

Penetration of surface-evaporated brines into the Proterozoic basement and deposition of Co and Ag at Bou Azzer (Morocco): Evidence from fluid inclusions

Samira Essarraj ^a, Marie-Christine Boiron ^{b,*}, Michel Cathelineau ^b,
David A. Banks ^c, Mohamed Benharref ^d

^a *Faculté des Sciences et Techniques, Département de Géologie, BP 618, Marrakech, Morocco*

^b *UMR CNRS G2R 7566 and CREGU, BP 23, 54501 Vandoeuvre-lès-Nancy Cedex, France*

^c *School of Earth Sciences, University of Leeds, Leeds LS2 9JT, UK*

^d *MANAGEM-Groupe ONA, Twin Center-Tour A, BP 16016 Casablanca, Morocco*

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Abstract

Ag-ores occur in a specific zone of the Bou Azzer Co–As deposit in the Precambrian basement of the Anti-Atlas belt (Morocco), especially in highly microfractured quartz-depleted diorite. They formed after the main Co–As stage of mineralization, but both ore stages (Co–As and Ag-ore) appear linked to similar immiscible fluids: an hyper-saline Na–Ca brine (5.5–22 wt.% eq. NaCl and 13.5–18.5 wt.% eq. CaCl₂, with Na/Ca ranging from 0.4 to 1.2 during Ag-mineralization) occurring as L + V ± halite fluid inclusions and CH₄–(N₂) gas dominated fluids. Pressure–temperature estimates for the Ag-stage range from 40 to 80 MPa and 150 to 200 °C e.g. at a temperature slightly lower than that of the preceding Co–As stage (200–220 °C).

Chlorinity, cation (Na/Ca ca. 2.2) and halogen ratios (Cl/Br from 300 to 360) are typical of deep basinal brines, especially of surface-evaporated brines that have exceeded halite saturation. The primary brines were modified by fluid–rock interaction during burial and migration through the basement. Ag-deposition was probably favoured by dilution and cooling due to the mixing of brines with less saline fluids. Similarities between the Ag-brines from Bou Azzer, Zgounder and Imiter suggest a regional scale circulation of basinal brines during extension probably later than the Triassic, during the early stages of rifting of the Atlantic.

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1. Introduction

Silver mineralization in the cobalt district of Bou Azzer constitutes one of the Ag-occurrences from the Precambrian basement of the Anti-Atlas belt (Morocco), which also hosts the Zgounder and Imiter silver

deposits, amongst others. Previous studies of the mineral assemblages have shown similarities between the Bou Azzer silver mineralization and the Cobalt–Gowganda (Canada) type of silver-deposit (Andrews et al., 1986). In both deposits: (i) veins cross-cut metamorphosed Precambrian rocks, (ii) the first Co–Ni sulphur–arsenides association is followed by silver ores, (iii) the average silver grade is similar (500–600 g/t Ag) and (iv) a K-feldspar–albite hydrothermal alteration affects the wall rocks (Leblanc and Lbouabi, 1988). At Cobalt–Gowganda, the Ag-deposit is interpreted to

* Corresponding author. Tel.: +33 3 83 68 47 30; fax: +33 3 83 68 47 01.

E-mail address: marie-christine.boiron@g2r.uhp-nancy.fr (M.-C. Boiron).

result from the cooling and/or dilution of brines (Godwin et al., 1986; Marshall et al., 1993). At Bou Azzer, Leblanc and Lbouabi (1988) have associated silver deposition with K–Na metasomatism at an inferred temperature between 200 and 350 °C and a relatively high pressure of around 200–300 MPa. This P – T range is based on the alteration mineralogy and geochemical data. Previous fluid inclusion studies, based on microthermometry, a few qualitative Raman data and SEM observations on secondary fluid inclusions in quartz and calcite from the Co–As ores, have reported the existence of brines, sharing “surprisingly, a number of common characteristics with trapped brines associated with paleo-evaporites” (En-naciri et al., 1997). However, no detailed determination of ore fluid chemistry nor precise P – T evolution based on isochore calculation was available, and no data was available on the Ag-rich zones.

New investigations of the Bou Azzer ores, especially the Ag-ore zones, have shown a more complex evolution of fluids, especially the co-existence of brines with meth-

ane-nitrogen-rich fluids. Thus, the main objective of this study was to determine the nature of the ore fluids in the Ag-rich zones and their possible origin, and to compare ore fluids in the Ag-rich zones with those from the Co–As ores. Special attention has been paid to the fluid composition (gas, major cations, halogens) determined by Raman spectroscopy, microthermometry and bulk-leachate analysis, in order to examine the significance of the main fluid event which resulted in the genesis of the Bou Azzer deposit.

2. Geological setting

The Bou Azzer polymetallic deposit is located about 320 km east of Agadir in the Precambrian formations of Bou Azzer-El Graara (central part of the Anti-Atlas mountains, Fig. 1). The deposit has been exploited for cobalt since 1933 by the CTT company (ONA group), and silver exploitation began in 1988.

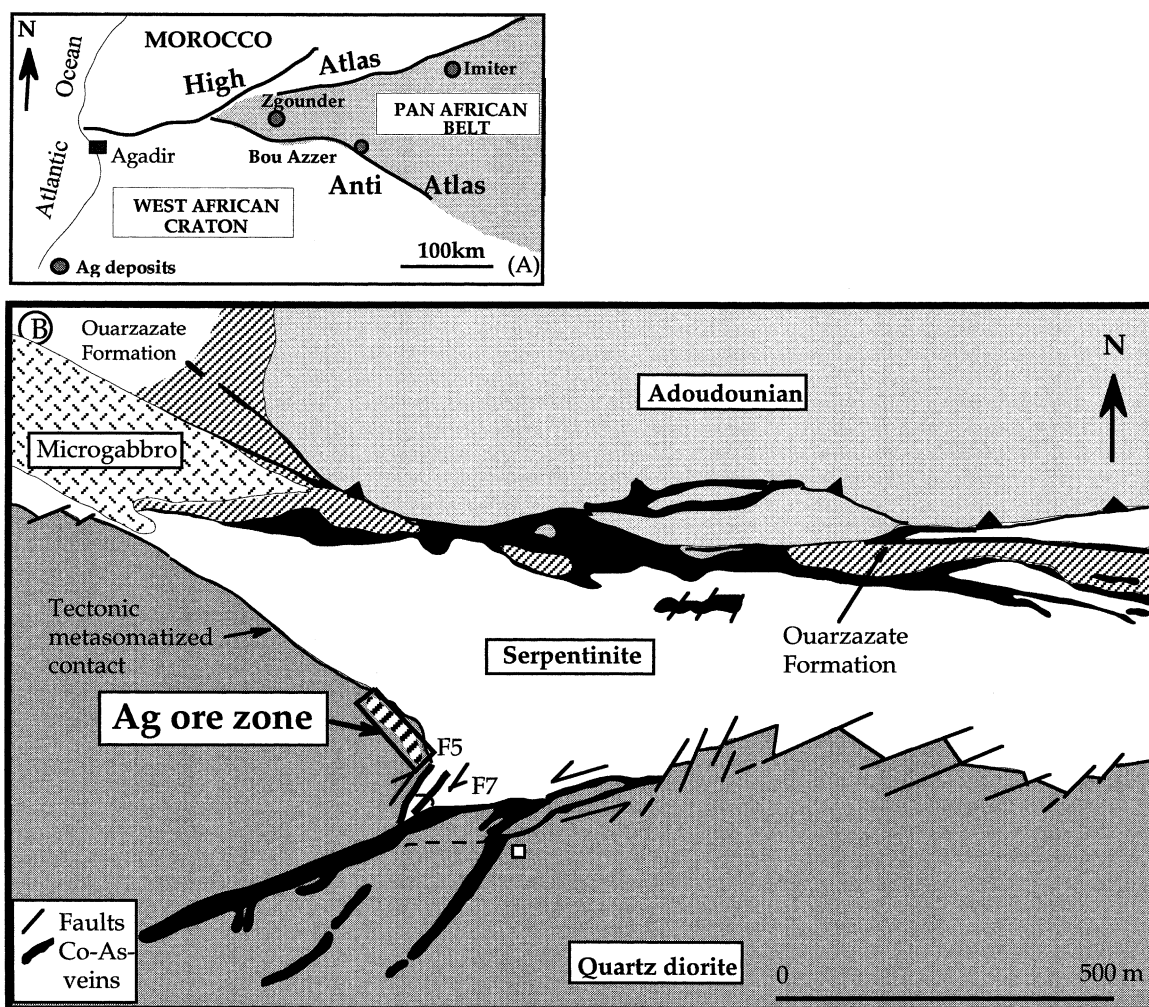


Fig. 1. Regional geology of the Bou Azzer deposit. (A) Location of the silver deposits in the Precambrian belt in the south of Morocco (Leblanc and Lbouabi, 1988) and (B) local geology of the Bou Azzer mine (Leblanc, 1975), with location of silver ore zone (box detailed in Fig. 2).

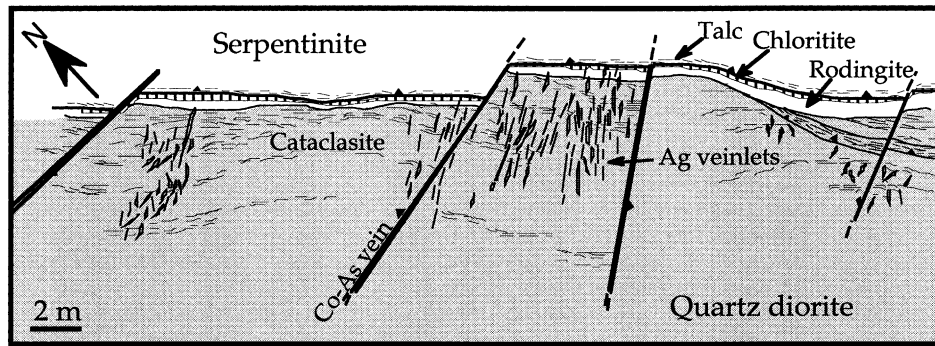


Fig. 2. Structural sketch of the silver ore zone in the serpentinite-quartz diorite contact and distribution of silver mineralization (from Leblanc and Lbouabi, 1988).

The Bou Azzer-El Graara area is a part of the 680–580 Ma Pan-African orogenic belt. It is located along the main Anti-Atlas thrust, a major east-west trending fault zone which constitutes the northern boundary of the West African Eburnean craton with an age of 2000 Ma, (Caby, 1970; Leblanc, 1975). The Pan-African orogeny started by rifting and formation of an ophiolitic complex during the Middle Precambrian (so-called PII), around 788 ± 9 Ma (Rb/Sr dating; Clauer, 1976). Two tectonic phases are distinguished. The first and major B1 phase (Leblanc, 1975), dated at 685 ± 15 Ma (Rb/Sr; Clauer, 1976) consists of the obduction of the ophiolitic complex in a southerly direction onto the northern margin of the West African craton and serpentinisation of its ultramafic rocks. The B2 tectonic phase is dated at 623 ± 18 Ma (Rb/Sr; Clauer, 1976), and at 615 ± 12 Ma (U–Pb; Ducrot, 1979). A back-arc basin formed and was filled by a syn-orogenic volcano-sedimentary series at the end of the Middle Precambrian (PII–PIII), and finally by the Ouarzazate volcano-sedimentary formations during late Precambrian (PIII). At the end of the Precambrian (PIII), a marine transgression, over the Anti-Atlas, led to the deposition of the Adoudounian marine sediments at 534 ± 10 Ma based on U/Pb data of Ducrot and Lancelot (1977) from the Jbel Boho volcano.

The Bou Azzer deposit is mainly exploited for Co–As ores which occur along the borders of serpentinite massifs, (Fig. 1b), and consists of quartz–carbonate–(Co–As) veins with a low Ag content (30 g/t). The Ag-mineralization (500 g/t) occurs in a limited ore zone in the western part of the mine (Figs. 1b and 2) characterised by a specific hydrothermal alteration along the contact between the altered quartz diorite and the serpentinites.

3. Ore mineralogy and paragenesis in silver ore zone

Ag-ores are found in the altered quartz diorite as disseminated ores within a vuggy alteration facies (quartz depleted diorite so-called “episyenite”), and in the

microfractured chloritized quartz diorite. This altered and Ag-mineralised contact is the so-called “silver ore zone”. The genesis of the ores is however later than the hydrothermal alteration which produced the formation of the reservoir rock for the subsequent mineralising event.

3.1. Pre-ore stage: Reservoir rock formation

Quartz depleted rocks, so-called “episyenites” (Cathelineau, 1986) were found in the quartz diorite, in the vicinity of metasomatic transformation zones that occur along the tectonic contact between serpentinite and quartz diorite. Thus, a zoning of rock types occur from the fresh quartz diorite to the serpentinite (Fig. 2): massive quartz diorite, cataclastic quartz diorite, rōdingite, talc, chloritite and serpentinite (Leblanc and Lbouabi, 1988).

In the episyenite zone, the host diorite was affected by the following succession of events: (i) quartz diorite underwent ductile deformation, and displays cataclastic textures, (ii) a strong hydrothermal alteration caused the complete dissolution of magmatic quartz grains, leaving empty vugs (Fig. 3A). The total dissolution of quartz led to the formation of a porous altered rock (episyenite), resulting in a major depletion of Si, Mg, Ca and gains in Fe (Leblanc and Lbouabi, 1988), (iii) the episyenite was then affected by fluid circulation which were responsible for the ore deposition and further alterations such as the crystallisation of adularia and albite (gains in Na and K).

3.2. Ore stages

Two mineral associations are distinguished in the ores as shown in Fig. 4:

- Ore stage I (Co–Fe–arsenide): this stage is characterised by polymetallic ore assemblages disseminated in the quartz diorite: (i) a Co–As–Fe mineralization with rare cobaltite followed by safflorite (Co–As)

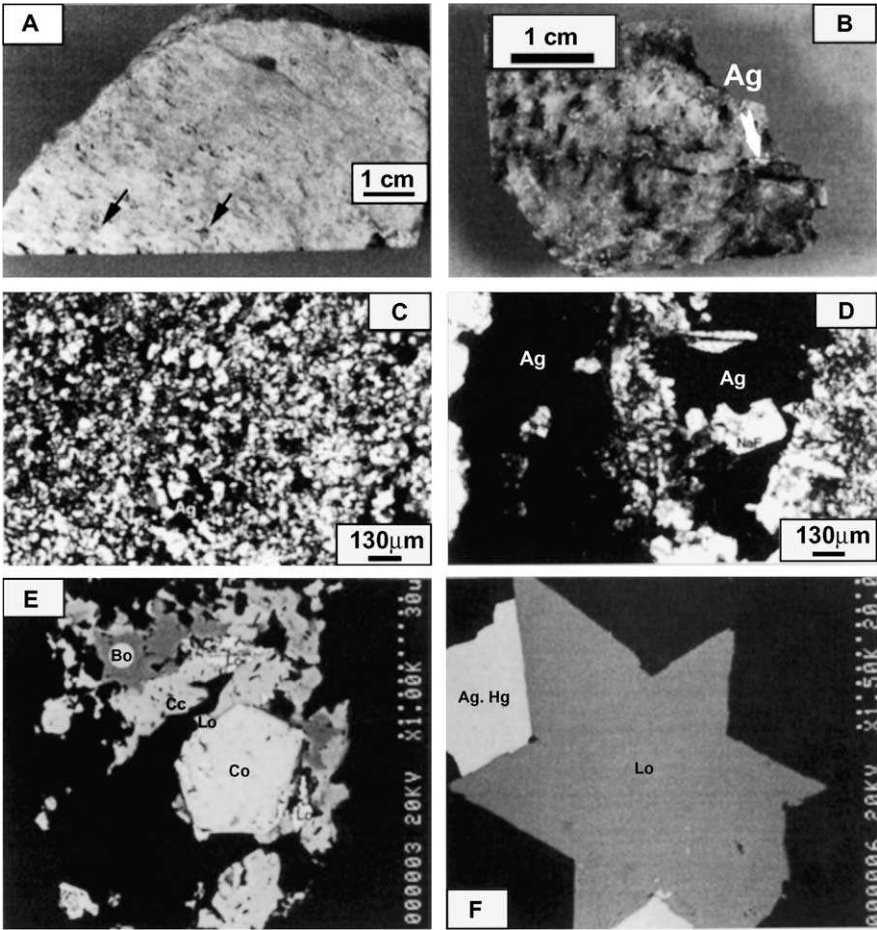


Fig. 3. (A) Hand specimen of Bou Azzer quartz depleted quartz diorite (episyenite) formed in a rather deformed zone (mylonitic area) with Ag-minerals (arrows) crystallising both in vugs resulting from quartz dissolution and in grey albite–adularia veinlets. (B) Hand specimen of non-altered quartz diorite from the silver ore zone, showing that Ag-minerals crystallised only in micro-fractures (arrows). (C) Ag-minerals (opaque minerals) are localised in a cryptocrystalline albite–adularia matrix. (D) Photomicrograph of a sample from the episyenite Ag-mineralised zone of Bou Azzer showing that no corrosion of albite (NaF) and adularia (KF) crystals is observed when in contact with Ag-minerals (Ag). (E) Early cobaltite (Co) with löllingite (Lo) and bornite (Bo). Bornite is altered into chalcocite (Cc) (SEM, backscattered photomicrograph). (F) Crystallisation of Ag–Hg amalgam onto löllingite (Lo) from the preceding stage (SEM, backscattered photomicrograph).

Minerals	Co - As stage	Ag-Hg stage
Cobaltite	—	
Safflorite	—	
Löllingite	—	
Quartz-calcite-chlorite	—	
Sphalerite	—	
Tennantite	—	
Chalcopyrite	—	
Bornite	—	
Galena	—	
Albite-Adularia		—
Ag-Hg Amalgam		—
Native Ag		—
Fluid inclusion types		
Lws (and Vm-n)	—	
Lw/Lwh and Lm-n	—	—

Fig. 4. Paragenetic sequence of the Bou Azzer silver ore zone and associated fluid types (see text for abbreviations concerning fluid types).

and loellingite (Fe–As) similar to those found in quartz–calcite veins from the Co–As veins (Fig. 3E), and (ii) base metal sulfides and sulfosalts showing a succession of sphalerite–tennantite–chalcopryrite–bornite and galena. Ore stage I minerals are less abundant in the Ag-ore zones than in the main Co–As rich ore-bodies. It can be noted that Co–As minerals, in the main carbonate veins, are undeformed.

- Ore stage II (Ag–Hg–paragenesis): as already described in Leblanc and Lbouabi (1988), Ag-minerals are Ag–Hg amalgam, acanthite and native silver (Fig. 3C and F). In the chloritized quartz diorite, the minerals fill microfractures (a few millimeters in width, Fig. 3B), and crystallise sometimes in close association with clear quartz overgrowths. In the altered quartz diorite (episyenite), they fill vugs resulting from quartz dissolution, and crystallise onto euhedral albite and adularia crystals which appear closely linked with the Ag-ores (Fig. 3D). Small Ag-grains are also found in the corrosion zones of early arsenides and sulfides disseminated within the chloritized quartz diorite. Therefore, Ag-minerals crystallise in apparent equilibrium with quartz–albite and adularia, but corrode early sulphides.

Mineral assemblages from the two stages are undeformed and precipitated in opened fracture or vugs.

4. Fluid inclusion study

4.1. Methods

The description of fluid inclusions follows the convention of Boiron et al. (1992). It is based on the type of total homogenisation T_h (L–V to the vapor noted V, L–V to the liquid noted L) and the nature of the fluid components (subscript c, when C–H–O–S species are dominant; m or n, for CH₄ and N₂ species, respectively; w for water, s for solids and h for halite cube). The subscripts consist in a combination of the letters as a function of the abundance of the various species in the fluid.

Fluid inclusions were studied by microthermometry on doubly polished wafers, from approximately 20 samples, using a Chaix-meca heating-freezing stage (Poty et al., 1976). For microthermometric data, abbreviations are used as follows: T_c : temperature of ice–first melting; T_{mice} : final melting temperature of ice, T_{mh} : final melting temperature of hydrohalite, T_{mh} : final melting temperature of halite crystal, T_h (L–V): total homogenisation temperature (L + V to liquid or L + V to vapor). Salinity calculations for Ca-bearing aqueous fluids were carried out using the algorithm of Naden (1996) based on the data from Oakes et al. (1990). Chlorinity was also analysed in individual fluid inclusion by Raman spectroscopy following the methodology described by

Dubessy et al. (2002). Molar fractions of CH₄ and N₂ were determined in individual inclusions by micro-Raman analysis performed on a DILOR LABRAM Raman spectrometer at CREGU, Nancy. Bulk composition and molar volume were computed from the P – V – T – X properties of individual inclusions using the data of Holloway (1981) for variable proportions of CH₄ and N₂.

Bulk crush-leach analyses were performed on samples of quartz and calcite devoid of mineral inclusions. Samples were prepared and cleaned using the methods in Banks et al. (2000). Analysis of anions Cl, Br, I, and SO₄ were carried out by ion chromatography on doubly distilled water leachates. Na, K and Li were determined on the same solutions by flame emission spectroscopy, and cations Na, K, Li, Ca, Mg, Ba, by ICP-AES.

4.2. Results

In the silver ore zone, fluid inclusions have been studied mainly in healed microfractures from the Ag-mineralized quartz diorite. Microfractures cross-cut all previous ductile deformation textures and are well preserved, in a few cases, fluid inclusions in calcite as well as feldspars from the quartz-depleted diorite have been studied. The discrimination of fluid generations, their relative chronology and the fluid inclusion typology in the different ore zones has been determined from the fluid inclusion composition, vapor filling, presence of daughter crystals and textural relationships. Microthermometric data and Raman analyses are summarised in Tables 1 and 2.

4.2.1. Pre-ore stage: ore reservoir formation

Several types of inclusions occur as cluster-like associations in magmatic quartz grains (Fig. 5) or in secondary fluid inclusion planes. Only diorite samples from the contact zone with the episyenite show the specific relationships between these fluids and the quartz dissolution event. Two-phase inclusions (L_w , and V_w) are found with variable vapor filling (10–90%) which are interpreted as the result of heterogeneous mixing between liquid and vapor. T_c is mostly around -40 °C, T_{mice} has been recorded between -13 and -0.1 °C, and T_h between 200 and 360 °C (to the liquid phase). V_w inclusions are difficult to study because of the small size of liquid phase but T_{mice} has been recorded at -2 – 0 °C and total homogenisation determined in a few cases between 380 and 400 °C.

In the T_{mice} – T_h plot (Fig. 7), several sets of fluid inclusions can be distinguished: (i) a first group is characterised by T_{mice} around $-0.5/0$ °C and highly variable T_h , and (ii) series of fluid inclusion planes displaying smaller ranges of T_h – T_{mice} pairs for a given fluid inclusion plane, the whole set of data covering however a

Table 1

Summary of the microthermometric data from the different types of fluid inclusions at the Bou Azzer silver ore zone and chemical composition of volatile fluid inclusions obtained by Raman microprobe analysis

Inclusion types			Microthermometry					Raman data
			T_e	$T_{m\text{ ice}}$	T_h (L–V)	T_{mh}	T_h (CH ₄ –N ₂)	
<i>Pre-ore stage</i>								
L_w (<20 μm)	Primary and secondary FI in magmatic quartz of quartz diorite		–57/–40	–13/–0.1	200/360 L			
H ₂ O–NaCl–CaCl ₂			–40	–6 and –1				
V_w (<10 μm)			38	263	186			
				–2/0	380/>400 V			
<i>Co–As stage</i>								
L_{ws} (5–40 μm)	Primary and mostly secondary FI in hydrothermal quartz from Co–As veins (Co–As ore zone)		–79.9/–67.1	–52/–33.1	111/208 L	191 to >274 (> T_h (L–V))		
H ₂ O–NaCl–CaCl ₂			49	–40; –34	180	220		
V_{m-n} (<20 μm)							–104.8/–64.1 V	CH ₄ : 43–65 mol%
CH ₄ –N ₂ –(CO ₂)		halite?					–95	N ₂ : 35–57 mol%
							24	CO ₂ : traces
<i>Ag–Hg stage</i>								
$L_{w'}$ and L_{wh} (<10 μm)	Secondary FI in magmatic quartz of quartz diorite (Ag-ore zone)		–80/–67.1	–46/–16	90/220 L	126/230 (< T_h (L–V))		
H ₂ O–NaCl–CaCl ₂			–74	–28	140			
L_{m-n} (<15 μm)			114	170	180	22	–99/–81.8 L/C	CH ₄ : 82–100 mol%
CH ₄ $\pm$ N ₂							119	N ₂ : 0–18 mol%
								CO ₂ : nd

Ranges, modes and number of measurements (in bold) are given for each microthermometric parameter. T_e : eutectic temperature, $T_{m\text{ ice}}$: melting temperature of ice, T_h : homogenization temperature, T_{mh} : melting temperature of halite. All values in °C. L: liquid, V: vapor, nd: not detected.

Table 2

Summary of the Raman data and corresponding T_h for CH_4 – N_2 fluids

	Sample	Inclusion	T_h °C	Mode	CH_4 (mol.%)	N_2 (mol.%)
Co–As stage V_{m-n} inclusions	BZ7-1	2	–90.7	V	45	55
	BZ7-1	3	–69.1	V	43	57
	BZ7-1	5	–64.1	V	46	54
	BZ7-2	8	–104.8	V	55	45
	BZ7-2	9	–97.1	V	65	35
Ag–Hg stage L_{m-n} inclusions	BO3-10	15	–82.8	C	98	2
	BO3-10	16	–84.2	C	100	0
	BO5-1	4	–97.7	L	83	17
	BO6-2	3	–94.1	C	83	17
	BO6-2	12	–93.4	L	82	18
	BO7-8	1	–91.8	C	86	14
	BO7-8	4	–94.8	C	87	13
	BO7-8	8	–91.3	L	85	15
	BO7-9	1	–85	L	100	0
	BO7-9	5	–84.1	L	98	2

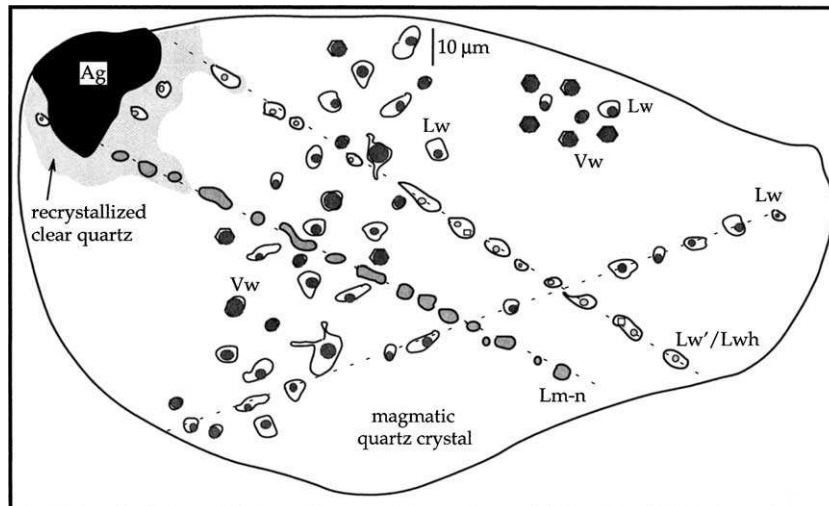


Fig. 5. Sketch showing textural relationships between fluid inclusion types and silver mineralization (Ag) in a magmatic quartz crystal from quartz diorite in the silver ore zone.

rather extended range of T_h (200–400 °C) and T_{mice} (–10/–1 °C). Few T_{mice}/T_h pairs are available for V_w fluid inclusions with T_{mice} from –1 to –2 °C, but no T_h could be obtained precisely for the vapors of very low salinity (Fig. 6). For L_w and V_w fluid inclusions, salinities are calculated in the H_2O – NaCl system and range between 0.3 and 17 wt.% eq. NaCl .

4.2.2. Co–As-ore stage

Healed microfractures cross-cutting quartz and carbonate in the Co–As mineralised veins from the Co–As ore zone, and micro-fractured Ag-mineralised diorite contain two fluid inclusion types: (i) three-phase ($L + V + H$, noted L_{ws}) containing an aqueous liquid, a vapor bubble and halite and (ii) rare one-phase dark fluid inclusions dominated by methane and nitrogen (Fig. 6A to E).

Three-phase inclusions (L_{ws}) are brines with low T_e , ranging from –79.9 to –67.1 °C. T_{mice} occurs in the range of –52 to –33.1 °C (Fig. 8A). Occasionally, metastable melting temperatures of a salt hydrate (probably hydrohalite) are recorded between +1° and +20 °C. T_h (L – V) occurs between 111 and 208 °C and T_m h between 191 °C and 274 °C. Numerous fluid inclusions with large halite crystals decrepitated before halite dissolution. Salinities calculated in the H_2O – NaCl – CaCl_2 system, on the basis of T_{mice} , T_m h and T_m h are 16–24 wt.% NaCl and 21–23 wt.% CaCl_2 with a Na/Ca ratio ranging from 0.7 to 1.1. Raman analyses show that the vapor phase contains traces of CH_4 and N_2 and sometimes CO_2 , but no clathrates were observed.

One-phase dark inclusions (V_{m-n}) (Fig. 6D) contain CH_4 and N_2 vapor and minor amounts of CO_2 . The

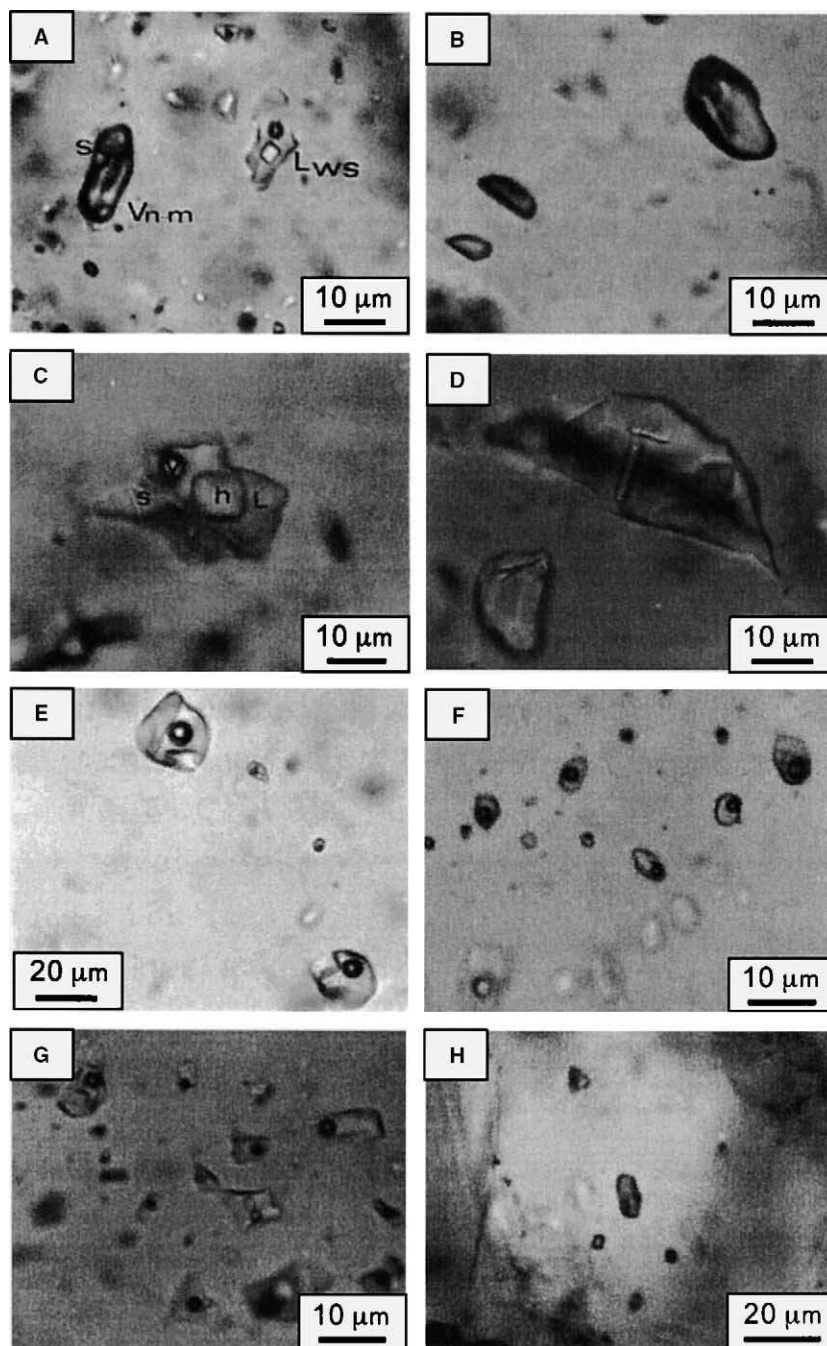


Fig. 6. Photomicrographs of the different types of fluid inclusions. (A) V_{m-n} inclusions coexisting with L_{ws} inclusions in the Co–As mineralised veins. (B) V_{m-n} inclusions in Co–As-bearing quartz. (C) and (D) L_{ws} saline inclusions showing a liquid phase (L), a vapor phase (V), a halite cube (h) and non-identified solids (s). (E) L_{ws} fluid inclusion plane in Co–As-bearing quartz. (F) $L_{w'}$ fluid inclusion plane in quartz from the diorite (Ag stage). (G) L_{wh} inclusions in quartz from the diorite (Ag stage). (H) L_{m-n} inclusions in late feldspar closed to the Ag-minerals.

CH_4 content is between 43 and 65 mol.% and N_2 between 35 and 57 mol.% (Table 2).

4.2.3. Ag-ore stage

The identification of the Ag–Hg ore fluids was based on the textural relationships between fluid inclusions and Ag-minerals. Thus, two phase ($L_{w'}$), associated with rare three phase (L_{wh}) and volatile-rich fluid inclusions (L_{m-n}) were found in close association with Ag–Hg ore

(Fig. 6F–H). They are especially observed as scarce inclusions in small clear quartz preceding or synchronous with silver minerals (Fig. 5) and as clusters in the adularia coating the Ag-mineralised vugs. Similar fluid inclusions occur as secondary inclusions in healed micro-fractures in quartz and calcite.

L_w and L_{wh} inclusions have T_e ranging from -80 to -67.1 °C, T_{mice} from -46 to -16 °C, T_h (L–V) from 90 to 220 °C and T_{mh} from 126 to 230 °C (T_{mh} only

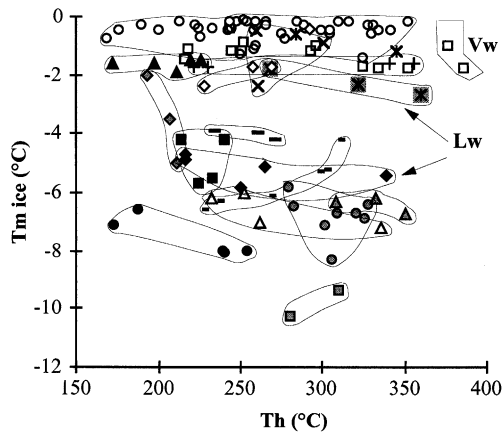


Fig. 7. T_{mice} versus T_h diagram applied to early aqueous fluid inclusions (L_w and V_w) from the altered quartz diorite in the silver ore zone (proximity of episyenite). Fluid inclusions that are secondary (L_w in microfissure planes, full symbols) in magmatic quartz from diorite are grouped by plane. Each group of full symbols are relative to a fluid inclusion plane.

for L_{wh} inclusions). Data interpreted in the H_2O – $NaCl$ – $CaCl_2$ system yield the following estimates: 5.5–22 wt.% eq. $NaCl$ and 13.5–18.5 wt.% eq. $CaCl_2$ with Na/Ca ranging from 0.4 to 1.2. Three distinct trends could be observed in the T_{mice} – T_h plot (Fig. 8B): (i) lower T_{mice} values at decreasing T_h from 240 to 150 °C; (ii) at sub-constant T_h (140 ± 10 °C), a wide range of T_{mice} ; and (iii) inclusions with a spread of T_h at constant T_{mice} values of around -30 ± 3 °C.

L_{m-n} fluid inclusions occur as (i) scarce inclusions in albite and adularia, in close association with L_w inclusions in the altered diorite and mostly as (ii) secondary inclusions along micro-fractures cross-cutting the quartz of the diorite with similar orientations to the brine inclusions (L_w/L_{wh}) (Fig. 5). L_{m-n} inclusions have T_h values ranging between -99 and -81.8 °C and homogenise to

the liquid state. They are dominated by CH_4 with minor amounts of N_2 (CH_4 from 82 to 100 mol.% and N_2 from 0 to 18 mol.%). No CO_2 has been detected in these inclusions by Raman spectroscopy (Table 2).

4.3. Comparison between fluids related to the Co–As and Ag-stage

Fluids associated with the deposition of Co–As assemblages in the Co–As ore area and those related to silver deposition in the silver zone are broadly similar being Na – Ca brines accompanied by $CH_4 \pm N_2$ -rich fluids. Nevertheless, some differences were found between the Co–As and the Ag-ores. Co–As brines are oversaturated with respect to halite at room temperature and Ag-brines are mostly halite undersaturated (L_{wh} represents approximately 15% of Ag-brine fluid inclusions). The T_{mh} – T_h (L – V) plot, applied to saturated brines, (Fig. 9)

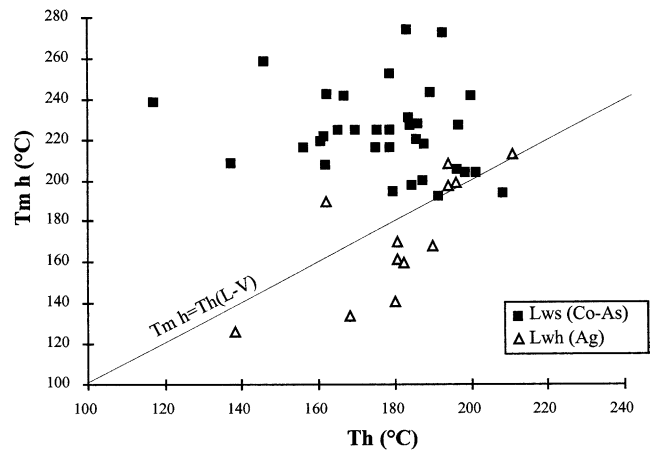


Fig. 9. T_m halite versus T_h (to the liquid phase) diagram representing brine fluid inclusions from the silver ore zone (L_{wh} –Ag) and Co–As ore zone (L_{ws} –Co–As).

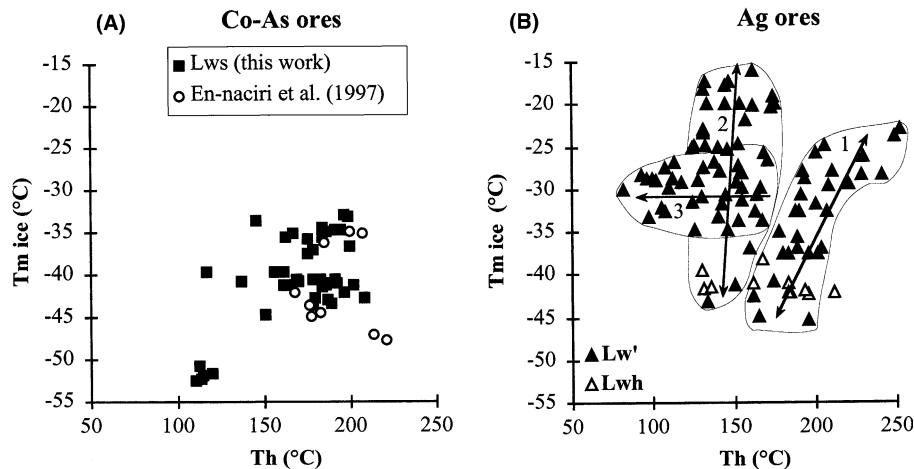


Fig. 8. T_{mice} versus T_h (L – V) for fluid inclusions from: (A) Co–As ore stage (Co–As ore zone) with a comparison of data from this work with those from En-naciri et al. (1997) and (B) Ag-ore stage (silver ore zone). 1, 2, 3 represent the three distinct trends described in the text.

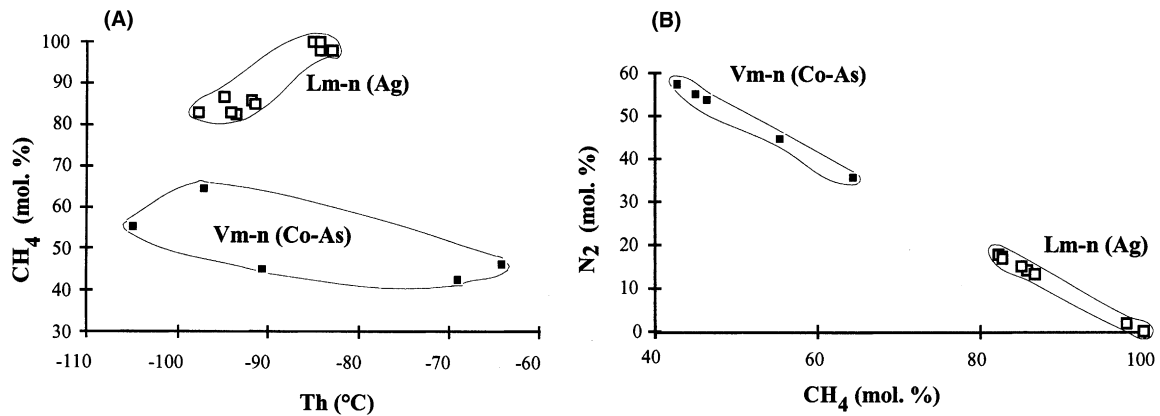


Fig. 10. CH₄ (mol.%) versus T_h diagram (A) and CH₄ (mol.%) versus N₂ (mol.%) diagram (B) for volatile fluid inclusions from the Co–As ore zone (V_{m-n} inclusions) and from the silver ore zone (L_{m-n} inclusions), analysed by Raman spectroscopy.

shows that T_{mh} is systematically higher than T_h (L–V) for Co–As brines, but mostly similar or lower than T_h (L–V) for Ag-brines. In addition, the $T_{mice}-T_h$ (L–V) diagram (Fig. 9) shows that the Ag-brines have similar or lower T_h (L–V) than the Co–As brines and have undergone a dilution process.

The V_{w-n} fluid inclusions, described for the first time in both Co–As and Ag-ores, can be considered as immiscible fluids trapped during the same event as the brines. Comparison of the gas composition (Fig. 10) shows that CH₄-volatile inclusions from the Co–As-ore are vapors enriched in N₂ and those from the Ag-ore are liquid inclusions, with minor amounts of N₂.

5. Physical and chemical conditions of ore stages

5.1. Pre-ore stage: The episyenite formation

The pre-ore stage is characterised by quartz dissolution within a quartz diorite and is related to the circulation of low salinity, high temperature aqueous fluids (V_w and L_w inclusions). The close association of vapors and liquids with highly variable densities are interpreted as the result of heterogeneous trapping. This feature is the most typical of boiling zones in geothermal systems where products of boiling (vapors and liquids) mix with the residual parent fluid (Ruggieri et al., 1999). It is shown by the contamination of the vapors which are abnormally enriched in salt because of mixing with parental fluids, or liquids produced by boiling. In these systems, liquids with very low salinities (close to 0 eq. wt.% NaCl) are found and considered as the products of vapor condensation, one of the only processes yielding hot, nearly pure water (Ruggieri et al., 1999). It is noteworthy that quartz dissolution has been considered as the result of interactions between a fluid of very low salinity from the condensation of aqueous vapors in other occurrences of episyenites (El Jarray et al.,

1994). Therefore, fluids at Bou Azzer in samples close to the episyenite are likely to be similar to those related to the main quartz dissolution stage.

5.2. Ore formation at Bou Azzer

The co-existence of the brines and CH₄-rich fluids suggest that they were probably immiscible and were trapped under similar conditions. An estimation of the P – T conditions for the Ag-ores may be obtained by the intersection of the isochores of the two fluid inclusion types (L_w and L_{wh} , and L_{m-n}), as no other mineralogical constraints are available. The steep isochores of L_w fluid inclusions provide a rather good temperature bracket of 150–200 °C, and the flat isochores of L_{m-n} fluid inclusions a pressure range of 40–80 MPa (Fig. 11). If a lithostatic pressure is taken into account, the pressure of 80 MPa corresponds to a burial depth of around 3 km if the mean rock density is considered to be around 2.6 g/cm³.

The temperatures of 150–200 °C are higher than those generally expected at a depth of 3 km, as a thermal gradient of around 40 °C/km would yield a temperature of 120–130 °C. Such temperatures are however frequently determined in deep parts of sedimentary basins where advective flow of hot fluids occur in faults or along unconformities, such as in the case of Mississippi Valley type deposits (Leach et al., 2001).

The preceding Co–As stage is characterised by a similar association of brines and volatile-rich fluids than the Ag-stage. The similarities between Co–As and Ag-brines suggest similar conditions of trapping, the Co–As brines being trapped slightly earlier, at probably higher temperatures, the T_h modes 180 and 220 °C being around 10–20 °C above those of the Ag-brines (Table 1).

In conclusion, fluids associated with metal deposition at Bou Azzer deposit are high-salinity brines trapped under moderate temperatures (150–250 °C) in conditions of immiscibility with methane-rich fluids.

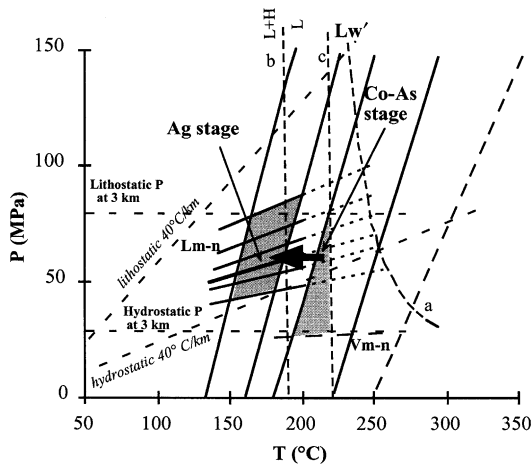


Fig. 11. P – T reconstruction for fluid circulation in the silver ore zone of Bou Azzer. The quartz dissolution stage (episyenite stage) is related to L_w fluid inclusions. Bubble curve (a) for CH_4 fluids was calculated from the data of Price (1979). Isoleths at 30 (b) and 35 (c) eq. wt.% NaCl showing liquidus ($L + H - > L$) (Bodnar and Vitik, 1994) have been drawn. Grey domains correspond to the probable P – T conditions for Co–As and silver deposition in the Bou Azzer silver ore zone. Thermal gradient (40 °C/km) is drawn in dashed lines for a lithostatic and hydrostatic pressure.

A cooling of approximately 50 °C is recorded between the two stages (Co–As and Ag). In both stages, the metals were likely precipitated by mixing of the brines with less saline fluids as shown by the rather large salinity range of the trapped fluids.

6. Ion chemistry of mineralising brines

The composition of the fluids was investigated on bulk samples of quartz and calcite hosting the brines. Three representative samples could be separated and perfectly cleaned of all contaminants. Magmatic quartz from the diorite was not crushed as it contains fluid inclusion generations that are earlier than the ore brines and it was also not possible to clean it of contaminants. The reconstructed fluid composition (Table 3) was calculated using the average salinity (5.5 mol/l Cl) determined from microthermometry and Raman spectroscopy.

The dominant anion in the analysed fluids is Cl, and there is no significant amount of SO_4 . The Ca content could be only obtained for the quartz sample (free of Ca-minerals) and is compatible with the microthermo-

metric results. Major cations are thus Na and Ca, with K and Mg much less abundant ($\text{Na}/\text{Ca} = 2.2$, Na/K between 8 and 15, $\text{Na}/\text{Mg} = 100$, $\text{Ca}/\text{Mg} = 45$). Fe, Mn, Zn, Ba, Sr (Li, Cu) have been found only in trace amounts.

The Bou Azzer brine composition has been compared to fluid compositions from representative crustal reservoirs: oil-field brines (Carpenter et al., 1974; Kharaka et al., 1987), intragranitic hot fluids (Michard, 1990), deep basinal brines (Fisher and Kreitler, 1987), Canadian Shield brines (Bohlke and Irwin, 1992), paleofluids trapped as inclusions: brines in Spanish evaporites (Ayora et al., 1994), brines resulting from halite dissolution in Colombian emeralds (Banks et al., 1995, 2000), magmatic fluids at SW England (Smith et al., 1996). Representative ion analyses for fluids from the Zgounder Ag-deposit (Essarraj et al., 1998) located approximately one hundred kilometers north-west from Bou Azzer (Fig. 11), have been reported in order to compare the chemistry of fluids in both Ag-deposits.

The Bou Azzer fluids are remarkably similar to the brines reported from the Zgounder Ag-deposit. The main ionic ratios (Na/K , Na/Li and Cl/SO_4) indicate that the Bou Azzer brines have compositions similar to sedimentary brines, especially to those reported by Carpenter et al. (1974) and Kharaka et al. (1987) from oil-fields (Fig. 12), with a small trend of Cl/SO_4 and Na/K ratios towards those fluids derived from evaporites (Ayora et al., 1994; Fig. 11C). The halogens, Cl, Br and to a lesser degree I, can be used to distinguish the source of fluids (Bohlke and Irwin, 1992), because they are conservative in solution and are relatively unaffected by fluid–rock interactions (Banks et al., 1991). At Bou Azzer, Br contents range from 15 to 18 mmol/l and I from 0.2 to 0.4 mmol/l, and the Br/Cl and I/Cl ratios are typical of deep basinal brines (Fig. 11D), in particular oil-field brines. In the Cl/Br versus Cl diagram (Fig. 11B), the composition of brines lies close to the seawater evaporation trend (Fontes and Matray, 1993), and correspond to evaporated seawater that has exceeded halite saturation. Such a low Cl/Br ratio, linked to a relative Br enrichment is typical of primary evaporitic brines, and distinct from that expected from evaporite dissolution (secondary brines such as those from Colombian emeralds, Banks et al., 2000). Besides, the rather low Na/Ca indicates a significant interaction between the Na-rich brines and Ca-rich rocks, as evaporitic brines having passed halite saturation have very high Na/Ca

Table 3
Reconstructed composition of fluid inclusions (in mmol/l) and molar ratios from crush-leach analyses

Sample	Na	K	Ca	Mg	Ba	Li	Cl	Br	SO_4	I	Na/K	Na/Li	Na/Ca	Cl/Br	Cl/ SO_4	Br/Cl	I/Cl $\times 10^5$
BZ-Qz	3194	210	1434	32	14.3	11.1	6786	19.1	5.5	0.2	15	234	2.2	356	1234	0.0028	3
BZ-Cal	2007	194	nd	nd	nd	20.8	6761	20.1	13.3	0.5	10.4	97	–	336	509	0.0029	7.5
BZ-Ca2	1880	235	nd	nd	nd	21.8	6754	21.9	14.3	0.5	8	86	–	309	472	0.0032	7.4

Qz: quartz, Ca: calcite, nd: not determined.

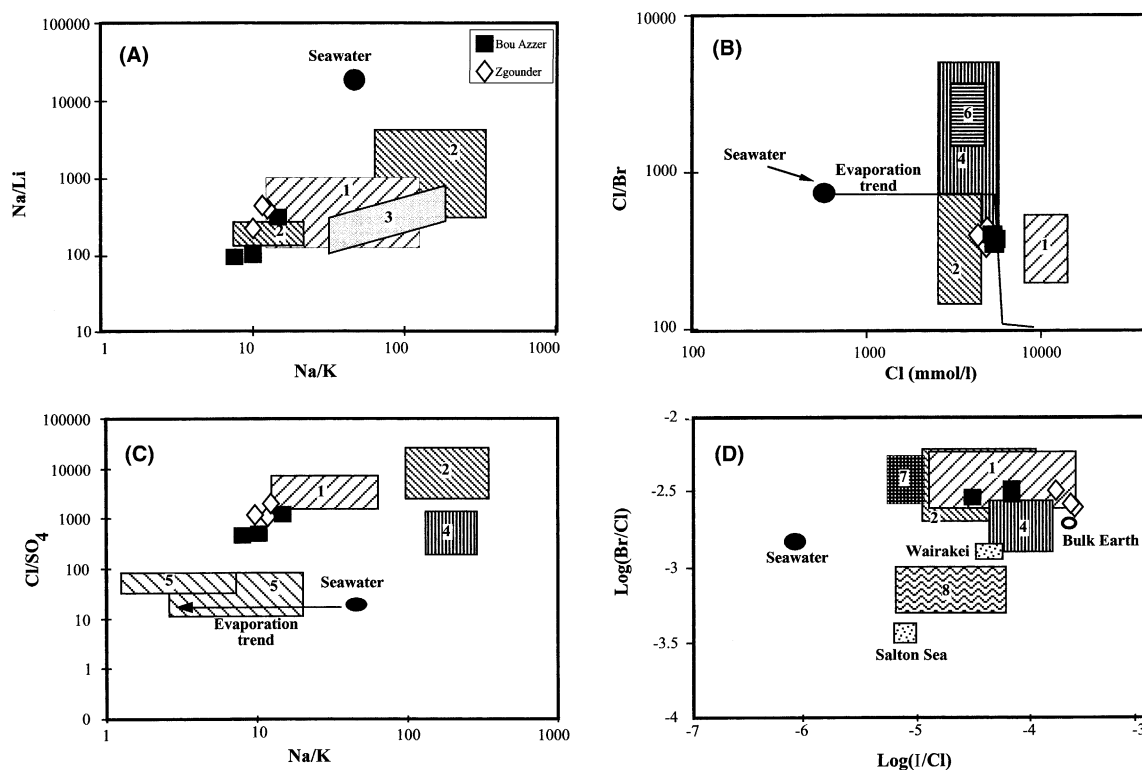


Fig. 12. Composition of brines of Bou Azzer determined by crush-leach analysis, compared to brines from the Zgounder silver deposit (Essarraj et al., 1998), together with some reference fluid compositions: (A) Na/K versus Na/Li, (B) Cl/Br versus Cl, (C) Na/K versus Cl/SO₄, (D) Log(Br/Cl) versus Log(I/Cl). Cation ratios are molar ratios. Reference fluids are: (1) oil fields (Carpenter et al., 1974); (2) oil fields (Kharaka et al., 1987), (3) Intragranitic hot fluids (Michard, 1990); (4) Deep basinal brines (Fisher and Kreitler, 1987), (5) brines from evaporites (Ayora et al., 1994), (6) brines from Colombian emeralds (Banks et al., 1995, 2000), (7) Canadian Shield, (Bohlke and Irwin, 1992), (8) Magmatic fluids (SW England, Smith et al., 1996). Sea-water evaporation trend from Fontes and Matray (1993).

ratios. Gains in Ca could be linked to Ca–Na exchange, dolomitisation or feldspar alteration (albitisation of plagioclase), the latter process being observed at Bou Azzer.

7. Discussion and conclusion

7.1. Ore fluids and silver deposition

The fluids responsible for the Ag-ore were highly saline Na–Ca brines (5–6 mol/ Cl) that occur as two- to three-phase fluid inclusions (L + V ± halite cube). The most likely trapping domain estimated for these fluids is a temperature between 150° and 200 °C and a pressure between 40 and 80 MPa. Ag deposition is primarily concentrated in zones of high permeability, in particular, the micro-fissured diorite and the vuggy episyenite.

The driving mechanism for silver deposition was probably a mixing of the brines with lower salinity fluids, as shown by the large range of salinities. As silver is transported more efficiently in high salinity NaCl fluids, as chloride complexes, the subsequent decrease in the fluid chlorinity results in the destabilisation of Ag-chloride complexes, because of the decrease in the ionic

strength of the solution. Similar mechanisms have been described by Godwin et al. (1986) for the Ag–(Co) Beaverdall deposit British Columbia, by Marshall et al. (1993) at Cobalt and by Essarraj et al. (1998) for the Zgounder Ag-deposit, or Imiter deposit (Baroudi et al., 1999) in the Anti-Atlas.

7.2. Source of brines

The geochemical features of the fluids are characteristic of those originating from sedimentary basins (Br/Cl and I/Cl ratios are typical of deep basinal brines), and, in particular, primary evaporitic brines that have exceeded halite saturation. The brines have a salinity close to halite saturation that was generated by surface evaporation, but subsequent burial of the evaporites and brines at the higher temperatures recorded for the fluid inclusions may have caused some modification (200–220 °C, Co–As stage, down to 160–180 °C, Ag-stage). Heating of primary brines in presence of halite would have increased the salinity by dissolving NaCl and therefore increased the Cl/Br ratio, but not significantly as the solubility of halite at 160–200 °C is only 20% higher than at 25 °C. However it is likely that as part of this processes recrystallisation of the halite

would occur and this would release more Br into the fluid leading to a decrease in the Cl/Br ratio. If however the brines percolated into the basement prior to burial, and were isolated from the evaporites, then no modification of Cl/Br would have taken place. Temperatures of 160–200 °C may indicate that the brines come from depths of ca. 4–5 km, considering thermal gradients of 30–40 °C/km.

Finally, the low Na/Ca ratio indicates that brines have undergone some extensive modification of the major cations during their migration. High salinity seawater evaporated brines should be dominated by Na and Mg with lesser amounts on K, but with no Ca. From the analyses of the fluids Ca is a major component of the fluid and Mg is depleted. [Davisson and Criss \(1996\)](#) propose that Na–Ca exchange through albitisation of plagioclase is the main process generating Ca-rich brines in sedimentary basins, but this is not the case here. Although this did occur it is not volumetrically important as the Na concentrations are not depleted to the levels required if this was the major processes. Instead it is clear that the loss of Mg is far more important and exchange of Mg for Ca through dolomitisation of limestones is a more likely mechanism for generating the high Ca concentrations in the fluid.

Percolation of the brines seems to have been a regional feature as the Zgounder and the Bou Azzer (or Imiter) deposits, which have similar fluids are more than 100 km apart. The nature of the brines, and conditions of percolation (minimum burial of 3 ± 0.5 km, temperatures of 150–200 °C) are similar to those described elsewhere, where there is a link between mineralization and the unconformity between the basement and overlying sedimentary basins: Proterozoic basins (Oklo (Gaboon): [Mathieu et al., 2000](#); Saskatchewan (Canada): [Kyser et al., 2000](#); Northern territories (Australia), [Derome et al., 2003](#)), Mesozoic basins (western Europe, [Boiron et al., 2002](#)), intracontinental rifts with Mesozoic to Cenozoic sediments such as the Rhine graben ([Pauwels et al., 1993](#)). In all these examples, brine migration occurred significantly later than the sedimentation. In Ag-deposits, [Canals et al. \(1992\)](#) described similar highly saline Ca–Na-rich fluids at Atrevida (Spain) originating from evaporites. Evaporites are recorded in Adoudounian series (Late Proterozoic, [Choubert, 1963](#); [Chbani et al., 1999](#)), but also in the late Triassic (latest Carnian and early Norian (218 Ma)), Late Rhaetian (203 Ma), and Early Jurassic (201 Ma) series, ([Laville et al., 1995](#); [Olsen et al., 2000](#)) from both south and north of the Atlas belt.

7.3. Age of percolation and causes of thermal anomalies

The age of ores is unknown, but similarities in the brine composition, conditions of trapping and the nature of the mineral association in the three Ag-deposits

(Bou Azzer, Zgounder, Imiter) tend to indicate that a major stage of brine and metal migration occurred in the Anti-Atlas. The formation of hot brines of sedimentary origin could have occurred after the Adoudounian, or more likely after the late-Trias, which corresponds to the major stage of evaporite formation. Although Moroccan Ag–(Co–As) deposits have been considered by several authors as synchronous of major metamorphic stages of Panafrican ages (680 Ma, [Leblanc and Lbouabi, 1988](#) at Bou Azzer), or of magmatic intrusions inferred as synchronous of the ores (550 ± 3 Ma, U/Pb on zircon from rhyolite, [Levresse, 2001a](#) at Imiter), no direct dating of the ores was available. Hypothetical ages were thus proposed in accordance with the preferred conceptual genetic models (metamorphic-hydrothermal). Early introduction of metals at Bou Azzer, e.g. Panafrican, seems however, incompatible with the fact that ore infillings in fractures were unaffected by late Panafrican or Paleozoic deformation or metamorphism, and with the nature of the brines as determined in the present study.

The only available date for Bou Azzer is an age of 218 ± 8 Ma (Norian) recently obtained by [Levresse et al. \(2001b\)](#) by $^{40}\text{Ar}/^{39}\text{Ar}$ dating on adularia from the Co–As ores. Adularia which precedes silver in the vug infillings can be attributed to a diagenetic feldspathisation at an age close to the Trias-Lias boundary. Thus, the major stage of thermal and fluid flows in this region during post-Proterozoic times has been attributed to upwelling of the upper mantle, within a thin continental crust during the early stages of the Atlantic rifting. It is marked in the basement and Triassic and Liassic series by a thermal impact which could have reached 185–210 °C for some 10–15 Ma, and is considered to have occurred during late Trias to early Lias ([Huon et al., 1993](#)). The youngest ages of 184 Ma were determined on the finest fractions (<0.4 mm) of Triassic sediments of Argana ([Huon et al., 1993](#)). North-East of the studied area, the “Atlasic rift” is considered to have opened at the same time. It is characterized by extensional tectonics, with the formation of sedimentary basins, the reactivation of basement faults, and then, during Liassic times, by the deposition of marine carbonate sequences which induced a post-rift thermal subsidence stage.

The overall consideration of the data concerning the Trias-Lias transition in Morocco, and the proposed model of circulation of Na–Ca brines expelled from buried evaporites is thus in favour of a model of brine penetration within the basement during a major extensional tectonic episode. The precise age is unknown, but it is likely to be related to periods synchronous or slightly later than the early stages of the Atlantic rifting. Such a model is an alternative to the previous conceptual models of syn-metamorphic or syn-magmatic episodes of Ag-ore formation in Anti-Atlas ([Leblanc and Lbouabi, 1988](#); [Levresse, 2001a](#); [Levresse et al., 2004](#)). These

considerations are in favour of a late stage of mineralisation linked to extensional tectonics during post-Norian times, when evaporite levels were sufficiently buried to produce hot basinal brines.

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