# C and O Isotopes of the Riópar Non-Sulfide Zn Ores (Albacete, SE Spain)

/ DIDAC NAVARRO-CIURANA (1*), MERCÈ CORBELLA (1), ESTEVE CARDELLACH (1), LUIS ALBERTO CAMPOS-QUISPE (1), DAVID GÓMEZ-GRAS (1), ALBERT GRIERA (1), ELENA VINDEL (2), LINDA DANIELE (3)

(1) Dpt. de Geologia. Edifici C. Universitat Autònoma de Barcelona. Bellaterra (España)
(2) Dpt. de Cristalografía y Mineralogía. Facultad de C. Geológicas. Universidad Complutense de Madrid. Madrid (España)
(3) Dpt. de Geología. Facultad de C. Físicas y Matemáticas. Universidad de Chile. Santiago (Chile)

## INTRODUCTION

Recent improvements in extraction technologies for the treatment of non-sulfide Zn ores (acid-leaching, solvent-extraction, electrowinning) paves the way for a renewal of economic interest for this ore-type (Boni et al., 2003). Although the term "*calamine*" is not recognized by the International Mineralogical Association (IMA), it is a convenient mining term used to designate a mixture of non-sulfide Zn minerals such as carbonates (smithsonite, hydrozincite), silicates (willemite, hemimorphite) and oxides (zincite, franklinite). *Calamine* ores may be originated by hypogenic or supergenic processes (Large, 2001; Hitzman et al., 2003). The hypogene *calamine* deposits usually contain willemite, zincite or franklinite, whereas the supergene deposits are mainly composed of smithsonite, hydrozincite or hemimorphite (Reichert, 2007). The "Reales Fábricas de Alcaraz" factory, located in Riópar (Albacete, SE Spain), were established in the late XVIII century. They constituted the first metallurgical brass plant of the Iberian Peninsula and the second of Europe. The Zn came from the nearby calamine mines which produced a minimum of ~20,000 t along its mining history (Navarro-Ciurana et al., 2014).

In this contribution the description of the Riópar *calamines* together with C and O isotope data are presented. Results constrain the non-sulfide Zn deposit-type, the formation temperature, the fluid origin and the carbon source involved in the *calamine* genesis.

## GEOLOGICAL SETTING

The Riópar area is located at the limit between the External and Internal Prebetic Basins, situated at the northern boundary of the Mesozoic Betic Rift. The Prebetic Zone consists of a transfer fault area with a succession of folds and thrusts of NE-SW direction verging towards the NE. The Riópar area is affected by W-E trending and S-dipping San Jorge and NW-SE trending Socovos strike-slip dextral faults (Navarro-Ciurana et al., 2014). Triassic age sandstones and carbonates of Lower to Middle Jurassic age crop out in the N block of the Socovos fault, whereas carbonates of Upper Cretaceous age appear in the S block of the San Jorge fault. Upper Jurassic to Lower Cretaceous age carbonates crop out between the two faults.

## ORE-TYPES

Two ore-types have been identified in the Riópar area: hypogene Zn-(Pb-Fe) Mississippi Valley-Type (MVT) sulfides and non-sulfide Zn-carbonates and hydroxides. The hypogene ore is hosted by hydrothermal dolostones which replace the Upper Jurassic to Lower Cretaceous age carbonates (Navarro-Ciurana et al., 2014). The old mines are aligned along the footwall block of the San Jorge fault, which probably focused most of the dolomitizing and ore-bearing hydrothermal fluids. The hypogene paragenesis consists of replacive to sucrosic dolomite, early saddle dolomite, Zn-Fe-Pb sulfides (marcasite, sphalerite and galena), late saddle dolomite and rombohedral dolomite replacing sphalerite (Fig. 1).

*Calamine* ores are found replacing the hypogene Zn-sulfides and as karst-infills. They consist of Zn-carbonates (smithsonite and scarce hydrozincite), associated with abundant Fe-(hydr)oxides (goethite and hematite) and minor Pb-carbonates (cerussite) (Fig. 1). Three smithsonite types have been recognized: Type-I consists of brown anhedral microcrystalline aggregates as encrustations replacing sphalerite. It presents bright to dull dark blue cathodoluminescence (Fig. 1a). Type-II refers to brownish botryoidal aggregates of rugged appearance, replacing sphalerite (Fig. 1b), showing a pink to red bright luminescence. Type-III smithsonite appears as grayish botryoidal aggregates of 400 µm to 1cm in size in karstic cavities (Fig. 1c). It presents alternating bands of bright to dark blue and pink luminescence. Hydrozincite is scarce and appears as milky white botryoidal encrustations in cavities replacing smithsonite (Fig. 1d). The non-sulfide Zn mineral assemblage

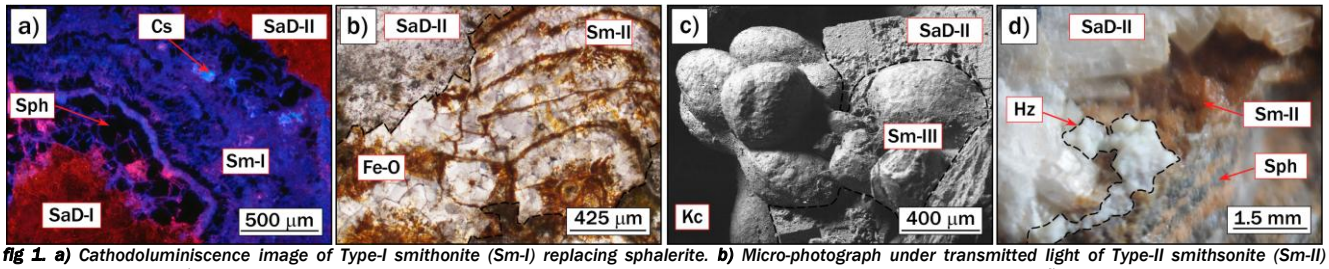


*fig 1. a) Cathodoluminiscence image of Type-I smithonite (Sm-I) replacing sphalerite. b) Micro-photograph under transmitted light of Type-II smithsonite (Sm-II) replacing sphalerite. c) Secondary electron microscopy micrograph of Type-III smithsonite (Sm-III) filling a karst cavity (Kc). d) Photograph of hydrozincite (Hz) replacing Type-II smithsonite as encrustation in cavity. SaD-I: early saddle dolomite; Sph: sphalerite; SaD-II: late saddle dolomite; Cs: cerussite; Fe-O: Fe-(hydr)oxides.*

**palabras clave:** Isótopos de O/C, Mineralizaciones de Zn no sulfuradas, Calamina, Prebético, Riópar.

**key words:** O/C Isotopes, Non-Sulfide Zn Ore, Calamine, Prebetic, Riópar.



* corresponding author: didac.navarro.ciurana@gmail.com

(smithsonite and hydrozincite) and their textures (replacements of hypogene Zn-sulfides and accumulations in karst-infill cavities) points to a supergene origin.

## C AND O ISOTOPE DATA

The different smithsonite-types exhibit a narrow range of $\delta^{18}O$ values, +27.8 to +29.6‰ V-SMOW (Fig. 2). This data points to an almost constant $\delta^{18}O$ composition and temperature of fluids during the *calamine* formation (Coppola et al., 2008). As calamine minerals appear to be supergenic, they must represent the product of oxidation of primary sulfides by meteoric waters. From late Miocene (Tortonian: Braga et al., 2003) to the present, the combined effect of regional uplift, as well as erosion, contributed to exhumation of the External Betics (e.g. Meijninger and Vissers, 2007). The lower Cretacous age rocks and associated hypogene sulfides were then exposed, resulting more vulnerable to the action of meteoric waters. The present day $\delta^{18}O$ value of meteoric waters in the Betic area is around -5‰ (Díaz-Tejeiro et al., 2009). Assuming that isotopic composition of local meteoric waters did not change significantly from Miocene to present-day a temperature range of 12 to 19ºC during smithsonite precipitation has been calculated (Fig. 3), using the $\delta^{18}O$ fractionation equation of Gilg et al. (2008). These temperatures are typical of continental near-surface environments in a temperate climate (Coppola et al., 2009). A climate with alternating wet and dry cycles could promote the formation of weathering and oxidizing solutions (Hitzman et al., 2003), which would facilitate karstic development and replacement of the sulfides.

The $\delta^{13}C$ of smithsonites vary from -6.3 to +0.4‰ V-PDB (Fig. 2). These values point to a mixing of $^{13}C$-enriched and $^{13}C$–depleted sources of carbon (Gilg et al., 2008). A $^{13}C$-rich source could result from: i) $CO_2$ from carbonate-bearing host-rocks; ii) atmospheric $CO_2$; and iii) soil $CO_2$ derived from decomposition of C4 plants (Cerling, 1984). The most probable carbon source for $^{13}C$-enriched values at Riópar are the host-limestones and the hydrothermal dolomites as they show $\delta^{13}C$ average values of +2.7‰ and -0.1‰ respectively (Navarro-Ciurana et al., 2013) (Fig. 2). The release of $CO_2$ by the dissolution of host-carbonates could have been promoted by acid solutions generated during oxidation of the hypogene sulfides (e.g. Williams, 1990).

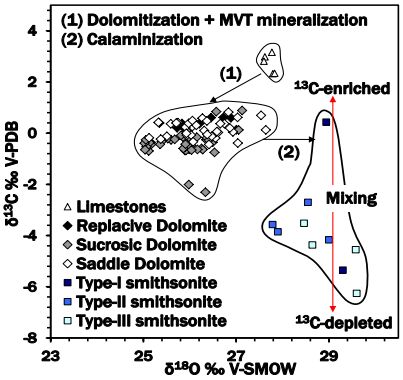


*fig 2. $\delta^{18}O$ vs. $\delta^{13}C$ cross-plot of smithsonite-types from the Riópar non-sulfide Zn ores. Limestone and dolomite values are reported by Navarro-Ciurana et al. (2013).*

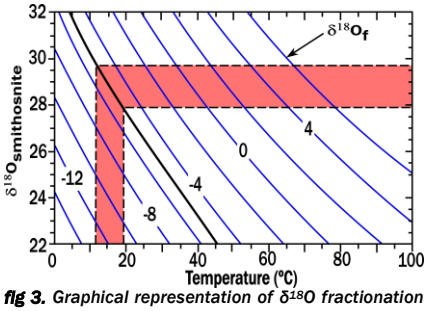


*fig 3. Graphical representation of $\delta^{18}O$ fractionation curves between smithsonite and water according to Gilg et al. (2008), as a function of fluid temperature. Calculated temperatures for the Riópar smithsonite precipitation (red area) are based on the $\delta^{18}O_f$ value of -5‰ V-SMOW for the fluid.*

Organic matter derived from decomposition of C3 vegetation in the soils covering the ore is the most probable source for $^{13}C$-depleted values (Boni et al., 2003) (Fig. 2). However, an additional $^{13}C$-depleted source resulting from the oxidation by bacterial activity of hypogene sulfides, as a consequence of a dropping water table, cannot be ruled out.

## CONCLUDING REMARKS

The Riópar non-sulfide Zn mineral assemblage consists of abundant smithsonite and scarce hydrozincite. Their textures and C-O isotope data ($\delta^{18}O$: +27.8 to +29.6‰ V-SMOW; $\delta^{13}C$: -6.26 to +0.43‰ V-PDB), puts constrains on: i) the *calamine* deposit-type, which is characterized by direct replacement and karst-fill, must have formed under supergenic conditions; ii) the oxidizing fluid, which was of meteoric origin with temperatures of 14 to 22ºC; and iii) the carbon source, that resulted from mixing between two components: $CO_2$ from the dissolution of host-dolomite ($^{13}C$-enriched source) and $CO_2$ derived from C3 vegetation decomposition ($^{13}C$-depleted component).

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