Dolomitization Related to Zn-(Pb) Deposits in the Río Mundo Area (Riópar, Albacete)

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INTRODUCTION.

The Río Mundo old mining area is situated in the External Prebetic Zone and constitutes the northern boundary of the Mesozoic Betic Basin. The area comprises carbonates and detrital rocks of Triassic, Jurassic and Cretaceous ages covered by sediments of Tertiary age. Zn-(Pb) Mississippi Valley-Type (MVT) deposits appear related to widespread dolomitization affecting carbonates of Middle Jurassic age. In the study area, several dolomitization episodes affecting carbonates of different ages have been identified.

The aim of this research is to characterize the dolomitization related to the MVT mineralization, using C and O isotopes and cathodoluminescence techniques. This will delineate the origin and evolution of dolomitizing fluids.

GEOLOGICAL SETTING.

The Río Mundo area, near the Riopar village (Albacete), consists of a transfer fault zone, crossed by a succession of folds and thrusts of NE-SW direction verging towards the NE. The old Zn mining works are aligned with the San Jorge fault (Corbella et al., 2012). The area is also affected by the NW-trending Socovos strike-slip dextral fault. It is considered to separate the Internal from the External Prebetic Zone (e.g. Rodríguez-Pascua and De Vicente, 2001). However, in the study area these two units seem to be limited by the San Jorge fault (Fig. 1).

Triassic sandstones and clays crop out along the Río Mundo valley, following the trace of the Socovos fault. Jurassic carbonates appear in both the northern and southern slopes of the valley but north of the San Jorge fault, whereas Cretaceous rocks only crop out in the southern slope and southern block of the San Jorge fault (Fig. 1).

METHODS.

70 thin-polished sections from host-limestones and dolostones related to the MVT mineralization were studied using a petrographic microscope. Staining with Alizarine Red-S and potassium ferricyanide allowed to distinguish calcite from dolomite and their ferroan equivalents. A Technosyn Cold Cathodoluminescence (CL) device (model 8200 MkII), operating at 15-18 Kv and 150-350 µA gun current, was used for CL study.

95 samples were analysed for their C and O isotope composition on a Finnigan MAT-252 mass spectrometer. Oxygen isotope values are reported in δ‰ relative to V-SMOW standard, whereas carbon values are reported in δ‰ relative to V-PDB. Precision was ±0.04‰ for $\delta^{18}O$ and ±0.03‰ for $\delta^{13}C$.

PETROGRAPHY AND GEOCHEMISTRY.

Jurassic host-limestones.

The host-limestones correspond to Jurassic marine wackstones, packstones and grainstones of peloids, ooids and miliolids (peloobiomicrites and peloobiosparites). Their isotopic signature varies from +27.55 to +27.83‰ for oxygen and from +2.32 to +3.16‰ for carbon.

Early dolomitization.

The early dolomitization stage of the host-limestone is identified on hand samples by white rhombohedral crystals. Two sub-phases have been distinguished under the petrographic microscope. Dolomite Ia corresponds to a dark brown replacive dolomicrite (≤100 µm in size) with penetrative and destructive or non-destructive fabric. Some relicts of the original limestones, predominantly ooids and pelletoids, are recognized. The light brown idiomorphic

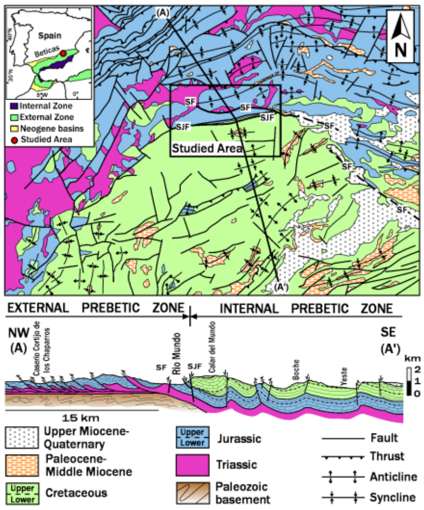

fig 1. Schematic geologic map (modified from Vera et al., 2004) and geological cross section (A-A') of the Internal and External Prebetic Zone and Río Mundo area (SF: Socovos fault; SJF: San Jorge fault).

dolomite Ib (≤1.5 mm in size) replaces dolomite Ia, which remains as ghost crystals (Fig. 2a). CL observations of dolomite Ia and Ib revealed the same bright red-orange patchy luminescence (Fig. 2a). The two sub-phases were sampled together for the isotopic study (dolomite I) and exhibits $\delta^{18}O$ ranges from +25.03 to +26.50‰ and $\delta^{13}C$ from -0.66 to +0.57‰.

Dolomitization associated to MVT ore.

The massive dolomitization associated with MVT mineralizations occurred in at least two sub-phases. Dolomite IIa consists of ivory white crystals in hand samples. The crystals appear as multizoned saddle dolomite (<3mm in size) with alternating clear and dark brown bands. This dolomite type replaces the previous phases preserving dolomite Ia and Ib as ghost crystals. IIa dolomite shows a high intercrystalline porosity (~25%), which is preferentially occupied by organic matter and dolomite IV. Dolomite IIa appears filling

palabras clave: Dolomitización, Zn-(Pb) MVT, Prebetico Externo. | *key words:* Dolomitization, Zn-(Pb) MVT, External Prebetic.

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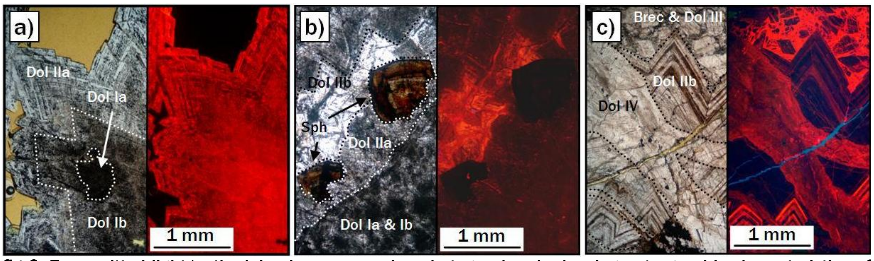

fig 2. Transmitted light/cathodoluminescence microphotograph-pair showing petrographic characteristics of Río Mundo dolostones: a) host-dolostone of Zn-(Pb) MVT ore; b) dolostone associated to Zn-mineralization; c) late dolomitization (Dol: dolomite; Sph: sphalerite; Brec: breccia).

milimetric fractures and associated with brown-reddish sphalerite zoned crystals (strongly altered to smithsonite). Dolomite IIa presents a zoned dark red dull luminescence (Fig. 2a and 2b). Their C and O isotope signatures overlap that of dolomite I ($\delta^{18}O$: +25.04 to +26.54‰; $\delta^{13}C$: -0.75 to +0.49‰), although some samples showed more ^{13}C-depleted values (as low as -2.01‰; Fig. 3). Dolomite IIb is present as clear white crystals in hand samples. Under the petrographic microscope, it is a clear-dark white multi-zoned saddle dolomite (<4 mm in size), partially replacing sphalerite of fracture zones. CL revealed bright red luminescence cores surrounded by non-luminescent bands (Fig. 2 b and 2c). Oxygen and carbon isotope values are similar to those of dolomite I and IIa ($\delta^{18}O$: +25.13 to +26.93‰; $\delta^{13}C$: -0.44 to +0.59‰). The last mineralizing sulphide stage was constituted by disseminated galena, marcasite and minor pyrite, filling intercrystalline, moldic and fracture porosity. Galena is partially altered to anglesite and cerussite.

Late dolomitization.

Some samples evidence post-ore brecciation, formed by angular dolomite fragments (<0.5 mm in size) and bright red luminescence dolomite III cement (<40 µm). They are cut by later fractures which are filled by dull patchy red luminescent dolomite IV crystals (<20 µm) (Fig. 2c). Dolomite IV has isotopic signature ranges from +25.38 to +26.15‰ in $\delta^{18}O$ and -0.60 to +0.30‰ in $\delta^{13}C$.

Calcitization.

The deposition of centimetric calcite crystals (CS) in pore-filings constitutes the latest cementation event. This calcite presents $\delta^{18}O$ isotopic composition from +23.90 to +24.32‰ and $\delta^{13}C$ of -7.28 to -6.99‰.

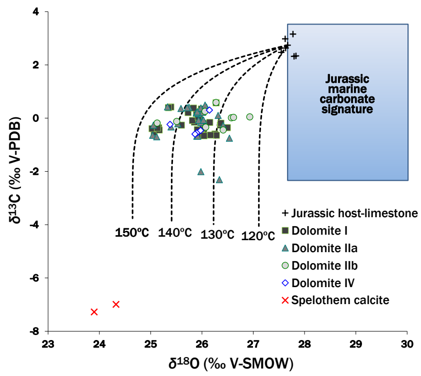

fig 3. $\delta^{18}O$ vs. $\delta^{13}C$ cross-plot of host-limestone, dolomites and calcites from the Río Mundo outcrops with a Jurassic marine carbonate box according to Veizer et al. (1999). C-O isotope model curves have been calculated in terms of fluid-rock interaction for dolomite (dashed lines) at different temperatures (Zheng and Hoefs, 1993). The dolomitizing fluid is assumed to have $\delta^{13}C$= -0.5‰ and $\delta^{18}O$= +12.0‰. H_2CO_3 is the dominant aqueous carbon species. The CO_2 mole fraction of the fluid is (X_f)= 0.2.

DISCUSSION AND CONCLUSIONS.

The petrographic microscope study combined with staining methods allowed to distinguish 7 dolomite phases. However, only 6 of these phases could be recognized by CL investigations. Dolomite IIb replaced most of Zn-mineralization, decreasing the volume of the primary sulphide ore, which was finally altered to smithsonite and calamines.

The data distribution on a C/O isotope plot may be explained by the interaction of a dolomitizing fluid and the regional limestone of Jurassic age. This interaction has been modeled assuming the Río Mundo Jurassic limestone and a fluid having a $\delta^{18}O$= +27.67‰ and a $\delta^{13}C$= +2.74‰, at temperatures ranging from 120 to 145°C and a CO_2 content of 0.2 mole fraction. Most data plot in a narrow $\delta^{13}C$ range, suggesting that interaction took place at low fluid/rock ratios. The more ^{13}C-depleted samples correspond to late calcite and could represent the involvement of waters enriched in soil-derived CO_2 and calcite precipitation in the vadose meteoric enviroment (telogenic fluid) (Fig. 3).

Petrographic and CL studies of dolomitization associated to MVT mineralization in the Río Mundo-Riopar area illustrate a complex paragenetic sequence. However, the isotopic composition of the different phases is very similar and does not seem to be a useful tool to discriminate the different dolomitization stages.

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