

## Hydrothermal fluids in barren quartz veins (Spanish Central System). A comparison with W-(Sn) and F-(Ba) veins

### Fluidos hidrotermales en filones estériles de cuarzo (Sistema Central Español). Comparación con filones de W-(Sn) y F-(Ba)

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**Abstract:** Late fluids trapped in barren quartz veins from the Spanish Central System and a comparison with earlier fluids associated with W and fluorite mineralization have been investigated in this paper. Special attention has been paid to fluid chemistry using microthermometry and bulk leachate chemical analysis. Three different fluids have been recognized: (i) early H<sub>2</sub>O-NaCl-CO<sub>2</sub>-CH<sub>4</sub> fluids associated with W-sulphide (ii) aqueous H<sub>2</sub>O-NaCl fluids related to fluorites (iii) aqueous fluids associated with barren quartz veins. Two different fluids characterized by H<sub>2</sub>O-NaCl and H<sub>2</sub>O-NaCl-CaCl<sub>2</sub> systems have been recognized in these latest fluids. Li is present too. Possible origins for dissolved ions in the fluids are discussed in this study. Different mineralizations have different origins.

**Key words:** fluid inclusions, Spanish Central System, "crush leach" analysis, barren quartz veins

**Resumen:** En el presente trabajo se han investigado los fluidos tardíos atrapados en filones estériles de cuarzo del Sistema Central Español, a la vez que se ha realizado una comparación con fluidos asociados a mineralizaciones de W y de fluorita. Se ha llevado a cabo el estudio mediante un análisis combinado de microtermometría y química del fluido. Se han identificado tres tipos de fluidos: (i) fluidos tempranos acuoso-carbónicos (H<sub>2</sub>O-NaCl-CO<sub>2</sub>-CH<sub>4</sub>) asociados a mineralizaciones de W-sulfuros (ii) fluidos acuosos (H<sub>2</sub>O-NaCl) asociados a fluoritas (iii) fluidos asociados a filones de cuarzo. En estos últimos se han reconocido dos fluidos acuosos diferentes caracterizados por los sistemas H<sub>2</sub>O-NaCl y H<sub>2</sub>O-NaCl-CaCl<sub>2</sub>, con presencia de Li.

En este estudio se discute el posible origen de los iones disueltos en los fluidos, que es diferente para cada tipo de mineralización.

**Palabras clave:** inclusiones fluidas, Sistema Central Español, análisis mediante "crush leach", filones estériles de cuarzo

## Introduction

The Spanish Central System has been subjected to repeat fluid incursions, which are responsible for different intragranitic and intrametamorphic mineralizations, W-Sn, Cu-Zn-Pb sulphides and F-Ba. These hydrothermal fluids spread around 200 Ma in time. Barren quartz veins record the last fluid events. Fluids associated to W-(Sn) sulphide veins have been studied in several deposits of the Spanish Central System, San Rafael, Cabeza Mediana, Collado Mediano, Cabeza Lijar, Garganta de los Montes, El Estepar (Quílez, 1994; Vindel et al., 1995), as the fluorite ores (Tornos et al., 1991). Very little is known about the fluid chemistry and conditions of the barren quartz deposition. The aim of this study is to analyze these late fluids and to compare them with the earlier fluids associated with the W-Sn and fluorite mineralizations.

Typical barren quartz veins have been selected in the central sector of the Spanish Central System, which hosts numerous occurrences of this type and provides excellent opportunities to sample the quartz veins and correlate to close W-polymetallic sulphide and fluorite veins.

## Geology and mineralization

The Spanish Central System is a northeast trending mountain chain located in the inner zone of the Hercynian Belt of Spain. The central part, called "Sierra de Guadarrama", consists of granites and high-grade metamorphic rocks, mostly pre-Hercynian orthogneisses and some pre-Ordovician metasediments. The late Hercynian granites were emplaced from 345 to 275 Ma (Ibarrola et al., 1987) after the main Hercynian orogenesis. They are mostly peraluminous monzogranites and leucogranites (Villaseca et al., 1998).

Mineralized veins containing W-Sn, sulphide, fluorite-baryte, barren quartz and hydrothermal alteration are widespread in the Spanish Central System (Fig. 1). Mineralization covers the period from 300 to 100 Ma ago. W (Sn) veins and greisens are the oldest at 302-290 Ma, followed by fluorite at 145-18 Ma (Galindo et al., 1994) and then barren quartz at 100 Ma. (Caballero et al., 1992).

Peraluminous granites and minor leucocratic granites host the W-Sn mineralizations. Sometimes, they crosscut high-grade metamorphic rocks usually orthogneisses or migmatites. W-Sn veins are characterized by multistage ore deposition consisting of the successive crystallization of W (Sn-Mo) minerals and Cu-Zn-(Pb) sulphides (Quílez et al., 1990; Quílez, 1994; Vindel et al., 1995; García, 1997).

Fluorite-baryte veins, with small amounts of sulphides (galena, sphalerite, chalcopyrite, pyrite and Bi-Ag sulphosalts), are common in the western part of the Spanish Central System. They are hosted by peraluminous porphyritic adamellites, and minor leucogranites and sometimes by orthogneisses. The veins display vertical and lateral zoning, a deeper and outer quartz zone, an intermediate fluorite zone and a shallow and inner barite zone (Ortega et al., 1988; Tornos et al., 1991). Minor amounts of carbonates are also present. Fluorite has distinct color zoning, the outer of which is yellow, with an intermediate purple tone and an inner green zone in contact with the barite.

Typical barren quartz veins (Martín Crespo et al., 1997) are the subjects of this study. They are hosted by the Zarzalejo-Valdemorillo porphyritic granite and have developed along extensional faults (striking N20-30°E with dipping of 80-90°E). The veins have a thickness of 1 to 5 m and can be several kilometers in length (maximum 4 km). They consist of quartz, which is

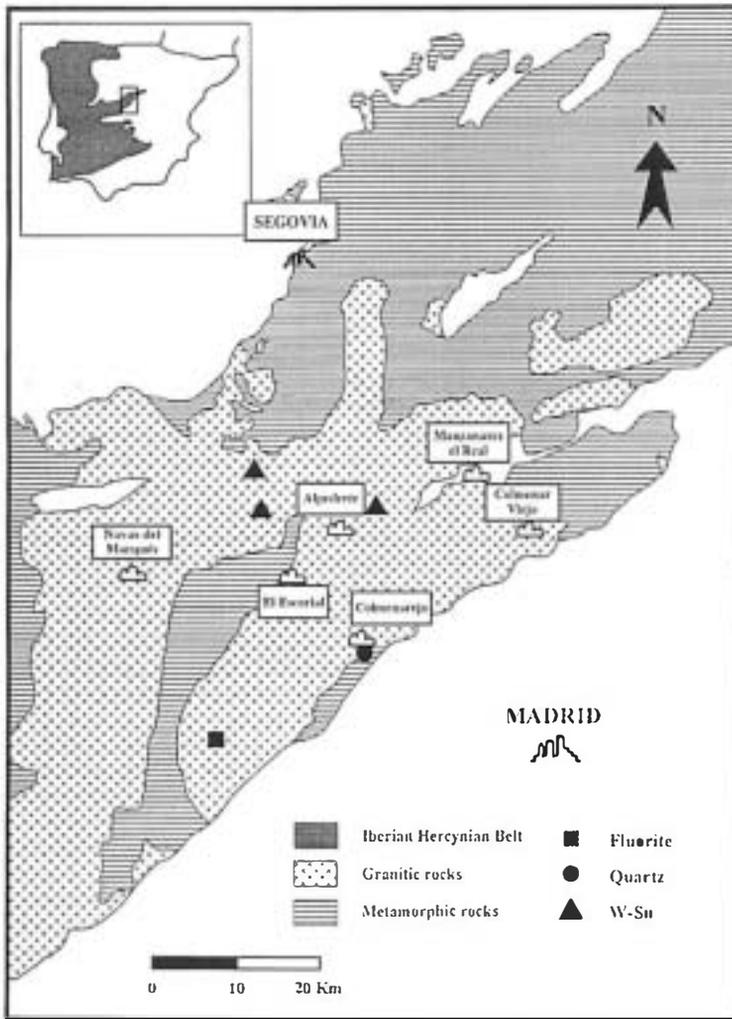


Figure 1.- Geological setting of the W-(Sn), fluorite and barren quartz mineralizations. Sample locations are represented too.

Figura 1.- Localización geológica de las mineralizaciones de W-(Sn), fluorita y cuarzo estéril. También se ha representado la localización de las muestras.

massive at the vein margins but euhedral in the center; some carbonates also occur at the margins of the crystals and filling fractures. Hydrothermal alteration is restricted to the proximity of the lodes due to the low temperatures of fluids and it is poorly developed. Sericitization and chloritization

are the usual and most important alterations. Sericitization is characterized by formation of of of hand, is restricted to the alteration of granite's biotites because a new generation of biotites not appears.

## Analytical methods

### *Individual fluid inclusion characterization*

Microthermometric characterization of the fluids was undertaken using a heating-freezing Linkham THG 600 stage. The stage was calibrated at high temperature with melting point standards and at low temperature with a pure CO<sub>2</sub> at the triple point (-56.6 °C), the melting point of toluene (-95 °C) and the T<sub>m</sub> ice in a pure water synthetic fluid inclusion (0 °C). Accuracy of ± 0.2 °C has achieved during freezing, ± 1 °C between 25-400 °C and ± 4 °C between 400-600 °C. Salinity is expressed in equivalent wt.% NaCl and was calculated from measurements of the ice melting temperatures (T<sub>m</sub> ice) using the equations of Hall et al. (1988).

Salinity of hypersaline inclusions (> 26.3 wt.% NaCl) were calculated from the halite dissolution temperature (T<sub>s</sub>) using the equation of Bodnar & Vityk (1994). This equation is theoretically valid only when halite and vapor bubble disappear at the same temperature, but will provide a reasonable approximation of the salinity when these conditions are not present. The errors range from an underestimate of the salinity by ~ 1.3 wt.% for a halite dissolution temperature of 200 °C, to an overestimate of the salinity by ~ 2.6 wt.% for a halite dissolution temperature of 600 °C (Bodnar & Vityk op.cit.). P-T properties were obtained using data from Zhang & Frantz (1987) for the H<sub>2</sub>O-NaCl system.

Notation of the fluid inclusion types follows the nomenclature of Boiron et al. (1992), which takes into account the nature of the dominant chemical phases and the type of phase change.

### *Bulk ion analysis*

Bulk crush-leach analysis was performed on samples of quartz and fluorite that were prepared and cleaned using the methods of

Botrell et al. (1988) modified by Yardley et al. (1993). The amount of sample crushed in an agate pestle was typically between 0.5 and 1 gr. of clean mineral grains, free from contaminant minerals. Analysis of anions, Cl and Br was performed by Ion Chromatography on double distilled water leaches using a Dionex 4500I HPLC. Sodium was determined on the same solution leached with an acidified LaCl<sub>3</sub> solution by Flame Emission Spectroscopy (FES).

## Fluid data from different types of veins

### *W-Sn-polymetallic sulphide veins*

Fluid inclusions data of W-Sn-polymetallic sulphide veins from several deposits of the Spanish Central System (Cabeza Mediana, Collado Mediano, Cabeza LÍjar, Garganta de los Montes, El Estepar, San Rafael) were previously published (Quílez et al., 1990; Quílez, 1994; Vindel et al., 1995; García, 1997). Three main types of fluids have been identified:

Magmatic hypersaline aqueous fluids represented by three phase Lw-s inclusions including one ore more solid phases (dominantly halite and/ore silvite and unknown trapped minerals) with total homogenization temperatures ranging from 200 °C to 400 °C and salinity from 29 to 48 wt.% eq. NaCl.

Metamorphic aquo-carbonic fluids; represented by three different types of fluid inclusions: (i) H<sub>2</sub>O-NaCl-CO<sub>2</sub>-CH<sub>4</sub> liquids (Vc-m-w inclusions, density 0.4/0.6, Th 350/400), (ii) H<sub>2</sub>O-NaCl-CO<sub>2</sub>-(CH<sub>4</sub>) liquids (Vc-w inclusions, density 0.5/0.8, Th 350/410) and (iii) H<sub>2</sub>O-NaCl-(CO<sub>2</sub>)-CH<sub>4</sub> liquids (Lw-c and Lw-m inclusions, density 0.55/0.70, Th 210/370). The salinity of the aquo-carbonic fluid, where could be calculated, ranging between 0.2 and 2 wt.% eq. NaCl.

Aqueous fluids (H<sub>2</sub>O-NaCl) liquids represented by Lw1 and Lw2 inclusions)

are characterized by low to moderate salinity (1 to 9 wt.% eq. NaCl) and Th ranging between 140 and 380 °C.

#### *Fluorite-barite veins*

Fluid inclusions in fluorite are aqueous and show homogenization temperatures in the range 150-270 °C and salinity between 0 and 10.5 wt.% eq. NaCl. Fluid inclusions in baryte are more saline (3.4-14 wt.% eq. NaCl) and lower Th (120-200 °C). Fluid inclusions in quartz older than the mineralization show Th 260-300 °C and final melting temperature of ice >2 °C (Tornos et al., 1991). Analyses of volatiles contained in fluid inclusions in fluorites and barytes by decrepitation under vacuum and mass spectrometry show that the fluid are pure water with small amounts of CO<sub>2</sub> and traces of H<sub>2</sub>, CH<sub>4</sub> and CO (Galindo et al., 1994).

#### *Barren quartz veins*

Typical barren quartz veins from the Colmenarejo zone are the subjects of this study. Fluid inclusions have been studied in well-formed quartz crystals in the central part of the barren quartz veins where the optical conditions were suitable. In the outer part, the milky and massive quartz made not possible the observation and the microthermometric study. Although, the size of fluid inclusions in this outer zone were very small to get suitable data.

Three major stages of mineral crystallization and fluid migration have been recognized: stage 1: central part of well-formed quartz crystals (Q1) enriched in primary and pseudosecondary Lw1 inclusions and Lw2 secondary inclusions in fluid inclusion planes; stage 2: outer part of the quartz crystals (Q2) containing primary Lw2 inclusions and stage 3: carbonates crystallization. During the third stage of fluid migration Lw-s inclusions in FIP resulting from the annealing of microcracks are observed in the both quartz types. No primary

Lw-s inclusions were recognized.

Three types of fluid inclusions have been identified. Microthermometric data including ranges and modes are presented in Table 1; they are all aqueous and no C-N-S species were detected.

Lw1 inclusions represent H<sub>2</sub>O-NaCl fluids, with L+V at room temperature. They are primary inclusions located in the centre of the quartz crystals. Bulk salinity of this fluids is lower than 1 wt.% NaCl. Homogenization temperatures ranging between 170-295 °C, with 250 °C as the modal valor.

Lw2 inclusions are primary inclusions, located in the margins of the crystals and also scattered along healed fractures in the centre of the crystals. They contain L+V at room temperature. The eutectic temperatures, ranging for -67 to -57 °C, corresponding to H<sub>2</sub>O-NaCl-CaCl<sub>2</sub> fluids (Yanatieva, 1946; Borisenko, 1977). These temperatures are lower than theoretic eutectic temperatures (-52 °C). According to Zwart & Touret (1994), two possible explanations for this are: (I) the system follows the melting sequence according to the model univariant curve (Spencer et al., 1990; Davis et al., 1990) with a metastable eutectic point around -70 °C for this system or (II) a mixture of H<sub>2</sub>O-NaCl-CaCl<sub>2</sub> contains other salts like KCl and/or LiCl. Preliminaries analyses of these fluids using LA-OES (Laser Ablation Optical Emission Spectroscopy) have demonstrated the presence of Li. The composition of these fluids lies in the high salinity part of the H<sub>2</sub>O-NaCl-CaCl<sub>2</sub> system, below the ice-hydrohalite cotectic curve around 27 wt.% eqNaCl (Fig.2). They show lower homogenization temperatures than Lw1 fluids (90-160 °C), and 120 °C as the modal valor.

Lw-s inclusions contain, at least, three phases at room temperature including daughter crystal (halite). Also trapped carbonates, plagioclase and phyllosilicates have been identified by SEM+EDS. Homogenization temperatures ranging

Table 1.- Representative microthermometric data for the different types of fluid inclusions. Barren quartz veins.

Tabla 1.- Datos microtermométricos representativos de los diferentes tipos de inclusiones fluidas. Filones de cuarzo estéril.

Inclusion types	Lw1	Lw2	Lw-s
Main components	H <sub>2</sub> O-NaCl	H <sub>2</sub> O-NaCl-CaCl <sub>2</sub>	H <sub>2</sub> O-CaCl <sub>2</sub> -NaCl
Occurrence in veins	Primary	Primary (Secondary)	Secondary
Habitus at room temperature	Two phases	Two phases	Three phases
Gas infilling (%)	5-30	5-10	5-10
Tm eutectic (°C)	--	-67 / -57 mode: -63.5	--
Tm ice (°C)	-0.4 / 0 mode: -0.2	-26.7 / -24.2 mode: -25	-47.5 / -41 mode: -46.5
Tm hydrohalite (°C)	--	-13.5 / -5.8 mode: -8	--
Tm solidus (°C)	--	--	120-205 mode: 145
Th vapour (°C)	170 - 295 mode: 250 (L)	90-160 mode: 120 (L)	60-165 mode: 130
Salinity (wt.% NaCl eq.)	0 / 0.7	16 / 19 wt.% NaCl 7 / 12 wt.% CaCl <sub>2</sub>	10 / 15 wt.% NaCl 22 / 27 wt.% CaCl <sub>2</sub>
NaCl / (NaCl + CaCl <sub>2</sub> )	--	0.60 / 0.70 mode: 0.65	0.25 / 0.35 mode: 0.30

between 60 °C and 165 °C and dissolution temperatures of halite between 120 °C and 205 °C. Modal temperatures are closed in both intervals: 130 °C and 145 °C respectively. High bulk salinity has been calculated for this Lw-s inclusions between 36 and 37 wt.% eq.NaCl. They are secondary inclusions, postdating the other two types and represent the last hydrothermal event.

#### *Chemistry of fluid inclusions*

The halogens, Cl and Br, can be used to distinguish ions from different sources (Bohlke & Irwin, 1992). This arises because they are conservative in solution and are relative unaffected by fluid-rock interactions

(Banks et al., 1991). Unlike halogens, the cation content of the fluid inclusions almost certainly reflects fluid-rock interactions. Cl, Br and Na were analyzed in this paper (Table 2). For waters made saline by halite dissolution, Na/Br and Cl/Br molar ratios are strongly increased over that for seawater. Halite precipitation from evaporatively concentrated seawater strongly decreases the Na/Br and Cl/Br ratios of the residual brines (Kesler et al., 1995).

The oldest fluids (W-Sn veins) have Cl/Br ratios (Fig. 3) ranging between 995 and 1094 which are similar to magmatic fluids associated with mineralizations in the Hercynian granites of England (Banks et

al., 1993). Intermediate age fluorite fluids have Cl/Br ranging between 3844 and 4346 that combined with the low salinity is suggestive of dissolution of evaporites by low salinity water. This is in accordance with the data from Galindo et al. (1994). They propose a source derived from a marine/evaporitic environment for this fluorite mineralization. The youngest fluids in the barren quartz veins have Cl/Br 703 to 753, representative of the higher salinity

Lw2 fluids. This is close to the ratio for evaporating seawater prior to halite precipitation.

### Discussion

Barren quartz veins show two main types of fluids: (i)  $\text{H}_2\text{O}$ -NaCl, moderate temperature and low salinity fluid, represented by Lw1 inclusions, and (ii)  $\text{H}_2\text{O}$ -NaCl- $\text{CaCl}_2$ , low

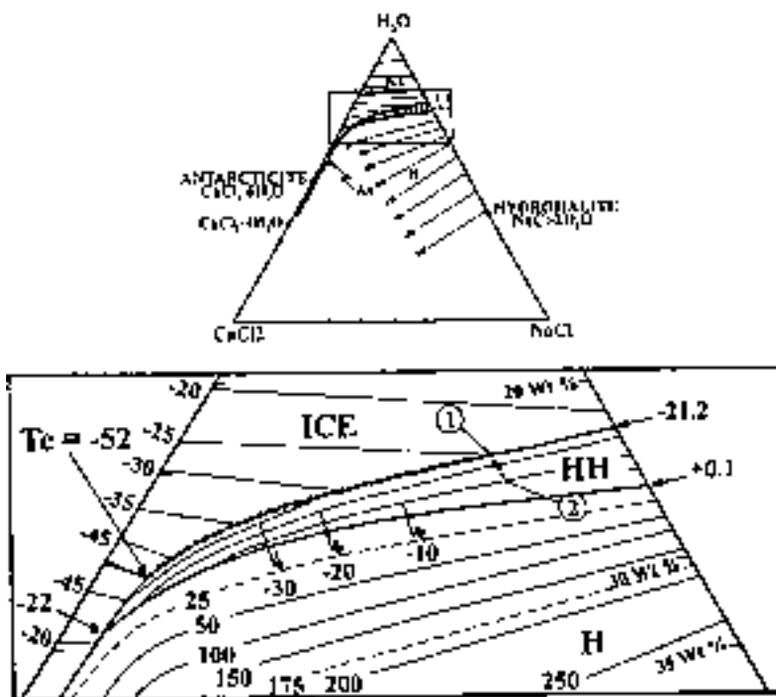


Figure 2.- Phase diagram for the ternary system  $\text{H}_2\text{O}$ -NaCl- $\text{CaCl}_2$  (after Zwart & Touret, 1994) with the outlined part representing the area of interest. Solid lines are isotherms and dashed lines are extrapolated isotherms. Bold solid lines are cotectic curves that separate the ice, hydrohalite (HH) and halite (H) regions. Melting path of Lw2 inclusions is represented by a trail of small black squares with the temperature modes: 1. Ice melting and 2. Hydrohalite melting. At this point, the fluid composition can be determined.

Figura 2.- Diagrama de fases del sistema ternario  $\text{H}_2\text{O}$ -NaCl- $\text{CaCl}_2$  (a partir de Zwart & Touret, 1994) con la zona de interés en detalle. Las líneas continuas finas son isotermas y las discontinuas isotermas extrapoladas. Las líneas más gruesas representan curvas cotéticas que separan los campos de estabilidad del hielo, hidrohalita (HH) y halita (H). Se ha representado con cuadrados negros la trayectoria de fusión de las inclusiones fluidas Lw2 tomando las temperaturas modales: 1. Fusión de hielo y 2. Fusión de hidrohalita. En este punto, se puede determinar la composición del fluido.

Table 2.- Cl/Br and Na/Br molar ratios in fluid inclusions of different vein types.

Tabla 2.- Relaciones molares Cl/Br y Na/Br en inclusiones fluidas de los distintos tipos de filones.

Vein types	Samples	Cl/Br (m)	Na/Br (m)
W - (Sn) Sulphide	SR 0	1094	1296
	SR 0.5	995	698
	SR 22/1	1012	1326
	SR 22/2	1057	1080
Fluorite	FA	3941	2865
	FG 1	3244	2341
	FG 2	4346	3104
	FG 3	3844	2702
Barren Quartz (Lw2 fluid)	QTG 15	723	794
	QTG 27	753	1054
	BQTG 27	703	508

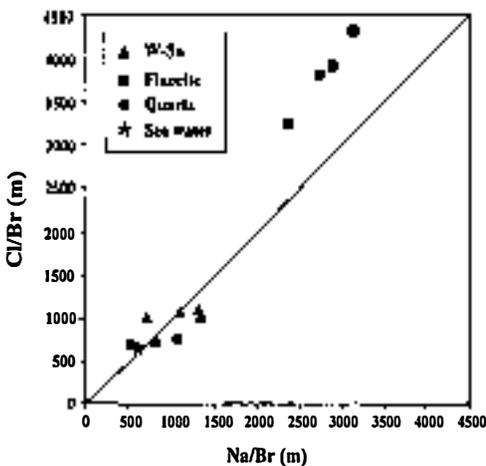


Figure 3.- Na-Cl-Br composition of fluid inclusions hosted in quartz from barren quartz, W-(Sn) veins and in fluorite from F-(Ba) veins.

Figura 3.- Composición en Na-Cl-Br de los fluidos en filones de cuarzo estéril, W-(Sn) y F-(Ba).

temperature, high salinity fluid, represented by Lw2 and Lw-s inclusions.

The salinity-Th plot (Fig. 4) shows a clear evolution of the salinity-Th pairs indicating an increase of salinity with decrease in temperature. A low salinity fluid and moderate temperature characterize the first hydrothermal stage. Quartz precipitation could have been favored by progressive cooling of solution and fluid-rock interaction, which cause an increase in the Ca content (plagioclase alteration). Cooling, salinity increase and finally decrease of Ca due to carbonate crystallization characterize later fluid input in the veins. This high-salinity fluid represents the latest event in the hydrothermal evolution of the Spanish Central System.

These fluids are similar to other post-variscan fluids, e.g.: in Germany (Behr et

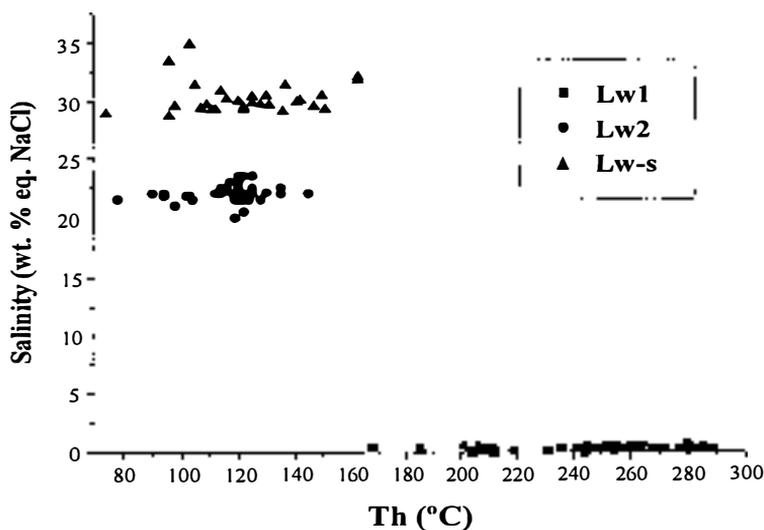


Figure 4.- Salinity (wt.% eq.NaCl) vs. Th diagram in fluid inclusions from barren quartz veins.

Figura 4.- Diagrama Salinidad-Temperatura de Homogeneización de las inclusiones de los filones de cuarzo.

al., 1987; Peucker-Ehrenbrink & Behr, 1993), and Belgium (Muechez et al., 1995). They are widespread in the hydrothermally altered parts of the Hercynian crystalline basement of middle Europe, and related to veins originated during Hercynian fracturation events. Similar brines are known from many sedimentary basins, most of them are genetically related to evaporites (Behr & Gerler, 1987; Mullis & Stalder, 1987; Lodemann et al., 1998). They were probably originated in the Permian and/or Triassic evaporites. A Lower Cretaceous coastline has been defined at the north from the area (Alonso et al., 1982). All data obtained up till now in the barren quartz veins are in accordance with a marine/evaporitic environment, but the sedimentary record is scarce and discontinuous (Gil & García, 1996).

## Conclusions

The data suggest that the different types of hydrothermal ores of different age came

from different sources. Na-Cl-Br chemistry and age indicate the following pattern of fluid migration in the Spanish Central System: (1) Early CHON fluids associated with W mineralizations are quite distinct from late aqueous fluid, their halogen chemistry indicates features similar to magmatic fluids associated with mineralizations in the Hercynian granites of southwestern England. (2) Intermediate fluids related to fluorites appear to have been controlled by dissolution of evaporites. Thus, these fluids appear to be related to Early Mesozoic evaporites. (Galindo et al., 1994). (3) Barren quartz veins are the latest hydrothermal event of the Spanish Central System. The dominance of evaporated and concentrated seawater as the salinity source is consistent with their geological setting. However, the high  $\text{CaCl}_2$  concentrations can not be explained only by alteration of carbonates, because no carbonate deposits were recognized close to this area. The Ca content could be explained by a fluid-rock interaction with a significant plagioclase alteration.

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