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Abstract

Origin of the mineralizing fluids from the Carboniferous sedex deposits of L'Alforja (SW Catalonian Coastal Ranges, Spain)

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Abstract

Fluid inclusions were studied in stratiform ore deposits hosted in Namurian sedimentary series near L'Alforja (southernmost part of the Catalonian Coastal Ranges, NE Spain). Primary fluid inclusions in quartz crystals from L'Alforja ore bodies are twophase (L–V), with salinity between 1.1 and 18.0 wt.% NaCl eq. and homogenization temperature mainly in the range of 220– 260 °C. δD values analyzed in chlorite range between -63% and -33%, and $\delta^{18}O$ values range between +2.7%and +6.8% in chlorite, and from +8.6% to +10.7% in quartz. Fluid inclusions and oxygen-hydrogen stable isotopes indicate that the mineralizing fluid of L'Alforja was mainly seawater. The hydrothermal fluid had lower density than seawater, so producing buoyant plumes on debouching at the seafloor, and the metals precipitated with the decrease of temperature. Hydrothermal fluids related to late-Hercynian porphyritic granite dykes produced local recrystallization of the ores, as well as a younger generation of high saline fluid inclusions, and locally caused isotopic reequilibration. © 2003 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Carboniferous series from the southwest of the Catalonian Coastal Ranges (NE Spain) host several stratiform and stratabound sulfide deposits, defined as sedex type by Melgarejo (1992). Some of these deposits were mined during the XIX and XX centuries. Those of L'Alforja are the most important in

volume. Two areas can be distinguished: Mas del Mestre and Pou del Cobus (Fig. 1).

Fluid inclusions and $\delta^{18}O-\delta D$ isotopic compositions were studied in L'Alforja ore deposits to obtain information about the fluids and so constrain the metallogenetic history of the Carboniferous sedimentary basin from the SW of the Catalonian Coastal Ranges.

2. Geological setting

The Catalonian Coastal Ranges comprise a Hercynian folded basement unconformably overlain by a Mesozoic sedimentary cover. In the southernmost

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Fig. 1. Geology and location of the Carboniferous sedex deposits of L'Alforja.

domains, the Hercynian basement is made up of a thick Carboniferous series that unconformably overlies sedimentary sequences of Cambrian to Late Devonian ages.

The Carboniferous sequence is characterized by sharp lateral changes of facies and thickness, by the abundance of olistoliths and breccias, and by the local presence of alkaline volcanism at the base (Melgarejo, 1992). These features are consistent with a subsiding sedimentary basin divided in sedimentary highs and depressions by synsedimentary faults (Melgarejo, 1992). Generally, the Carboniferous series starts with a cherty unit (up to 10 m in thickness) regionally attributed to the Tournaisian. Visean to Middle Namurian turbiditic series, up to 2000 m thick, unconformably cover all the above units and contain several stratiform Pb–Zn–Cu–Ag sediment-hosted sulfide deposits (Melgarejo, 1992; Canet, 2001).

During the Hercynian Orogeny, the Paleozoic series was deformed by two main episodes of folding and thrusting trending roughly NW–SE. The regional metamorphism took place at epizonal levels and produced mineral assemblages characteristic of very low grade to anchimetamorphic conditions. Late Hercynian granitic stocks, accompanied by late porphyritic dykes of similar composition, intruded these series. As a consequence of these intrusions, contact metamorphism was locally developed in the area. Some late NE–SW and NNW–SSE Hercynian faults have been reactivated during the Alpine Orogeny, and allowed episodes of hydrothermal circulation that produced Ba-Pb-Zn-Ni-Ag veins (Melgarejo, 1992).

The sulfide deposits of L'Alforja are hosted in the Namurian detrital series, mainly formed by gray shales and sandstones (Melgarejo, 1992). The Mas del Mestre deposit consists of massive pyrrhotite beds, more than 2 m thick, interbedded with scarce decimeter-thick sphalerite beds. At the top, some massive pyrite beds, up to 1 m in thickness, occur. These sulfide beds are interbedded with chlorite-rich beds and with cryptocrystalline feldspar-rich beds, both interpreted as metaexhalites (Canet, 2001). Massive sulfide beds contain chlorite aggregates and disseminated euhedral quartz crystals, 500 μ m to 2 mm in length. In addition, minor amounts of chalcopyrite, galena, and Ag and Bi sulfides and tellurides occur.

The Pou del Cobus occurrence consists of an interbedding of quartz, magnetite and chlorite-rich beds. Chlorite-rich beds are mainly composed of chlorite, with quartz and minor amounts of epidote and actinolite. Pyrite, galena, chalcopyrite and scheelite are scarce. Magnetite is weathered to maghemite.

Hercynian deformation affected the mineral deposits. Minor structures as boudinage and axial plane cleavage are evident in all the above-described mineral assemblages. Furthermore, the contact metamorphism produced annealing of the sulfide associations. Finally, pyrrhotite is partially replaced by a very late generation of marcasite and pyrite, with bird's eye-like textures.

3. Fluid inclusions

Fluid inclusions were studied in authigenic quartz crystals embedded within sulfides in Mas del Mestre deposit and within the magnetite layers in the Pou del Cobus occurrence. The measured fluid inclusions are isolated and randomly distributed. They are two-phase (L+V) aqueous inclusions. Fluid inclusions have regular morphology, small size, usually between 2 and 5 µm, and the bubble represents 5–15 vol.% of the inclusion. According to Roedder (1981) criteria,



Fig. 2. Salinity versus homogenization temperature (Th) plot for the studied fluid inclusions. The sample Mestre 3 was taken near a porphyritic dyke.

these inclusions can be considered of primary origin. Furthermore, there are numerous fluid inclusions distributed in planes, but they were discarded, as being of secondary origin.

Microthermometric measurements were performed on a Linkam THMS-600 heating and freezing stage in the University of Barcelona. Calibration was made with standard compounds between -56.6 and 308.9°C. The precision was ± 0.2 °C for the freezing measurements and ± 1 °C for the heating measurements.

Freezing measurements were carried out on the fluid inclusions until they froze. First melting temperature only could be measured in some samples; it is usually close to -22 °C, indicating that the dissolved salt is mainly NaCl (Crawford, 1981). The temperature of ice melting ranges between -1 and -15 °C. Salinity was calculated from the ice melting temperature using the equation of Potter et al. (1978). Salinity is mainly between 1.1 and 14 wt.% NaCl eq. in Pou del Cobus and it reaches up to 18 wt.% NaCl eq. in Mas del Mestre (Fig. 2). The values of salinity are roughly distributed in two groups, one close to the seawater salinity (3.2 wt.% NaCl eq.), and the other of higher salinity, from 8 to 18.9 wt.% NaCl eq. The inclusions of the second group are especially abundant in one sample of Mas del Mestre located close to the contact with a late Hercynian granitic porphyritic dyke. Homogenization temperatures are between 140 and 310 °C, with most of values distributed between 220 and 260 °C (Fig. 2). The calculated densities for the first inclusions group range mainly from 0.7 to 0.9 g/cm³.

4. Oxygen and hydrogen stable isotope ratios

 δ^{18} O values were obtained in quartz and chlorite, and δ D values in chlorite. δ D values range between -63 ‰ and -33 ‰, and δ^{18} O values vary between +2.7 ‰ and +6.8 ‰ in chlorite and from +8.6 ‰ to +10.7 ‰ in quartz.

The δ^{18} O and δ D of the fluids in equilibrium with the analyzed minerals were calculated from the fractionation equations of Wenner and Taylor (1971) and Matsuhisa et al. (1979), considering a range of temperature between 220 and 260 °C. Most of the calculated δ^{18} O- δ D values are close to seawater isotopic composition of around 0% (V-SMOW). Only one sample, obtained in the vicinity of the contact with a porphyritic dyke, shows $\delta^{18}O-\delta D$ values consistent with metamorphic and magmatic waters.

5. Discussion

The homogenization temperature of the fluid inclusions mainly varies from 240 to 260 °C. This range is comparable to that found in other ancient exhalative deposits, and with the temperatures of most recent submarine vents (Peter and Scott, 1988).

Salinity of fluid inclusions indicates the presence of two different fluids, one with low salinity and the other with high salinity. This fact could be explained by the coexistence of two fluids at the time of mineral formation, as in the case of many massive sulfide deposits (Lüders et al., 2001). Another possibility is that one of the two populations of fluid inclusions has a secondary origin. Two facts support the second option. The first relates to the distribution of the saline fluid inclusions, which are more abundant and with highest values in the sample obtained near the porphyritic dyke. The second is the stable isotope data, since the only sample that presents a magmatic affinity is the same that yielded the highest salinity values. These data indicate the existence of a magmatic fluid related to the porphyritic dyke. Thus, a late interaction with late-Hercynian magmatic fluids took place.

Therefore, assuming that the first type of fluid inclusions is primary, the salinity of the mineralizing solutions would range from 1 to 7 wt.% NaCl eq., lower than most values reported for fluid inclusions in sedex deposits (Gardner and Hutchinson, 1985; Samson and Russell, 1987; Ansdell et al., 1989). Nevertheless, several modern analogues of sedex deposits, as those from Guaymas basin, vent hydrothermal fluids with densities significantly lower than that of seawater (Peter et al., 1986).

The oxygen and hydrogen stable isotope data from L'Alforja occurrences and the values of salinity of fluid inclusions indicate that the fluid that formed the stratiform mineralizations was dominantly seawater. The low density of that fluid, from 0.7 to 0.9 g/cm^3 , suggests that the ore mineralization was formed from a buoyant hydrothermal plume and not as a brine pool.

6. Genetic model of ore formation

Fluid inclusion and oxygen-hydrogen isotopic composition of the Carboniferous sediment-hosted ore deposits from the Southern Catalonian Coastal Ranges are consistent with a primary marine origin of mineralizing fluids.

The sharp lateral sedimentary facies and thickness changes, as well as the existence of olistoliths, breccias and alkaline volcanism at the basis of the Carboniferous basin (Melgarejo, 1992), suggest a tectonic activity contemporaneous to Carboniferous sedimentation. Therefore, this area would be a subsiding basin affected by abundant synsedimentary normal faults, which acted as permeable areas that favored fluid circulation. As this fluid has lower density than seawater, when it rises to the seafloor, it produced buoyant plumes, instead of the brine pools that Sangster (2002) proposed for most sedex deposits. The base metals from this buoyant plume would precipitate by the quenching of this fluid due to the contact with the cool seawater, generating seafloor ore deposits.

7. Conclusions

The fluid that originated the mineralizations of L'Alforja was mainly seawater, that in a process of deep circulation would reach a minimum temperature of 240 °C. Salinity of the hydrothermal fluid, at those temperatures, implies a fluid density lower than that of seawater, so that the vent system formed a buoyant plume.

The deposits have been later affected by contact metamorphism, and late hydrothermal fluids related to porphyritic granite dykes produced local recrystallization of the ores.

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