

Research Article

Fluid Origin and Evolution of the Roc Blanc Silver Deposit (Jebilet Massif, Variscan Belt, Morocco): Constraints from Geology and Fluid Inclusions

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The Roc Blanc Pb-Zn-Ag-Au vein deposit is located in the NW of Marrakech, in the Central Jebilet massif. It is spatially related to Bramram-Tabouchennt-Bamega (BTB) granodioritic pluton (ca. 330 Ma) metamorphism aureole. The main veins hosted in black shales are oriented N-S to NNW-SSE. Pb-Zn-Ag-Au ore is associated with quartz, chlorite, sericite, and carbonate gangue minerals. Two major stages of ore deposition were distinguished. The preore stage (stage I) comprises two quartz-mineralised vein generations with Fe, As, Zn, and Cu ores (vg1 and vg2). The main ore stage (stage II) consists mainly on Ag, Au, Pb, Zn, Cu, and Sb ores, which is hosted by carbonaceous vein (vg_3) and by two late quartz generations veins $(vg_4$ and vg_5 with a geodic quartz). Three types of fluid inclusions have been recognized in silver mineralisation bearing quartz veins according to petrographic investigations, microthermometry, and Raman spectroscopy studies: (i) liquid-rich H₂O-N₂-CH₄±CO₂-(salt) fluid inclusions (type 1), (ii) vapour-rich H₂O-CO₂-CH₄-N₂-(salt) fluid inclusions (type 2), and (iii) aqueous H₂O-(salt) fluid inclusions (type 3). The interpretation of fluid inclusion data shows a mixing of two fluids that are metamorphic and surface to subsurface origin, trapped at boiling state. The first mineralised stage was deposited at $350 \pm 20 \circ C$ (this temperature of ore deposition was supported also by chlorite geothermometry) with salinity of 13.7 wt% NaCl equiv., while the deposition of the argentiferous stage, which consists of the main economic mineralisation of the Roc Blanc deposit, occurs during decreasing temperature at 150°C with a salinity of 12.1 wt% NaCl equiv. The all-mineralised ore was deposited at relatively low pressure, below ~1-1.1 kbar. So, fluid dilution and cooling are probably the main factor for silver deposition in the Roc Blanc polymetallic vein deposit. In addition, fluid inclusion studies reveal that the mineralising fluid corresponds to a mixture of metamorphic fluid (H₂O-CH₄-N₂-CO₂) with surface to subsurface aqueous gas-free fluids (H₂O-salt, meteoric, or brine).

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1. Introduction

The Roc Blanc Pb-Zn-Ag-Au deposit is located on the central unit of the Jebilet Hercynian massif, which is the most important part of the Jebilet Pb-Zn-Ag-Au metallogenic province. It is hosted by metamorphic Visean-Namurian shales (spotted schists) in the contact metamorphic aureole of the Bramram-Tabouchennt-Bamega (BTB) granodioritic plutons (Figure 1). The Roc Blanc silver deposit is spatially related to the BTB granodioritic plutons and probably displays a typical concentric base and precious metal zonation of Sn, W, Au, Cu, Pb, Zn, Ag, and Au, covering an area of approximately 10 km [1, 2]. The Pb-Zn-Ag-Au mineralisation of the Roc Blanc is similar to some other deposits in the central Jebilet (i.e., Koudiat el Hamra polymetallic mineralisation) which have been mined for silver in the past [2].

The Roc Blanc deposit is located in the central part of the Jebilet massif, 20 km north of Marrakech city. Discovered in 1925, the deposit is a silver-rich ore, with indicated and inferred resources which have been estimated around 200,000 t at 297 g/t and >56,000 t at 234 g/t Ag, respectively. Resources contain about 0.8% Pb and 1.01% Zn and a significant amount of copper and gold [3].

Mineralisation in the Roc Blanc deposit occurs as veins displaying banded or brecciated structures. It consists mainly of pyrrhotite, pyrite, arsenopyrite, chalcopyrite, sphalerite, galena, Ag-tetrahedrite, Pb-Ag-Sb sulphosalts, argentite, native silver, Ag-Au amalgam, and Ni-Co minerals [4, 5]. These minerals form different paragenesis, and they are precipitated during successive mineralising fluid events [4–6]. The mineralogy of the Roc Blanc ore corresponds to an intermediate- to low-sulphidation deposit [4].

The formation of the Roc Blanc deposit has been subject of many studies that are complementary, but often controversial [4, 7], questioning the nature of the mineralising fluids. The ore-forming fluids play a major role in any hydrothermal mineralised system. Therefore, the characteristics, origin, and evolution of these fluids are important for metallogenic studies. Several mechanisms, like boiling, fluid mixing, cooling, decrease of fluid salinity and pressure, and fluid rock-interactions, have been considered for mineral precipitation factors [8, 9]. More of them are taken account for the initiation of polymetallic silver precipitation, such as boiling, mixing, cooling, salinity, and pressure decreases (e.g., [4, 10-18]). In the present paper, we present paragenetic sequences of the Pb-Zn-Ag-Au veins of Roc Blanc deposit, with new analysis of fluid inclusions (petrography and microthermometry coupled with Raman spectroscopy analysis). The purpose of this study is to discuss the fluid composition and sources since fluid inclusion studies, timing, and metallogenic nature of the deposit through estimating the PT conditions of ore vein formation.

2. Geological Setting

2.1. Central Jebilet Geological Setting. The central Jebilet massif is part of the Moroccan Variscan belt, represented by the Meseta domain and the Palaeozoic blocks of the High Atlas [19]. The Meseta domain is structurally limited by the

Haut Atlas Mountain in the south and the Rif domain in the north. It is separated into two sectors (the Western and the Eastern Meseta) by the Mesozoic mountains of the Middle Atlas [20]. The Jebilet massif is located in the western part of the Moroccan Meseta, at 7 km north of the Marrakech city (Figure 1(a)). The massif is outcropping in E-W direction with 170 km in long and 40 km in wide.

The Jebilet massif consists of three tectonostratigraphic units, subdivided into eastern, central, and western parts (Figure 1(b)), separated by major shear zones [21, 22]. The western Meseta Shear Zone (WMSZ) separates the western units from the central one [23], and the Marrakech Shear Zone (MSZ) separates the central from the eastern unit [24]. Their original sedimentary relationships are masked by these complex tectonized contacts. The eastern unit is composed of Visean rocks including allochtonous terranes of Ordovician to Devonian ages. The western units consist of weakly deformed and metamorphosed Cambrian and Ordovician rocks, whereas the central units consist mainly of very low-grade metamorphism of the Visean Sarhlef Formation. Recently, new biostratigraphic results on metamorphosed conodonts studied by Lazreq et al. [25] have been attributed to the Sarhlef Formation. These new biostratigraphic investigations have yielded an age ranging from the Frasnian to late Famennian for the Sarhlef serie [25]. According to these authors, this new age is more compatible with the previous radiometric data of the intrusive magmatic rocks [26–30]. The central units are intruded by three generations of syntectonic intrusions. The earlier igneous activity has been started at c.a. 330 Ma [31] with the emplacement of an early bimodal mafic-ultramafic to felsic suite, comprising olivine to quartz-bearing gabbro and peridotite locally intruded by a ca. 279 ± 7 Ma gabbro dike. The whole was intruded by late Variscan granitoid stocks, leucogranite dike, and microdiorite sheets. Granitoid intrusions correspond to a syntectonic I-type and/or S-type, strongly peraluminous, largely evidenced by the Bamega-Tabouchennt-Bramram stocks and Oulad Ouaslam laccolith [32-34]. These plutonic rocks have been dated to 327 ± 4 Ma (whole-rock Rb-Sr ages; [30]). Two highly differentiated micas ± tourmaline-bearing leucogranites have been recognized in the studied area, and they correspond to a NW-trending, subvertical sheet dikes, dated at 296 ± 12 Ma (Rb-Sr isotopes; [30, 35]). However, Ar-Ar dating method on white micas from regional shear zones that also affects the leucogranite, gives an oldest age 305.9 ± 0.9 Ma [7]. Microdioritic dikes correspond to the youngest intrusive rocks, dated from ca. $255 - 241 \pm 5$ Ma (K-Ar and 40 K- 40 Ar on kaersutite [36–38]) to ca. 235 Ma (SHRIMP U-Th-Pb on zircon [27]). Before these intrusive magmatic rocks, a volcanic rock has been described in Central Jebilet, associated with pyrrhotite-rich massive sulphide deposits, attributed to Upper Visean (e.g., [22, 29, 39-41]).

The central Jebilet formations were metamorphosed at low-grade regional metamorphism achieving epizonal to anchizonal conditions [22, 42–44]. This metamorphism in the central Jebilet was contemporaneous with post-Visean crustal shortening ductile deformation [45]. Subsequently to the regional metamorphism, a contact metamorphism accompanied the magmatic intrusions emplacement.



FIGURE 1: Geological location. (a) Location of the Jebilet massif in the framework of the Palaeozoic outcrops of North Africa. (b) Geological sketch map of the Jebilet massif showing the location of the Roc Blanc deposit (modified from [22]). (c) Detailed geological map of the south eastern part of the central Jebilet massif [4].

Aureoles of hornblende and pyroxene hornfels metamorphic facies are particularly developed in the vicinity of felsic intrusions [33].

For deformation events in the central Jebilet unit, they are distributed unevenly, depending mainly on the relative competence of the rocks [43]. So, many deformation phases have been noticed in this central part of the massif. Four deformation phases named as D_0 , D_1 , D_2 , and D_3 have been recognized ([22, 46–48] and references therein). D_0 was identified as an early synsedimentary event related to extensive-transtension tectonics, allowing the setting up of the Devono-Carboniferous basin [46]. The D_1 and D_2 deformation phases were related to the closure of the basin. Those episodes begin in Upper Visean-Namurian (~325 Ma). The D_3 event was related to the emplacement of late Variscan, syn- to postkinematic granodioritic intrusions, which developed an HT-LP metamorphic aureole.

The Jebilet massif hosts have many metalliferous deposits, mainly represented by massive sulphides, followed by pyrometasomatic deposits and mineralised veins [22]: (i) massive sulphide deposits are the most studied ones. They are base metal pyrrhotite rich (Kettara, Koudiat Aicha, Draa Sfar, etc.) and are differently considered by authors as syngenetic or epigenetic mineralisation (e.g., [29, 39, 40, 44, 49, 50]). Their relative age is Upper Visean-Namurian, which would be reconsidered to Devonian for syngenetic affiliation

mineralisation, according to the recent biostratigraphic reconsiderations [25]. (ii) The pyrometasomatic mineralisation (e.g., Frag El Maa) is linked to syntectonic felsic intrusion emplacement [22]. (iii) The mineralised veins are polymetallic and rich in precious metals (e.g., [4, 6, 7]); their emplacement generally postdates the major regional S1 fabrics and before the microodioritic magmatism event which is dated at $255 - 241 \pm 5$ Ma [36]. The Roc Blanc Pb-Zn-Ag-Au deposit is part of this event.

2.2. The Roc Blanc Deposit Geological Setting. The Roc Blanc deposit is hosted by black shales of the Sarhlef schist serie. This serie covers most of the central unit (Figure 1(b)) and is composed of sedimentary rocks weekly metamorphosed to greenschist facies. The lithology is made up mainly of pelites (black shales), sandstones, and calcareous beds alternating with volcanic and subvolcanic rocks of mafic and felsic composition [22]. The schists are intruded by Bramram-Tabouchennt-Bamega (BTB) granodioritic plutons, leucogranites, and microdioritic dikes [1] at the western boundary of the Marrakech Shear Zone (MSZ), which limits the central part and the eastern part of the Jebilet massif. The deposit is located in the contact metamorphism aureole of the BTB plutons ([1], Figures 1(b) and 1(c)). These plutons contain numerous quartz-carbonate veins, pegmatitic veins, and aplitic rocks.

The Roc Blanc orebodies have been described as quartzcarbonate veins cutting the Sarhlef schists [12, 22]. The mineralisation is characterised by [4, 5] (i) a complex paragenesis; (ii) modest opening; (iii) direction substantially parallel to the major Hercynian fold axial plan, often slightly inclined on the schistosity; and (iv) its richness in silver and antimony minerals. Mineralogically, the Roc Blanc deposit is particularly distinguished by the presence of owyheeite and andorite, in addition to other Ag-rich bearing minerals (argentiferous tetrahedrite, ullmannite, miargyrite, pyrargyrite, polybasite, argentite, and native silver). Ag-rich minerals commonly are expressed as inclusions in galena, chalcopyrite, and other sulphide and occur sometimes as microfractures filling sulphides and quartz.

3. Sampling and Analytical Methods

Samples were taken from outcrops and from thirteen drill cores (RB-1, RB-2, RB-3, up to RB-13; Figure 2(a)) of the Roc Blanc deposit for ore descriptions. The mineralogical and petrological studies, already published by Arbaoui et al. [4], are based on results of a sample set, including eighty polished thin sections. Those samples were studied under transmitted- and reflected-light, polarized microscope, and scanning electron microscope (SEM), with an energy dispersive spectrometer (EDS, SE, and BSE) at the REMINEX Research Centre and Laboratory (Morocco). SEM operating conditions were an accelerating voltage of 30 kV, a beam current of 20 nA, and count times of 20 s.

Five samples were selected for fluid inclusion studies, carried out on double polished, 100-300 mm thick sections from quartz bearing mineralisation, including argentiferous phases. Various inclusions in quartz were selected for microthermometry and Raman spectroscopy analysis based on their petrographic characteristics. The petrographic studies of inclusions were mainly conducted according to Roedder [51], Van den Kerkhof and Hein [52], and Diamond [53].

Microthermometric studies were performed on thick sections using a Linkam THMS-600 heating-freezing stage mounted on an Olympus BX-50 microscope at the Laboratory of Metallogeny and Magmatism in the Geology Department of STHB University (Algeria). Liquid nitrogen was used for the freezing phase. The machine temperatures range from -196 to 600°C. For all inclusions, the accuracy was 0.2°C during the cooling stage and 0.5°C during the heating stage. The volumetric fraction of the aqueous phase was visually estimated using standard charts [51, 54]. The salinities of aqueous gas-free inclusions were calculated using the final ice melting temperatures with the Bodnar equation [55, 56]. Molar fractions of CO_2 , CH_4 , and N_2 were determined in individual fluid inclusions by semiquantitative analysis of Raman spectroscopy spectra and performed with a Labram Raman spectrometer at CNRS-CREGU (Nancy, France). The scanning regions were in the range of 1000-1500 cm⁻¹ for CO₂, 2250-2750 cm⁻¹ for N₂ and H₂S, and 2750-2950 cm⁻¹ for CH₄. Finally, isochoric curves of aqueous gas-free inclusions were calculated using the model of Zhang and Frantz [57] to estimate the PT condition of the main mineralising fluid.

4. Ore Descriptions and Typology

4.1. Morphology of Mineralised Veins. The Roc Blanc deposit is a Pb-Zn-Ag-Au mineralisation generally bearing vein structures. It consists of massive open-space fillings of a network subvertical veins, veinlets, and an echelon tension gashes [4]. Seven major ore structures (in extension) are identified in the deposit area, occurring as discontinued veins of several hundred meters long, hosted by black shales (Figure 2(a)). They show two major trends that are N135 to N150 (V_3 , V_4 , V_6 , and V_7) and N0 to N10 (V_1 , V_2 , and V_5) (Figure 2(a)). In most cases, hydrothermal veins in the study area are mainly oriented around N135 and dip from 45° to 65°E (Figure 2(b)). All of the major ore structures are located in the sinistral SSEtrending Marrakech Shear Zone. The mean extension of major ore structures varies from 300 to 600 m long and from 0.3 to $0.5 \,\mathrm{m}$ of thickness (Figure 2(a)). V_5 is the largest one, being more than 2 000 m long with an average thickness of 0.7 m. The veins cut across the S_1 cleavage, which strikes N10 to N45 and dips 70°-80°E (Figure 2(b)). Stretching lineations (L_e) are also observed; they are oriented toward the NNE direction, along with S_1 cleavage. The stratification in the deposit area is generally transposed into S_1 cleavage plan; however, some ESE strikes are occasionally observable. At map scale, microdioritic dikes, oriented NNE, also cut across all S_1 cleavage, Marrakech Shear Zone, and postdate the major ore structures. These dikes are clearly intersected by sinistral and dextral faults with local breccia mineralisation at their intersection (Figure 2(b)). The well relationship between these faults and mineralised veins is not observed, but generally, mineralised veins are stopped in front of these faults (e.g., V_2 and V_5).



FIGURE 2: (a) Geologic map of the Roc Blanc deposit showing the distribution and morphology of Pb-Zn-Ag-Au veins. Note the spatial relationship between the mineralised veins, microdiorite, and dolerite and the organic-rich black shale (Sarhlef schists). Location of drill cores (projected to surface) [4]. (b) Stereogram of hydrothermal veins from Roc Blanc deposit (n = 87 measured points). (c) Stereogram of S_1 (n = 202) and L_e (n = 22) values measured in the Roc Blanc area.



FIGURE 3: Photographs of representative samples from the Roc Blanc deposit, showing the structural relations between veins. (a) Vein (vg_1) consisting of quartz (Qtz1), chlorite, and ore minerals (Po, Sp, and Ccp) cutting across the bedding (S_0) . Note: hydrothermal alteration minerals (chlorite) are developed on vein boundaries. (b) Banded vein (vg_2) section, consisting of quartz (Qtz2), siderite, sphalerite, arsenopyrite, and pyrite. (c) Quartz (Qtz3) galena and silver mineral veins (vg_4) of the main stage crosscutting vg_2 . (d) Coexisting lightbrown sphalerite, coarse-grained galena, pyrite, and quartz (Qtz4) of the vg_5 . The silver mineralisation occurs as irregular patches and coarse-grained disseminations in the galena. Wall-rock (BS: black shale) fragments in the ore are altered to sericite and quartz.

4.2. Mineralogy and Paragenesis of the Pb-Zn-Ag-Au Veins. Mineralogical study revealed five vein generations (vg). The first mineralised vein (vg_1) is composed of quartz 1 (Qtz1) + chlorite + sericite-muscovite + pyrrhotite \pm chalcopyrite \pm Fe-rich sphalerite \pm galena (Figure 3(a)). The second vein (vg₂) generation is fracture filling quartz 2 (Qtz2) + siderite/ankerite + pyrite + arsenopyrite ore (Figures 3(b) and 3(c)). According to microscopic observations, this vein cut minerals of the first one. Both of these two veins types have been described in central Jebilet, where they are associated with pyrrhotite-rich massive sulphide deposits [50]. The third vein (vg_3) is made up of Fe-dolomite + Fe-rich sphalerite + galena + boulangerite + owyheeite + diaphorite + Ag-rich minerals (pyrargyrite, miargyrite, argentopyrite, polybasite, stephanite, Ag-tetrahedrite, argentite, and native Ag; Table 1). The fourth vein (vg_4) generates quartz 3 (Qtz3) + chalcopyrite + ullmannite + (Ag-Sb) sulphosalts paragenesis and clearly cross cut the second vein type bearing Qtz2 (Figures 3(c) and 3(d)). The fifth vein (vg_5) type contains quartz 4 (Qtz4) + calcite + Fe-poor sphalerite + Ag-tetrahedrite + Ag-Au alloy (Figure 3(d)). Here, Qtz4 occurs as geodic quartz overlapped by secondary pyrite.

All of these mineral assemblages in the Roc Blanc deposit were regrouped into three main ore forming stages ([4, 5]; Figure 4):

(1) The first stage is composed of Fe, As, Zn, and Cu mineralisation associated with quartz (Qtz1, 2), chlo-

rite, and sericite; it is represented by vg_1 and vg_2 mineral assemblages. Sphalerite and chlorite of this stage are Fe-rich. The mean value of Fe in sphalerite is 5.71 wt%. Chlorite corresponds to a ripidolites with a Fe[#](=Fe/(Fe + Mg) value ranging from 0.66 to 0.84 (Table 2 and Figure 5(a)). Kranidiotis and Mac Lean [58] geothermometry of these chlorites reveal temperatures between 330 and 380°C (Figure 5(b)). The quartz-chlorite-mineralised veins could be formed at $350 \pm 10 \circ C$, similar to those associated with the Kettara pyrrhotite-rich massive sulphide deposit [50, 59]

(2) The main ore stage is characterised by Ag, Au, Pb, Zn, Cu, and Sb mineralisation. The precipitation of Ag-bearing minerals is preceded by base metal sulphide minerals. This stage is formed by vg₃, vg₄ (Qtz3), and vg₅ (Qtz4) vein generation minerals. Late sphalerite of this stage is Fe-poor with 3.42 wt% Fe. Textural relationships among silverrich minerals indicate the following chronological order of precipitation: Ag-tetrahedrite → miargyrite → pyrargyrite → polybasite → stephanite → argentite → native silver. These minerals contain 32 to 35, 36 to 37, 59 to 61, 62 to 63, 65 to 66, 85 to 90,

Geofluids

Mineral	S	Fe	Ag	Au	Sb	Pb	Ni	Zn	Cu
			80.19	19.81					
Ag-Au			70.69	27.33					
			19.14	80.21					
			92.73	7.27					
Native silver			91.07	9.14					
			91.76	8.27					
Augontita	9.24	_	90.76						
Argentite	11.28	_	85.57		3.15				
Stephanite	17.9	_	66.75		15.33				
D	17.89	_	61.94		20.17				
Pyrargyrite	18	_	59.9		22				
	24.42	_	36.84		38.74				
Mlargyrite	22.72	_	37.96		39.32				
Oracle esite	19.2	_	17.2		28.7	35.1			
Owyneette	18.73	_	24.51		26.83	30.93			
Dianharita	23.94	_	28.49		22.8	24.76			
Diaphorite	27.35	_	25.68		24.67	22.3			
A]: (-	19	_	15.8		47.2	23			
Andorite	23.3	_	13.53		42.75	20.42			
Decile a servite	21.96	_	_		29.43	54.62	_	_	
Doulangerite	23.18	_	_		25.97	50.85	_	_	
Totuch a duita	30.23	5.94	_		35.71	_	_	_	29.12
Tetraneurite	25.38	2.42	_		34.8	_	_	_	37.4
Encile quaita	24.54	4.25	36.42		25.69	_	_	—	9.1
Freibergite	24.33	4.57	35.48		24.41	_	_	—	11.21
A a totrah adrita	22.96	4.75	34.7		24.26	_	_	2.27	11.05
Ag-tetralleunte	23.66	4.1	32.86		24.99	—	—	2.03	12.36
Dolyhasita	14.6	_	62.54		12.54	_	_	—	10.3
1 Ory Dashe	16.7	_	63		10.98	_	_	—	10.62
Illmannita	21.46	_	_		56.97	_	21.56	—	_
Ulimannite	19.29	_	_		61.27	_	19.43	_	_
Galena	12.73	_	0.1		_	87.17	_	_	_
Fe-poor sphalerite	32.42	3.42	_		_	_	_	64.2	_
Fe-rich sphalerite	38.21	5.71	_		_	_	_	56.08	_
Chalcopyrite	40.52	27	_		_	_	_	—	32.48

TABLE 1: Representative composition of SEM analysis (wt%) of silver and base metal minerals of the Roc Blanc deposit.

and >91 wt% Ag, respectively (Table 1 and Figure 5(c)). Ag-Au alloy is intergrown closely with argentite and typically cuts or replaces galena, argentiferous tetrahedrite, and chalcopyrite. It contains up to 80.21 wt% Au (Table 1)

(3) The postore stage is characterised by barren fluid circulation causing some alterations with chlorite, sericite, and quartz minerals. In addition, the primary ore of the Roc Blanc deposit is overprinted by supergene alteration marked by the formation of secondary pyrite, marcasite, magnetite, hematite, goethite, and malachite/azurite

5. Fluid Inclusions

Fluid inclusion studies were conducted on quartz in the studied five mineralised veins, including three early-stage and two late-stage samples. On the one hand, only one sample was collected at the early stage of the mineralised vg1-type which is characterised by quartz 1+chlorite \pm Fe-rich sphalerite \pm galena. On the other hand, the other two samples were sampled from the vg2-type consisting of quartz 2+siderite/ankerite + pyrite + arsenopyrite. The two samples of the late stage are from vg₄ with quartz (Qtz3) + chalcopyrite + ullmannite + (Ag-Sb) sulphosalts and geodic quartz vein (vg₅) with quartz (Qtz4) + calcite + Fe-poor sphalerite

Paragenetic			Main vein-filling stage	e II	Post-ore	Supergene
Minand	Pre-ore Fe-As stage I	Base metal-	 	1	barren stage III	alteration stage IV
Mineral		rich sub-stage 1	Ag-rich sub-stage 2	Au-rich sub-stage 3	ourren ouige m	alteration stage I (
Sulfides		1				
• Pyrrhotite				<u> </u>		
• Pyrite						
Arsenopyrite						
• Sphalerite						
• Galena			¦			
Chalcopyrite		F		F .		
• Marcasite		R		R		
Pb-Ag-Sb sulfosalts		A		A		
Boulangerite		C		C		
• Meneghinite		T	¦	T		
• Owyheeite		U	F	U		
• Andorite		R	R	R		
• Diaphorite		I	A	I		
Ni-Sb-bearing mineral		N¦	IC	N		
• Ullmannite		G	T	G		
Ag-Au-bearing minerals			U			
Argentopyrite			R			
Argentotennantite			I			
• Freibergite			N			
• Miargyrite			G			
Pyrargyrite						
• Stephanite						
Polybasite			· · · · · · · · · · · · · · · · · · ·			
• Argentite			: i — —			
 Native silver 				—		
• Ag-Au amalgam				—		
• Gold-electrum						
Gangue minerals						
Ca-Fe-Mg carbonates						
• Quartz 1						
• Quartz 2						
• Quartz 3						
• Quartz 4						
Sericite-muscovite						
• Chlorite						
• Graphite						
Tourmaline						
Rutile-ilmenite			l i l			
• Titanite						
Supergene minerals						
• Magnetite						
Geothite-hematite						
Malachite-azurite						

FIGURE 4: Paragenetic sequence of vein mineralisation of the Roc Blanc deposit (modified after [4]).

+ argentiferous tetrahedrite + Ag- and Au-bearing minerals. Carbonate minerals associated with the mineralisation are poor in fluid inclusions, and the scarce one observed is too small in size ($<5 \mu m$) and was not suitable for microthermometric studies.

5.1. Fluid Inclusion Petrography. Fluid inclusion studies were limited to primary fluid inclusions. They form isolated or fluid inclusion assemblage (FIA), [53] in host minerals and do not belong to any fractures. Based on distribution and shape, the vapour-filling ratio (R_{Flv}), microthermometric, and Raman spectroscopy analyses, three main fluid inclusion types are identified in the quartz-mineralised veins (Qtz1 (vg₁), Qtz2 (vg₂), Qtz3 (vg₄), and Qtz4 (vg₅)) of the Roc Blanc deposit.

Type 1 and type 2 are two-phase (L and V) aqueousgas-bearing fluid inclusions and are observed in Qtz1, Qtz2, and Qtz3. However, type 1 is liquid-rich (H₂O-N₂-CH₄±CO₂-(salt)) while type 2 is relatively vapour-rich (H₂O-CO₂-CH₄-N₂-(salt)). Type 3 is essentially twophase (L and V) aqueous fluid inclusions (H₂O-(salt)), existing in all quartz generations (Figures 6(a)–6(f)). These inclusions are associated with scarce one-phase fluid inclusions in some quartz. The three main types are distributed randomly and would correspond to primary fluid inclusions compared to the secondary fluid inclusions, which are arranged along transgranular trails [52]. These late inclusions consist of two-phase fluid inclusions, are small in size (<5 μ m), and were not suitable for microthermometric studies (Figure 6(d)).

Analysis	RB7-55	RB7-56	RB7-57	RB7-58	RB7-59	RB7-60	Chlorite RB7-61	es from pyi RB7-62	rrhotite b RB1-1	earing qu RB1-2	tartz vein RB1-3	RB1-4	RB1-5	RB1-6	RB1-7	RB1-8	RB1-9	RB1-10
SiO ₂	23.86	22.94	23.98	23.63	23.92	23.93	23.92	22.95	24.30	24.21	24.56	24.04	24.67	24.87	24.03	24.24	24.96	24.13
TiO_2	0.02	0.01	0.02	0.00	0.05	0.03	0.02	0.01	0.02	0.02	0.00	0.02	0.01	0.00	0.05	0.00	0.00	0.00
Al_2O_3	21.93	22.05	21.63	22.83	21.71	21.46	21.90	22.26	22.53	22.15	22.69	22.66	22.60	22.57	22.78	22.59	23.02	22.95
FeO	37.15	38.40	37.41	35.91	37.10	36.97	37.35	38.43	33.80	32.41	31.04	32.59	33.12	32.22	34.27	33.90	32.73	33.87
MnO	0.15	0.37	0.21	0.64	0.20	0.21	0.22	0.27	0.56	0.44	0.41	0.45	0.55	0.41	0.68	0.62	0.48	0.54
MgO	5.35	4.08	5.34	5.43	5.18	5.26	5.35	4.70	7.20	9.41	10.37	8.53	7.72	9.07	7.41	7.69	8.56	7.73
CaO	0.01	0.01	0.01	0.02	0.01	0.02	0.02	0.02	0.01	0.01	0.00	0.05	0.02	0.02	0.02	0.00	0.02	0.05
Na_2O	0.03	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.03	0.04	0.08	0.00	0.01	0.00	0.00	0.00	0.04
K_2O	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.01
BaO	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	00.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr_2O3	0.00	0.00	0.00	0.02	0.02	0.02	0.01	0.01	0.01	0.02	0.02	00.00	0.05	0.00	0.01	0.00	0.00	0.00
Total	88.52	87.94	88.69	88.77	88.29	88.11	88.80	88.66	88.47	88.72	89.14	88.43	88.75	89.21	89.30	89.04	89.83	89.39
Calculated s	tructural)	formula																
Si	5.29	5.18	5.32	5.19	5.31	5.32	5.30	5.14	5.29	5.24	5.24	5.22	5.33	5.31	5.20	5.26	5.30	5.20
$Al^{(IV)}$	2.71	2.82	2.68	2.81	2.69	2.68	2.70	2.86	2.71	2.76	2.76	2.78	2.67	2.69	2.80	2.74	2.70	2.80
Al ^(VI)	3.05	3.07	2.99	3.14	3.02	2.98	3.03	3.04	3.10	2.89	2.95	3.03	3.11	3.02	3.04	3.05	3.09	3.06
Ti	00.00	0.00	00.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	00.00	00.00	0.00	0.01	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	00.00	0.01	0.00	0.00	0.00	0.00	0.00
Fe^{3+}	0.19	0.17	0.20	0.26	0.24	0.25	0.18	0.10	0.23	0.08	0.10	0.12	0.24	0.20	0.17	0.17	0.23	0.16
Fe^{2+}	6.71	7.08	6.74	6.33	6.65	6.62	6.74	7.11	5.92	5.78	5.44	5.79	5.74	5.55	6.04	5.98	5.58	5.95
Mn	0.03	0.07	0.04	0.12	0.04	0.04	0.04	0.05	0.10	0.08	0.07	0.08	0.10	0.07	0.12	0.11	0.09	0.10
Mg	1.77	1.37	1.77	1.78	1.71	1.74	1.77	1.57	2.34	3.03	3.30	2.76	2.49	2.89	2.39	2.49	2.71	2.48
Ca	00.00	0.00	00.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01
Na	0.03	0.01	00.00	0.00	0.00	0.01	0.01	0.01	0.01	0.02	0.04	0.07	0.00	0.01	0.00	0.00	0.00	0.04
K	00.00	0.00	00.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.01
Total	35.78	35.78	35.75	35.65	35.68	35.65	35.73	35.85	35.71	35.91	35.89	35.88	35.70	35.74	35.78	35.79	35.70	35.81
Fe/Fe+Mg	0.80	0.84	0.80	0.79	0.80	0.80	0.80	0.82	0.72	0.66	0.63	0.68	0.71	0.67	0.72	0.71	0.68	0.71
T (°C)	364	379	362	374	362	362	364	382	359	360	357	364	354	352	368	362	355	367

TABLE 2: EPMA analysis (wt%) of chlorite from the Roc Blanc deposit.



FIGURE 5: (a) Projection of Roc Blanc chlorites in the classification diagram of Hey [60]. (b) Histogram of temperatures calculated for the crystallization of Roc Blanc chlorites based on the geothermometer of Kranidiotis and Mac Lean [58]. (c) Triangular Pb + Cu-Ag-Sb diagram showing the chemical composition of the Ag-rich and sulphosalt minerals from the Roc Blanc deposit.

- (i) *Type 1* consists of a liquid-dominated two-phase fluid inclusions with R_{Flv} ranging from 10 to 30%. The inclusions are oval or elongated and have regular to subregular shapes with 5 to $15 \,\mu\text{m}$ in size. These inclusions are abundant and can represent approximately 40% in single quartz. They form fluid inclusion assemblages (FIA) with other types or can be found isolated (Figures 6(a), 6(b), and 6(e))
- (ii) *Type 2* is composed of two-phase vapour-rich fluid inclusions with an R_{Flv} varying from 10 to 50%

(av. $R_{Fl\nu} = 30\%$). They appear dark, and their size is between 10 and 15 μ m. The inclusions have regular shapes and represent approximately 20% of inclusion populations. These inclusions are isolated or occur as clusters throughout quartz crystals. They are closely associated with type 1 and are not all time distinguishable from them by only petrographic observations (Figures 6(a)–6(e))

 (iii) Type 3 consists of two-phase aqueous (liquid + vapour) fluid inclusions showing a bright aspect. These inclusions are generally elongated, regular to

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FIGURE 6: Photomicrographs showing different types of fluid inclusions in mineralised veins of the Roc Blanc deposit in transmitted light. (a) Quartz- (Qtz1-) chlorite-pyrrhotite-mineralised vein (vg₁) with assemblage of two-phase $H_2O-N_2-CH_4\pm CO_2$ -(salt) inclusions (type 1), $H_2O-CO_2-CH_4-N_2$ -(salt) inclusions (type 2), and aqueous fluid inclusions (type 3). (b, c) Quartz- (Qtz2-) mineralised vein (vg₂) with abundant two-phase $H_2O-N_2-CH_4$ -(salt) fluid inclusions (type 1) coexisting with $H_2O-CO_2-CH_4-N_2$ -(salt) inclusions (type2) and H_2O -(salt) inclusions (type 3); and secondary inclusion trails in (c). (d, e) Quartz- (Qtz3-) (Pb-Ag-Sb) sulphosalt vein (vg₄) with two-phase $H_2O-N_2-CH_4\pm CO_2$ -(salt) inclusions (type 1), $H_2O-CO_2-CH_4-N_2$ -(salt) inclusions (type 2), and aqueous fluid inclusions (type 3). (f) Two-phase aqueous fluid inclusions (type 3) of the geodic quartz (Qtz4) vein (vg₅).



FIGURE 7: Representative laser Raman spectra of type 1 (a, b) and type 2 (c, d) fluid inclusions from the Roc Blanc deposit.

subregular with 5-15 μ m in size. They have a very consistent low vapour-filling ratio, generally around 5 to 10%. Contrary to types 1 and 2, type 3 inclusions are present in all samples studied. They form generally FIA with type 1 and type 2 in Qtz1, Qtz2, and Qtz3 (Figures 6(a), 6(c), and 6(e)), and they can be dominant with proportion up to 50% or exist alone as in the Qtz4 (Figure 6(f))

5.2. Microthermometry and Raman Spectroscopy. Application of laser Raman spectroscopy indicates the presence of volatile components in the vapour phase of type 1 and type 2 fluid inclusions. The Raman spectra collected correspond mainly to nitrogen, methane, and carbon dioxide (Figures 7(a)-7(d)). Type 3 fluid inclusions are essentially gas-free, whereas one inclusion analysed from a scarce one-phase fluid inclusions contains methane and nitrogen (Qtz2, 57% CH₄, and 43% N_2). Although the volatile phases (CH₄, N₂, and CO₂) are detected in many inclusions, twophase transitions have been noticed during freezing and heating runs: ice melting temperature $T_{m(ice)}$ and bulk homogenisation temperature (T_h) (Table 3). Clathrates form generally in the freezing stage of these inclusion types; however, clathrate melting temperatures were difficult to observe.

5.2.1. Type 1 Fluid Inclusions. These inclusions have been identified in Qtz1, 2, and 3. Their microthermometric data

show a variable ice melting temperature. $T_{m(ice)}$ are generally between -15 and -1°C in Otz1, Otz2, and Otz3, with an average value of -6.9, -7.6, and -10°C, respectively (Figure 8(a)). In the Qtz1 and Qtz3, scarce fluid inclusions yield a low $T_{m(ice)}$ up to -18 and -21.8°C, respectively. During the heating stage, all of these inclusions have been homogenised into the liquid phase. T_h are relatively similar in the Qtz1 and Qtz3; they range from 104 to 237°C in the Qtz1 and from 117 to 248°C in Qtz3, with average values of 164 and 190°C, respectively (Figure 8(b)). In the Qtz2, T_h are slightly higher, with values between 215 and 288°C, with a mean around 250°C. Raman spectroscopy analysis was carried out in these inclusion types in the Qtz1 and Qtz2. Their vapour phase is mainly composed of variable proportions of nitrogen and methane, whereas carbon dioxide is detected as traces in two inclusions of Qtz1 (Figure 9). According to the semiquantitative composition (X in mole percent) of gases calculated from Raman spectra areas, in the Qtz1, nitrogen is relatively dominant; X_{N2} ranges from 59 to 77 mol%, and X_{CH4} ranges from 23 to 39 mol%. Their average composition is approximately $70 \mod N_2$ and 30mol% CH₄. In the two inclusions where carbon dioxide is detected, X_{CO2} is 2 mol%. In the Qtz2, methane is prevalent, $X_{\rm CH4}$ ranges from 52 to 74 mol% with a mean of 60 mol%, and X_{N2} is between 26 and 48 with an average value of 40 mol%. CO_2 is missing in all inclusions of type 1 in the Qtz2 or its content is lower than the detection limit.

FI type	Range	T_m (ice)	Th °C	Salinity wt% NaCl equiv.	R flv	Taille <i>u</i> m	CO ₂ %	N ₂ %	CH ₄ %
Quartz 1				<u> </u>					
Type 1	Min	-18	104		10	5	2	59	23
$H_2O-N_2-CH_4\pm CO_2-(salt)$	Max	-1	237		30	15	2	77	39
	Mean	-6.9	164		20	8	2	69	31
	N	21	21				2	8	8
Type 2	Min	-15.8	250				24	20	25
H ₂ O-CO ₂ -CH ₄ -N ₂ -(salt)	Max	-8	310				56	40	36
	Mean	-10.8	280				40	30	30.5
	N	6	6				2	2	2
Туре 3	Min	-19.2	85	7.9					
H ₂ O-(salt)	Max	-4.8	169	19.4					
	Mean	-11.6	125	15.9					
	N	13	13	13					
Quartz 2									
Type 1	Min	-15	215				0	26	52
H ₂ O-N ₂ -CH ₄ -(salt)	Max	-2	288				0	48	74
	Mean	-7.6	246				0	40	60
	N	16	21				5	5	5
Type 2	Min	-24	300		10	10	34	27	36
$H_2O-CO_2-CH_4-N_2-(salt)$	Max	-12.8	377		50	15	37	27	38
	Mean	-18	338		30	12	35.5	27	37
	N	6	6				2	2	2
Туре 3	Min	-9.5	150	3.7					
H_2O -(salt)	Max	-2.2	162	13.4					
	Mean	-6.5	157	11.5					
	N	3	3	3					
Quartz 3									
Type 1	Min	-21.8	117						
H ₂ O-N ₂ -CH ₄ -CO ₂ -(salt)	Max	-1	248						
	Mean	-10	190						
	N	20	26						
Type 2	Min	-23	250				78	13	9
H ₂ O-CO ₂ -CH ₄ -N ₂ -(salt)	Max	-5	309				78	13	9
	Mean	-12.1	278				78	13	9
	N	13	13				1	1	1
Type 3	Min	-9.4	100	6.2					
H ₂ O-(salt)	Max	-3.8	110	13.3					
	Mean	-6.7	104	10.7					
	N	5	5	5					
Quartz 4									
Type 3	Min	-17.4	74	4.1	5	10			
H ₂ O	Max	-2.4	202	19.6	10	12			

-10

32

Mean N 134

40

13.5

32

8

11

TABLE 3: Summary of microthermometric and Raman microspectrometric data of fluid inclusions in mineralised veins of the Roc Blanc Ag-Pb-Zn deposit.



FIGURE 8: Histogram frequency of homogenisation temperatures (T_h) and ice melting temperature $(T_{m(ice)})$ based on microthermometric data of fluid inclusions in mineralised quartz veins of the Roc Blanc deposit. (a, b) $T_{m(ice)}$ and T_h of H₂O-N₂-CH₄±CO₂-(salt) inclusions (type 1). (c, d) $T_{m(ice)}$ and T_h of H₂O-CO₂-CH₄-N₂-(salt) inclusions (type 2). (e, f) $T_{m(ice)}$ and T_h of H₂O-(salt) inclusions (type 3). Homogenisation occurs into liquid phase or vapour phase (see description in the text).



FIGURE 9: Compositional ternary diagram showing the repartition of gas phases in fluid inclusions of quartz-mineralised veins of the Roc Blanc deposit.

According to the abundance of nitrogen and methane, a relative absence of CO_2 , and the ice melting temperature variation, the type 1 fluid inclusions are considered to belong to $H_2O-N_2-CH_4\pm CO_2$ -(salt) system.

5.2.2. Type 2 Fluid Inclusions. They show a relative lower ice melting and higher bulk homogenisation temperatures than the other fluid inclusion types of the Roc Blanc mineralising systems (Figures 8(c) and 8(d)). Contrary to the type 1, the type 2 fluid inclusions have almost homogenised into vapour phase. In the Qtz1, $T_{m(ice)}$ ranges from -15.8 to -8°C and T_h from 250 to 310°C, with means of -10.8 and 280°C, respectively. In the Qtz2, these inclusions bear a moderate saline fluid according to their low ice melting temperature; $T_{m(ice)}$ are between -24 and -12.8°C with an average value of -18°C. Their T_h are also higher than those of the type 1 with values ranging from 300 up to 377°C and a mean around 340°C. This type in Qtz3 shows $T_{m(ice)}$ between -23 and -5°C, mean $T_{m(ice)} = -12 \circ C$, and their T_h values ranging from 250 to 309°C, with a mean of about 280°C (Figures 8(c) and 8(d)). The type 2 is also aqueous-gasbearing fluid inclusions, with gas composed of CO_2 , N_2 , and CH_4 ; their average compositions are, respectively, 40, 30, and 30 mol% in the Qtz1; 36, 27, and 37 mol% in the Qtz2; and 78, 13, and 9 mol% in Qtz3 (Figure 9). Compared to the type 1, it is not argued with the few Raman spectroscopy data that CO_2 is systematically present in all inclusions of the type 2; however, its content here is relatively dominant (Table 3). According to the microthermometric and Raman spectroscopy data, type 2 fluid inclusions belong to the H₂O- CO_2 -CH₄-N₂-(salt) system.

5.2.3. Type 3 Fluid Inclusions. They are two-phase (L and V) aqueous bearing fluid inclusions, with very low vapour filling ratio (\approx 5%) indicating low trapping temperature. In the Qtz1, the $T_{m(ice)}$ ranges from -19.2 to -4.8°C and T_h from 85 to 169°C with mean values of -11.6 and 125°C, respectively (Figures 8(e) and 8(f)). In Qtz2 and Qtz3, $T_{m(ice)}$ have similar values that are between -9.5 and -2.2°C and average values of -6.5 and -6.7°C, respectively. However, their T_h are different and occur at about 160°C in the Qtz2 and 110°C in the Qtz3. In the Qtz4, where only type 3 fluid

inclusions have been observed, $T_{m(\text{ice})}$ are variable, ranging from -17.4 to -2.4°C (mean = -10 ° C) and T_h are between 74 and 202°C (mean \approx 135 ° C).

These inclusions are being gas-free; their salinities have then been calculated from ice melting temperatures using the Bodnar equation of state [55, 56]. In the Qtz1, salinities are between 7.9 and 19.4 wt% NaCl equiv. with an average salinity of 16 wt% NaCl equiv. Qtz2 and Qtz3 yield a narrow salinity range (3.7 and 13.4 wt% NaCl equiv.) with a mean around 11 wt% NaCl equiv. For the Qtz4, salinities are between 4.1 and 19.6 wt% NaCl equiv. (mean = 13.5 wt%NaCl equiv). Type 3 fluid inclusions belong therefore to the H₂O-(salt) system.

6. Discussion

6.1. Fluid Compositions and Sources. Microthermometric study and Raman spectroscopy analysis show similar fluid inclusion types in three quartz-mineralised veins (Qtz1, Qtz2, and Qtz3) that are $H_2O-N_2-CH_4\pm CO_2$ -(salt) (type 1), $H_2O-CO_2-CH_4-N_2$ -(salt) (type 2), and H_2O -(salt) (type 3). These similarities indicate the formation of these veins in the same contexts and relatively short interval times. The main fluid inclusion types, forming FIA in Qtz1 (vg_1), Qtz2 (vg_2), and Qtz3 (vg_4) mineralised veins, have not systematically the same compositions. The coexistence of these fluid inclusions with different contents could be explained here by two main hypotheses, which are mixing or boiling. A bivariate plot of $T_{m(ice)}$ (depending on salinities) versus T_h of representative fluid inclusions shows linear distribution of inclusions along $T_{m(ice)}$ axis (Figures 10(a)-10(c)). This distribution mode suggests a variation of salinities at nearly constant homogenisation temperature that are characteristic of a boiling process (e.g., [10]). If this process is true for fluid inclusions of the same type in the same mineral, it does not explain the coexistence of all fluid inclusion types due to the different T_h recorder between types 1, 2, and 3 in Qtz1, Qtz2, and Qtz3. However, type 1 fluid inclusions are always plotted between type 2 and type 3 (Figure 10), and results probably from the mixing of these two latest which are aqueous-gas-rich and aqueous gas-free fluids, respectively. This process tends to equilibrate the two fluids, generating an intermediate fluid composition and temperatures as in the type 1 (which is gas-poor, especially in CO₂). To resume, the fluid inclusions in the mineralised veins $(vg_1, vg_2, and vg_4)$ would result from the mixing of at less two fluids trapped at boiling state as

$$\begin{aligned} H_2 O-CO_2-CH_4-N_2-(salt)_{(type\,2)} &+ H_2 O-(salt)_{(type\,3)} \\ &= >H_2 O-N_2-CH_4 \pm CO_2-(salt)_{(type\,1)}. \end{aligned}$$

Note that CO_2 exists only in two inclusions of type 1 in minor proportion (2 mol %).

According with the mixing process and a relative structural time of emplacement of the veins (post S_1 cleavages), the source of the aqueous gas-bearing fluid (type 2) can be linked either to retrograde pseudo metamorphic fluids

(H₂O, CO₂, CH₄, and N₂ mixtures) or to the mesothermal fluid, whereas the aqueous fluid (type 3) is typical for epithermal quartz veins [61, 62]. The type 3 fluid inclusions yield similar salinities and T_h range especially in the Qtz2 and Qtz3 (3.7-13.4 wt% NaCl equiv., 110-160°C, respectively) that are characteristic of epithermal fluids (salinities = 1 - 12 wt%NaCl equiv. and $T_h = 100 - 300$; [62]). The fluid inclusions of geodic quartz (Qtz4) are typical gas-free and yield also an epithermal characteristic (mean $T_h = 134 \circ C$ and mean salinities = 13.5 wt%NaCl equiv.). For aqueous gas-bearing fluid inclusions which can have metamorphic or mesothermal origin, if the T_h values (250-380°C) argued with these sources, the volatile components (mixtures of CO₂, CH₄, and N₂) and low $T_{m(ice)}$ (-10.8°C) of type 2 fluid inclusions relative to moderated salinities (c. >14 wt% NaCl equiv. estimated from [55]) are not consistent with mesothermal quartz veins. Indeed, after Wilkinson [62], fluids of mesothermal quartz veins are predominantly CO_2 -N₂ or CO_2 -CH₄ mixtures, where intermediate compositions are rare and salinities are low. On the other hand, the contribution of magmatic fluids has not been ruled out for type 2 fluid inclusions. It is possible that these fluids represent magmatic derived or surface to subsurface fluids (meteoric or brine) driven through metamorphic rocks during retrograde cooling, where they have been enriched in volatile components. This could take place during uplift and extensional tectonics, and the resulting convection cells are open to the surface [63]. This can also explain the low $T_{m(ice)}$ recorded, relative to moderate salinities, in addition to the boiling hypothesis for salinity variation. Otherwise, although the type 2 and type 3 coexist in the same FIA (Figures 6(a)-6(e)), they display different homogenisation temperatures (e.g., in Qtz2 T_h mean = 340, 160°C, respectively). This difference can result for fluids trapping at an immiscible state [64] in the aqueous-gas-bearing fluid inclusions (type 2), where T_h reaches 377°C. But these high T_h are consistent with temperature from chlorite geothermometry ($350 \pm 10 \circ C$). Therefore, the mixing of two fluids with different temperatures is more convincing.

In the type 1 fluid inclusions, the volatile content is dominated by a mixture of N_2 and CH_4 , with minor proportions or absence of CO₂, whereas in the type 2, CO₂ is abundant and can be dominant, forming a mixture with CH_4 and N_2 (Figure 10). N_2 - CH_4 mixture indicates reducing conditions which could characterise the mineralisation genesis conditions in vg₁ (Qtz1 + chlorite + sericite-muscovite + pyrrhotite ± chalcopyrite ± Fe-rich sphalerite ± galena). This hypothesis is argued by the formation of pyrrhotite which is deemed to form under reducing conditions [65]. A similar fluid composition has been observed in quartz-chlorite-mineralised veins (mineralisation dominated by pyrrhotite) associated to massive sulphide deposit in the central part of Jebilet massif (e.g., Kettara pyrrhotite-rich massive sulphide deposit) where reducing conditions are also advanced [50, 66].

The presence of CH_4 in the studied inclusions would derive from the organic matter in the host black shales, explaining the higher proportions of CH_4 in the trapped fluids of the area. In the case of N_2 , according to Bastoul [67], a release of nitrogen occurs by the breakdown of NH_4 -bearing micas during the



FIGURE 10: Plot of representative microthermometric data of type 1, type 2, and type 3 fluid inclusions in T_h vs. $T_{m(ice)}$ binary diagram. (a) Quartz-chlorite-mineralised vein (Qtz1 and vg₁). (b) Qtz2-mineralised vein (vg₂). (c) Qtz3-mineralised vein (vg₄). (d) T_h mean of all fluid inclusion types in all quartz veins (see description in the text).

prograde metamorphic reactions. The black shales of the central Jebilet are enriched in organic carbon and phyllosilicates, so the production of CH_4 - N_2 fluids could be possible during prograde metamorphism, and they entrapment during ore forming process which postdate the pic of regional metamorphism.

In summary and based on the arguments presented above, the aqueous-gas-bearing fluid inclusions at the Roc Blanc deposit are consistent with the contribution of metamorphic fluids in the mineralising system and were probably mixed with aqueous relatively low temperature fluids. The mineralised fluids were eventually trapped at boiling state.

6.2. Timing of Mineralising Events and P-T Conditions. The mineralised veins postdate S_1 cleavage, which is axial planar to folds generated during the post-Visean tectonometa-morphic event ([45], [4]). So, the mineralisation was formed during or after the retrograde cooling phase of the metamorphism; indeed, the composition of aqueous gas-bearing fluid inclusions yields partly a metamorphic origin as emphasised

above. The presence of aqueous fluid inclusions (type 3) in all quartz-mineralised veins argued the retrogression metamorphic cooling, which largely involves rehydration reactions caused by waters from outside [63, 68] and that have probably flooded the sink site.

To constrain the P-T conditions of mineralised vein formations, the batch of isochoric curves was calculated from representative aqueous gas-free fluid inclusions (type 3) using the model of Zhang and Frantz [57] (Figure 11). The Qzt1 (vg₁: quartz + chlorite + sericite-muscovite + pyrrhotite \pm chalcopyrite \pm Fe-rich sphalerite \pm galena) and Qtz4 (vg₅: geodic quartz + calcite + Fe-poor sphalerite + Ag-tetrahedrite + Ag-Au-alloy) show a large field, giving unrealistic pressure trapping conditions. Contrariwise, the Qtz2 (vg₂: quartz + siderite/ankerite + pyrite + arsenopyrite) and Qtz3 (vg₄: quartz + chalcopyrite + ullmannite + (Ag-Sb) sulphosalts) yield a narrow field. The intersection of an approximate maximal T_h of type 3 fluid inclusions of Qtz2 (200°C) and Qtz3 (150°C) gives a maximum trapping



FIGURE 11: Representative isochores of two-phase aqueous gas-free fluid inclusions (type 3) in the Roc Blanc mineralised quartz veins. Isochores are calculated after the model of Zhang and Frantz [57].

pressure of about 1 and 1.1 kbar, respectively, relative to the deposition of the argentiferous stages (Figure 11). This must represent the pressure around which the Roc Blanc deposit was formed, potentially near 500 bars. Indeed, the mineralised veins at Roc Blanc deposit cross-cut each other, showing successive emplacement in time, but their inclusions yielded similar fluid compositions, which show that veins were formed relatively in the same context short spaced times.

On the other hand, the highest homogenisation temperatures are generally recorded in the Qtz2 (Figures 8(b), 8(d), 8(f), and 10(d)); the T_h of its fluid inclusions would represent an upper limit temperature of the Roc Blanc mineralising fluids ($350 \pm 20 \circ C$). These conditions work with the formation of the first quartz vein generations (vg₁ and vg₂). For the argentiferous phases, its deposition occurs at c. 100 to 210°C according to the T_h value of aqueous gasfree fluid inclusions of Qtz3 (vg₄) and Qtz4 (vg₅).

For ore deposition factors, no major characteristic has been observed under fluid inclusion studies to explain the difference in mineralogy of the ore stages. Considering all quartz-mineralised veins, a few significant observations are done in the type 3 fluid inclusions (observed in all quartz) where the mean T_h increases from Qtz1 (vg₁) to Qzt2 (vg₂) and decreases progressively towards Qtz3 (vg₄) and Qtz4 (vg₅) (Figure 10(d)). The same temperature evolution is shown also by type 1 and 2 fluid inclusions in vg₁, vg₂, and vg₄ quartz. These statements can indicate a rapid heating (vg₁ to vg₂) followed by progressive cooling (vg₄ to vg₅) in the general system. Note that silver-bearing minerals form in the latest veining system (Qtz3 and Qtz4); their genesis can then be linked to the cooling of mineralising fluids. 6.3. Metallogenic Type. The Roc Blanc Pb-Zn-Ag-Au veins are located at 2 km towards the NNE of the BTB Hercynian granodiorites. It is then spatially associated with the contact metamorphic aureole of this intrusion which reaches 5 km in diameter. The granodiorites and their surrounding aureoles (black shales) host several mineralised veins that are Sn-W mineralisation and Cu, Au, Sb, Pb, Ag, and Zn mineralisation, respectively, suggesting a metallic zoning around the BTB granitoids [2, 22]. This zoning could be represented by likely: Sn-W (1) \rightarrow Au-Cu (2) \rightarrow Pb-Cu-Zn (3) \rightarrow Sb-Ag-Au (4) zonations according to the model intrusion-related mineralisations established by Blevin [69].

The mineralisation of the Roc Blanc deposit containing As, Zn, Cu, Pb, Ag, Sb, Au, and Ni can then be related between the two later metallic zones around the BTB granodiorites: Pb-Cu-Zn-As $(3) \rightarrow$ Sb-Ag-Au ± Ni (4) mineralisation.

According to the structural relationship in the Roc Blanc area, the genesis of the deposits took place after regional schistosity elaboration; then, it occurred between the emplacements of late Variscan BTB granodiorite (327 ± 4 Ma; [30]) and post Variscan microdioritic dykes (255 to 241 Ma, [27, 36–38]). After Huon [70] and Huon et al. [71], the ore deposition occurs more probably around 290 Ma as the bulk of mineralisation formed syn- to postpeak greenschist-amphibolite facies metamorphism dated at 290 ± 4 Ma, while for Essaifi et al. [7], the genesis of mineralisation is related to the greisenhydrothermal system associated with emplacement of the Stype leucogranites at 305.9 ± 0.9 Ma, which also lead to the metal zonation around BTB intrusions.

According to our results, any direct link has been established between magmatism events and the deposit genesis (leak of clear magmatic fluids in studied inclusions). However, Pb and Sr isotopes from ore minerals indicate a magmatic origin of these elements [4], while calculated $\delta^{18}O_{\text{fluid}}$ (15 to 18‰) and C stable isotopes (-7.1 ± 1.2‰) obtained on carbonate mineral gangues are consistent with interactions of metamorphic fluids and organic-rich black shale [4]. Therefore, with respect to these data and the results from fluid inclusion studies presented here, two hypotheses could be set for the formation of the Rock Blanc deposit:

- (i) The first is the mobilisation of metals by metamorphic fluid (i.e., type 2 H₂O-CO₂-CH₄-N₂-salt fluid inclusions) from magmatic rocks and/or its surrounding host black shales and the deposition of ore into N-S fractures along the Marrakech Shear Zone at low pressure (below 1 to 1.1 kbar). This fluid was probably mixed with surface to subsurface fluids (i.e., type 3 aqueous fluid inclusions), with eventually cooling and boiling in the system, leading to the deposition of ore
- (ii) The second hypothesis is the circulation of surface to subsurface fluids (meteoric or brine) as convection cells through magmatic and host metamorphic rocks during retrograde cooling, where they have been enriched in metals and volatile components (CO₂-CH₄-N₂). This can lead to the formation of immiscible fluids (types 1 and 2). The ore deposition will occur by progressive cooling when mineralised fluid is driven toward the surface. After Pohl [63], this could take place during uplift and extensional tectonics where convection cells are open to the surface. So, this hypothesis will bring the formation of the Roc Blanc deposit near to Triassic basin opening

In all cases, the precipitation of the first mineralisation (preores Fe-As stage I, vg_1 , and vg_2) is linked to reducing conditions characterised by high temperature (c. $350 \circ \pm 20 \circ C$), and the argentiferous mineralisation (main vein-filling stage II; vg₃, vg₄, and vg₅) precipitated during decreasing temperature (below 200°C), where all the mineralised systems were cooling. The salinity of these two main mineralising fluids, stage I and stage II, is similar with values ranging from 3.7 to 19.4 wt% NaCl equiv. (mean = 13.7 wt%NaCl equiv.) and 4.1 to 19.6 wt% NaCl equiv. (mean = 12.1 wt%NaCl equiv.), respectively. The ore-forming fluids were trapped into N-S fractures, near surface to subsurface conditions at pressure below 1.1 kbar, potentially around 500 bars and at boiling state. According to Chouhaïdi [12] and Benchekroun and Essarraj [11], the precipitation of silver-bearing minerals is likely due to the decrease of salinity, fluid temperature, and fO_2 and the increase of fluid pH. However, in our case, just a slight decrease of salinity was observed from vg_2 to vg_4 .

The age of ore deposition remains a main question of debate. According to structural relationship, it may occur around the period of the leucogranite dyke emplacement or more after all Variscan-related magmatic events, during the extensional phase. Our data combined with literature review argues more with a link with late Variscan leucogranite intrusions emplacement, e.g., [7]. In fact, an abrupt increasing temperature in the mineralising system is recorded in the Qtz2 vein (vg_2) (Figure 10(d)). This would be related to a rapid heating which can be caused only by a shock temperature of magmatic rock emplacements because the hosting rocks were in retrograde metamorphism sequence. On the other hand, any magmatic fluid has been detected through fluid inclusion studies; therefore, ore forming fluid circulated around leucogranite intrusion when it was cooling. Then, the leucogranite dyke contributed by its temperature and may also provide some metallic elements to ore-forming fluid.

To conclude, a metamorphic fluid would have played a major role for metals collecting from intrusions and their surrounding host organic-rich black shales and their deposition at near surface environment.

7. Conclusion

The Pb-Zn-Ag-Au deposit of Roc Blanc occurs as N-S to NNW-SSE veins hosted in the contact metamorphism area of the BTB intrusions. The mineralisation was deposited in three main stages (through five generations of quartz- and carbonate-mineralised veins): (1) a preore stage represented by vg_1 and vg_2 , with Fe, As, Zn, and Cu mineralisation (stage I); (2) the main stage composed mainly by Ag, Au, Pb, Zn, Cu, and Sb bearing minerals, observed in vg_3 , vg_4 , and vg_5 (stage II); and (3) the postore stage corresponding to an unmineralised phase made up of chlorite, sericite, and quartz minerals (stage III).

Fluid inclusion studies carried out on quartz-bearing ores (Qtz1, Qtz2, Qtz3, and Qtz4, from vg1, vg2, vg4, and vg₅, respectively) show the presence of three fluid types which consist of H2O-N2-CH4±CO2-(salt) fluid (type 1), H₂O-CO₂-CH₄-N₂-(salt) fluid (type 2), and H₂O-(salt) fluids (type 3). Microthermometric data of the type 2 aqueous gas-bearing fluid inclusions (H₂O-CO₂-CH₄-N₂-salt) gave a homogenisation temperature ranging from 250°C to 380°C and a relative moderate salinity estimated at 14 wt% NaCl equiv.; this fluid is related to metamorphic origin. For the type 3 aqueous fluid $(H_2O(salt))$, the homogenisation temperatures and salinities give an average value of 150-160°C and 13 wt% NaCl equiv., respectively. These characteristics are consistent with epithermal fluids, originating from surface to subsurface. The type 1 fluid inclusion $(H_2O-N_2-CH_4\pm CO_2-(salt))$ would result from the mixing of these two latest types which are aqueous-gas-bearing and aqueous gas-free fluids. This process tends to equilibrate the two fluids generating an intermediate fluid composition and temperatures as in the type 1 ($T_h = 104 - 288 \circ C$).

Interpretation of fluid inclusion data in the mineralised veins indicates that fluid is resulted from the mixing of at least two fluids trapped at boiling state. The P-T conditions of ore formation are below 1.1 kbar, and $350 \pm 20 \circ C$ for stage I and c. 150°C for stage II. Their mean salinities are 13.7 and 12.1 wt% NaCl equiv., respectively. Dilution and cooling were the main mechanism of argentiferous ore mineral precipitation in the Roc Blanc deposit, caused by the mixing probably of metamorphic fluid (H₂O-CH₄-N₂-CO₂) with surface to subsurface aqueous gas-free fluids (H₂O-salt, meteoric, or brine).

Data Availability

This study constitutes a continuum of the first author's PhD thesis of Ag-Pb-Zn ores in the Roc Blanc deposit. The studies were carried out at the DLGR Laboratory (Cadi Ayyad University, Marrakech) and at the REMINEX Research Center and Laboratory (Morocco).

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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