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Recrystallised (Fe-)Zn-Pb ores of the Portel-Ficalho region (Ossa Morena Zone, Portugal)

A. Mateus$^{(a,b,1)}$, **J. Figueiras**$^{(a,b,2)}$, **V. Oliveira**$^{(c)}$ **& J. X. Matos**$^{(c,b,3)}$

a - Departamento de Geologia, Faculdade de Ciências da Universidade de Lisboa, Portugal
b – Centro de Recursos Minerais, Mineralogia e Cristalografia (CREMINER), Fac. Ciências da Universidade de Lisboa, Portugal
c – Instituto Geológico e Mineiro, Beja, Portugal
1 – amateus@fc.ul.pt; 2 – jmvf@fc.ul.pt: 3 – joao.matos@igm.pt

ABSTRACT

Keywords: (Fe-)Zn-Pb sulphide ores; variscan metamorphism; Ossa Morena Zone; SEDEX-Ireland type mineralisation.

In the Portel-Ficalho region, metavolcanic rocks and/or metadolostones of the *Dolomitic Formation* (Lower Cambrian) host sulphide (Fe-)Zn-Pb mineralisation that shows strong metamorphic and post-metamorphic reworking and occur with late disseminated and fracture-controlled mineralisation. P-T conditions of metamorphism inferred on the basis of *sph* and *apy* compositions are 2.6kbar/≈440ºC for Enfermarias and ≈4.5kbar/465-475ºC for Algares, the log$a$(S_2) values varying from –8.5 to –6.5 and from –9 to –8, respectively. Retrogradation evolved roughly from ≈400ºC, log$a$(S_2)≈ –8, log$a$(O_2)≈ –26 to ≤300ºC, log$a$(S_2)≥–11, log$a$(O_2)≤–33.5. Under these conditions, substantial amounts of Fe, Zn and Pb are expected to be remobilised, their further redeposition taking place under ≈260-220ºC. Considering the mineralogical nature of the recrystallised mineralisation and the geochemistry of their host rocks, a SEDEX-Ireland type model is indicated for the primary mineralisation, the variations in redox and pH conditions of metal deposition being responsible for some particular features observed.

Introduction

The Magnetite-Zinc Belt, roughly running NW-SE from Montemor-o-Novo to Ficalho, is one of the most important ore districts in the Ossa-Morena Zone (Oliveira, 1986). It comprises different mineralisation types formed in distinct geological settings that usually display strong tectonic deformation and textural-mineral transformations, both developed either during Variscan metamorphism or during the subsequent retrogradation and/or hydrothermal activity triggered by the formation of Late-Variscan fault zones. The direct characterisation of the pristine mineral and textural relationships of the mineralisation and of the correlative hydrothermal alteration haloes eventually developed in host rocks is, therefore, impossible. The important question is: is it possible to obtain adequate data to unravel properly the origin and evolution of the mineralising systems prior to their physical and chemical readjustments in Variscan and Late-Variscan times? The main goal of this work is to discuss this problem by examining the effects of Variscan metamorphism and deformation on some (Fe-)Zn-Pb mineralisation hosted in the *Dolomitic Formation* of Lower Cambrian age (Oliveira *et al*., 1991).

Sulphide (Fe-)Zn-Pb mineralisation in the Magnetite-Zinc Belt are apparently limited to the Portel-Ficalho region, forming several ore showings and deposits, some of them extensively explored in the past. The deposits of Algares and Balsa, located a few kilometres SW of Portel, were subjected to intense geological and geophysical surveys in the sixties by the SFM (Goinhas, 1971a) and a first characterisation of the drilled mineralisation was made by Gaspar (1967), Andrade (1966, 1969) and Carvalho (1988). The deposits of Preguiça and Vila Ruiva, located in the Moura-Ficalho area, also belong to this mineralisation type, although data on the primary mineralisation is rather scarce since the mining works concerned mainly the very rich supergene secondary Zn-ores (Goinhas, 1971b; Oliveira, 1986). In the Moura-Ficalho area, two other (Fe-)Zn-Pb prospects were recognised by SFM: Carrasca and Enfermarias. In the former prospect, only small amounts of disseminated base metal sulphides were observed. In the second prospect, a systematic geological and geophysical exploration program (including drilling) carried out in the eighties, enabled the identification of hidden mineralisation (Oliveira & Matos, 1992). In this extended abstract, the sulphide mineralisation found at Algares, Balsa and Enfermarias, will be briefly reviewed in order to identify what features were preserved from the Variscan metamorphism and deformation.

Main geological aspects of the Portel-Ficalho region

The recrystallised (Fe-)Zn-Pb mineralisation known in the Portel-Ficalho region is typically associated with a thick, metamorphosed and deformed (volcano-)carbonate sequence, particularly with its deeper part where metavolcanic rocks may form a relatively continuous series (like those identified in the Moura-Ficalho area) or metric horizons of variable extension intercalated in a thick metadolostone package (apparently predominating in the Portel area). Oliveira *et al* (1991), define this (volcano-)carbonate sequence as the *Dolomitic Formation*, dated from the Lower Cambrian by correlation with a very similar succession outcropping in the Elvas, Estremoz and Aracena regions. However, as Araújo (1995) points out, a simple comparison between the Moura-Ficalho and the Portel areas is problematic because: 1) the presence of distinct allochthonous and parautochthonous units hinders the establishment of a "simple" lithostratigraphical column; and 2) the effects of Variscan metamorphism and deformation, being quite different in both areas (much more intense and complex in Portel), masks the original lithology of some silicate rocks. Despite these problematic issues, it can be shown that: 1) the lithostratigraphical sequence of Oliveira *et al.* (1991) is appropriate for the Moura-Ficalho area, despite the controversy concerning the detailed internal framework, age and geodynamic interpretation of its upper units known as the *Moura-Ficalho Volcano-Sedimentary Complex* (Middle Cambrian? – Ordovician) and the *Xistos de Moura Formation* (Ordovician? – Silurian); 2) the polyphase Variscan deformation, observed at all scales, is responsible for the development of stacking folds with axial plane cleavage and of various thrust zones that, in general, record the effects of strain accommodation in a progressive, tangential regime; 3) tectonic dismembering is rather strong in the Portel area, creating a complex imbricate pattern that includes several allochthonous and parautochthonous folded units, similar to those found all over the Portel-Viana do Alentejo-Alvito region (Araújo, 1995); 4) the Variscan metamorphism is transitional between greenschists and amphibolite facies in Moura-Ficalho and amphibolite facies in Portel, although some of the parautochthonous units in the latter area preserve evidence for an early metamorphic event developed under eclogite facies conditions; and 5) the recrystallised (Fe-)Zn-Pb mineralisation, comprising mostly sulphides, are preferentially located in the hinges and/or along the short limbs of the major anticline-antiformal stacks whose cores are dominated by the afore-mentioned (volcano-)carbonate sequence.

(Fe-)Zn-Pb ores: occurrence, morphology, mineralogy and host rocks

In Algares, the massive sulphide mineralisation occurs mainly along the contacts of intermediate-mafic metavolcanics with metadolostones, its most important lenses (20-30 m thick) being limited to the hinge domains and short limbs of second order, NNW-SSE-trending, antiformal folds and occurring as concordant horizons, sometimes interstratified with the host rocks (Gaspar, 1967; Andrade, 1969; Goinhas, 1971a). Disseminated and fracture-controlled mineralisation can also be observed, forming discontinuous haloes of variable extension surrounding the massive mineralisation either in metadolostones or in metavolcanic rocks. In Balsa, the massive (10 m thick) and disseminated to fracture-controlled mineralisation occurs exclusively within a metadolostone horizon located above felsic metavolcanics and below intermediate-mafic metavolcanics, the whole package defining a second order, NNE-SSW-trending synformal fold (Goinhas, 1971a). In Enfermarias, the massive mineralisation occurs as stacked centimetric lenses sub-parallel to the metamorphic foliation showed by strongly chloritised intermediate-mafic metavolcanics located in the hinge of a second order NW-SE to NNW-SSE-trending anticline-antiformal stack; disseminated and fractured-controlled mineralisation also exists both in hydrothermally altered metavolcanics and in fractured metasomatised metadolostones (Oliveira & Matos, 1992; Barroso, 2002; Martins, 2003).

In Algares, the massive mineralisation is mainly composed of *py*, *sph*, *po* and *mgt*, the main accessory phases being *cpy*, *gn*, and *apy*; rare mackinawite, and Sb(-Ag?)-sulphosalts can also be observed (Gaspar, 1967; Andrade, 1969). Pyrite prevails largely in the massive mineralisation, usually occurring as fractured aggregates of euhedral grains often surrounded by fine-grained amphibole ± chlorite masses that occasionally include relics of barite; its composition is close to ideal FeS_2, although trace amounts (<0.05 *at. p.f.u.*) of Zn and Cd seem to be typical of *py* grains included in the deepest drilled mineralised levels. The core domains of many euhedral *py* grains comprise relics of *py-marc* intergrowths containing rare and tiny *po* inclusions, strongly suggesting that *py* is mainly a recrystallisation product of *py-marc* intergrowths formerly developed through *po* reaction with H_2S-rich fluids; fractures affecting *py* grains are usually filled with *cpy ± po ± apy*. Recrystallised *po* aggregates preserving foam textures are locally seen in the massive mineralisation. *Po* also occurs as inclusions in *mgt*, which forms fractured aggregates commonly observed along the contact between metasomatised metadolostones and the massive sulphide mineralisation; the former rocks are usually enriched in tremolite ± talc (surrounding corroded barite aggregates) and in late *ank* + *dol* + *cal* mostly deposited along different fracture sets. Locally, *mgt* is seen replacing *po*, enclosing also *py* grains, thus indicating a late depositional stage. Irregular masses of *cpy* postdates *apy* (with ≈ 32-33 at.%As) and surround also *po* aggregates in the peripheral domains of the massive mineralisation, replacing them partly; however, there are no clear textural relationships between *cpy* and *mgt* indicating their relative depositional chronology. The peripheral domains of the massive mineralisation are relatively enriched both in deformed *sph* [$(Zn_{0.86}Fe_{0.13}Cd_{0.01})S_{1.00}$, on average] that occasionally show tiny *cpy* exsolutions, and in *gn* [$Pb_{1.01}Sb_{0.01}S_{0.98}$] often occurring as irregular inclusions in *py*, *cpy* and *sph* but also forming interstitial aggregates that display abundant exsolutions of Sb(-Ag?)-sulphosalts. A late, iron-poor and non-deformed *sph* generation [$(Zn_{0.91}Fe_{0.09})S_{1.01}$] is found in fracture-controlled mineralisation along with *py* + *cal* ± *ank* ± *qtz*; in metadolostones, the early mineral infillings of multiphase veinlets comprise *py (± marc)* + *apy* ± *gn* + *ank* ± *dol*. Disseminated mineralisation in Algares is mostly composed of *py* ± *sph*.

Information concerning the sulphide mineralisation of Balsa is much more limited. Massive mineralisation is chiefly composed of fractured aggregates of *py* and *sph* [$(Zn_{0.84}Fe_{0.15}Cd_{0.01})S_{1.02}$] that include rare relics of *po* and are embedded in a *dol* + *cal* ± *ank* matrix variably enriched in tremolite-actinolite ± talc; no evidence exists of significant *mgt*. Grains of *sph* do not show *cpy* exsolutions. Two main generations of *py* can be recognised, the latest one containing rounded inclusions of *gn* that usually display tiny irregular inclusions of (Ag-bearing?) sulphosalts. The fracture-controlled mineralisation is mainly composed of *py* + (yellow) *sph*, forming fine-grained aggregates deposited along with *ank* + *cal* ± *qtz*. The disseminated mineralisation comprises mostly very fine-grained *py* ± *sph*.

Five different mineralisation types were recently characterised in the Enfermarias prospect (Barroso, 2002), the most important being the massive sulphide one. This is composed of fractured *py* and deformed *sph* aggregates that contain accessory amounts of *gn*, *cpy*, *apy*, *Ag-tt* and *mgt*; the gangue mineralogy is dominated by chlorite, actinolite-tremolite, Mg-hornblende, talc, serpentine, quartz, biotite and stilpnomelane. In this mineralisation type, *sph*, *apy*, *py* and *mgt* show usually evidences of strong recrystallisation and deformation; *gn* and *cpy* form irregular, interstitial aggregates heterogeneously distributed without preferred orientations; the deposition of *Ag-tt* is shown to be a late process. The available mineral chemistry data show that *py*, *cpy* and *gn* are quite close to their respective ideal compositions; deformed *sph* has the average $(Zn_{0.86}Fe_{0.18}Cd_{0.02})_{1.06}S_{1.02}$ composition; the As at.% contents of *apy* range from 30.5 to 32.4, although more often confined to the interval 30.5-31.0. A comprehensive characterisation of the chemical composition displayed by the silicates and carbonates can be found in Martins (2003). A different type of massive mineralisation is shown to occur in this prospect intimately associated with strong metasomatised domains (usually denoting a dolomitic precursor) close to sub-horizontal shear zones, thus post-dating the massive sulphide lenses; this tectonically controlled mineralisation is chiefly composed of *mgt* + *py* ± *po* ± *cpy* embedded mostly in a silicate matrix that comprises chlorite, talc, serpentine and actinolite-tremolite. Two different styles of late, disseminated and fracture-controlled mineralisation were also pointed out by Barroso (2002); one of them, typically associated with hydrothermally altered metavolcanics, includes *py* + *sph* $[(Zn_{0.88}Fe_{0.07}Cu_{0.02})_{0.97}S_{1.02}]$ ± *gn* ± *cpy* + *qtz* + *chl* ± *bt* ± *ms* + *dol* ± *cal*; the other, better developed in strongly modified metadolostones, comprises *gn* + *sph* $[(Zn_{0.93}Fe_{0.04}Mn_{0.01})_{0.98}S_{1.02}]$ ± *py* ± *cpy* ± *po* ± *Ag-tt* ± golden silver ± realgar? + different carbonate types + serpentine + chlorite + talc. With the exception of *sph* and *Ag-tt*, all these late sulphides display chemical compositions close to their ideal formulas (Barroso, 2002); the golden silver particles show 60 at.%Ag and 39 at.%Au; data on the chemical compositions of the silicate and carbonate phases can be found in Martins (2003). The fifth mineralisation type clearly results from a late, superimposed Cu-ore forming system related to the development of a sub-vertical strike-slip fault zone, as reported in Barroso (2002).

Discussion and conclusions

At a mesoscopic scale, it is evident that the (Fe-)Zn-Pb mineralisation here briefly described reflects largely the influence of metamorphic, structural and metasomatic controls. This is mainly caused by Variscan, ductile deformation and fluid remobilisation of a pre-existing (syngenetic or epigenetic?) mineralisation along with externally derived post-metamorphic mineralising events, involving intense metasomatism of a reactive Ca-Fe(-Mg-Mn)-rich precursor.

Although fluid inclusion and isotopic data are not available, some key issues related to ore metamorphism can be generally addressed evaluating both the thermodynamic conditions of sulphide stability and the T- or P-composition dependence shown by several minerals. Some thoughts on pre-metamorphic mineralisation and post-metamorphic metal remobilisation can also be done assessing thermochemically the Zn, Pb and Cu solubilities as a function of T and/or of fluid salinity. *Apy* and *sph* are the most useful minerals in the recrystallised sulphide mineralisation for such reasoning. In buffered sulphide mineral assemblages, the As content of *apy* depends on T, as demonstrated by many experimental and theoretical studies, which also show that this geothermometer may be used in greenschist to lower amphibolite facies conditions. In Algares, *apy* is a pre-metamorphic mineral coexisting with early *py-marc* intergrowths, probably post-dating *po* but preceding *cpy*; a relatively narrow temperature range (≈ 465-475ºC) can be deduced on the basis of its arsenic content, the $\log a(S_2)$ values varying from –9 to –8. In Enfermarias, *apy* is also a pre-metamorphic mineral coexisting mostly with *py*; following the same numerical approach, the calculated temperature varies from 440 to 360ºC and $\log a(S_2)$ values from –8 to –6.5. Considering the FeS content of deformed *sph* equilibrated with *py* and *po* (which is useful in deciphering the metamorphic pressures), values of ≈ 4.5 kbar and around 2.6 kbar are obtained for Algares-Balsa and Enfermarias, respectively. Note that the P-T conditions inferred on the basis of *sph* and *apy* compositions are just slightly below the values independently inferred for the Variscan metamorphic peak at the Portel and Moura-Ficalho areas (Araújo, 1995 and references therein).

The onset of significant post peak-metamorphic metasomatism in Enfermarias is marked by the deposition of *mgt* + *py* ± *po* ± *cpy*, later followed by the development of disseminated and fracture-controlled mineralisation largely dominated by *py*. This suggests that retrogradation evolved roughly from the *mgt* stability field (at ≈ 400ºC and $\log a(S_2) \approx -8$, $\log a(O_2) \approx -26$) to the *py* stability field (≤ 300ºC, $\log a(S_2) \geq -11$ and $\log a(O_2) < -33.5$) most of the time along the *mgt-py* boundary, reaching occasionally and locally the triple point *po-py-mgt*, thus enabling the deposition of trace amounts of the former sulphide under pressures below 2.5-2 kbar. According to the chemical nature of the host rocks, the fluids involved in these processes were presumably aqueous-carbonic, low saline and somewhat acidic. Assuming pH values in the range 4 to 5, $aCl^- \approx 3\text{-}4$ and $a(\Sigma S) \approx 0.01\text{-}0.001$, it can be shown that considerable amounts of Fe, Zn and Pb might be remobilised from the pre-existing mineralisation along the aforementioned P–T–log$a$(S$_2$)–log$a$(O$_2$) path. Under these conditions, the hydrothermal leaching and transport of copper is rather difficult, thus suggesting that the pre-metamorphic mineralisation was indeed originally Cu-poor. Further redeposition of Fe, Zn and Pb as disseminated sulphides or as fine-grained fracture infillings (always in the *py* stability field) depends mostly on T decrease and/or local aH$_2$S increase and/or pH rise, if Cl-complexes are assumed to be the most efficient way for metal transport; this seems indeed to have occurred under decreasing temperature conditions, mainly from 260ºC to 220ºC as indicated by the composition of late chlorite aggregates developed in Al and Si-saturated rock domains. The late Cu-enrichment is therefore envisaged as a consequence of a superimposed hydrothermal activity, that led to *py* + *cpy* ± *po* + *qtz* + *chl* deposition at *ca.* 260-300ºC. Data presently available for the Algares and Balsa deposits do not enable to discribe in detail the post-metamorphic evolution of the mineralisation; however, a similar trend is believed to have occurred.

As in all highly deformed and metamorphosed mineralised environments, the nature of pristine mineralogy and its origin are contentious issues, with textural relationships largely reflecting the last significant overprints. The recystallised sulphide mineralisation of Algares, Balsa and Enfermarias occur in a very similar lithostratigraphical setting, and apart from some detail differences caused by Variscan metamorphism and deformation, they show several distinct features that are believed to represent the inheritance of original characteristics that allow to unravel distinguishing depositional environments: 1) primary *mgt* is relatively abundant in the peripheral domains of massive pyrite mineralisation of Algares, denouncing a relatively late, incipient oxidation; 2) *sph* and *gn* are more abundant than *po*, but form massive lenses only at Enfermarias; and 3) an Fe-Mn carbonate envelop seems to exist in Enfermarias, its poor preservation being a result of metamorphic redistribution and subsequent Fe-Mn incorporation in new mineral structures. At all locations, *py* largely prevails and *cpy*, when present, is always an accessory phase. Moreover, (Fe-)Zn-dominated mineralisation is preferentially hosted in siliceous rocks (commonly hydrothermally altered mafic-intermediate metavolcanics), whereas metasomatised carbonate rocks seem to be the favoured setting for Pb(-Ag)-dominated mineralisation. All these features together with the lithological nature of the host rocks, suggest that all these massive mineralisations were formed through exhalation processes in marine environments, the differences inferred from the geological record tentatively interpreted as a consequence of variations in redox and pH conditions of metal deposition. In fact, the scarcity of primary *cpy* strongly suggests that these metal accumulations might have precipitated from high salinity, low temperature (< 300ºC), reduced and fairly acidic fluids quite poor in S but carrying large amounts of Fe and Zn (and lead). Fluid discharges in anoxic basins, together with temperature decrease and reduction, might have led to the formation of the original mineralisation of Balsa and Enfermarias (with characteristics of both SEDEX and Ireland-type categories). Fluid discharges in slightly more oxidised basins, accompanied by temperature decrease, and/or further oxidation coupled by pH increase, explains the particular features observed at Algares, particularly the peripheral enrichment in *mgt* showed by the pyrite massive mineralisation.

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