Evidence for Hot MVT Brines in the Mesozoic Prebetic Basin: the Riópar Zn-Pb Deposits

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INTRODUCTION

The small Riópar deposits (~20,000 t extracted Zn), located at the limit between the External and Internal Prebetic Basins (northern boundary of the Mesozoic Betic Rift, Fig. 1), correspond to Zn-Pb Mississippi Valley-type (MVT) mineralization. They occur within a Middle Jurassic to Lower Cretaceous carbonate sequence (Grandia et al., 2001; Navarro-Ciurana et al., 2013a; b).

The old mines (San Agustín, Rosita and San Jorge) are aligned on the W-E-trending and S-dipping San Jorge fault that is believed to have channelled the ore-bearing fluids. The area is also affected by the NW-trending Socovos strike-slip dextral fault (Corbella et al., 2012). The MVT mineral paragenesis consists of an early dolomite, marcasite, sphalerite, galena and a late dolomite phase (Navarro-Ciurana et al., 2013a).

Zn-Pb MVT deposits in the Maestrat and Basque-Cantabrian basins (Fig. 1) have been dated as Early to Late Tertiary respectively (Grandia et al., 2003; Symons et al., 2009). As the Mesozoic basin in Riopar is tectono-stratigraphically akin to those basins, a similar age for the studied deposits cannot be discarded. If this is the case, mineralization could have formed as a consequence of the circulation of basinal brines related to the rift system developed during the break-up of Pangea.

In the current study, data from microthermometry of fluid inclusions and Sr isotope analyses from the Riópar district are presented. These and the O isotopes data previously reported by Navarro-Ciurana et al. (2013a) have been used to develop a conceptual model for the formation of the Riópar mineralization.
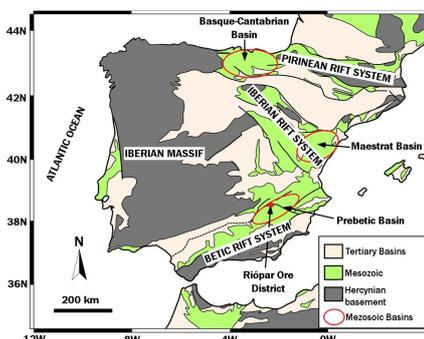

fig 1. Schematic geological map of the Iberian Peninsula, showing the location of the rifting systems during the Mesozoic and Betic, Basque-Cantabrian and Maestrat Basins (modified from Grandia et al., 2003).

MICROTHERMOMETRICAL DATA

A microthermometric study has been performed on 63 primary fluid inclusions in sphalerite and late dolomite samples from San Agustín mine. Measurements were made on a Linkam THMS-600 heating-freezing stage at the Dpt. de Geologia of the Universitat Autònoma de Barcelona.

Fluid inclusion (FI) sizes range between 3 to 15 µm and are found along growth bands. They show a variable vapor/liquid ratio, ranging from 5 to 25. The first melting (T_e) occurs at temperatures between -65 and -45ºC; below these temperatures the frozen phase acquires a brown to yellowish colour, characteristic of the H_2O-NaCl-$CaCl_2$ system (Reynolds and Goldstein, 1994). Melting of hydrohalite ($T_{m,hydrate}$) was observed at temperatures of -21.9± 0.7ºC.

Melting ice ($T_{m,ice}$) temperatures are different for sphalerite and late dolomite fluid inclusions. $T_{m,ice}$ of FI in sphalerite occur between -9.9 and -6.5ºC, representing bulk salinities of 10.1 - 13.9 wt.% NaCl+$CaCl_2$ (Fig. 2a), with 9.1 - 12.5 wt.% NaCl and 1.0 - 1.4 wt.%

$CaCl_2$, according to Bakker (2003). FI in late dolomite show $T_{m,ice}$ ranging from -7.5 to -1.6ºC; corresponding to bulk salinities (Bakker, 2003) of 2.6 - 11.3 wt.% NaCl+$CaCl_2$ (Fig. 2a), with 2.3 - 10.2 wt.% NaCl and 0.3 - 1.1 wt.% $CaCl_2$.

Homogenization temperatures in both sphalerite and late dolomite fluid inclusions are between 157 and 241ºC, with a mode at 215ºC for sphalerite and at 195ºC for late dolomite (Fig. 2b).

Microthermometric data indicate that fluids trapped in primary FI are hot brines with moderate to low salinity. The relatively higher salinity of trapped fluids in sphalerite with respect to late dolomite may be due to either different mixing proportions of fluids or to transient variations in the fluid composition, and possibly in the source as well, or both, during the mineral precipitation event.
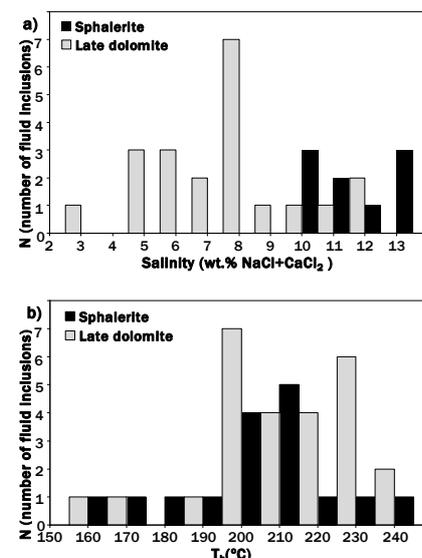

fig. 2. Frequency histogram showing the distribution of bulk salinity (a) and homogenization temperature (b), distinguishing the fluid inclusions trapped in sphalerite and late dolomite crystals from the San Agustín mine area.

Sr-O ISOTOPES

8 samples of host-carbonates, and 3 samples of hand-picked late dolomite were selected for Sr and O isotope characterisation. Sr isotope composition were analysed at the Universidad Complutense de Madrid using a TIMS-Phonix mass spectrometer. The reproducibility (2σ) was better than ±0.03%. The O isotope compositions were performed on a Finnigan MAT-252 mass spectrometer at the Serveis Científico-Tècnics of the Universitat de Barcelona. Oxygen isotope values are reported in δ‰ relative to V-SMOW standard with a precision of ±0.04‰.

The Middle Jurassic to Lower Cretaceous carbonates, which host the MVT mineralization, exhibit $^{87}Sr/^{86}Sr$ ratios between 0.7072 and 0.7074 and $\delta^{18}O$ values from +25.7 to +28.9‰. Some Sr-O isotope data are similar to those of Middle Jurassic to Early Cretaceous limestones (Veizer et al., 1999). The more $\delta^{18}O$-depleted samples (+25.7 to +26.5‰) suggest recrystallization or replacement (early dolomitization and late calcitization) of the host-limestones (Fig. 3).

Sr isotope ratios in late dolomite vary from 0.7074 to 0.7083 and their $\delta^{18}O$ from +25.1 to +26.7‰ (Fig. 3). The isotopic difference with the host rock suggests the presence of a fluid that has partially equilibrated with the host-carbonates. The Sr radiogenic signature can be explained by the interaction of the fluid with Rb-bearing minerals, which are found in the Cretaceous and Triassic rocks of the area.

CONCEPTUAL MODEL OF RIÓPAR ORE FORMATION

One of the most significant findings of this study is the high homogenization temperatures (< 240°C) and low salinity (< 14 wt.% NaCl equiv.) fluids encountered in sphalerite and dolomite fluid inclusions, reflecting the temperatures of advecting hydrothermal mineralizing brines. Similar Th/salinity data have been reported in some deposits of the Basque-Cantabrian Basin (Simón et al., 1999).

Fluid inclusion and Sr-O systematic isotope values do not provide evidences of fluid mixing, as described in some deposits of the Maestrat and Basque-Cantabrian Basins (Grandia et al., 2003a; b). Nevertheless, the presence of
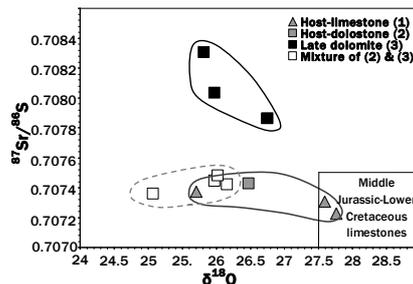

fig. 3. $^{87}Sr/^{86}Sr$ vs. $\delta^{18}O$ plot of the host-carbonates and ore-bearing dolomite from the Riópar ore deposit with Middle Jurassic to Lower Cretaceous limestones box (Veizer et al., 1999).

a minor dilute fluid component cannot be ruled out and merits further investigations.

The proposed model of ore deposition for Riópar consists of a hot basinal brine of moderate salinity that circulated upwards through the San Jorge Fault. Originally this fluid could have been more saline and might have mixed with a lower salinity fluid, although no clear evidences of mixing have been found. These hot brines, partially equilibrated with the host-carbonates, generated the precipitation of small amounts of Zn-Pb-Fe sulfides in the footwall block of the fault wherever sulfide was available. The brine was probably metal poor in response to its moderate salinity, compared to other MVT deposits. After the precipitation of sulfides, a decrease in salinity of the fluid preventing the transport of enough metals, or the lack of sufficient H_2S to precipitate sulfides caused the cease of ore deposition. However, this fluid was able to continue the precipitation of a late dolomite generation.

CONCLUDING REMARKS

Fluid inclusion and Sr-O isotope data from the Riópar MVT mineralization puts constrains on the origin and evolution of the ore-forming hydrothermal fluid. Even though more work is needed to confirm the proposed model, the following conclusions can be drawn:

i) High homogenization temperatures and relatively low salinities of FI in sphalerite and dolomite confirm the presence of a hot and dilute brine as responsible for the MVT ore formation in the Prebetic Basin.
ii) The Sr-O isotope data suggest the mineralizing fluid was partially equilibrated with the host-carbonates. The most radiogenic samples are explained from the

interaction with siliciclastic rocks.
iii) The fluid inclusion and isotope data obtained so far, suggest the presence of a single mineralizing brine that evolved in time to a lower salinity fluid probably by mixing, although evidences of such a process have not been recognized.

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