

Fluids in Hercynian Au veins from the French Variscan belt

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Abstract

Fluids, together with alteration and ore mineral assemblages, were studied in representative hydrothermal gold-bearing quartz veins from the western part of the Variscan belt in France (La Bellière, Montagne Noire district, Villeranges-Le Châtelet district, and Limousin province). Petrographic studies of the relationships between ores, fluid inclusions, microfracturing and quartz textures show that chronological and genetic relationships between gold deposition and fluid trapping may be very complex and difficult to establish for veins which show multi-stage fracturing and shearing. Systematic studies of secondary fluid inclusions in microcracks and recrystallized zones of the early quartz veins indicate two contrasting physical-chemical conditions: 1 relatively high temperature (250–400°C) and pressure (>1 kbar) event with CO₂-CH₄-H₂S-N₂ (±H₂O-NaCl)-rich fluids related to the early sulphide deposition; 2 lower temperature (150–250°C) and pressure with aqueous fluids related to the late native-gold-sulphide (or sulphosalt) assemblage, which constitutes the economic ores in some deposits.

In deposits where gold occurs predominantly in a combined state within arsenopyrite and pyrite (Châtelet and Villeranges), primary fluid inclusions in authigenic quartz combs cogenetic with arsenopyrite are almost purely aqueous (H₂O-NaCl) and have a low salinity (1–4 wt. % NaCl). P-T conditions (150–250°C, nearly hydrostatic pressures) are similar to those of the second stage in the multi-stage quartz veins.

Consideration of chemical equilibria in the C-O-H-N-S system using microthermometric and Raman spectrometric analysis for the fluids, together with data obtained from mineralogical studies, show that during gold deposition, f_{O_2} was below hematite-magnetite buffer at Villeranges and around the Ni-NiO buffer at La Bellière and Montagne Noire. f_{S_2} calculations based on H₂S analyses are in good agreement with mineral assemblage estimates and close to that fixed by the pyrite-pyrrhotite boundary at high temperature. Ore fluid pH was significantly lower than in the host rocks as shown by the complete alteration of the host rocks into a quartz-K-mica assemblage. The data illustrate that during the late Hercynian, fluid circulation evolved from high P-T conditions, in some cases linked to late magma intrusions, towards conditions typical of later hydrothermal systems of the geothermal type.

KEYWORDS: fluids, Hercynian, gold veins, Variscan belt, France.

Introduction

THE Hercynian belt in Europe hosts several gold districts with numerous showings and a few mined deposits. In France, most of the deposits are located within the Hercynian basement, in metamorphic series, and to a lesser degree in granitic rocks, mostly peraluminous granites (Bache, 1980; Crouzet *et al.*, 1979) and volcano-sedimentary series (Villeranges; Boiron, 1987). With the exception of a few concentrations considered as early (massive sulphides at Salsigne, Bonnemaïson *et al.*, 1986), most gold ores formed during the latest deformational stages affecting the Hercynian basement (Bouchot, 1989; Lépine, 1989),

within the age range 325–290 Ma (Boiron, 1987; Bouchot, 1989).

In most cases, the quartz veins are characterized by a multi-stage ore deposition, which consists of the successive crystallization of Fe-As minerals, Pb-Zn-Cu sulphides and Pb-Ag sulphosalts. These mineral assemblages crystallize during specific stages of microfracturing and fluid migration which affect the previously deposited quartz infilling of the vein. However, the superimposition of the different stages on the same vein hinders the reconstruction of the chronological and genetic relationships between fracturing, fluid trapping and mineral deposition.

The purpose of this work was to estimate the f_{O_2} , f_{S_2} , pH and fluid composition of the ore fluids by studying the fluid inclusions and mineral assemblages related to the most significant stages of the fluid migration and trapping in the quartz veins in order to constrain the factors controlling gold transport and deposition during the late Hercynian stages.

Materials

Geological setting of the Au deposits

Quartz veins were sampled in four representative gold districts of the French Hercynian belt: (1) the south Armorican Massif; (2) the Marche-Combrailles; (3) the Limousin area in the northern part of Massif Central; and (4) the Montagne Noire district in the southern part of Massif Central (Fig. 1).

In the southern Armorican zone, the La Bellière Au deposit (Bache, 1980) is located north of the Montagne batholith in the mica-schist series of the Mauges plateau. The La Lucette gold ore is developed in Silurian to Carboniferous mica-schists and sandstones.

Along the Marche-Combrailles shear zone, Au showings and deposits have been discovered within a 50 km long band. Au veins are seen to cut the Hercynian basement (Guéret monzogranite, anatectic biotite-cordierite gneisses (Le Châtelet: Zappettini, 1983), the Visean basins (Viges, Villeranges: Boiron, 1987) and late intrusive bodies (peraluminous granites at Le Châtelet, and lamprophyres).

In the Limousin area, Au deposits and showings (Ambazac, Vaulry, Nouic, Janailac), and the St-Yriex district (Ahmadzadeh, 1984) with the Bourneix (Hubert, 1986; Calli, 1988) and L'Aurieres mines (Essarraj, 1989) occur mainly within metamorphic series surrounding large granitic intrusives. However, Au veins frequently cross-cut late sills and dykes of peraluminous granites, as well as granites exhibiting subsolidus quartz dissolution and albitization (e.g. Bourneix). Some spatial relationships between the location of the gold veins and the presence of partially hidden leucogranite belt are suspected (Sandras, 1988; Bouchot, 1989).

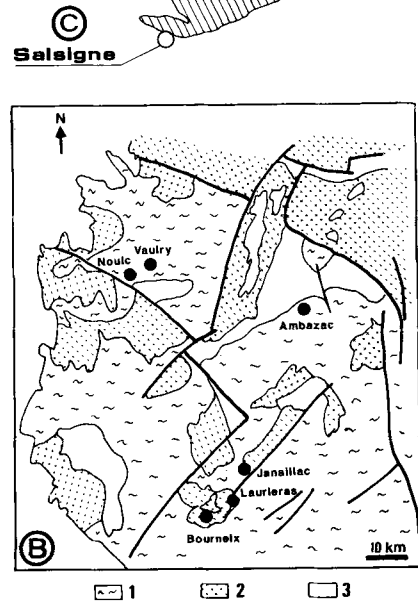
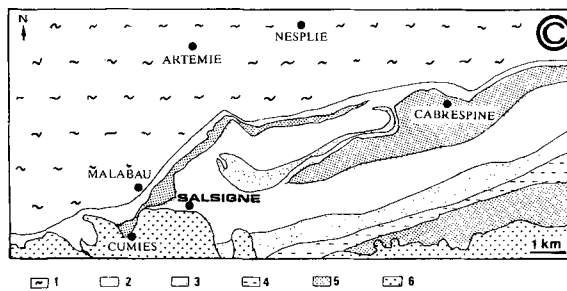
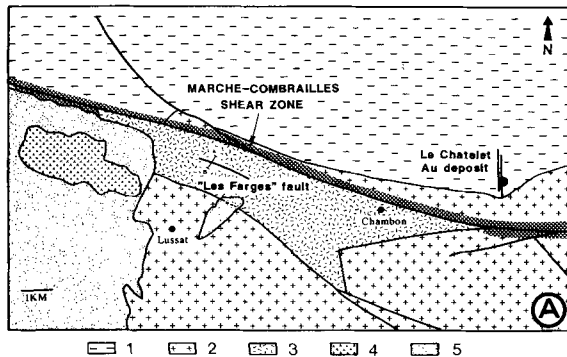
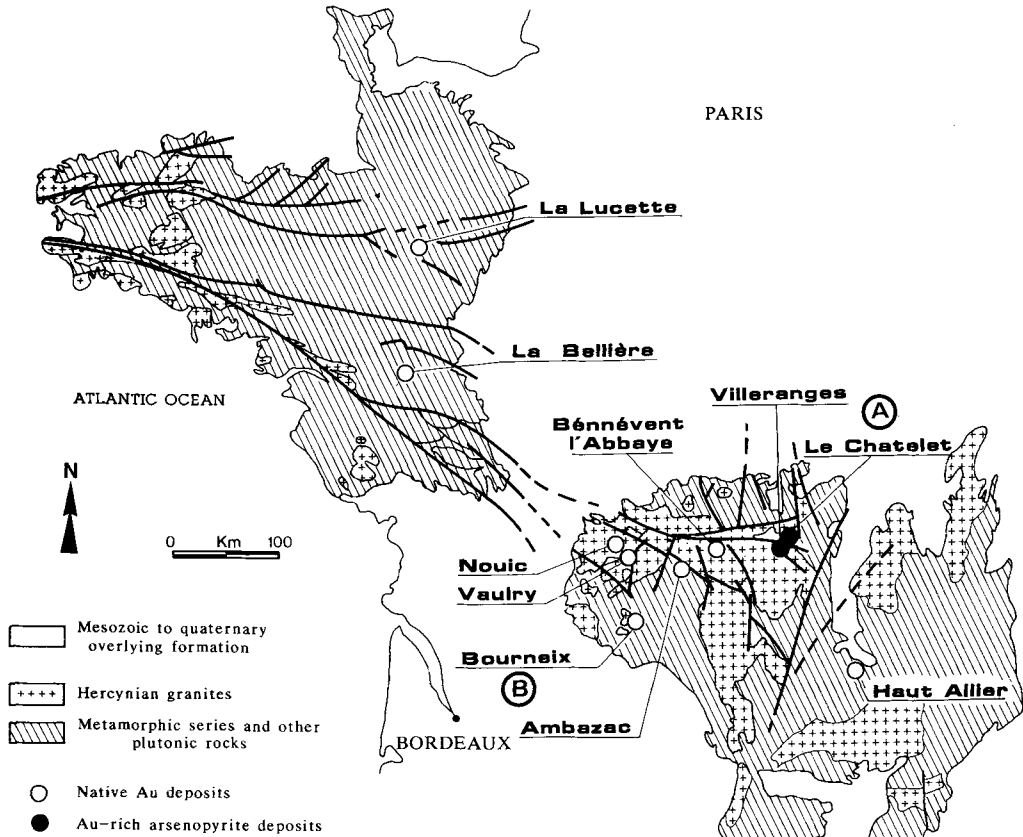
The Salsigne district is located in the southern part of the Montagne Noire (southern part of the

Massif Central). This important gold district, with the Salsigne mine and the numerous gold showings (Nesplé, Cabrespine, Malabau, Cumiès, Artemie from the Montagne Noire) is characterized by a multi-stage metallogenesis which includes an early stage yielding the constitution of massive sulphide layers ('Sedex' type sulphide mineralization) and different ductile to brittle deformational stages which produced folding and recrystallization of some sulphide masses (Bonnetmaison *et al.*, 1986), and late Hercynian quartz-sulphide veins (Lépine, 1989; Boiron *et al.*, 1989a). The latter from the Montagne Noire series were only presented in this study.

Ore assemblages

Gold occurs either as native gold or as a trace element (30 to 5000 ppm) within sulphides. There are several different mineral associations involving native gold, but many previous descriptions have ignored the difficulties in estimating the time relationships between gold deposition and other mineralization. For instance, part of native gold may be supergene or very late in the mineralogical sequence, and occur as a late infilling of cavities or microcracks. This is difficult to distinguish from gold deposited during the early stages. A second difficulty arises from the varied mineralogical assemblages of the different deposits. In the Marche-Combrailles zone, gold occurs only in a combined state in arsenopyrite and pyrite included in ankerite-bearing quartz combs (Boiron, 1987; Marion *et al.*, 1986; Marion, 1988; Cathelineau *et al.*, 1988). By contrast, other deposits are characterized by multi-stage metallogenesis (Bellière, Limousin veins, and quartz veins from the Salsigne and the Montagne Noire districts): the early crystallization of Fe-As minerals, later Pb-Zn-Cu sulphides, followed by complex sulphide-sulphosalts. However, Table 1 shows that significant differences characterize the deposits studied, especially the lack of some stages, the typical metal association of the deposits and the combined-to-metallic ratio for gold ores. Thus, a definitive global sequence describing all the occurrences as the result of a single general process, valid for the whole Variscan belt, seems unlikely, contrary to the interpretations of Picot and Marcoux (1987), and Bonnetmaison and Marcoux (1987).

FIG. 1. Location of gold deposits in the French part of the Variscan range. (A) Marche-Combrailles district: 1, augen gneisses; 2, Guéret granite; 3, Visean volcanosedimentary series; 4, Stephanian rhyolites; 5, post-Stephanian overlying sedimentary formations. (B) Limousin district: 1, metamorphic rocks; 2, monzogranite; 3, leucogranite. (C) Montagne Noire district: 1, Cambrian metamorphic schists; 2, schists and sandstones, Lower Georgian; 3, Georgian limestones; 4, schists and sandstones, Acadian; 5, Lower Devonian; 6, Eocene.



			BELLIERE	MONTAGNE NOIRE	LIMOUSIN district	MARCHE COMBRAILLES	
						VILLERANGES	CHATELET
Native gold	Qtz veins breccia microsaccharoid qtz		arsp - pyr (?)		arsp - pyr		
Native gold Combined gold	Microfracturing recrystallized qtz qtz veinlets	* P.F.I. * P.F.I.	sph - gal-cpy Au	arsp - pyr	arsp Au - Arsp		(?)
Native gold		* F.I.T.	(?)	cpy-Au-Bi-bism	gal - cpy sulfosalts		
Combined gold	Authigenic qtz combs	* P.F.I.				Au-arsp-pyr-qtz-ank qtz - stib	Au-arsp-pyr-qtz-ank

TABLE 1. Mineralogical assemblages for the gold-bearing quartz veins. Arsp, arsenopyrite; Au-arsp, gold-bearing arsenopyrite; pyr, pyrite; cpy, chalcopyrite; sph, sphalerite; gal, galena; stib, stibnite; bi, native bismuth; Au, native gold; bism, bismuthinite; qtz, quartz; ank, ankerite; P.F.I., primary fluid inclusion; F.I.T., fluid inclusion trail.

Alteration assemblages

The typical alteration assemblage of gold-vein wall-rocks consists of dioctahedral K-micas (illite, phengite series), ankerite and quartz, irrespective of the original rock litho-geochemistry. K-micas are also found within the quartz veins syncrystallized with sulphides, mostly arsenopyrite. In the Villeranges deposit, three alteration stages have been recognized (Boiron, 1987; Boiron *et al.*, 1989b). The first one of regional extent is characterized by chlorite rather than phengite, the second one, the phengite stage is then followed by illite crystallization which is typical of mineralized zones. K-micas exhibit significant compositional differences as a function of their crystallization temperature, especially variations in the interlayer occupancy (K) and the tetrahedral Si content of illites and phengites respectively. The use of the geothermometers proposed for phengites (Velde, 1965) and illites (Cathelineau and Izquierdo, 1988) indicate relatively large ranges of crystallization temperatures for the two minerals. However, estimated temperatures for a given stage of the mineral sequences may be relatively well constrained: for instance, $200 \pm 20^\circ\text{C}$ for the illites from the Villeranges deposit (Boiron and Cathelineau, 1989a).

Time/space relationships between fluid and solid phases

Multistage quartz veins

The study of the ore fluids was carried out using fluid inclusions in recrystallized microfaulted

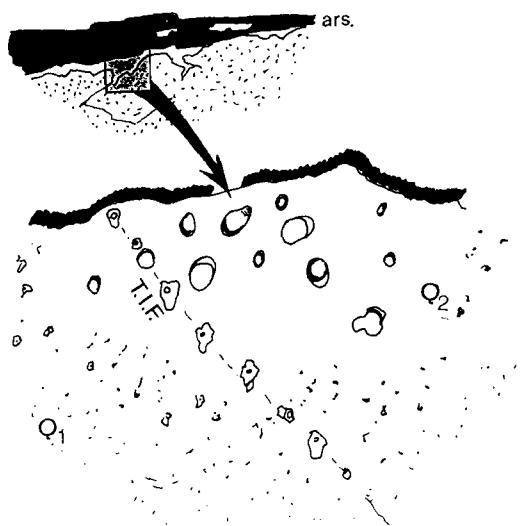


FIG. 2. Distribution and features of fluid inclusions in recrystallized quartz (Q2) surrounding the early sulphides (dominant arsenopyrite) in a quartz vein (Q1).

zones in early quartz veins from the La Bellière and Montagne Noire samples. Recrystallization of the quartz (Q2, Fig. 2) is related to the early sulphide deposition which occurs after the microfissuring of previously deposited quartz (Q1). Microcrack infillings consist of pyrite-arsenopyrite in Montagne Noire, and sphalerite-galena at La Bellière. In these two cases, fluid inclusions may be considered as nearly primary (Lc, Vc, L1)

and are scattered within the recrystallized quartz which occurs as irregular patches or bands along microcracks and sulphides (Fig. 2), and more rarely as rare euhedral forms in open spaces. These quartz grains also contain trails of secondary fluid inclusions (L2) along healed microcracks crosscutting both Q1 and Q2 quartz (Fig. 2) related to later microfracturing.

At other localities in the Limousin area (Vaulry, Nouic, Ambazac, Janaillac), fluid inclusions from healed microcracks were studied in the quartz Au ores. The relationships between native Au particles, sulphides, microcracks and fluids were unclear.

Authigenic quartz

In the case of the Marche-Combrailles deposits (Villerranges and Evaux showings), inclusions trapped in quartz veinlets are considered to be primary since the quartz and arsenopyrite are cogenetic. At Châtelet, similar quartz comb development is observed together with partial recrystallization of quartz grains of various origins (magmatic and metamorphic), yielding more complex patterns and hence causing greater difficulties in correctly identifying these fluids specifically related to the gold-rich arsenopyrites.

Methodology

Analytical procedure

Microthermometric measurements were performed on a Chaixmeca heating-freezing stage (Poty *et al.*, 1976). Salt concentration, expressed as wt.% NaCl equivalents, and fluid density of gas-poor fluid inclusions were determined by microthermometry (Zhang and Frantz, 1987). In gas-rich fluid inclusions, CO₂ was identified by melting of a solid below -56.6°C. The volumetric fraction of the aqueous liquid (Flw) and the volumetric fraction of the carbon-rich liquid in the carbon-rich phase (Flc) were estimated at room temperature by reference to the volumetric chart of Roedder (1972). Molar fractions of CO₂, CH₄, H₂S and N₂ were determined in individual inclusions by micro-Raman analysis performed on a DILOR X-Y multichannel Raman spectrometer.

Geochemical parameters

f_{O_2} and f_{S_2} were calculated from the P - V - T - X properties of individual inclusions in the C-O-H-S system (Dubessy, 1984; Ramboz *et al.*, 1985; Dubessy *et al.*, 1987, 1989). Estimation of f_{O_2} , f_{S_2} and pH, were also obtained by using stability diagrams for the sulphide and silicate assemblages (Boiron *et al.*, 1988).

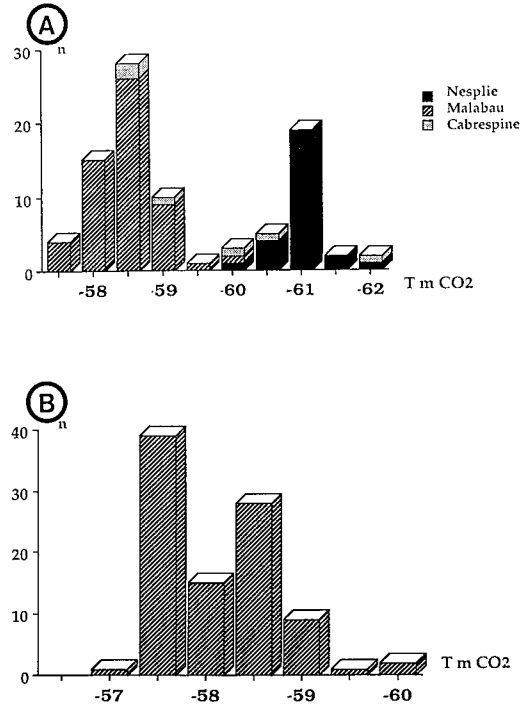


Fig. 3. Histogram illustrating the CO₂ melting temperature of the CO₂-rich fluid inclusions: A, Montagne Noire showings; B, La Bellière deposit.

Analytical data on fluid inclusions (Tables 2, 3, 4, 5)

Recrystallized quartz

Lc and Vc inclusions are carbon dioxide-rich and have variable water content. They present homogenization of the non aqueous part (ThCO₂) mostly to the liquid, and bulk homogenization (TH) to the liquid or vapour. L1 and L2 inclusions are almost purely aqueous and homogenize to the liquid state.

The primary fluid inclusions (Lc, Vc and L1) exhibit distinct phase relations at room temperature: apparent monophasic inclusions; liquid-vapour inclusions with relatively variable liquid/vapour ratios, and rare three-phase (V_{CO₂}-L_{CO₂}-L_{H₂O}) inclusions (i.e. La Bellière). These inclusions do not exhibit any clear spatial or chronological relationships and are randomly distributed in the recrystallized quartz. Lc and Vc inclusions have solid CO₂ melting temperature (T_mCO₂) (in presence of carbonic liquid and vapour) which are significantly lower than the triple point of pure CO₂ (Fig. 3A and B) indicating the presence of other volatile species. As con-

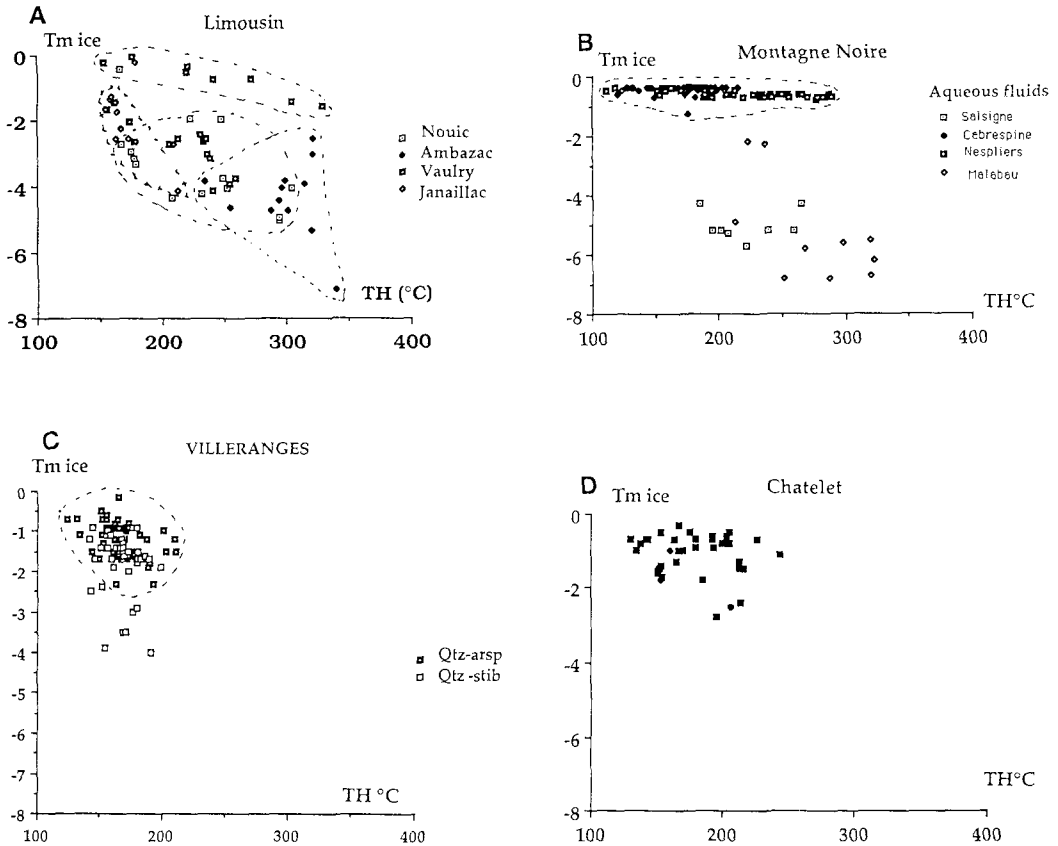


Fig. 4. $T_m\text{H}_2\text{O}$ -Th plot for aqueous fluid inclusions from: A, Limousin gold-bearing quartz veins (Ambazac, Nouic, Vaulry, Janailiac); B, Montagne Noire gold-bearing quartz veins (Nesplé, Cabrespine, Malabau, Salsigne), Boiron *et al.*, 1983a; C, Villeranges gold-bearing arsenopyrite; D, Châtelet deposit.

firmed by Raman microprobe analysis, the CH_4 content ranges between 0.1 and 10 mole % at Montagne Noire, 0.1 to 5 mole % at La Bellière and 0.8 to 13 mole % at L'Aurieras. N_2 and H_2S are present in trace amounts in almost all the inclusions analysed, but can reach up to 2.5 and 0.10 mole % respectively. Combined microthermometric and Raman analyses of gases have proved that no significant chemical differences could be found for either the carbon-rich phase or the aqueous-rich phase of the inclusions exhibiting variable liquid/vapour ratios. Decrepitation of Vc and Lc fluid inclusions containing visible water is common, making it difficult or impossible to estimate TH (TH L-V(L or V)). In the Malabau showing, bulk homogenization temperature in the range 310–360 °C of aqueous-carbonic inclusions could have been measured before decrepitation. $T_m \text{CO}_2$ or $T_m \text{ice}$ could

not be obtained. TH are in the range 240–320 °C for Montagne Noire, mostly in the range 300–350 °C at La Bellière and 260–370 °C for L'Aurieras (Table 2). Fluids with similar microthermometric properties have been described at Le Bourneix (Hubert, 1986) and in the Bennevent l'Abbaye district (Bril and Nenert, 1987).

Secondary (H_2O -NaCl)-rich L2 inclusions are observed as trails in quartz veins from Montagne Noire, La Bellière, L'Aurieras and gold showings from the Limousin area (Vaulry, Nouic, Ambazac, Janailiac). L2 inclusions are generally characterized by relatively low salinity ranging from 0.5 to 8 wt.% NaCl equiv. in Limousin (Fig. 4A), from 1 to 2 and 7 to 10.5 wt.% NaCl equiv. in the Cabrespine-Nespliers and Salsigne-Malabau veins (Montagne Noire, Fig. 4B) respectively. TH cover a relatively wide range (150–350 °C), even within the same quartz vein or microcrack, sug-

	Tm CO ₂ range	mode (n)	Tm ice range	mode (n)	Th CO ₂ range	mode (n)	TH range	mode (n)	Tm Clat range	mode (n)
NESPLIE	-60,-62	-61 (30)	-5,7		-1,7, -6,9	-5,5 (21) L				
MALABAU	-57,5,-60	-58,5 (63)	-5,4,-7,1	-6,3 (14)	-5,1,11,4	3,5 (59) L	232, 404 (46) L	*240-260 *320	1,5, 7,5	2 (7)
CABRESPINE	-58,1, -62,3	-58,5 (6)	-7,1,-7,2	-7,1 (3)	-12,1, 12,6	L			3,5,4	
LA BELLIERE	-56,9, -60	-57,5 (94)	-5		12,2, 27,9	22 (26) L, C or V	192-358 L	310 (25)		
LAURIERAS	-58,-64	-59 (13)	-4,5,-1	-4 (12)			260-370	300 (26)	8, 12	11 (12)

TABLE 2. Microthermometric data for aqueous-carbonic fluids from Montagne Noire, Bellière and L'Aurieras deposits. TmCO₂, melting temperature of solid CO₂; TmH₂O, melting temperature of ice; ThCO₂, homogenization temperature of CO₂; TH, homogenization temperature; Tm Clat, melting temperature of clathrate; L, liquid; V, vapour; C, critical. All values in °C.

	Tm ice range	mode (n)	TH range	mode (n)
NESPLIE	-0,8, -0,4	-0,6 (63)	152, 288 L (66)	*190-200 *240-250
MALABAU	-6,8,-0,5	-6 (13)	223, 318 L	(12)
CABRESPINE	-1,3, -0,4	-0,4 (58)	128-251 L	185 (61)
SALSIGNE	-3,4, -5,8	-5 (31)	144, 287 L	200-240 (37)
JANAILLAC	-0,4, -4,3	-1,8 (16)	150,208 L	165 (14)
NOUIC	-0,9, -5,2	-3,5 (24)	152, 291 L	175 (16)
VAULRY	-0,4, -3,3	-2,5 (24)	149, 325 L	230 (20)
AMBAZAC	-2, -7,3	-4,2 (12)	250,330 L	190 (11)
LAURIERAS	-5, -1	-2,5 (61)	150,280 L	200 (62)
VILLERANGES	-0,5 -2,3	-1,5 (54)	141,211 L	170 (76)
CHATELET	-0,3, -3,3	-0,8 (47)	143,244 L	200 (33)

TABLE 3. Microthermometric results for aqueous fluids from different gold deposits. Tm H₂O, melting temperature of ice; Th H₂O, homogenization temperature of H₂O; L, liquid. All values in °C.

		H ₂ O	CO ₂	CH ₄	N ₂	H ₂ S	T _m CO ₂	T _h CO ₂	T _m ice	density
1	CAB	33	59	5	2,5	0,04	-58,7	4,2 L		0,8
2	CAB	65	25	10	1	0,06	-62,3	-12,1 L		0,75
4	MAL	55	39	5	1,25	0,06	-58,4	6,5 L	-6,1 ^v	0,8
5	MAL	78	18	1,5	0,4	0,01	-57,6	6,3 L	-6,4	0,9
7	NESP	68	20	9	1,6	-	-61,5	-6,9 L		0,75
8	NESP	68	23	8	0,44	-	-61,8	-6,7 C		0,75
3	CAB	97,5	2,5	0,01	-	-	-60,5	6,6 L	-7,2	0,9
6	MAL	98	2	0,07	-	-	-58,1	1,7 L	-6,3	0,9
9	NESP	95	3,5	2	0,22	-	-61,5		-5,7	0,7

TABLE 4. Chemical compositions of fluid inclusions from Montagne Noire gold quartz veins obtained by Raman microprobe spectrometry and microthermometric data. Compositions are given in mole %. T_m CO₂, melting temperature of solid CO₂; T_h CO₂, homogenization temperature of CO₂; T_m H₂O melting temperature of ice; L, liquid; V, vapour; C, critical. All values in °C. Density is given in g/cm³.

Samples	H ₂ O	CO ₂	CH ₄	N ₂	H ₂ S	T _m CO ₂	T _h CO ₂	TH	Density
1/1 - 2	17	81	2,5	0	0,15	-57,2	22,5 L		0,63
1/2 - 1	37	61	2,5			-57,6	18,5 C		0,75
1/8 - 1	45	55	0,2			-57,4	24,4 L	310 V	0,76
1/1 - 6	63	33	3	1		-57,1	21,5 L		0,68
1/B - 1	66	31	1,5	0,9	0,1	-57,5	25,5 C		0,62
1/1 - 4	69	30	1			-57,2	21 L		0,8
1/B - 3	75	24	1	0,25	0,02	-57,6	24 C		0,51
1/8 - 3	78	20	1,5			-57,2		337	0,8
1/8 - 6	82	14	3	0,7		-58		315 L	0,68

TABLE 5. Chemical compositions of fluid inclusions from La Bellière gold-quartz veins obtained by Raman microprobe spectrometry and microthermometric data. Compositions are given in mole %. T_m CO₂, melting temperature of solid CO₂; T_h CO₂, homogenization temperature of CO₂; TH, homogenization temperature; L, liquid; V, vapour; C, critical. All values in °C. Density is given in g/cm³.

gesting repeated reopening of the microcracks and multi-stage trappings of fluids.

Authigenic quartz

Primary fluid inclusions (L) are randomly distributed within authigenic euhedral quartz crystals from the Villeranges deposits. They are characterized by low salinity (<4 wt.% NaCl equiv.) aqueous fluids. Slightly higher salinities are recorded in the stibnite bearing authigenic quartz which ends the ore sequence (Fig. 4C). Traces of CO₂ and CH₄ have been only identified by Raman spectroscopy. Their partial pressure is around 1 atm which results in a gas-poor fluid ($\chi_{\text{gas}} < 0.02$). TH_L-V(L) occurs in the range

150–200°C. In the rhyodacitic tuffs, secondary fluid inclusions are observed in healed microcracks of the quartz phenocrysts and display very similar compositions, but a wider range of TH. The scattering of TH values increases in quartz phenocrysts from chlorite to phengite and illite alteration zones (Fig. 6). In addition, the minimum TH values decreases along this sequence. By contrast, T_m ice remains constant (Boiron, 1987).

At Châtelet, very similar fluid compositions and TH (Fig. 4D) are noted for the primary fluid inclusions in the euhedral quartz which carries gold-rich arsenopyrites. It is however difficult to decipher the spatial and genetic relationships between

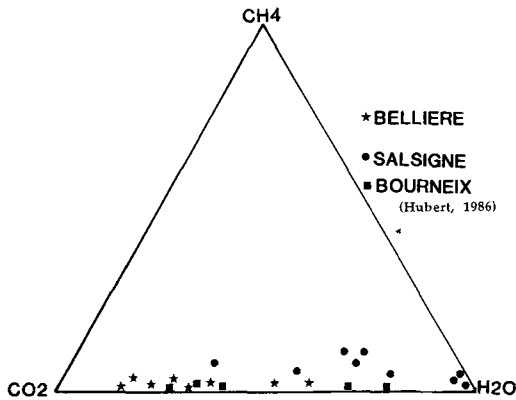


FIG. 5. Ternary plot of bulk compositions of aqueous-carbonic fluids from Bourneix (data from Hubert, 1986), Montagne Noire and La Bellière.

the volatile-rich inclusions observed by Wu *et al.* (1989) in samples from the Châtelet area and the stages of gold-rich arsenopyrite deposition.

Interpretation of the fluid-inclusion data

Bulk chemical evolution

For each case study, the ternary plot (Fig. 5) of the bulk chemical compositions of the Vc, Lc inclusions shows a continuous water increase and CO₂ decrease. Variations of CH₄, N₂ and H₂S are less clear. No significant variations of salinity were observed. This suggests a dilution by aqueous fluids during the first stage.

The second stage of gas-poor fluids, located in recrystallized quartz (Q2), from Limousin and Montagne Noire are characterized by the same range of salinity and minimum trapping temperature of 150–350 °C. Tm ice–TH plots (Fig. 4A and B) for the Vaulry (Limousin) and Nesplé and Cabrespine (Montagne Noire) show a linear trend with little variation in salinity. This indicates mainly variations of fluid trapping temperature under more or less isobaric conditions. The constant salinity suggests the same source of fluids. For other deposits, TH occurs in the same range but the salinity displays more scattered values (3 to 9 wt.% NaCl), suggesting slight variations in the fluid sources during cooling.

Aqueous fluids located in authigenic quartz from Châtelet and Villeranges show a narrow range of TH values. At Villeranges (Fig. 4C), fluids associated with gold-bearing arsenopyrites exhibit very small variations in salinity and density. This shows that gold-bearing arsenopyrite was deposited under restricted *P–T–X* conditions. It is worth noting that fluids associated with the

stibnite stage (later than the arsenopyrite crystallization) display higher salinities from 2 to 6 wt.% NaCl but similar TH. At Châtelet, the fluids related to the gold-rich arsenopyrite exhibit the same features (Fig. 4D).

P–T evolution

Multi-stage quartz veins: the *P–T* properties of aqueous-carbonic inclusions were modelled for the system H₂O–CO₂–CH₄ using *V–X* data (Tables 4 and 5) and the equations of Kerrick and Jacobs (1981) and Jacobs and Kerrick (1981).

Montagne Noire district. Probable minimum pressure of trapping is around 2–3 kbars in a temperature range 350–400 °C, and probably represents a lithostatic pressure indicative of relatively deep structural level (7–10 km). This indicates that the first stage of vein emplacement occurred during or at the end of metamorphism. However, the same recrystallized quartz grains also display very dense Lc inclusions, together with Vc inclusions displaying much lower densities. The Lc inclusions were trapped at pressure as high as 4 kbars whilst the Vc inclusions were trapped in the range 0.5–1.5 kbar. Such variation could be explained by successive pressure drops within the veins from lithostatic to intermediate to hydrostatic conditions through a more general decompression process.

Pressure estimates for L1 and L2 fluids in the 250–350 °C temperature range are around 1 kbar. Therefore a minimum pressure reduction of 1–2 kbars occurred between the circulation of carbonic fluids and aqueous. Decompression events suggested by the decreasing density of the trapped aqueous-carbonic fluids may have favoured the influx of such aqueous fluids within the fault system. Trapping pressures for L2 inclusions are probably intermediate between the lowest pressures given by the less dense Vc inclusions, and hydrostatic pressures.

La Bellière. High pressures in the range 1–2 kbars are recorded for both the carbonic fluids and aqueous fluids. Considering the estimated crystallization temperature of phengites, which crystallized together with sulphides and gold, using the clay geothermobarometer from Velde (1965), the probable trapping conditions were around 400 °C and 1.5–2 kbars.

Limousin area. At L'Aurieras, minimal *P–T* conditions for aqueous-carbonic fluids are relatively high, around 0.75 ± 0.25 kbar and 300–350 °C (Essarraj, 1989). Aqueous fluids related to the latest stage have probably been trapped under hydrostatic pressure ($P_{min.} \geq 100$ bars) at temperatures around 200 ± 20 °C. At Le Bourneix, Hubert (1986) calculated high

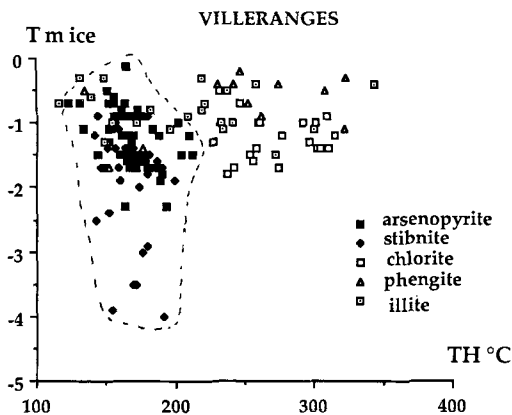


FIG. 6. $T_m\text{H}_2\text{O}$ -Th plot for aqueous fluid inclusions from the Villeranges deposit.

pressures around 2 kbar for the early stage, assuming that the early H_2O ($\pm\text{CO}_2$, CH_4) fluid from the first stage was trapped at higher pressure than that prevailing during the second stage (CO_2 , CH_4 -rich fluids). Pressure during the second stage was around 0.8 kbar, being related to the vapour pressure of boiling carbonic fluids.

Marche-Combrailles district. At Villeranges, useful data on pre-ore stages have been obtained from the study of fluid inclusions trails in tuff grains (Fig. 6). The evidence of the superimposed alteration envelopes (Boiron, 1987; Boiron *et al.*, 1989b) is shown by the important scattering in TH values of the secondary fluid inclusions in tuffs from the illite zone. By contrast, in the chlorite zone, quartz has only been affected by the earlier stage (chlorite episode) as demonstrated by the smaller dispersion and TH in the range 230–320°C. TH values for the illite-ore stage are given by the primary fluid inclusions in authigenic quartz combs which are strictly synchronous with the gold-rich arsenopyrite deposition. Fluid pressure is calculated from the ore fluid densities and the temperature derived from the clay geothermometers applied to illite and chlorite compositions (Cathelineau and Nieva, 1985; Cathelineau and Izquierdo, 1988): chlorite stage ($T 290 \pm 30^\circ\text{C}$, $P 900 \pm 300$ bars); phengite stage ($T 250 \pm 30^\circ\text{C}$, $P 500 \pm 300$ bars); illite stage ($T 200 \pm 20^\circ\text{C}$, $P 400 \pm 200$ bars).

Fluid pressure was hydrostatic during the ore stage (illite). Therefore fluids responsible for the gold-rich arsenopyrite crystallization along the Marche-Combrailles shear zone belong to a long-lived hydrothermal circulation within the basement and the volcano-sedimentary formations on a regional scale. In these environments, fluid cir-

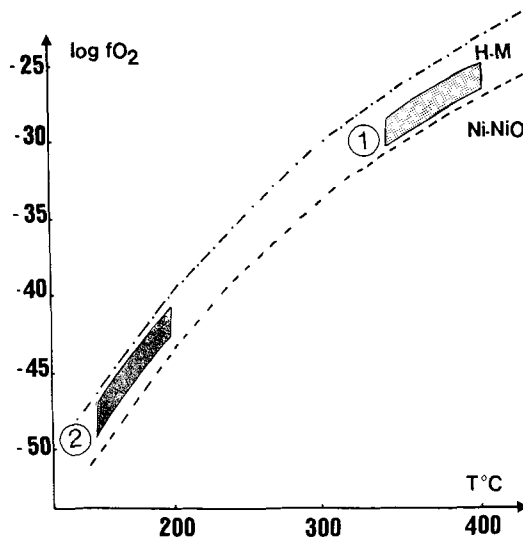


FIG. 7. $\log f_{\text{O}_2}$ -temperature diagram: 1, high P - T deposits; 2, intermediate to low P - T deposit.

ulation was of the geothermal type with a temperature around 300°C for the first stage, decreasing to 150°C. The temperature range for gold deposition is relatively similar to temperatures of trapping of L2 inclusions in the multi-stage veins.

Estimations of pH , f_{O_2} , f_{S_2}

High-temperature fluids

In the high-temperature deposits ($350 \pm 50^\circ\text{C}$, Salsigne and Bellière) characterized by Lc and Vc inclusions, f_{O_2} was around that fixed by the Ni-NiO oxygen buffer ($10^{-30 \pm 2}$) (Fig. 7) and are typical of metamorphic fluids generated by carbon-bearing environments. f_{S_2} is relatively high around $10^{-10 \pm 1}$, as at Montagne Noire and close to the pyrite-pyrrhotite boundary. At Le Bourneix (calculation by Dubessy, in Touray, 1987) f_{O_2} was around the Ni-NiO buffer.

Low-temperature fluids

Authigenic quartz of lower temperatures ($200 \pm 50^\circ\text{C}$, Marche-Combrailles deposits) contain combined gold in closely associated arsenopyrite and pyrite. Isotopic and mineralogical studies of these ores yielded f_{O_2} estimates between the H-M and the Ni-NiO oxygen buffer (Fig. 7; Boiron *et al.*, 1989b).

pH

Most of the rocks in the vicinity of the gold veins are frequently altered to a quartz + K-mica

assemblage, which preferentially replaces feldspars and chlorite (Boiron, 1987). The instability of K feldspars and the crystallization of a quartz-K-mica assemblage indicates a shift towards low pH during deposition, provided that the K^+ activity remains constant in the fluid. The constant K^+ activity is suggested by mass balance calculation which does not show any significant K^+ supply or loss (Boiron and Cathelineau, 1989b).

Factors controlling gold deposition

In quartz veins from the Montagne Noire or Bourneix-L'Aurieras district, the genetic relationships between the trapping of aqueous-carbonic fluids during the recrystallization of early quartz and the precipitation of early arsenopyrite are well established. The gold content of such arsenopyrites is mostly in the range 1–50 ppm (Cathelineau *et al.*, 1988, 1989) but may reach exceptionally 1000 ppm (L'Aurieras; Essarraj, 1989). At this stage, gold introduction is generally minor and represents less than 5%, exceptionally 15%, of the present-day mined ores. Most of the native gold is found as late inclusions of microcracks affecting either the recrystallized quartz or the previous arsenopyrite crystals, and is associated with late mineral assemblages involving Bi-Pb minerals (Montagne Noire district) or Pb-Ag-Sb-Cu minerals (Bourneix-L'Aurieras). f_{O_2} - f_{S_2} values are favourable for gold transport during the early stages. However, gold seems to precipitate mainly during the second stage. L2 fluids are considered to be linked to the crystallization of late sulphides and sulphosalts and subsequently to the late native-gold-sulphide assemblage which constitutes the economic ores.

Whatever the temperature range, the f_{O_2} conditions are compatible with bisulphide stability in the fluid phase. Bisulphide ligands are known as efficient gold complexing agents (Seward, 1973, 1984). In addition, the pH shift towards low values as evidenced by alteration mineral assemblage is favourable for gold precipitation (Romberger, 1986; Shenberger and Barnes, 1989).

The presence of both CO_2 and CH_4 in the early stages is considered to be more a reflection of the general redox state at high temperature ($T > 350^\circ C$) where CO_2 - CH_4 -producing reactions are favoured (i.e. fluid-graphite equilibria, decarbonization). This redox state is later noted during the late aqueous stage as demonstrated by the mineralogical assemblages. In addition, the presence of gases, for instance CO_2 , cannot be interpreted directly as a metallogenic tool, con-

trary to the suggestion of Smith *et al.* (1984) and Wood *et al.* (1986).

Time relationships between gold metallogeny and French late Hercynian events

During the first stage of sulphide deposition in intra-metamorphic veins, pressures were probably lithostatic and above 1.5 kbar at the Salsigne and Bellière deposits, with temperatures in the range 350–400°C (Fig. 8). Such P - T conditions are similar to those recorded at the end of the Hercynian metamorphism. In the early stage of fluid trapping, fluid migration involved mostly metamorphic-derived aqueous-carbonic fluids. Similar conditions are recorded in the early stages of deposits from the northern part of Massif Central (Bourneix and Limousin showings). Heat, fluid circulation and associated metal transfer are the result of the intrusion of late magmatic peraluminous granites. Then, P - T conditions changed progressively from high- P - T towards high- T -low- P and then low- T -low P (Fig. 8). Such changes in the P - T conditions may be partly attributed to the progressive uplift of the basement at the end of Hercynian orogeny.

At the very end of the brittle deformational events affecting the Hercynian basement, heat flows were related to late thermal anomalies which were distributed along deep crystal structures. Fluid convection and thermal activity were thus spatially associated with earlier shear zones, such as the Marche-Combrailles shear zone. The presence of early shearing followed by brittle deformation probably plays a major role in increasing rock permeability, which in turn favours fluid infiltration and hydrothermal leaching of metals through extensive microfaulting. However, only the brittle deformation occurring during the late reactivation stage of the shear zones has clear genetic relationships with economic ore deposition. Aqueous fluids responsible for the main stage of gold deposition for the Villeranges deposit were meteoric in origin as proved by isotopic data (Boiron, 1987) and invaded the system during periods of decompression associated with new deformational events. Temperatures are in the range 180–250°C and pressures are hydrostatic. Such conditions are typical of late Hercynian geothermal mineralizations. Rather similar conditions have been recorded in most other deposits, especially during the sulphide-sulphosalt stages responsible for most economic mineralizations.

However, the relative importance of early high- P - T stage and later stages for the genesis of gold mineralization remains poorly known. The timing

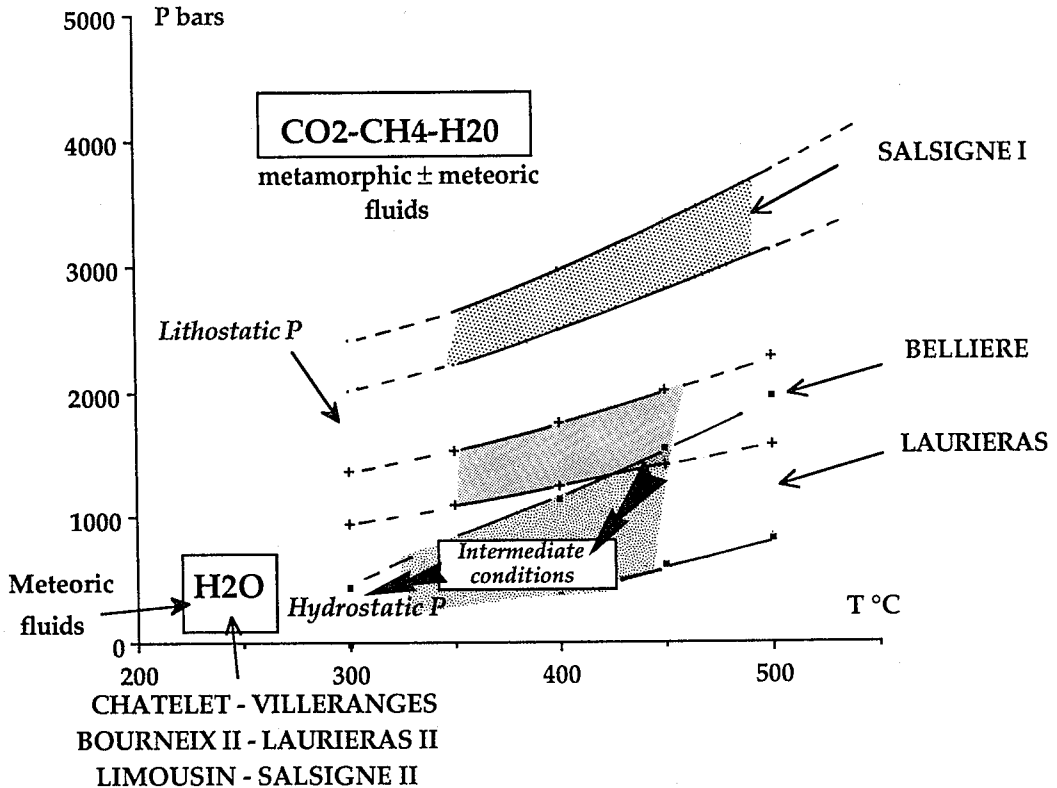


Fig. 8. P - T reconstruction of conditions prevailing for the Hercynian gold veins. Salsigne I and II refer to data obtained on quartz veins (Cabrespine, Malabau, Nesplé) from the Montagne Noire (Salsigne district; Boiron *et al.*, 1989a).

of gold introduction in the system is especially difficult to determine. Thus, gold may be introduced either early in the system, and only affected by later *in-situ* remobilization, or through distinct and independent stages.

Conclusion

This study demonstrates three significant changes in the physical-chemical conditions and metal deposition in the late French Hercynian quartz veins.

(a) Changes in the bulk chemical composition from early aqueous-carbonic fluids of metamorphic derivation, to late aqueous fluids probably related to the general meteoric fluid migration affecting the basement at the end of the Hercynian orogeny.

(b) Changes in the P - T conditions from an early stage of sulphide deposition within quartz veins, under lithostatic pressures and relatively high temperatures (relatively deep structural levels), towards hydrothermal conditions typical of geo-

thermal systems, with lower temperatures in the range 150–300°C and hydrostatic pressures (shallow levels).

(c) Changes in the factors controlling fluid migration: (1) an initial stage induced by the late-metamorphic conditions and periods of decompression around fault zones partly related to the progressive uplift of the basement; (2) a fluid convection linked to the late intrusions of peraluminous granites; (3) thermal anomalies developed around deep crustal structures.

Optimal conditions for gold transport and deposition are the following: f_{O_2} close to that fixed by the Ni-NiO oxygen buffer, high f_{S_2} around that fixed by the triple point hematite-pyrite-pyrrhotite and a shift toward lower pH.

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