# Metallogenesis of lead-zinc deposits of the Alcudia Valley, Spain

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ABSTRACT: Neoproterozoic and Palaeozoic sedimentary rocks in the Alcudia Valley, Spain, host a large number of Pb-Zn(-Ag-Cu) deposits which can be classified into five types. With the exception of the minor syn-diagenetic stratabound type V mineralisation, other deposits occupy fractures generated during the Hercynian Orogeny. Types I, II and III are syn-tectonic veins whereas the most abundant deposits, type IV, are post-tectonic veins showing a spatial relationship with late Hercynian granite intrusions.

## **1 INTRODUCTION**

The Alcudia Valley in the eastern Sierra Morena, Ciudad Real Province, Spain (Figure 1) has been mined since Roman times and was an important mining field in the last quarter of the 19th century and the early part of the 20th century. This district, along with the neighbouring Linares and La Carolina fields, made Spain one of the leading Pb-producing countries during that period. The district is remarkable for the intensity of mineralisation, with a total of 484 mines and prospects hosted by Neoproterozoic and Palaeozoic sedimentary rocks in an area of approximately 2500 km<sup>2</sup> (Palero 1991). The deposits are dominantly Pb-Zn veins with significant contents, but irregular distribution, of Ag and Cu.

## 2 GEOLOGICAL SETTING

The Alcudia Valley lies within the southern sector of the Central Iberian Zone of the Iberian Massif. A prominent feature of the geology is a series of major WNW-ESE trending anticlines and synclines formed during the Hercynian Orogeny.

The Neoproterozoic rocks, generally referred to as "Alcudiense" (Tamain 1972), are equivalent to the schist-graywacke complex that forms a broad zone in the central and western parts of the Iberian Peninsula. The "Lower Alcudiense" unit is a monotonous sequence of shales and graywackes, and is overlain unconformably by the more heterogeneous "Upper Alcudiense" unit consisting of sandstones, shales,



Figure 1. Location of the Alcudia Valley mineral field

graywackes, conglomerates and limestones. The contact between the "Upper Alcudiense" and Lower Palaeozoic rocks is marked by a disconformity. The Ordovician-Devonian sequence is almost continuous from Tremadocian to Gedinnian and consists of alternating orthoquartzites, shales and sandstones.

Lower Carboniferous rocks crop out in a wide belt in the southern part of the area and form a characteristic unit known as "Culm de Los Pedroches" consisting of a monotonous sequence of shales and sandstones, with some intercalated lenses of conglomerate. Deposition of the "Culm" was followed by the Hercynian Orogeny and the postorogenic sediments of the Puertollano coal basin of Stephanian age.



Figure 2. Location of the major examples of the five types of Pb-Zn deposits in the Alcudia Valley and contours of Ag grades of type IV deposits

The rocks of the Alcudia Valley have been subjected to several phases of deformation. Two pre Ordovician deformation events affected the Precambrian rocks; the first folded the "Lower Alcudiense" rocks whereas the second followed deposition of the "Upper Alcudiense" sediments and involved vertical displacement of blocks controlled by major NW-SE fractures. The most important deformation took place during the Hercynian Orogeny, with two phases that affected almost the entire Precambrian and Palaeozoic sequence. The first phase (H<sub>D1</sub>) was responsible for the major WNW-ESE trending folds and longitudinal fractures parallel to fold axes. HD1 post-dated deposition of the "Culm" but preceded Stephanian sedimentation. The second phase of Hercynian deformation  $(H_{D2})$ produced ductile-brittle shear zones, the majority of which are sinistral, trending NE-SW, with some dextral, trending NW-SE. The impact of these shear zones on HD1 structures resulted in interference folds

Alcudia Valley were deposited. Magmatic activity in the region is represented by Palaeozoic and Tertiary-Ouaternary volcanism and

and fractures in which most of the Pb-Zn veins of the

Palaeozoic and Tertiary-Quaternary volcanism and both pre- and syn-Hercynian granite intrusions. Volcanic rocks, mainly pyroclastics, are found interbedded with sediments at several stratigraphic levels in the Palaeozoic sequence. Pre-Hercynian intrusive rocks are found in the northwestern part of the district, and consist of small stocks of calcalkaline porphyries. Of much greater significance are the Hercynian granites which crop out in the northwest and southwest of the area as the Fontanosas stock and Los Pedroches batholith (Figure 2). Two distinct facies are present in these intrusive bodies: a biotite granodiorite with enclaves and a porphyritic cordierite monzogranite with feldspar megacrysts. Recent investigations on equivalent granites in nearby areas have shown that the granodiorites were emplaced either during the interval between the two

Hercynian deformations ( $H_{D1}$  and  $H_{D2}$ ) or at the beginning of  $H_{D2}$ , whereas the monzogranites clearly post-dated  $H_{D2}$  (Palero, Zuazo & Fernández-Carrasco, unpubl.).

## 3. MINERALISATION

#### 3.1 Mineral deposit types

Five distinct types of deposits (Figure 2) have been recognised on the basis of morphology, host rocks, structural setting and mineral assemblages (Palero 1991). Type I deposits (e.g. Tres Ventas) are Zn-Pb veins in HD2 shear fractures in Neoproterozoic rocks. Type II deposits (e.g. El Hoyo group) are strongly deformed Zn-Pb-Cu veins in HD1 fractures in Ordovician rocks. Type III deposits (e.g. La Nava) are Zn-Pb veins exhibiting a greater variation in morphology and degree of deformation compared with other types, and are found in both HD1 and HD2 fractures in Late Ordovician and Early Silurian rocks. Type IV deposits (e.g. San Quintín) are the most abundant and economically most important type. These are Pb-Ag-Zn veins occupying HD2 fractures and are widely distributed through the district in rocks ranging from Neoproterozoic to Late Ordovician, although most common in Neoproterozoic host rocks. Type IV veins are characterised by complex mineralogy and paragenetic sequence and show a spatial relationship with porphyritic monzogranites emplaced at around 290 Ma (Penha & Arribas 1974). Ag grades of these deposits show a zonation in three "corridors" extending out from post-H<sub>D2</sub> intrusions (Figure 2). The zonation also correlates with a trend from early stage minerals close to granite contacts to later stage minerals further out. Type V (e g. Peña del Aguila) is a minor type of stratabound Zn-Pb mineralisation occurring as disseminations and small veins in Late Ordovician limestone

## 3.2 Metallogenesis

Deposition of Type V mineralisation preceded the Hercynian Orogeny. A syn-diagenetic origin is suggested by the limited stratigraphic distribution of the mineralisation and anomalous base metal contents of Late Ordovician-Early Silurian black shales overlying the mineralised limestone (Palero & Martín-Izard 1988).  $\delta^{34}$ S values of 8.3 to 13.6‰ are compatible with bacteriogenic reduction of Late Ordovician-Early Silurian seawater sulphate. Minor remobilisation of disseminated sulphides into veins took place during late diagenesis or early Hercynian deformation.

The origins of the other four types of deposits are intimately related to the Hercynian Orogeny. Type II deposits were  $syn-H_{D1}$  veins. Fluid inclusions in

quartz are mainly aqueous and rarely aqueo-carbonic, with mean homogenisation temperatures (Th) of 176°C and 344°C, respectively. The mean salinity of each fluid inclusion type is approximately 3.5 wt. % NaCl equivalent.  $\delta^{34}$ S values of sulphides are -0.7 to 17.0‰ and calculated  $\delta^{18}O_{H_2O}$  values are approximately -1 to 2.5%. Lithogeochemical studies (Delgado et al. 1988) have shown depletion in metal contents of host rocks adjacent to the veins of El Hoyo group, suggesting a lateral secretion process involving mobilisation of metals by a surface-derived fluid, either seawater or meteoric water. The former is more likely on the basis of  $\delta^{34}$ S data, which may be explained by thermochemical or inorganic reduction of seawater sulphate. The aqueo-carbonic fluid inclusions may represent a minor influx of metamorphic fluid.

Type III veins formed during both H<sub>D1</sub> and H<sub>D2</sub> in localised hydrothermal systems. Fluid inclusions in quartz are aqueous with a mean Th of 206°C and mean salinity of 6.2 wt % NaCl equivalent. The stratigraphic distribution and  $\delta^{34}$ S values of sulphides (7.3 to 13.3‰) are similar to type V deposits, suggesting an origin involving either remobilisation of syn-diagenetic type V mineralisation or derivation of metals from the same source (viz. Late Ordovician-Early Silurian black shales).  $\delta^{13}$ C values of carbonates (-7.5 to -7.1‰) are within the possible range for dissolution of limestone (Ohmoto 1986) but an organic-derived component is also probable. Calculated  $\delta^{18}O_{H2O}$  values are approximately 5 to 7‰, in keeping with formation waters.

Type I deposits were syn-H<sub>D2</sub> veins. Fluid inclusions in quartz contain a higher temperature aqueo-carbonic fluid (mean Th of 270°C and salinity up to 8 wt % NaCl equivalent) and a lower temperature aqueous fluid (mean Th of 228°C and mean salinity of 9 wt % NaCl equivalent), and may represent mixing of a metamorphic fluid with formation water. Calculated  $\delta^{18}O_{H_2O}$  values are approximately 2 to 7‰.  $\delta^{34}S$  values of sulphides of -12.7 to 4.7‰ and  $\delta^{13}C$  values of carbonates of -12.5 to -9.3‰ are in keeping with black shales of the Neoproterozoic sequence as the major source of sulphur and a partial source of carbon.

Fluid inclusions in ankerite in type IV veins record relatively low temperatures (Th values from 89° to 145°C) and a wide range of salinities (12 to 41 wt % NaCl equivalent), typical of basinal brines (e.g. Munoz et al. 1994, Wilkinson et al. 1995). Calculated  $\delta^{18}O_{H_2O}$  values are approximately 0 to 4‰. The veins are located in H<sub>D2</sub> fractures and the spatial relationship to monzogranite outcrops indicates that late Hercynian magmatism was the source of heat driving fluid migration through the fracture system. Reaction of the fluid with black shales of the Neoproterozoic sequence is suggested by  $\delta^{34}S$  values of sulphides (-10.0 to -2.7‰) and  $\delta^{13}C$  values of carbonates (-11.8 to -8.2‰) of the main

stages of the paragenetic sequence. The final paragenetic stage consists of barite ( $\delta^{34}S = 13.4$  to 19.0‰), with calcite and pyrite (single  $\delta^{34}S$  value = -23.8‰). In the adjacent Linares and La Carolina fields, barite veins associated with Pb veins similar to the Alcudia type IV deposits reach, and are hosted by, the lower part of the Triassic sequence overlying the Palaeozoic sedimentary rocks and granites (Azcárate et al. 1971). This suggests that the final stage of the Alcudia type IV veins may have been deposited during a later hydrothermal event than minerals of the main stages.

#### 4 CONCLUSIONS

The Pb-Zn(-Ag-Cu) deposits of the Alcudia Valley represent a sequence of mineralising events over a time span of at least 200 Ma, commencing with syndiagenetic type V mineralisation in Late Ordovician sediments. Syn-tectonic mineralisation was deposited during both major phases of Hercynian deformation, with type II deposited syn-H<sub>D1</sub>, type I syn-H<sub>D2</sub> and type III deposited during both H<sub>D1</sub> and H<sub>D2</sub>. The economically most important mineralisation event was post-tectonic, when deposition of the main stages of type IV veins was associated with the emplacement of late Hercynian granites. The final stage of type IV mineralisation was apparently deposited during the Triassic.

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