Bulletin de Minéralogie

# Scheelite-bearing quartz veins from Poblet (Catalonian Coastal Range). Characterization of fluid inclusions and genetic model

Carlos Ayora Ibañez, Nicole Guilhaumou, Jean-Claude Touray, Juan Carlos Melgarejo

**Resumen**

Los filones de cuarzo y scheelita de Poblet, con una orientación NE-SO, se hallan encajados en los granitos calcicos tardi-hercinicos del sector Sur de las Cadenas Costeras Catalanas.

El estudio de las inclusiones fluidas en el cuarzo y la scheelita de estos filones se ha llevado a cabo mediante microtermometria, microespectroscopia Raman y microscopia electronica con analisis EDS. En ambos tipos de minerales se han observado los mismos tipos de cavidades intracristalinas, con excepción de las inclusiones de tipo I, que no han sido identificadas en la scheelita. Se han caracterizado sucesivamente :

— Inclusiones hipersalinas de tipo I, conteniendo unicamente halita, o varios sólidos asociados : silvina y cloruro ferroso (minerales hijos) ankerita, siderita, moscovita, feldespato potasico (minerales atrapados).

— Inclusiones acuosas de tipo II (L), de salinidad débil (1 à 6 % eq. NaCl), que homogeneízan en fase liquida entre 300 y 400 °C, o en condiciones críticas alrededor de 400 °C.

— Inclusiones acuosas de tipo II (V), de salinidad débil, con una fase carbónica de baja densidad, que homogeneízan en fase gaseosa entre 350 y 420 °C inclusiones trifasicas de tipo II (V'), en las que la fase gaseosa esta compuesta de $CO_2$ practicamente puro, de densidad 0,26. Estas inclusiones de tipo II parecen representar la evolución continua de un fluido supercrítico hacia dos subcríticos.

— Inclusiones tardías de tipo III, que indican la circulación de un fluido acuoso más frío y diluído (150 a 300 °C y de 0 a 3,5 % eq. NaCl).

La abundancia en las inclusiones de tipo I de cloruro ferroso sugiere una temperatura elevada (400 a 600 °C) de atrape de una fase fluida en equilibrio con un granito biotítico (Whitney et al., 1985). Las condiciones de P-T compatibles con las medidas obtenidas en las inclusiones de tipo II se situan alrededor de 400 °C y 0,8 kbar, valores comparables con los obtenidos en el yacimiento de tungsteno de Jebel Aouam, Marruecos (Cheilletz, 1984). Estas condiciones podrían corresponder a las de la cristalización de la scheelita.

**Résumé**

Les filons de quartz à scheelite de Poblet, d'orientation générale NE-SO, sont encaissés dans des granitoïdes calciques tardihercyniens du secteur Sud des chaînes côtières catalanes.

L'étude des inclusions fluides a été effectuée par microthermométrie, microspectrométrie Raman et microscopie électronique (analyse EDS) dans le quartz et la scheelite. A l'exception des inclusions de type I qui n'ont pas été observées dans la scheelite, les mêmes remplissages ont été observés dans les cavités intracristallines des deux minéraux. On a pu caractériser successivement :

— Des inclusions hypersalines de type I, avec dépôt de halite seule, ou plusieurs phases solides associées ; ankérite, sidérite, muscovite, felspaths potassiques (minéraux piégés), sylvite et chlorures ferreux (minéraux fils).

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— Des inclusions tardives de type III, marquant la circulation d'un fluide aqueux plus dilué et plus froid, (150 à 300 °C et 0 à 3,5 % equ. NaCl).

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**Abstract**

Scheelite-bearing quartz veins from Poblet, trending in a NE-SW direction, are hosted by calcic granitoids of Late Hercynian age in the southern part of the Catalonian Coast Range. Fluid inclusions

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Type I inclusions containing brine, daughter phases (halite, sylvite and sometimes iron chloride) and incidentally trapped minerals (ankerite, siderite, muscovite, K-felspar and unidentified species). Type II(L) inclusions have a low salinity (1 to 6 % eq. NaCl) and homogenize in the liquid phase in the range of 300-400 °C or under critical conditions near 400 °C. Type II(V) are low density, $CO_2$-poor aqueous inclusions, homogenizing in the gas phase in the range of 350-420 °C. Type II(V') have higher $CO_2$ contents. Type II inclusions appear as samples of an initially hypercritical fluid, trapped at different stages of its evolutions towards two subcritical fluids. Type III inclusions indicate later circulation of a colder, low-salinity solution (Th : 150 to 300 °C ; salinity : 0 to 3.5 % NaCl wt %).

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# Scheelite-bearing quartz veins from Poblet (Catalonian Coastal Range) Characterization of fluid inclusions and genetic model

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**Abstract.** — Scheelite-bearing quartz veins from Poblet, trending in a NE-SW direction, are hosted by calcic granitoïds of Late Hercynian age in the southern part of the Catalonian Coast Range. Fluid inclusions from quartz and scheelite have been characterized using microthermometry, Raman microspectrometry and Scanning Electron Microscopy. Except for type I inclusions (not observed in scheelite), similar inclusions have been observed in both minerals. One recognizes, in order of formation :

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**Key-words :** scheelite, quartz, fluid inclusions, Catalonia.

*Les filons de quartz à scheelite de Poblet (chaînes catalanes). Caractérisation des fluides associés et modèle de dépôt.*

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*Los filones de tungsteno de Poblet (Cadenas Costeras Catalanas). Caracterizacion de los fluidos asociados y modelo genetico.*

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# I. INTRODUCTION

## I.1. Geological Framework

The Catalonian Coast Range has a sedimentary and volcanic Paleozoic basement intruded by late Hercynian granites (leucogranites and granodiorites-tonalites). Above this basement, Mesozoic sediments lie unconformably upon a pre-Triassic erosion surface. After Neogene activity of NE-SW faults, a horst and graben configuration was developed with formation of small sedimentary basins (Figure 1). In the Southern zone, near the Poblet monastery outcrop tungsten bearing quartz lodes as well as disseminated scheelite occur in Carboniferous rocks.

## I.2. Tungsten-bearing quartz lodes

A detailed description of these scheelite-bearing quartz veins with accessory wolframite has been previously published (Melgarejo and Ayora, 1984). They have a general NE-SW orientation and are mostly hosted by the high-Ca facies (granodiorite, tonalite) of the granitic intrusions. Minor occurrences are hosted by late porphyry dykes and Carboniferous rocks metamorphosed at the pluton contact. One should note that NE-SW veins cross-cutting leucogranitic facies are barren. Meteoric weathering is a serious problem for characterizing the hydrothermal alteration at the veins walls. However, two mineralogical assemblages may be described (Melgarejo, 1983) :

— at the very contact of the quartz vein, which contains limited amounts of albite and orthoclase one has sometimes a centimetre scale fine grained association of quartz + orthoclase + albite + chlorite + residual muscovite.

# II. FLUID INCLUSIONS

## II.1. Fluid inclusion (F.I.) types

Fluid inclusions have been studied in massive

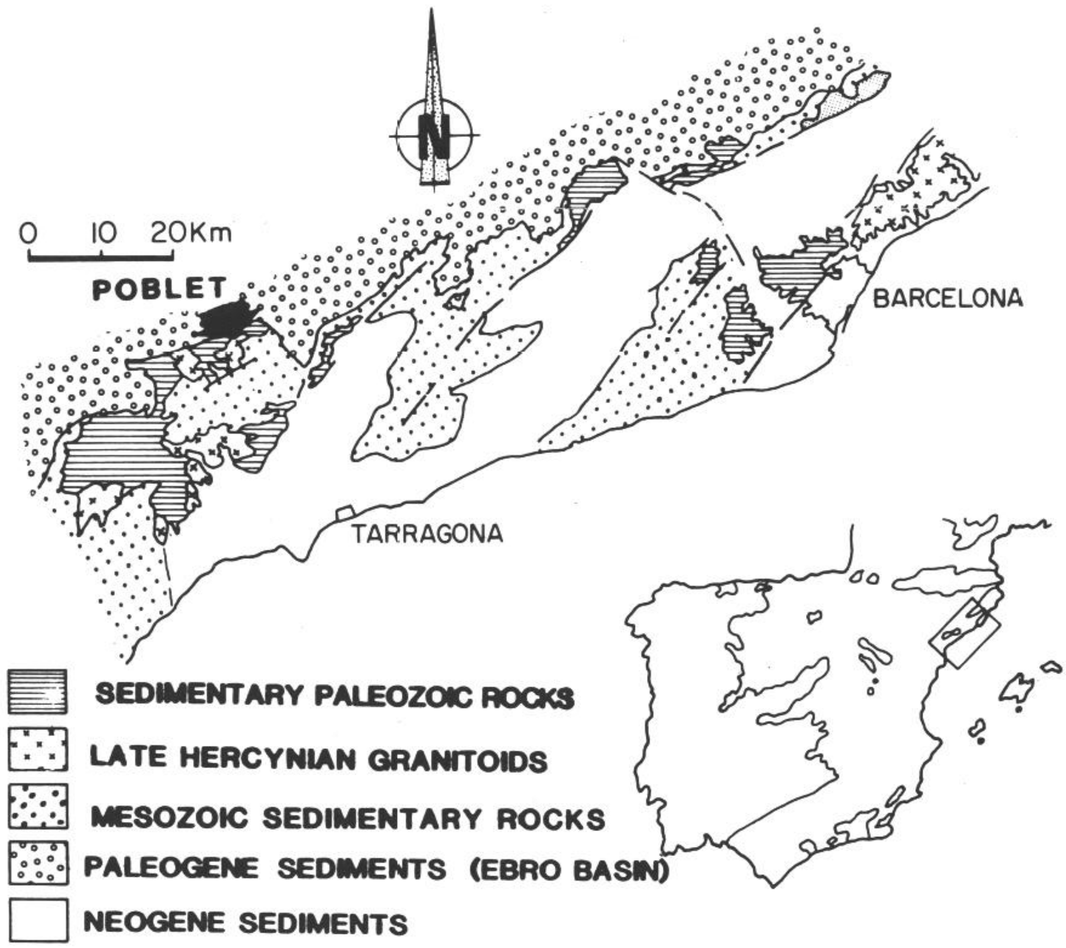


FIG. 1. — *Geological sketch map of the southern Catalonian Coast Raange.* (simplified from Julivert and Martinez, 1980).

*Schéma géologique du secteur sud des chaînes côtières catalanes, simplifié d'après Julivert et Martinez (1980).*

microcrystalline quartz, geodic quartz and massive scheelite. Microthermometry, Raman microspectrometry (for analyzing gas phases) and SEM with EDS were used for the analysis of solid phases. Inclusion sizes range from 1 to about 50 micrometers. Three main types have been recognized : types I and II are fluid samples mostly entrapped in early F.I. by microcrystalline quartz. In contrast, type III inclusions are scattered in healed cracks of the same samples.

Primary inclusions from geodic quartz belong to type III. Excepting brine inclusions (type I), the same F.I. have been detected in both quartz and scheelite.

*Type I inclusions*

These are brine F.I. with halite and usually other daughter crystals. They form small clusters without evident geometrical relations with other F.I. types. In the particular case of large quartz crystals, they are mostly present in the central core of the sample. Their apparent lack in scheelite samples is possibly related to the limited number of large transparent crystals.

*Type II inclusions*

These are two-phase bearing F.I. Vapour occupies between 30 and 70 % of the bulk volume. They are more or less geometrically-shaped, the smallest ones having a negative-crystal morphology. They are scattered along a large number of small anastomosing healed fractures cross-cutting grains of the quartz-scheelite agregates. In the particular case of large quartz crystals, they are abundant in the core and rare in the outer part. Three subtypes have been recognized :

— subtype II L, with dominant liquid water,

— subtype II V, with a low density carbonic phase,

— subtype II V′, similar to the former one with visible liquid $CO_2$ at room temperature.

*Type III inclusions*

Two-phase aqueous inclusions irregularly shaped with vapour bubbles amounting to about 20 % of the total volume. In geodic quartz, they are scattered in three dimensions and considered as primary F.I. In the massive quartz, they are late secondary.

## II.2. Microthermometric data

Microthermometric investigations have been performed with a Chaix-Meca heating and freezing stage using a procedure described earlier (Guilhaumou, 1982). With respect to the small size of F.I. and the practical problems at high temperatures, thermometric measurements were performed only at temperatures lower than 450 °C. The data are collected in figures 3 to 8.

*Type I inclusions*

The disappearance of the vapour phase occurred at $T_B$ in the range +243 to +437 °C ; total dissolution of halite occurred at $T_S$ in the range +216 to +415 °C. The total homogenization (at temperature $T_H$) was not always achieved at 450 °C mostly for inclusions with several daughter crystals, and decrepitation often occurred around +430 °C before homogenization. In different cases, one has $T_H = T_S$ or $T_H = T_B$. The correlation between $T_S$ and $T_B$ is illustrated in figure 2.

*Type II inclusions*

Eutectic temperatures range between −24.6 and −21.1 °C, very near the eutectic point of the system $H_2O$-NaCl. Accordingly, one may discard the presence of significant amounts of $CaCl_2$ or $MgCl_2$ (Crawford, 1981). Melting temperatures of ice, $Tm_i$, are in the range 0 to −3.5 °C (Figure 3.A), corresponding to salinities between 0 and 5.5 wt % equivalent NaCl. $CO_2$ has been detected by the presence, in several instances, of a solid melting very near the triple point of $CO_2$ (about −56.6 °C) and the formation of hydrates.

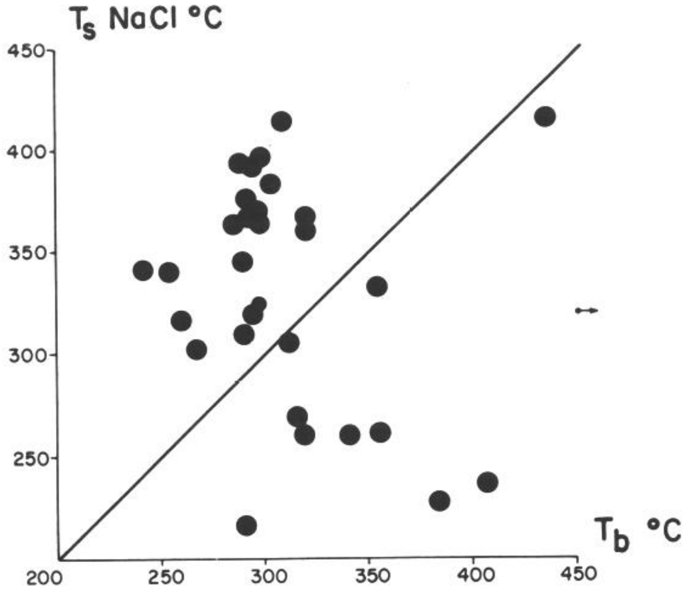


FIG. 2. — *Correlation plot between Ts (total dissolution temperature of the daughter halite) and Tb (temperature of disappearance of the vapour bubble) in type I inclusions.*

*Diagramme de corrélation entre Ts (température de dissolution du cube de halite) et Tb (température de disparition de la bulle de vapeur) dans les inclusions du type I.*

At high temperature, three different behaviours have been noticed (Figure 4) :
— Transition L + V → V with $T_H$ ranging from +338 to +422 °C in the massive quartz and +327 to 391 °C in the scheelite (subtype II V).
— Transition L + V → L with $T_H$ ranging from +298 to +409 °C in the massive quartz and +300 to +396 °C in the scheelite (subtype II L *pro parte*).
— Critical homogenization between +379 and +414 °C in the massive quartz only (subtype II L *pro parte*).

In the carbonic part of the II V′ inclusions, the only phase transition is L + V → V and it occurs from +24.2 to +27.8 °C (Figure 5) indicating $CO_2$ densities in the range 0.23 to 0.28. $CO_2$ clathrate melt, in the presence of liquid $CO_2$, between +7.4 and +9.3 °C (Figure 6) ; the salinities derived from these data are in good agreement with the figures deduced from $Tm_i$. The solids grown at low temperature melt around −56.6 °C, indicating pure $CO_2$. The mean composition of II V′ inclusions, following Ramboz-type calculations (1980), is $X_{CO_2}$ = 13 % ; $X_{H_2O}$ = 85.4 % ; $X_{NaCl}$ = 1.6 %.

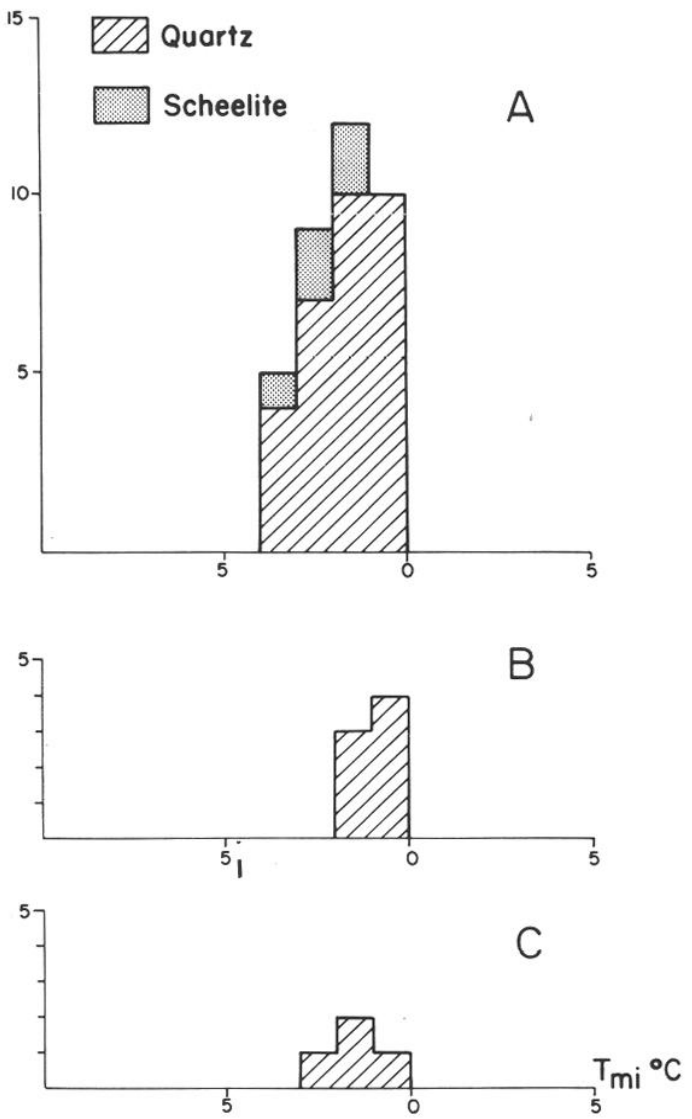


FIG. 3. — *Histogram of the melting temperature of ice $Tm_i$.* A : type IIL in microcrystalline massive quartz and in scheelite. B : type III in geodic quartz. C : type III in healed fractures of the microcrystalline quartz.

*Histogramme des températures de fin de fusion de la glace $Tm_i$.* A : type IIL dans le quartz massif et la scheelite. B : type III dans le quartz géodique. C : type III dans les fractures recicatrisées du quartz microcristallin.

## *Type III inclusions*

The $Tm_i$ values scatter in the range −0.3 to −2.1 °C (Figures 3B and 3C) implying salinities in the range 0 to 3.5 wt % equivalent NaCl. Homogenization always occurs through the L + V → L transition between +190 and +300 °C (Figure 7). There is no significant difference between secondary F.I. in the massive quartz and primary ones from the geodic quartz, confirming its late origin.

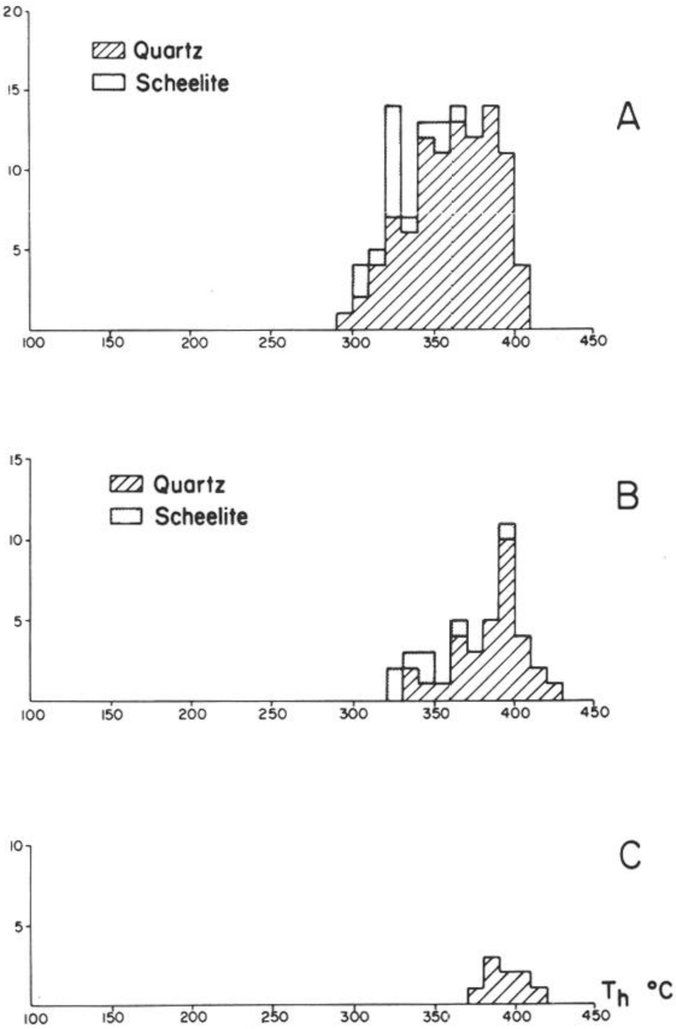


FIG. 4. — *Histogram of the homogenization temperature in type II inclusions from massive quartz and scheelite.* A : L+V L (subtype IIL). B : L+V V (subtype IIV). C : critical homogenization (subtype IIL).

*Histogrammes des températures d'homogénéisation des inclusions de type II dans le quartz massif et la scheelite.* A : L+V L (sous-type IIL) ; B : L+V V (sous-type V) ; C : homogénéisation critique (sous-type IIL).

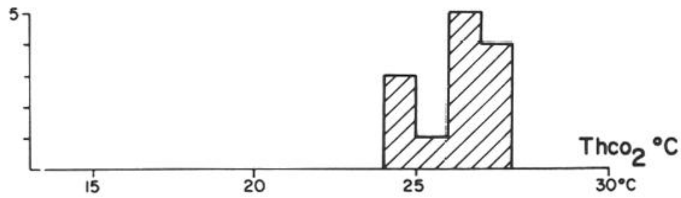


FIG. 5. — *Histogram of the homogenization temperature of the carbonic phase, Th $CO_2$.* (L+V V).

*Histogramme des températures d'homogénéisation de la phase carbonique, Th $CO_2$* (L+V V).

## II.3. Raman microprobe data

Analysis have been performed in collaboration with J.M. Bény (Orléans) using a U-1000 machine, with a procedure previously described (Bény *et al.*, 1982 ; Touray *et al.*, 1985). As a result, the vapour phase of II V and II V′ F.I. is mostly made of $CO_2$ with trace amounts of $CH_4$, $N_2$ and $H_2S$ (Table I) in good agreement with freezing data.

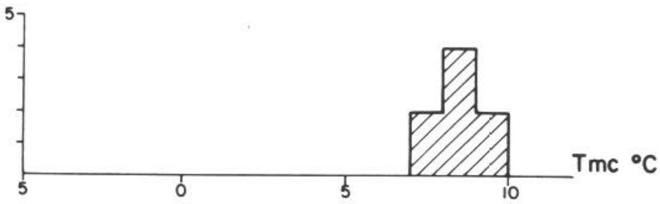


FIG. 6. — *Histogram of the melting temperature of the $CO_2$-clathrate $Tm_c$.* (Determined in the presence of liquid $CO_2$ in IIV′ subtype inclusions).

*Histogramme des températures de fusion du clathrate de $CO_2$ $Tm_c$.* Déterminé en présence de $CO_2$ liquide dans les inclusions de type IIV′.

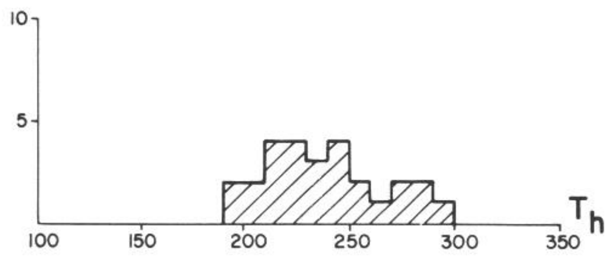


FIG. 7. — *Histogram of homogenization temperatures of type III inclusions.*

*Histogramme des températures d'homogénéisation des inclusions de type III.*

## II.4. Scanning electron microscope data

Solid phases present in type I inclusions have been identified by SEM with an EDS analytical system (Barcelona University). Combining morphological data (Figure 8) with qualitative chemical analysis, the following determinations were performed :

— Halite cubes (Na, Cl)
— Sylvite cubes with rounded corners (K, Cl)
— Manganese-rich iron chloride crystallized as hexagonal prisms (Fe, Cl, Mn). The number of associated water molecules remains unknown (possibly $FeCl_2$-$2H_2O$, Kwak *et al.* (1986), but more likely $FeCl_2$, because of the hexagonal morphology).
— Iron-rich rhombohedral carbonates : ankerite (Fe, Mg, Ca) and siderite (Fe, Mg).
— Muscovite flakes (Si, Al, K), K-feldspar massive crystals (Si, Al, K) and undetermined Si-Ca-Mg-Al-Fe compounds.

Halite and sylvite are daughter phases, formed inside inclusions during temperature drop, as demonstrated by total dissolution during heating runs. Iron chloride is probably a daughter phase too, however only partial dissolution was observed at + 450 °C. Carbonates and silicates have probably been mechanically entrapped.

## III. INTERPRETATION AND CONCLUSION

From F.I. data, two contrasted types of fluids appear to have played a part in the history of the tungsten-bearing quartz lodes of Poblet :

| Inc | Vb/Vc | Microthermometry | | | | | | % Raman | | | | V | Dt |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Tfm | Tmi | Th | $Tf_{CO_2}$ | $Th_{CO_2}$ | TfC | $X_{CO_2}$ | $X_{CH_4}$ | $X_{H_2S}$ | $X_{N^2}$ | | |
| 1 | 0.6 | -23 | -1 | +400 | -56 | +25V | +7.4 | 98.2 | 0.1 | 0.5 | 0.3 | 38.8 | 0.56 |
| 2 | 0.2 | -23 | -3.5 | +350 | nd | - | - | 99.9 | | traces | | 27.7 | 0.82* |
| 3 | 0.8 | -23 | -0.5 | +400 | nd | - | - | 99.9 | | traces | | 88.6 | 0.80* |

TABLE I. — *Compositions of fluid inclusions, calculated from microthermometric data and Raman microspectroscopy.* (Ramboz, 1980). Vb : vapour phase ; Vc : total volume of inclusion ; Tfm : first melting temperature of ice ; Tmi : ice melting temperature ; Th : homogenization temperature ; Tf $CO_2$ : melting temperature of $CO_2$ ; Th $CO_2$ : homogenization temperature of $CO_2$ (V : in vapour phase) ; Tfc : melting temperature of the $CO_2$ clathrate ; V : molar volume ; Dt : total density of inclusion. 1 : type II V′ ; 2 : type II L ; 3 : type II V ; * : for $d_{CO_2} = 0.1$.

*Composition des inclusions fluides calculées à partir des données microthermométriques et des analyses à la microsonde Raman.* (Ramboz, 1980).

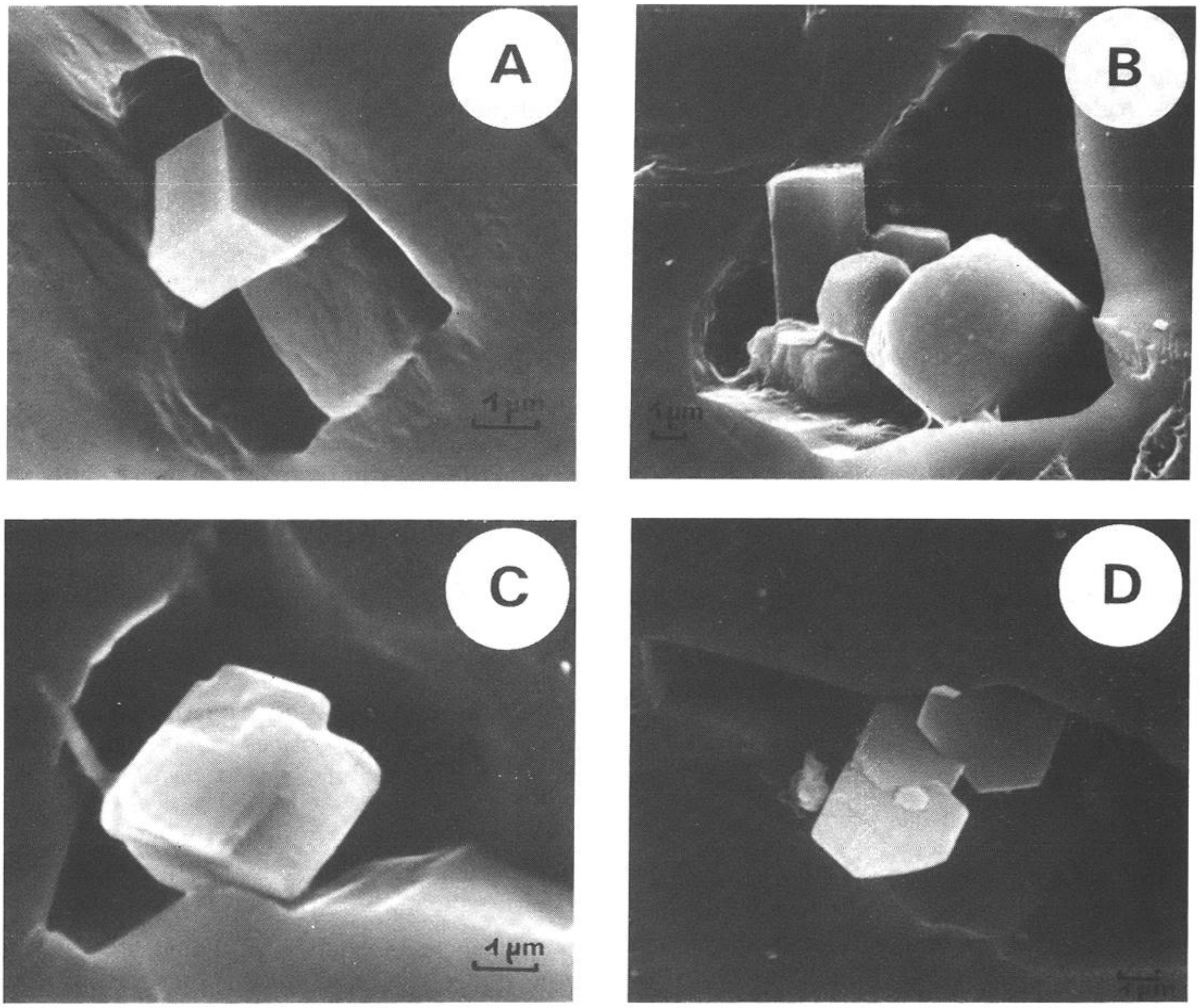


FIG. 8. — *Analysis of the solid phase by SEM and EDS.* A : (Fe,Mn)$Cl_2$, hexagonal prisms ; NaCl partly dissolved cube. B : back left : (Fe,Mn)$Cl_2$ prisms, front : NaCl and KCl cubes. C : siderite. D : muscovite.

*Analyse des phases solides dans les inclusions par MEB et EDS.* A : (Fe,Mn)$Cl_2$, prisme hexagonal ; cube de NaCl en partie dissous. B : en bas à droite : (Fe,Mn)Cl prismatique, devant : NaCl et KCl en cubes. C : sidérite. D : Muscovite.

— Complex brines belonging to the system $H_2O$-NaCl-KCl with high amounts of $FeCl_2$.
— Solutions and vapours in the system $H_2O$-$CO_2$ (NaCl).

The first question to be answered is to determine the T-P conditions at the time of trapping. With respect to experimental alteration of granites by strong brines (Whitney *et al.*, 1985), the presence of iron chloride in type I inclusions as a daughter phase suggests entrapment temperatures significantly higher than 400 °C, in good agreement with microthermometrical data. Indeed, in 3 molar brines, one has higher Fe/Na ratios at higher temperatures (0.75/0.67 at 600 °C and 0.3/1.7 at 400 °C). The temperature dependence of the Fe/Na ratio could explain the presence in a same cluster of type I inclusions with or without iron-chloride daughter phase, the later reflecting a T decrease during the granite-brine interaction. Alternatively, post entrapment evolution (*e.g.* necking down) could be invoked. The numerical difference $T_S$-$T_B$ may give information about F.I. formation pressure when mother-brine salinities are buffered by extra-halite, as examplified by diapiric environments (Perthuisot *et al.*, 1978). However, in this regard, no unequivocal interpretation may be derived from figure 2, because at Poblet, saturation of hydrothermal fluids with respect to

NaCl is difficult to admit. Finally, the formation pressure of type I inclusions remains unknown. Boiling at low P of magma derived saline solutions, followed by an increase of both T and P (Burnham, 1979), could explain the origin and evolution of early fluids at Poblet.

Similar brine F.I. have been described in the Sn-W deposit of Aouam, Morocco ; the $T_S$-$T_B$ diagram (Figure 7, p. 267, Cheilletz, 1984) is similar to figure 3. However, at Aouam, the geological history is probably more complex than at Poblet because brine F.I. have been observed in three successive W-bearing quartz generations.

Type II inclusions are known as subtypes V and L and one may ask whether they represent immiscible fluids. The scarcity of heterogeneous groups of II V and II L F.I. does not suggest such a conclusion. Moreover, one has a significant shift between $T_H$ values for II V and II L inclusions (Figures 4A and 4B) and critical homogenizations are not uncommon. These facts suggest a continuous evolution of an hypercritical fluid in the direction of two subcritical fluids. This evolution has been discussed in detail at Aouam (Cheilletz, 1984) and applies as well at Poblet. The molar volumes of several II V' inclusions have been estimated from phase volume ratios, microthermometric and Raman data. With respect to the $H_2O$-NaCl-$CO_2$ system (Gherig, 1980), minimum trapping pressures of about 0.8 kbar have been computed, for minimum temperatures of 400 °C. In our interpretation, the II V' inclusions represent fluids belonging to the same generation as II V inclusions : no indications of later trapping of such fluids after dissolution-redeposition of quartz have been derived from careful optical examinations. Accordingly, 400 °C and 0.8 kbar are approximate minimum estimations of T and P at the time of trapping of type II inclusions.

The second question is related to possible genetic links between the two fluids. At Poblet, as well at Aouam, and other occurrences (Krusne-Hary, Tchecoslovaquia ; Durisova *et al.*, 1979), no intermediate compositions have been observed. Accordingly, one may suppose that the two fluids belong to two distinct hydrothermal episodes. This conclusion is in agreement with the early character of the brine inclusions and the later trapping of the type II inclusions (see above).

The last question is the nature of the W-bearing fluid. No brine inclusions have been observed in scheelite and one may presume that circulation of saline solutions occurred prior to $CaWO_4$ precipitation. However, with respect to the limited number of investigated scheelite crystals (size, transparency), this lack of brine inclusions may only be apparent. A precise mineralogical-paragenetic study of quartz containing the hypersaline brines and scheelite could help to overcome this problem. Unfortunately, the scarcity of scheelite precludes any definite conclusion.

In this model, a "host quartz lode", grown from hydrothermal brines, is thought to have been fractured and then to have hosted a W mineralization transported and deposited by $CO_2$-$H_2O$ fluids. A similar conclusion has been proposed for gold-bearing quartz veins from auriferous shear-zones (Hubert, 1986).

On the other hand, one should note that barren quartz veins (hosted by leucogranites) contain the same fluid inclusions as W-bearing lodes (this study). This observation underlines the rôle of fluid-rock interaction as controlling factor for $CaWO_4$ precipitation. Indeed, leucogranites are Ca-poor rocks (mean CaO content : 0.58 %) whereas calcic granites contain about five times more CaO (mean content : 2.75 %, Melgarejo and Ayora (1984)).

Finally, most of the F.I. data collected at Poblet are similar to those established at Aouam (Central Morocco, Cheilletz (1984)), underlining the possible rôle of fluid inclusions in helping to classify W-Sn deposits from the Hercynian domain.

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