Geoquímica isotópica do chumbo em mineralizações hidrotermais antimoníferas do Sul de Portugal

Lead isotope geochemistry in hydrothermal, antimony-bearing mineralising systems of Southern Portugal

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SUMÁRIO

A geoquímica isotópica do Pb em antimonites do Maciço Ibérico é consistente com as observações geológicas, indicando que as mineralizações de antimónio reflectem evolução metalogenética polifásica, onde o Pb derivou de diferentes reservatórios durante a tectónica tardi-Varisca. Antimonites das Zonas CI e SP são mais radiogénicas (μ ~10), derivando de reservatórios crustais; as da Zona OM são menos radiogénicas (μ ~ 9.5), incorporando fontes de Pb com valores U/Pb inferiores aos da composição média da crusta regional Varisca.

Palavras-chave: Geoquímica isotópica do chumbo; Minérios sulfuretados antimoníferos; SW da Ibéria

SUMMARY

Stibnite Pb isotope data support field/petrographic observations, indicating that antimony mineralizations in the Iberian Massif reflect a multistage metallogenic evolution, with lead derived from different reservoirs during Late-Variscan tectonics. Radiogenic CIZ and SPZ stibnite samples (μ ~10) are though to derive their Pb from dominantly upper crustal reservoirs; OMZ stibnites have lower $^{207}Pb/^{204}Pb$ ratios and their sources should have been characterized by U/Pb values significantly lower than the average regional Variscan crustal compositions.

Key-words: Lead isotope systematics; Sb-bearing, epigenetic sulphide ores; SW Iberia

1. Introduction

Sb-bearing sulphides occur in several epigenetic, hydrothermal, and structurally controlled quartz-carbonate lodes of Southern Portugal, sometimes as the main ore-mineral phases [*e.g.* 1,2]. The Palmas, Ventosa, and Cortes Pereira prospects are the three main examples of the known Sb-dominant mineralising systems. The former two are located in the southern border of the Ossa-Morena Zone (OMZ), near Montemor-o-Novo and Beja, respectively, whereas Cortes Pereira is located in the southeastern domain of the Iberian Pyrite Belt, South Portuguese Zone (SPZ), close to Alcoutim. In addition to their relative prevalence of stibnite aggregates, these sulphide-rich systems share a similar metallogenesis related to multistage focusing of hydrothermal fluids into major fault zones during successive reactivation events. From field criteria, a Late-Variscan timing of faulting and ore deposition is favoured [3]. Field and petrographic observations, experimental results, and numerical modelling [*e.g.* 4] also support the hypothesis of extensive metal scavenging from substantial volumes of Palaeozoic formations (meta-sedimentary and meta-volcanic sequences, in particular), specially if the initial in-

crements of the Late-Variscan crustal uplift proceeded under, at least, moderate rates (*ca.* 3-5 mm.year^{-1}).

The main purpose of this work is to report, for the first time, lead isotope data from pure stibnite concentrates of Palmas, Ventosa, and Cortes Pereira systems and, on their basis, discuss some relevant features concerning metal sources.

2. Main features of the selected prospects

The three prospects selected for this study were actively explored and mined in the past. Present-day sampling in these prospects is limited to old mine tailings and, with the exception of Palmas, to some preserved galleries and outcrops.

2.1 Palmas prospect

The prospect is sited *ca.* 15 km WSW of Montemor-o-Novo, close to the tectonic boundary between the OMZ and SPZ. The lodes, following N25ºW and NE-SW directions with variable dips, are chiefly composed of milky and slightly hardened quartz + sulphides ± non-deformed calcite. They correspond to hydrothermal mineral infillings of strike-slip fault zones hosted in a biotite-schist - gneissic sequence with abundant black quartzite intercalations, which has been correlated to the Proterozoic *Black Series* [5]. Stibnite prevails largely over pyrite and arsenopyrite. Chalcopyrite is rare and no other primary ore-mineral phase was observed. The examined samples record a large variety of textural arrangements. Macroscopic massive stibnite grades from non-oriented coarse grains into strongly oriented fine-grained aggregates. In some samples, the grain size reduction is clearly associated with foliation development parallel to the lode walls. Wavy extinction of oriented stibnite core-grains and formation of sub-grain mantles indicate progression of dynamic recrystallisation processes. Deformation bands and deformation twins are also common microstructures. Considering the mechanical response of coeval quartz aggregates, it seems that stibnite deformation took place slightly after its precipitation. Therefore, P-T conditions of stibnite deformation estimated on the basis of the observed microstructures represents a rough approximation to the P-T conditions of sulphide deposition. Pressure ranging from 0.6 to 1 kbar and temperatures between 175ºC and 250ºC are the most likely conditions if experimental results are considered [*e.g.* 6].

2.2 Ventosa prospect

The prospect is located *ca.* 4.5 km SE of Beja, near the southeastern border of the Ventosa – Senhora das Neves – São Brissos structure [7]. The mineralization is controlled by a complex structural arrangement, including WNW-ESE shears with strong SW dip and a late sub-vertical N-S fault zone. The lodes are mainly hosted in silicified amphibolites of Upper Proterozoic age, locally with abundant disseminated pyrite. They comprise a multistage quartz-carbonate hydrothermal precipitate that contains randomly distributed aggregates of sulphides and sulphosalts (mainly stibnite, tetrahedrite, pyrite, arsenopyrite, and berthierite, complemented by minor amounts of chalcopyrite, marcasite, gudmundite, famatinite, aurostibite, chalcostibite, chalcocite, and covellite). Besides the development of inter- to trans-granular fracturing no other evidence exists of strain accommodation by sulphide-sulphosalt minerals, thus supporting the late character of their deposition. Deposition took place mostly during two stages separated by a major fracturing event, along a cooling path from *ca.* 330ºC to 250ºC and/or subjected to significant changes in fS_2 e fO_2 under $4.5 \leq pH \leq 5.5$ [8].

2.3 Cortes Pereira prospect

The prospect, to be found at *ca.* 4 km NW of Alcoutim, shows different (brecciated) lodes intimately associated with a WNW-ESE thrust fault zone that dips ~65º towards the NNE, affecting meta-sediments of the Mértola Formation (flysch sequence) of Visean age [*e.g.* 9]. These lodes comprise different quartz generations, the early ones showing effects of strong cataclasis Accessory amounts of siderite can be observed in some samples, as well as rare barite and calcite. Calcite seals very late veinlets or interstitial voids of multiphase quartz breccias. As in the Palmas prospect, stibnite dominates, being locally accompanied by accessory amounts of fine-grained pyrite and arsenopyrite. The main stibnite generation form massive aggregates where very fine deformation twins are deformed by shear bands and discrete micro-shear zones. The local development of polygonal aggregates composed of equant, fine grains is interpreted as a result of a complete dynamic recrystallisation due to the heterogeneous high strain accommodation along the thrust fault zone. Late stibnite generations comprise slightly deformed to undeformed aggregates that invariably fill up randomly distributed interstitial spaces of reworked quartz breccias, even though they precede calcite infillings whenever present. Thus, it seems plausible to admit a narrow time span between the main event of stibnite deposition and its deformation, surely related to the early evolution stages of the thrust fault zone in Upper Visean times. Accepting this interpretation, the P-T conditions under which the main event of sulphide deposition/deformation occurred should be similar to that referred for the Palmas prospect. Therefore, late stibnite precipitation must have happened under temperature conditions below *ca.* 175 ± 25ºC.

3. Lead isotopes

Andráš et al. [10] report Pb isotope data on stibnite from different deposits/prospects in Dúrico-Beirão and Bragança (Northern Portugal) regions of the Central-Iberian Zone (CIZ). CIZ stibnite Pb isotope data are characterised by $^{206}Pb/^{204}Pb = 18.19 – 18.52$ ($\mu = 9.6 – 10.0$), $^{207}Pb/^{204}Pb = 15.59 – 15.67$, $^{208}Pb/^{204}Pb = 38.13 – 38.54$ ($w = 35 – 39$) ratios and

variable model ages [11] (~100 Ma to ~400 Ma), which have been interpreted as lead that was (re-)mobilised at different times from continental crustal sources.

The present study provides complementary Pb isotope data on stibnites from Palmas, Ventosa (OMZ) and Cortes Pereira (SPZ) prospects in Southern Portugal. The new OMZ and SPZ stibnite Pb isotope results are summarised in figure 1, together with CIZ stibnite isotope data given in [10]. The OMZ and SPZ stibnite Pb isotope values are fairly homogeneous, with a range of $^{206}Pb/^{204}Pb$ values from 18.19 to 18.22, $^{207}Pb/^{204}Pb$ values from 15.56 to 15.61 and $^{208}Pb/^{204}Pb$ values from 38.12 to 38.30. The lowest and the highest $^{207}Pb/^{204}Pb$ values are those of the Palmas and Cortes Pereira stibnite samples, respectively, with the latter also displaying the highest $^{208}Pb/^{204}Pb$ ratio (fig. 1). Model ages (Palmas: 201 Ma; Ventosa: 278 Ma; Cortes Pereira: 313 Ma) and the subtle observed isotopic variations are in agreement with both field criteria and available Pb isotope data on regional ore deposits [12, 13], and are also consistent with multistage leaching of metals, during the Late-Variscan, from sources isotopically equivalent to those of the Iberian Pyrite Belt massive sulphides (SPZ) and late/post-Variscan OMZ Pb-Zn vein mineralizations (fig. 1). On the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (fig.1) the Cortes Pereira stibnite plots, together with CIZ stibnites, between the orogen and upper crustal growth curves of Zartman & Doe [14] and its lead isotope signature (μ = 9.7) supports an upper crustal derivation without significant juvenile contamination. Palmas and Ventosa (OMZ) stibnites are less radiogenic (μ = 9.5 - 9.6), indicating lead contributions from more primitive sources. In the $^{208}Pb/^{204}Pb$ - $^{206}Pb/^{204}Pb$ diagram (fig. 1), OMZ, SPZ and CIZ stibnites display similar $^{208}Pb/^{204}Pb$ values, and most samples plot above the upper crust, mantle and orogen average values, indicating a potential contribution of Th-derived lead. The observed broad correlations between stibnite Pb isotope ratios ($^{208}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$) and model ages, suggest that the variable μ and relatively high *w* ratios could be interpreted as to indicate U/Th decoupling during ore remobilisation related to multistage focusing of hydrothermal fluids into major fault zones subjected to successive reactivation events.

4. Discussion and conclusions

Stibnite lead isotope geochemistry is consistent with field and petrographic criteria, all indicating that Sb ore systems in the Iberian Massif reflect a complex multistage metallogenic evolution with Pb derived from different reservoirs during Late-Variscan tectonics. The less radiogenic reservoir has μ values close to 9.5 and *w* values of 36, whereas the more radiogenic reservoir has μ values of 10.0 and *w* values of 39. The first is interpreted to incorporate primitive, mantle derived, Pb, and the second should include a dominant upper crustal component. CIZ and SPZ stibnite samples with $^{207}Pb/^{204}Pb$ ratios above the orogen global growth curve [14] and the evolutionary curves of regional shales and volcanic-sedimentary rocks, respectively (fig. 1), are thought to derive their Pb from dominantly upper crustal reservoirs. In contrast, OMZ stibnite samples, particularly that from the Palmas prospect (fig. 1), have significantly lower $^{207}Pb/^{204}Pb$ ratios for equivalent $^{206}Pb/^{204}Pb$ values, demonstrating that distinct local source rocks characterized by U/Pb values significantly lower than the average regional Variscan crustal composition (*e.g.* mantle derived mafic rocks) must have also contributed to the compositional characteristics of these ore systems.

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Figure 1: Diagrams of $^{206}Pb/^{204}Pb$ versus $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ for CIZ (Dúrico-Beirão - black circles; Bragança - white squares; [10]), OMZ (white triangles), and SPZ (white circle) stibnites. Schematic location of the fields for OMZ ores (OMZ granitic ores (W): types 15 and 18; OMZ Pb-Zn: type 20; late/post-Variscan CIZ Pb-Zn; [13]), Iberian Pyrite Belt (IPB) ores and age corrected (300-250 Ma) IPB volcanics [12], Iberian granites [15], CIZ post-Tremadocian and Tremadocian sediments [17], CIZ Precambrian shale evolution curve (CIZ PC: equivalent to the OMZ Série Negra, [16]) and Zartman & Doe [14] "upper crust" and "orogen" curves are also shown for comparison.