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Paleozoic of the Tethys

Late and post-Hercynian low temperature veins in the Catalonian Coastal Ranges

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ABSTRACT

Many of the veins enclosed within the Paleozoic basement of the Catalonian Coastal Ranges show several common characteristics: low temperature of formation (between 75 and 200°C), the presence of complex polisaline fluids and a certain relationship to the pretriassic paleosurface. Mineralogical composition and age are variable, ranging from Pb-Zn veins with carbonate gangue of late Hercynian age through metal poor fluorite rich veins to barite rich veins of Triasssic age. Mineralizing fluids are not related to late Hercynian magmatism and deposition took place in active fractures developed either in extensional as in compressive regimes.

Key words: Low temperature. Ba-F-(Pb-Zn) veins.

RESUMEN

La mayoría de mineralizaciones filonianas encajadas en el zócalo Paleozoico de la Cadenas Costeras Catalanas, presentan una serie de características comunes: baja temperatura de formación (entre 75 a 200°C); presencia de fluídos polisalinos complejos y una cierta relación con la paleosuperficie pretriásica. La composición mineralógica y la edad son variables, comprendiendo desde filones de edad tardi-Hercínica con Pb-Zn y ganga carbonatada, filones de fluorita, pobres en metales, hasta filones con baritina dominante de edad Triásica. Los fluídos mineralizantes no tienen relación con el magmatismo tardi-Hercínico, y la deposición tuvo lugar en fracturas activas, tanto en regímenes compresivos como distensivos.

Palabras clave: Baja temperatura. Filones de Ba-F-(Pb-Zn).

INTRODUCTION

Enclosed within the Paleozoic materials of the Catalonian Coastal Ranges a large number of mineralized veins and minor occurrences are found. They are mainly composed of barite, fluorite and base metal sulfides (Pb, Zn, Ni, Co, Ag...). The characteristic features common to most of them are the low temperature of formation (between 75 and 200°C), the presence of complex polysaline fluids and a certain relationship to the pre-Triassic Paleosurface. However, several differences among them do exist either in the mineralogical composition as in the chemistry of the fluids and age. According to this, they can be classified into the following groups (fig. 1):

1) Pb-rich veins with gangue predominantly carbonatic (dolomite and ankerite) with an important vertical development (hundreds of meters), enclosed exclusively within the Hercynian basement. Veins appear to fill strike-slip faults, developed during a compressive period. The most outstanding example is the Bellmunt del Priorat area (S of the Ranges).

2) Metal poor and fluorite rich veins also enclosed within the basement such as Osor and Sant Marçal mines (Montseny-Guilleries area).

3) Barite rich veins associated to normal faults with minor sulphides (mainly galena) as in Martorell area

or with sulphides and arsenides of Pb, Zn, Cu, Ni, Co, Ag... as in Atrevida mine. They are enclosed within the basement occasionally crosscutting the lower Triassic materials (Buntsandstein). They are frequently associated to barite, partially cementing the overlying detrital sediments (red-beds) of lower Triassic age.

4) Metal poor (Pb-Zn(Cu)) veins are located within the basement associated to important silicifications. Although they are not mineralized, the fractures crosscut the Triassic cover. Examples of this type are the Argentera and La Selva areas (S of the Ranges).

The 1, 3 and 4 types are well developed in the central and southern zone of the Catalonian Coastal Ranges, whilst type 2 veins are better developed in the northern area.

Although some actual geothermal waters precipitate fluorite in the Paleozoic basement of the Ranges as in La Garriga-Samalus area, this type of occurrence will be not dealt with here.

MINERALIZATION TYPES

Northern zone

Within the Northern Zone (Montseny-Guilleries area) the best developed veins belong to type 2, among which, the most outstanding examples are the Osor (Girona) and Sant Marçal mines (Montseny, Barcelona). According to Font (1983), the fluorite stock of this area can be estimated in 3.5 to 4 Mt with a 40-50% in CaF_2.

In Osor, the mineralization consists of a composed vein of approximately E-W direction with more than 250m in depth and 1 km in length, divided into two other veins (N and S lodes) that crosscut the Paleozoic materials of the pre-Ordovician (Cambrian?) Osor series as well as the Hercynian pegmatites and porphyries of the area. The vein minerals found are: fluorite, sphalerite, galena, calcite, quartz, barite, pyrite, marcassite and chalcopyrite. According to Font (1983), homogenization temperatures in fluid inclusions from these fluorites are lower than 100°C (between 60 and 95°C). No data on the salinity of the fluids are available. Fluorite is the dominant mineral; barite is also present in small amounts in the upper levels of the mine. On the contrary, sulphides (galena and sphalerite) are more abundant at depth.

In the Sant Marçal area (Rigros vein, center of the Montseny massif) veins are enclosed within the Santa Fe-Arbucies granitoids (Viladevall, 1975). These veins are oblique with respect to the main faults of the region, of NW-SE trend, and parallel to a porphyry dyke which encloses the mineralization. The wall rocks are sericitized and carbonatized.

The Rigrós vein has a N050-N090 direction and a size of 700x160x0,5 to 3m. The vein filling consists of fluorite and quartz with minor amounts of barite, calcite, galena and chalcopyrite. As in Osor, barite is found mainly in the upper parts of the vein. Fluid inclusion data from fluorites (Canals, 1989a) show the presence of two mineralizing fluids: a first with T<100°C and salinity around 21% eq NaCl and negative anomalies in Eu and Ce and a second with a temperature between 160 and 230°C, salinity around 17% NaCl eq with a smaller Eu anomaly. All inclusions have euthectic temperatures close to -60°C, indicating the presence of complex polysaline solutions. Fluorite precipitation took place due to temperature decrease (and possibly small pH changes) from fluids generated in two different reservoirs (Canals, 1989a).

Observing the Montseny-Guilleries district as a whole, the mineralizations, clearly younger than the late-Hercynian intrusives are constituted by fluorite as the dominant mineral and minor barite. It is also interesting to point out that together with the low T of formation and the presence of complex polysaline fluids, the veins show a clear vertical zonation with a progressive decrease in the barite/fluorite ratio and increase of sulphides with depth.

Central and Southern Zone

The Central-Southern area of the Catalonian Coastal Ranges considered here, extends from Barcelona to the Priorat in the south. From geological and geochemical data three types of veins can be distinguished: A) Pb-Zn veins with dolomitic gangue, important vertical development (down to 500m) as in Bellmunt del Priorat area (Eugenia, Regia and Mineralogia mines) and enclosed exclusively within Hercynian materials (metasediments as well as intrusives). They seem to be of late-Hercynian age (pre-triassic). B) Veins related to the pre-Triassic paleosurface, with barite as the dominant mineral and variable amounts of Pb, Zn, Cu, Ni, Co, Ag sulphides and arsenides (Atrevida and Martorell mines). In some cases these veins crosscut the lower Buntsandstein red-bed facies and are usually associated to barite cementing these lower Triassic detrital materials. Veins are enclosed within any type

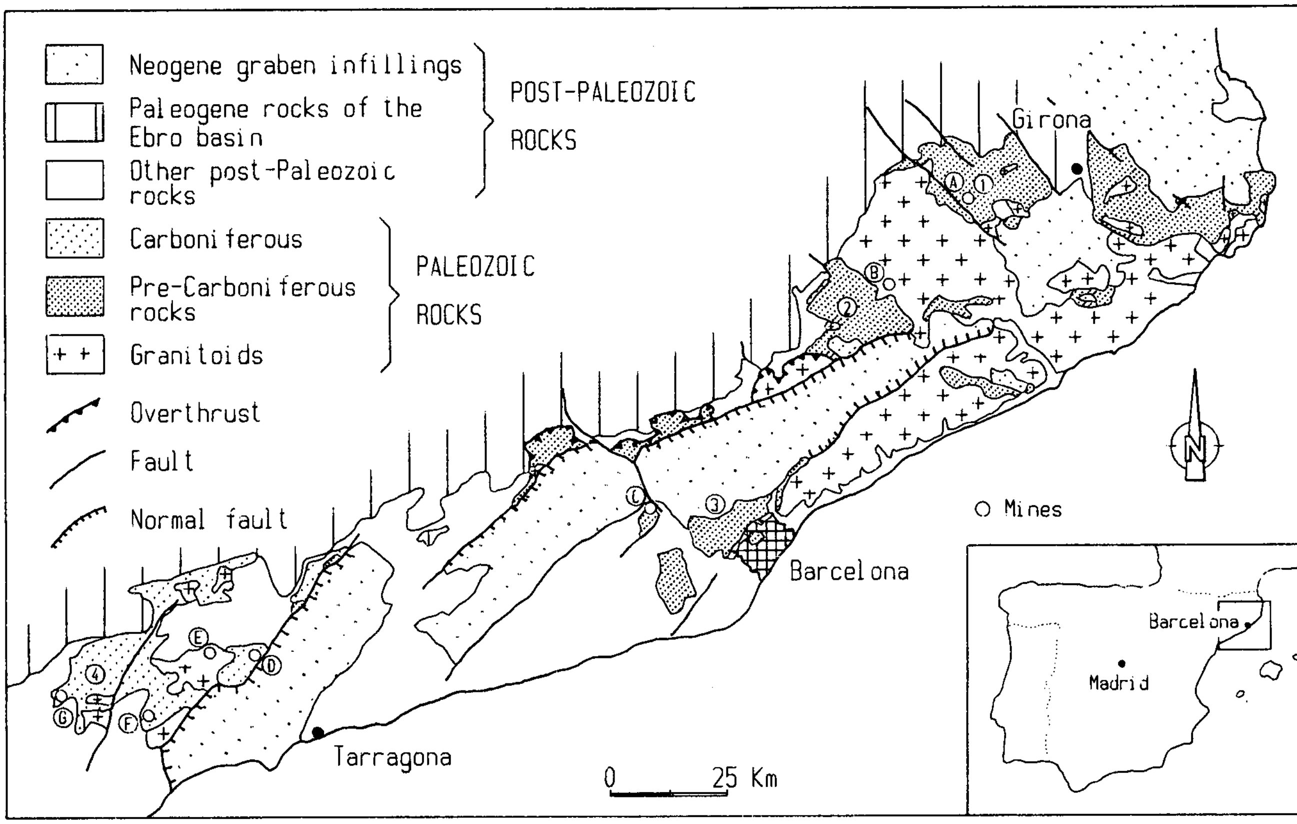

Figure 1.- Simplified geological map of the Catalonian Coastal Ranges. 1= Guilleries massif; 2= Montseny massif; 3= Collcerola massif; 4= Priorat area. Mines: A= Osor; B= Sant Marçal; C= Martorell; D= La Selva; E= Atrevida; F= Argentera - Escornalbou; G= Bellmunt.

of Hercynian materials including granites and are Triassic in age. C) Veins enclosed in the basement with galena and carbonatic gangue, associated to important silicifications as in the Argentera and La Selva areas.

Type A veins.- They are found in the Bellmunt area and have been studied in detail by Melgarejo (1987), and Canals et al. (1989). It has been the most important mining district of the NE of the Iberian Peninsula, situated within the Baix Priorat structural domain (Melgarejo, 1987). It is characterized by detrital series of Carboniferous age, flanking exposing pre-Carboniferous rocks, which cropout in a NW-SE trending anticline structure. The Paleozoic metasediments are intruded by late calcalkaline granites. All these rocks are cross-cut by a large number of granitic dykes of porphyric texture, dominantly intruded along a SW-NE trend. The mineralized veins intrude either the dykes as the metasediments and are oriented parallel to the dykes. These Hercynian materials were eroded to a peneplane and are now covered by a transgressive sequence of Triassic red-beds. Mineralized veins can reach up to 500 m in depth.

One of the most outstanding examples of this type of veins is the Eugenia mine. It is partially enclosed within the porphyries, which show sericitic and chloritic alteration. The mineralogy consists of galena, sphalerite, chalcopyrite, dolomite and ankerite with minor millerite and occasional kaolinite that fill a set of veinlets showing a vertical zonation with galena in the upper levels and sphalerite in the lower ones. Intrakarst fillings have been observed in the upper levels. From mineralogical and fluid inclusion data of dolomites and ankerites, stable isotopes of C, O and S of carbonates and sulphides, Canals et al. (1989) found that the precipitating conditions of the deposit were: log fO_2 between -50.5 and -48.5; temperature around 150°C; salinity of the fluids of 15% wt NaCl eq.; $\partial^{13}C_{CO2}$=-8.1 per mil; $\partial^{18}O_{H2O}$=3 per mil and $\partial^{3}S_{\Sigma S}$=1 per mil. These data seem to indicate the presence of non magmatic fluids, probably of evolved meteoric origin which leached metals, carbon and sulphur from metasediments and the enclosing intrusives.

This type of mineralizations do not cross-cut the overlying Triassic sediments. Thus, their age can be bracketed between late-Hercynian and pre-Triassic, clearly later than the emplacement of the Hercynian intrusives. Similar geological environments have been described in the Bohemian massif (Prhibram), French Massif Central (St Salvy) and Northern Africa, (Jebrak et al., 1983). All of these deposits are characterized (as Bellmunt) by an emplacement in strike-slip faults which in Bellmunt have a E-W trending in direction as a result of a ENE-WSW compression. This latter compression is of lower Permian age in France and middle Permian in Morocco, events that correspond to large late-Hercynian movements described by Arthaud and Matte (1975, in Jebrak, 1984).

Type B veins.- Are those clearly related to the pre-Triassic Paleosurface. Among them, the Atrevida mine is the best developed example. It consists of a 4 km long, 200 m deep and 1 to 6 m thick vein situated in a fracture of NNW-SSE direction which has been active during the Mesozoic and the Alpine orogeny. During the vein filling the fault acted distensively (symmetrical structure of the barite, presence of open space fillings and vertical striae). The mineralized fault was reactivated during the Alpine orogeny. As a result of this polyphasic history, the vein is enclosed within carboniferous metasediments, granodiorite and lower Triassic sediments, the latter containing disseminations of barite as cement. The mineralogy of the Atrevida vein is quite complex and has been described in detail by Melgarejo and Ayora (1985). According to the structure and the mineralogy, the vein system can be divided into three parts: upper, middle and lower.

The lower part is composed of an association of sugar-like quartz and small amounts of fluorite. Some of this quartz replaces a former mineralization of anhydrite as evidenced by the presence of relicts of this mineral in the quartz (Canals, 1989b). Fluid inclusion data of this quartz gave homogenization temperatures of 80°C and salinities of around 0% wt. NaCl eq. (almost pure water). $\partial^{18}O$ of this quartz ranges from 21 to 22.5 per mil (5 samples). At 80°C and assuming isotopic equilibrium $\partial^{18}O_{water}$ is around 0 per mil, value consistent with a water of meteoric origin.

The upper part is constituted by symmetrical bands of barite with some disseminations of galena, fluorite and sphalerite. Galena is the most important sulphide and is syngenetically replaced by anglessite showing near to atmospheric fO_2 conditions during its deposition.

The central zone of the vein is formed by symmetrical bands of barite with a brecciated zone; these breccias correspond to these so-called gravitational ones described by Jebrak et al. (1983) and are constituted by fragments of barite and enclosing wall rocks cemented by a complex association of sulphides and arsenides of Ni-Co-Fe together with sulfides of Pb, Zn and Ag. These minerals develop skeletic and spherulitic intergrowths indicating a fast precipitation process from an oversaturated solution.

From mineralogical and geochemical data,Canals (1989b) and Canals et al. (1988) showed that arsenides and sulphides from the central breccia precipitated at T=90°C and log aS_2=-22. Fluid inclusion data from fluorite and sphalerite (Th=110°C) are consistent with this temperature and point to a very low pressure of formation, the salinity of the solution being between 21 and 22% wt. NaCl eq. Euthectic temperatures lower than -60°C indicate again the presence of complex ($NaCl$-$CaCl_2$ rich) polysaline fluids. Late stages of mineralization are represented by an association of calcite and marcassite. Calcite Tmi of -0.3°C (very low salinity) indicates an important change in the type of fluid invading the system during late stages.

Stable isotope data of S and O in vein barite and in barite cementing the lower Triassic red beds ($\partial^{34}S$ between 14 and 17 per mil; $\partial^{18}O$ between 9.5 and 11 per mil) are very close to those of overlying evaporitic gypsum of middle Triassic age ($\partial^{34}S$=15 per mil). This suggests that sulphate was introduced into the system from a marine source or from leaching evaporitic levels of Triassic age. Sulphide isotopic compositions are variable: -8 per mil in galena from the upper levels of the vein to -16 per mil in galenas associated to the central breccia. These data, together with the geological evidences (age of the mineralization, relationship between vein and cement barite, etc.), have enabled a genetic model based on a two fluid mixing process to be established: a descending sulphate rich solution of marine (and/or from leaching evaporites) origin of lower to middle Triassic age that would saturate the basement fractures and an ascending hot brine (evolved meteoric waters) which carried the metals and barium. As a consequence of the mixing, barite and sulphides were precipitated (Canals et al. 1988; Canals, 1989b).

Similar situations can be found in other zones as in Martorell (Tritlla and Cardellach, 1988; Tritlla, 1989) and Escornalbou (Canals and Ayora, 1988). However, in these cases, sulphur isotopic data of barites give heavier values (19 per mil, mean of 8 samples in Martorell and 17 per mil, mean of 8 samples in Escornalbou) than in the Atrevida mine. Because the geological environment is identical such geochemical difference could indicate a different age (younger) than Triassic. Thus, mineralizing processes within basement fractures can have taken place during post-Triassic ages. Fluorite appears occasionally associated to this type of veins and seems to precipitate before the quartz. Fluid inclusion data from these fluorites show the presence of complex polysaline fluids (Te=-60°C) and salinities between 20 and 24% wt NaCl eq. with homogeneization temperatures around 90°C. According to Canals (1989a) in the fluorite crystals a zonation of the temperature of melting of the ice (Tmi) can be observed. This fact has been interpreted as the result of a salinity loss in the mineralizing solution from the beginning to the end of the crystal formation, thus suggesting a deposition mechanism caused by a mixing process of a hot ascending brine and a cold water of meteoric origin.

From the available data on this type of mineralizations, the evolution of these systems can be summarized as follows:

a) development of an erosive Paleosurface on the folded and fractured Paleozoic and intrusives.

b) sedimentation of Triassic materials, with conglomerates, sandstones, carbonate and evaporitic levels (sebhka environment) which could supply sulphate rich solutions to the system. Some basement fractures became active during this period.

c) formation of sulphate rich solutions either of marine origin as from leaching evaporitic levels and flowing towards the fractures through permeable strata (conglomerates).

d) the movement of the basement faults would cause an ascending flux of deep polysaline brines that carried metals. When mixing with the sulphate rich solutions barite precipitated.

e) continuous movement of the faults locally gave rise to brecciations and fast ascending of the deep fluid (Atrevida mine) and caused the sudden precipitation of sulphides and arsenides.

These active fractures are generally situated in areas close to ancient coast-lines and the mineralizations probably coincide in time with a general distensive phase (dominant regime during the Triassic), and with a crust thinning period (anomalous thermal fluxes) which facilitated the circulation and upflow of crustal fluids.

Type C veins.- Are those enclosed within the basement, Pb-Zn-Cu rich, of poor development and carbonatic gangue characterized to show important silicification phenomena. In some cases, indices of Ni-Co are found associated to Pb and Zn (Argentera area).

In the Argentera area, veins are enclosed within fractures of N30 direction affecting the Paleozoic basement. The basement is constituted by intrusive rocks and metasediments of Carboniferous to Devonian age (Melgarejo, 1987). Although fractures are of hectometric size, the mineralized zone is relatively small and is essentially formed by silicified breccias of enclosing rocks (hydraulic type breccias according to the description of Jebrak et al., 1983). Wall rocks are altered to sericite and no vertical zonation has been observed (Melgarejo, 1987; Canals, 1989b). Mineralogy is quite complex with Ni-Co arsenides, galena, sphalerite, chalcopyrite, bismuthinite, native bismuth and pyrite. Frequently, Ni and Co arsenides show spherulitic textures which are fragmented and cemented by quartz. The overall structure of these veins is similar to that described as «quars-haché» by Chegham (1985) in some veins in Morocco.

Deposition temperatures obtained from fluid inclusion data in calcite are close to 115°C; the available data from quartz fluid inclusions show similar temperatures (110°C) and a salinity of 2% wt NaCl eq. These data are very similar to those obtained in the sugar-like quartz formation of the Atrevida mine; $\partial^{18}O$ of this quartz is 22.0 per mil and $\partial^{18}O_{H2O}$ in equilibrium with it at 110°C is around 2 per mil, suggesting that late phases of silicification are caused by hot, low salinity, evolved waters of probable meteoric origin (Canals 1989b).

Regarding the age of these brecciated veins, it is important to point out that the faults to which they are associated have been active over several periods of time and that brecciations probably correspond to the last phases of deformation. The fractures, although less visible, also affect the Triassic cover. Consequently, the hypersilicified breccias could be of post-Buntsandstein age, probably related to the Alpine compression (Canals, 1989b).

The veins of La Selva area could be related to this type of mineralization. Occassionally, they crosscut the Triassic cover, have a calcitic gangue and contain metals such as Pb, Zn and small amounts of Cu, Ni, Co and Ag. A late silicification with quartz and adularia replacing the carbonate gangue, seems to remobilize a previous mineralization rich in Co, Ni, Ag, and Bi minerals.

CONCLUSIONS

The low temperature veins situated within the Paleozoic of the Catalonian Coastal Ranges are of late to post-Hercynian age and not related to Hercynian magmatism. Mineralizing fluids are, in general, brines with a high Na, Ca and K concentration and temperatures of deposition between 70 to 200°C.

Some of the veins show the presence of a quartz rich phase as in the Atrevida mine lower levels and Argentera area (silicified breccias). In this case, the salinity of the fluids is very low (between 1 and 5% wt. NaCl eq.) and temperatures around 100°C. Oxygen isotope data of this quartz indicate the presence of surficial waters in the systems during some stages of development.

The main mineralizing phase with fluorite-barite-sulphides, took place from evolved, highly saline brines which probably circulated down to great depths (several km) through basement fractures. This situation is similar to that found by Behr et al. (1987) and Durisova (1988) in the post-Variscan systems of Germany and Czechoslovakia. Circulation of the fluids is caused by the movement of the fractures, specially active during the Triassic. Fluids could be heated due to the regional geothermic gradient in a crust-thinning regime.

Where veins developed close to a coast-line (Atrevida mine, for example), sulphate-rich waters could invade the fractures, flowing through permeable strata. Barite precipitated when these waters mixed with upflowing deep fluids, as evidenced by stable isotope data.

The source of metals may be related to the type of material leached by the ascending solutions. In areas where veins have a complex mineralogy as in the Atrevida mine or the Priorat area, several stratiform mineralizations of sedex type have been described within the Paleozoic (Melgarejo, 1987 and Melgarejo et al., 1989, this volume) whereas the veins enclosed mostly within granites are fluorite-rich, suggesting that the vein mineralogy might reflect the regional stock-metal present in the leached area.

As a general rule, ore veins are related to active fractures through which circulation of fluids can take place. Some of these fractures developed in a extensional regime (Atrevida type) and the dominant metals are Ba, F, Pb and Zn carried by hot, reduced sulphur bearing, ascending brines that leached the enclosing and surrounding rocks. Sulphate barite seems to be of seawater origin. Other fractures developed in a compressive regime (Argentera veins). They show the presence of hydraulic breccias and are related to important silicifications and have Pb-Zn as dominant metals.

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