Mineralogy and geochemical characteristics of different superimposed mineralisations at the Enfermarias prospect (Moura, Portugal)

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ABSTRACT

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The Enfermarias prospect, located in the Magnetite-Zinc Belt of the Ossa-Morena Zone, has five different mineralisation types, preferentially hosted in basal horizons of the *Dolomitic Formation* (Lower Cambrian). The most important mineralisation of this hidden prospect is mainly composed of pre-metamorphic pyrite and sphalerite massive aggregates. During metamorphic retrogradation, rather massive aggregates of pyrite and magnetite were generated, accompanied by new sulphide disseminations (veins/veinlets) resulting from ore remobilisation or from new metal inputs in the system (Pb, Cu, Ag, As and Sb). These inputs are also responsible for the development of new mineral assemblages in the pre-metamorphic ores. The later development of pyrite and chalcopyrite aggregates, in fault breccias and veins or bands, is related to the evolution of sub-vertical strike-slip fault zones and records an independent Cu ore-forming system. The Enfermarias ores are thus a result of several different and largely unrelated superimposed events, the earlier ones having been much reworked. Simple geochemical indices may be used to detect and evaluate the mineralised domains without prior knowledge of their detailed mineral assemblages.

Introduction

The Enfermarias hidden prospect was drilled by the Serviço de Fomento Mineiro (nowadays Instituto Geológico e Mineiro - IGM) in the eighties, following evidence collected by geological, geochemical and geophysical exploration (Oliveira & Matos, 1992). The prospect is located in the Moura-Ficalho region of the Magnetite-Zinc Belt of the Ossa-Morena Zone. The regional litostratigraphical sequence consists of dark schists and metacherts ascribed to the Série Negra (Late Proterozoic), overlain in paraconformity by a thick (more than 300 meters) metadolostone sequence with basal metavolcanic intercalations known as Dolomitic Formation (Lower Cambrian). Above, there is a stratigraphic hiatus, locally recorded by a siliceous horizon. The overlying Middle Cambrian? – Ordovician Volcanic-Sedimentary Complex of Moura-Ficalho includes strata of calcitic marbles, calc-schists and metavolcanics. The uppermost formation is the Xistos de Moura Formation, also known as the Volcanic-Sedimentary Complex of Moura - Sto Aleixo (Ordovician? - Silurian), represented in this area by sericitic-chloritic schists and intercalated metavolcanics (Oliveira et al., 1991; Barroso, 2002; Martins, 2003). In the Moura-Ficalho region the meso-macroscopic Variscan folding led to the development of three NW-SE to NNW-SSE antiformanticlinal stacks, one of them at Enfermarias (Oliveira et al., 1991). In the Enfermarias area, several small angle WNW-ESE thrusts cause lamination and sometimes tectonic thickening of the litho-stratigraphic units; the whole stratigraphic and structural framework is cut by sub-vertical strike-slip faults (N-S, NNE-SSW and ENE-WSW trends) with kinematics indicating a NE-SW maximum compression, the same described elsewhere for late-Variscan times (e.g. Mateus, 2001; Marques et al., 2002).

The mineralised domains are hosted by the basal horizons of the *Dolomitic Formation of Moura-Ficalho*, mostly composed of metavolcanic rocks. The drilled metavolcanic sequence comprises different metavolcanic facies (felsic to intermediate-mafic) with interbedded (decimetric) horizons of silicate-bearing marbles and metasomatic rocks (mostly composed of chlorite/serpentine, actinolite/tremolite and talc), the latter often developed close to the sub-horizontal shear zones (Barroso, 2002; Martins, 2003). Anisotropic fabrics, metamorphic banding and multi-scale folding are quite common; abundant structural corridors also exist and may be divided in two groups: an older one developed with shallow dip and W vergence in a semi-brittle regime, and a later one represented by sub-vertical strike-slip fault zones (Barroso, 2002; Martins, 2003).

The main purposes of this work is to describe and characterize the different mineralisation types present in Enfermarias and correlate them with the events that took place during the evolution of this geological system.

Materials and Methods

This study was performed on three drill holes – SDM-3, SDM-5 and SDM-15 – chosen because of their unique petrological, mineralogical and textural characteristics. The sampling and logging of the drill cores allowed the subsequent petrographic, mineral chemistry and whole-rock chemistry studies. Whole-rock analyses were performed

in *Activation Laboratories Ltd.* (Ancaster, Canada) using a combination of different analytical methods (ICP, ICP-MS and INAA), and the individual minerals were analysed by electron microprobe in the Centro de Geologia da Universidade de Lisboa and Instituto Geológico e Mineiro, Porto.

Mineralisation types

The mineralogical, textural and geochemical study led to the individualization of five different sulphide (and/or oxide) mineralisation types (Barroso, 2002).

The mineralisation termed MS is mainly composed of strongly fractured pyrite (py I) and of deformed sphalerite (sph I) aggregates subparallel to the rock foliation, with minor amounts of galena (gn I), chalcopyrite (cpy I), magnetite (mgt I), arsenopyrite and sparse Ag-bearing tetrahedrite. Occasionally, the chalcopyrite-richer domains show this mineral altering to digenite, bornite or covellite. Sphalerite, magnetite, arsenopyrite and most of the pyrite (py I) show evidence for strong recrystallisation and deformation. The sphalerite aggregates record the recrystallisation and plastic deformation coeval of the Variscan metamorphism. Pyrite (py I), arsenopyrite and magnetite only exhibit fracturing and local brecciation. Galena and chalcopyrite grains (py I), sometimes sealing their fractures. Occasionally, neoformation of pyrite (py II) can be seen. Chlorite, actinolite-tremolite, Mg-hornblende, talc, serpentine, quartz, biotite and stilpnomelane, the latter always included in the sphalerite aggregates, compose the gangue minerals. These silicates involve the ore minerals and sometimes cut them.

The mineralisation termed *MM* comprises moderately massive aggregates of magnetite (*mgt II*) and pyrite (*py IIa*). These aggregates are strongly fractured and the two minerals appear to have crystallized in equilibrium, as can be seen by the local presence of "comb textures". Small chalcopyrite (*cpy I*) and, more rarely, pyrrhotite (*po I*) aggregates can be found sealing the pyrite and magnetite fractures. The silicate-gangue minerals involve the pyrite and magnetite aggregates of chlorite (*chl I*), talc, serpentine and actinolite-tremolite.

The mineralisation termed *FDS* occurs as late, millimetric veins/veinlets or bands of sphalerite (*sph IIa*), pyrite (*py II*), galena (*gn I*), hydrothermal milky quartz, biotite, sericite, chlorite and Fe-Mn oxides. This second generation of sphalerite has lower Fe concentrations (between 2,5 and 5,5 wt%) than *sph I* (between 5 and 9 wt%).

The mineralisation termed *DFS* mainly consists of fine disseminations of galena (*gn I* and *gn II*), sphalerite (*sph IIb*), pyrite (*py II*), Ag-bearing tetrahedrite (with Ag contents from 1,4 to 25,2 wt%) and, more rarely, gold-silver alloy particles. Whole-rock analyses and petrographic observations showed realgar to be present in this mineralisation type, but it was not possible to determine its chemical composition by electron microprobe. Grains of *sph IIb* have the lowest Fe concentration (between 2 and 3 wt%) of all sphalerite found at Enfermarias.

The mineralisation termed *TS* is composed of pyrite (*py III*), chalcopyrite (*cpy II*) and minor amounts of pyrrhotite (*po II*) as coarse aggregates in fault breccias and late veins or bands with abundant hydrothermal quartz and chlorite aggregates. Siderite and calcite veins or veinlets cut the sulphide mineralisation.

Some of the most important features of the whole-rock chemical composition of each mineralisation type are shown in Table 1. These chemical features, together with the whole-rock chemical composition of the country rocks and the detailed mineral assemblages characterising each mineralization type (Barroso, 2002; Martins, 2003), allowed the development of geochemical indices, able to detect and discriminate the different ores, especially *MS* and *TS*, in the absence of detailed mineralogical studies; the values of these indices take along borehole SDM-3 are shown in Fig. 1. The zinciferous index, $IZ = (Zn/(Zn+Pb+Fe+Mn)\times100)$, and the plumbiferous index, $IP = (Pb/(Zn+Pb+Fe+Mn)\times100)$ show good correlation with one another, although their peaks do not entirely overlap. The copper-argentiferous index, $ICA = [(Cu+Ag+As+Sb)/(Cu+Ag+Sb+Zn+Pb+Fe+Mn)\times100]$, has a distinct distribution along all the boreholes studied.

| Table 1 – whole-tock concentrations in the five initialisation types. | | | | | | | |
|---|-----------|-----------|-----------|-----------|------------|----------|----------|
| Mineralisation | S (%) | Fe (%) | Zn (%) | Pb (%) | Cu (ppm) | Sb (ppm) | Ag (ppm) |
| MS | 17,8-24,8 | 14,2-27,1 | 2,3-25,5 | 0,03-2,67 | 55-6900 | 18-102 | 2,9-75,6 |
| MM | 6,31 | 40,0 | 0,03 | 0,01 | 420 | 30 | 1,9 |
| FDS | 8,4-10,0 | - | 0,6-4,7 | 0,02-1,76 | 77-941 | 18-132 | 2,0-19,3 |
| DFS | 1,1 | - | 0,6 | 2,87 | 648 | 746 | 300 |
| TS | 14,0-21,0 | 22,9-25,5 | 0,01-0,03 | 0,00-0,01 | 6300-15900 | 139-461 | 4,0-10,1 |

Table 1 – Whole-rock concentrations in the five mineralisation types.

Discussion

The *MS* mineralisation occurs in lenses or massive aggregates that are sub-parallel to the metamorphic layering displayed by strongly chloritised intermediate to mafic metavolcanics. The *MM* mineralisation forms fractured aggregates in strongly metasomatised rock domains, mainly composed of chlorite, actinolite-tremolite, talc and serpentine aggregates, close to sub-horizontal shear zones. The *FDS* mineralisation mostly occurs within quartz-feldspar metavolcanics as late millimetric veins/veinlets or bands developed in pre-existent discontinuities, such as



Figure 1 – Geochemical indices (**IZ**, **IP**, **ICA**) in SDM-3: 1 – dolomitic marble; 2 - dolomitic marble with phyllosilicates; 3 – calcitic marble; 4 – calcitic marble with phyllosilicates; 5 – strongly metasomatized rock; 6 – felsic metavolcanic; 7 – intermediate-mafic metavolcanic; 8 – MS mineralization. The individual index values are represented by squares (point sample analyses) and by dots (original IGM analyses on samples 1 m long). The polygonal lines are moving averages of three points.

rock foliations. The DFS mineralisation is commonly found as fine disseminations, that occasionally also fill small veinlets, in silicate-bearing marbles or in strong metasomatised rocks. The main differences between FDS and DFS are due to differences in permeability and fracturing between the metavolcanics on one hand, and the marbles and strongly metasomatised rocks on the other. Their mineral assemblages are also conditioned by the local chemical composition, as exemplified by the chemical differences observed between sph IIa and sph IIb (essentially, reflecting different Fe contents of their host rocks). The TS mineralisation occurs in fault breccias and late veins or bands of the basal horizons of the metavolcanic sequence, below MS, MM and FDS-DFS mineralisation types. Their development is related to the evolution of sub-vertical strike-slip fault zones (350°, 75-80°W), which allowed the circulation of copper-rich siliceous hydrothermal fluids. Since the mineralisations are known only in drill-cores and TS is controlled by late fault zones, it is not known what, if any, is the influence of the country rocks in its detailed distribution and chemical composition.

The use of geochemical indices in Enfermarias allows the identification of the main mineralised domains and is particularly useful whenever detailed studies, such as petrography, have not been done. The different distribution of IZ, IP and ICA along all the boreholes examined, clearly reflects the lack of genetic relationship between the lead-zinc (MS) and the copper mineralisation types (TS). The misalignment between IZ and IP peaks clearly indicate that Zn and Pb react in slightly different ways to the general processes governing metal deposition and/or remobilisation, resulting in similar, but not entirely overlapped, distributions. Additionally, the indices distribution may show important correlations with the different lithologies (this is especially true for SDM-5 and SDM-15). Since it has been shown that non-mineralised rocks have low values for all of these indices, this correlation confirms a strong lithological control of the mineralisation types.

Most of the ore forming minerals of the *MS* mineralisation (*py I, sph I, apy* and *mgt I*) were clearly formed before the metamorphism/deformation peak. The crystallisation of stilpnomelane, green biotite and magnesian hornblende took place during the prograde metamorphism. This mineral paragenesis indicates maximum Variscan metamorphic conditions in the

transition of Greenschist to Amphibolite Facies, $ca. 500 \pm 50^{\circ}$ C. At this temperature, the ore minerals are preserved, but some of them, namely sphalerite, are already well within the plastic deformation regime. The introduction of tetrahedrite, as well as the crystallisation of most of the gangue-forming minerals (actinolite-tremolite, talc, serpentine, brown biotite and chlorite, the latter at relatively lower temperatures) took place during metamorphic retrogradation and began, at least locally, at temperatures close to those characterising the metamorphic peak, as

shown by the stable association of some silicates. The variable enrichment in galena (gn I) and, in a lesser scale, chalcopyrite (cpy I) is promoted by the influx of later fluids allowed by the permeability created by the fracturing of the *MS* domains.

The origin of *MM* is ascribable to the circulation of oxidised aqueous-carbonic fluids, progressively concentrated along the sub-horizontal structural corridors after the deformation-metamorphic peak. These fluids presumably originated by metamorphic degassing of the volcanic-carbonate sequence, are also responsible for the remobilisation of *MS* ores and its re-deposition as disseminations and/or as fracture infillings in rock domains where open fracturing was more intense (*DFS* and *FDS*, respectively). It should be noted, however, that these fluids were also metal-bearing and were responsible for the introduction of at least Pb, Cu, Ag, As and Sb not only in *DFS* and *FDS* mineralisation itself.

The development of *TS* mineralisation records an independent Cu ore-forming system superimposed on the main, pre-existing, Zn-Pb(-Ag) geochemical halo. Its fluids were unable to cause extensive metasomatism of the country rocks and could circulate only in the open fractures and associated porosity related to the movement of the late N-S strike-slip faults.

Conclusions

The interpretation of the Enfermarias metal concentrations cannot be done in terms of a simple metallogenic model, because they record the superposition of several mineralising episodes and were subject to considerable reworking during Variscan prograde and retrograde metamorphism. The main mineralising event preceded the metamorphic peak and generated massive sulphide mineralisations whose original textural (and mineralogical?) relationships were almost completely obliterated by subsequent deformation, recrystallisation and chemical reequilibration, thus rendering an accurate reconstruction of its formation conditions. Late metamorphic fluid circulation caused remobilisation and dispersion of the metals previously deposited and at the same time introduced minor amounts of new metals, both in the newly haloes of dispersed mineralisations and in the original metal deposits, thus further obliterating their original nature. Finally, copper brought in by late, unrelated fluids circulating in vertical fragile tectonic accidents became spatially associated to the prior complex metal anomaly, introducing a signal, common to many other mineral occurrences known in southern Portugal, but alien to the main sulphide mineralisations of Enfermarias. Despite their problematic metallogenic reconstruction, mineralisation types similar to those of Enfermarias are very easy to detect and evaluate using simple geochemical indices solely based on whole-rock chemical compositions.

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