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Post-metamorphic evolution of the Lower Cambrian section at Enfermarias (Moura, Portugal); its record and metallogenic implications

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Abstract

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In the Moura-Ficalho sector (Ossa-Morena Zone), the *Dolomitic Formation* comprises a thick metadolostone sequence whose basal section includes several intercalated metavolcanic horizons that contain stacked lenses of pre-Variscan sulphide ores. During the Variscan Orogeny, all these rocks experienced a complex geological history involving: 1) strong heterogeneous strain accommodation; 2) metamorphic recrystallisation in transitional upper greenschist to lower amphibolite facies conditions; 3) substantial post-metamorphic metasomatism; and 4) late hydrothermal alteration of variable intensity. During retrogradation, as temperature decreases and fluid/rock ratios increase, many different chemical processes took place (namely hydration, alkali and earth-alkali metasomatism, dedolomitisation, decarbonation, silication, silicification, and sulphidation), the character of metasomatic products depending mostly both on the local permeability contrasts and the mineralogical nature of protoliths. Subsequent stages of mineral-textural adjustments proceeded under higher fluid/rock ratios and lower temperature conditions, favouring essentially the progress of hydrolysis, chloritisation and silicification processes. During this geological evolution, metals and related chemical elements were considerably redistributed and/or added to the system, thus modifying significantly the characteristics of pre-Variscan ores.

Introduction

The Enfermarias prospect is located 1.5 km SE of Moura (SE Portugal) and includes Zn-Pb(-Ag-Sb-Au) ores hosted in Lower Cambrian rocks belonging to the *Dolomitic Formation* (Oliveira & Matos, 1992). The prospect is known by drilling and coincides with small gravimetric and electric anomalies, which, according to geophysical modelling (Represas et al., 2003), are unrelated to the ores and can be fully explained by the local geological structure and prevalence of metadolostones. Several other prospects and abandoned mines similar to Enfermarias are known in the Moura-Ficalho region, occurring in the same lithostratigraphical context, but many of them are affected by strong supergene alteration. Therefore, the non-outcropping Enfermarias prospect is a good case study to characterise in detail the geological setting and the metallogenesis of such mineralisation type, thus contributing to our present understanding of the Magnetite-Zinc Belt (Oliveira, 1986), one of the major ore districts in the Ossa-Morena Zone (OMZ).

Recent work has enabled a thorough characterisation of the Enfermarias ores, of their structural and lithostratigraphical controls and of the coeval wall-rock metasomatism and late hydrothermal alteration (Barroso, 2002; Martins, 2003). Here we present petrographic, mineralogical and geochemical data on rocks of the *Dolomitic Formation* that help explain the metamorphic and post-metamorphic evolution of the ores. Similar data for the ores themselves can be found in Barroso et al. in this volume.

Methods

Thirteen boreholes were drilled at Enfermarias. Their drillcores were macroscopically examined in order to determine which boreholes best represent the different ores present, their host rocks and the different tectonic, metamorphic, metasomatic and hydrothermal events that affect them. Based on this macroscopic observation, holes SDM-3, SDM-5 and SDM-15 were selected for detailed logging and whole-rock chemical analysis, and SDM-3 for comprehensive petrographic and mineral chemistry studies. Whole-rock analysis was performed by ICP at the certified Activation Laboraties (Ancaster, Ontario, Canada) and mineral micro-analysis by electron microprobe (JEOL 733 Superprobe) at the Centro de Geologia da Universidade de Lisboa.

Geological Setting

Many uncertainties remain regarding the stratigraphy of OMZ and its subdivisions due to difficulties caused by lack of fossils, intense tectonic dismembering, metamorphism and igneous intrusions. The general lithostratigraphic sequence of the Moura-Ficalho region (Oliveira et al., 1991), wherein Enfermarias is located, begins with a sequence of dark schists and metacherts thought to be of Upper Proterozoic age (by comparison with the *Série Negra* of the northern OMZ sectors), and ends with the *Xistos de Moura Formation* dated, at least partially, by fossils of Silurian age. In between, thick accumulations of carbonate sediments that include several intercalations of metavolcanic rocks (*Dolomitic Formation*), overlain by a volcano-sedimentary complex with schists, marbles and both felsic and mafic metavolcanics (*Volcanic-Sedimentary Complex of Ficalho-Moura*, VSC) represent the Lower Cambrian to Ordovician Series. Unconformities or paraconformities exist both at the base and at the top of the *Dolomitic Formation* and can be recognised by the local development of metaconglomerates or thin silicic horizons (the latter under VSC). The nature of the lower surface of the *Xistos de Moura Formation* is not well known. All these formations outcrop or are known by drilling around Moura and Enfermarias.

Variscan metamorphism and deformation are intense and, apart from the expectable mineralogical transformations of the pre-existing rocks, resulted in the development of folds at all scales, mechanical and compositional foliations and low angle SW-verging ductile to semi-brittle thrust zones, that cause lamination and tectonic repetition of the lithostratigraphical sequence. Late, sub-vertical strike-slip fault zones trending from N-S to NE-SW with thick, sometimes mineralised, fault breccias and gouges cut all formations and structures.

Intense metasomatism and/or hydrothermal alteration occurred along many of the sub-horizontal thrust zones, sometimes leading to total obliteration of the original textural and mineralogical relationships. Similar evidence for metasomatism and hydrothermal alteration exists in some contacts between metavolcanics and metadolodstones (or marbles), but sometimes the very presence of the alteration minerals obscures the contact nature, whether tectonic or normal stratigraphical superposition.

The Enfermarias ores are hosted in the lower part of the *Dolomitic Formation* in close association with intermedian-mafic volcanic intercalations, and seem to be roughly confined to the hinge line of an anticline-antiformal stack structure. This host formation, which represents most of the cores drilled at Enfermarias, was completely sampled during exploration of this prospect and the processes leading to the deposition of the ores must be recorded in it, since no mineralisation is known from any other stratigraphical level at Enfermarias.

Major Features of the *Dolomitic Formation* at Enfermarias

The detailed study of the three bore-holes mentioned above showed that the lower part of the *Dolomitic Formation* is characterised by the presence of three distinct metavolcanic series (MV1, MV2 and MV3) intercalated with carbonate rocks, the latter classified on the basis of their textural and mineralogical features calcitic or dolomitic marbles (CM or DM), banded calcitic-dolomitic marbles (BCDM) and metadolomitic breccias (MDB); along many thrust zones, usually bringing metavolcanics and marbles to contact, two different metasomatic rock types occur (Fig. 1).

Metavolcanic rocks

The lowermost (felsic) metavolcanic series (MV1) includes rocks essentially composed of quartz, K-feldspar, albite and phengite in a blast-aphanitic porphyritic relict matrix. The rocks of the MV3 series are very similar to those of MV1, but do not have micro-porphyroclasts of K-feldspar. Both series show intense K-feldspar hydrolysis (resulting in phengitic-sericite and quartz), and disseminated pyrite and sphalerite grains. These sulphides also occur in late veins or veinlets together with quartz, Mg-rich biotite, calcite and, sometimes, phengitic-muscovite. Fe^{3+} is present in sericite resulting from feldspar hydrolysis, *e.g.* $(Fe^{3+}/Fe^{2+})_{MV1} = 1.74$. The intermediate-mafic MV2 metavolcanic rocks have Mg-bearing hornblende (± diopside) and albite as essential minerals, defining a blast-aphanitic porphyritic relict matrix. The major alteration processes are plagioclase hydrolysis and saussuritisation, resulting in cryptocrystalline aggregates of biotite, chlorite and quartz surrounded by epidote ($Fe^{3+} = 0.59 \pm 0.11$ a.p.u.f.), and transformation of hornblende to actinolite. Near the thrust zones, these rocks show intense matrix chloritisation and metamorphic banding. Pyrite and sphalerite occur disseminated in the matrix. As was the case with MV1 and MV3, the MV2 metavolcanic rocks are intersected by late veins or veinlets, filled with three major mineral assemblages whose relative chronology is not very well established: 1) Mg-chlorite and calcite; 2) K-feldspar and calcite and 3) quartz, Mg-chlorite, pyrite, sphalerite and minor chalcopyrite. The metavolcanic rocks show low REE contents ($\Sigma_{REE} = [43.78 - 78.14]$ ppm), have high LREE/HREE fractionation ($La/Yb = [2.7 - 6.1]$) and are relatively depleted in incompatible elements ($Zr/Nb = [18.5 - 29.3]$). Normalised concentration patterns reveal distinct negative anomalies in Sr for the felsic metavolcanic rocks. The original chemical signature of these rocks is, however, hard to establish because of the whole-rock transformations experienced during post-metamorphic metasomatism and hydrothermal alteration. Nevertheless, they still preserve clearly the bimodal character reported for volcanic rocks of the same general lithostratigraphical setting in many other places of the OMZ (for details, see Martins, 2003).

<u>*Marbles*</u>

Dolomitic or calcitic granoblastic marbles (DM/CM) are chiefly composed of carbonate grains sometimes with minor Mg-chlorite (often Al-deficient). Usually they have no mineralisation, apart from finely disseminated galena in some samples. The most common carbonate rocks are banded calcite/dolomite marbles (BCDM), with thin alternating carbonate (calcite and/or dolomite) and silicate bands; the carbonate bands have grano-lepidoblastic texture and the silicate ones are almost entirely composed of Mg-chlorite, sometimes including minor amounts of biotite relics, tremolite and talc. In these rocks different disseminated ore minerals occur: carbonate bands have pyrite, besides minor tetrahedrite and realgar; phyllosilicate-rich bands have disseminated pyrite and sphalerite along with minor amounts of chalcopyrite and galena. There are also metadolomitic breccias (MDB) with dolomitic clasts cemented by calcite and/or dolomite and/or Mg-chlorite, often cut by different sets of late veins sealed by chlorite and calcite aggregates. Usually, metadolomitic breccias have no mineralisation, but occasionally pyrite and magnetite disseminations are present. All the analysed marbles are essentially composed of CaO and MgO; silicate bands in banded marbles, although conspicuous, impart low amounts of SiO_2 and Al_2O_3 to the rocks (SiO_{2max}= 4.84% and Al_2O_{3max}=0.93%).

<u>*Metasomatic rocks*</u>

As already stated, there occur along shear zones, usually separating metavolcanics and marbles, two different metasomatic rock types. The first one, with a grano-lepidoblastic texture, is mainly composed of calcite, tremolite and minor clinochlore and talc with disseminated pyrite, sphalerite and minor galena. The second one is a massive chloritite with minor relic biotite and frequent late calcite veins; pyrite and sphalerite are the main ore minerals of these rocks, together with very minor golden silver. Metasomatic rocks have normalized patterns of REE and incompatible elements similar to those of marbles, suggesting that the former are the result of extreme metasomatism of the latter; typical features are as follows: $(La/Yb)_{marbles}$ = [3.53-5.28]; $(La/Yb)_{mts}$ = [2.11-4.72]; $Zr/Nb_{marbles}$= [0.96-1.93]; Zr/Nb_{mts} = [0.29 – 4.5] (additional details in Martins, 2003).

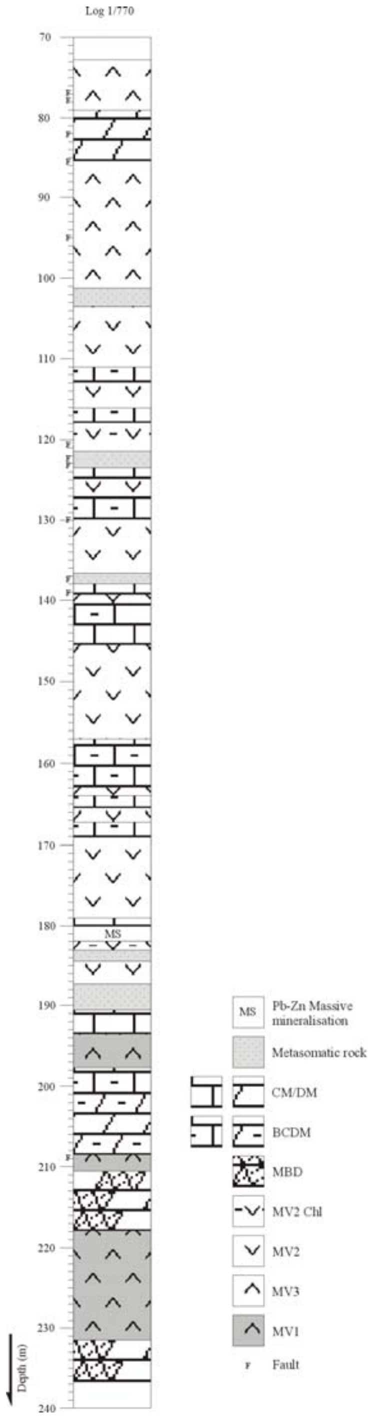

Fig.1 – Metacarbonate-metavolcanic sequence intersected by drill hole SDM-3. Symbols of different rock types as in text.

Discussion and conclusions

Most of the mineralogical and textural transformations observed in rocks belonging to the *Dolomitic Formation* drilled at Enfermarias record the effects of both Variscan metamorphism and post-metamorphic retrogradation, the latter including several events of metasomatism subsequently overprinted by variably focalised hydrothermal alteration.

Relics of the metamorphic mineral assemblage are fairly well preserved in MV2 metavolcanics and provides evidence for the chemical equilibrium *Mg-Amph + Ca-Plg ⇔ Ab + Ep + Ca-Amph + Chl*, thus positioning the P-T conditions of the Variscan metamorphic peak in the greenschists – amphibolite facies transition. The early stages of significant retrogradation are distinctly documented in sheared rock domains adjoining the main thrust zones, leading to the development of actinolite-tremolite (± talc ± lizardite) aggregates that may coexist with magnetite and pyrite (*MM* mineralisation – Barroso, 2002; Barroso et al. in this volume). Repeated fluid flow along these tectonic structures results in extreme mineralogical and textural transformations, converting pre-existent rocks in metasomatic products whose precursor is sometimes hardly to recognise. Also according to the mineralogical record, aqueous-carbonic fluids should have been dominant throughout a large part of the retrogradation stage.

During retrogradation, as temperature decreases and fluid/rock ratios increase, many different chemical processes took place, the character of products depending largely both on the local permeability contrasts and the mineralogical nature of rocks, and to a lesser extent on fluid chemistry. In carbonate rocks these processes involved mainly earth-alkali metasomatism, dedolomitisation, decarbonation, silication and hydration reactions; silicification processes can also be recognised locally. In metavolcanic rocks, the major chemical processes implicated hydrolysis, hydration, alkali and earth-alkali reactions, sometimes along with sulphidation and silicification. In general, the main end products of these reactions are: 1) actinolite-tremolite, talc, lizardite, calcite, chlorite and quartz in carbonate rocks; and 2) albite, Ca-amphiboles, quartz, epidote, biotite, sericite, chlorite and pyrite in metavolcanic rocks. Sulphide deposition as disseminations and/or as fracture infillings can be correlated with the last steps of this evolving stage, allowing to the development of *DFS* and *FDS* mineralisation types (Barroso, 2002; Barroso et al., this volume). Subsequent stages of mineral-textural adjustments proceeded under higher fluid/rock ratios and lower temperature conditions, favouring essentially the development of late chlorite aggregates and quartz, besides different fracture carbonate-infillings that may also include lately disseminated sulphides and sulphosalts. Finally, it should be noted that many features shown by the observed secondary mineral assemblages in distinct lithological settings, as well as by different new-formed minerals, are interpreted as a result of local chemical gradients and of important differences in fluid/rock ratios. Variations in time and space of: 1) CO_2 partial pressure and O_2 activity, for instance, strongly control redox and pH conditions, thus determining the oxidation of iron and manganese (as observed in some silicates) and the deposition of several mineral phases, particularly magnetite and carbonates; 2) strong Mg, Ca, and Fe chemical potentials, are also crucial to local development of tremolite instead of lizardite or other hydrated silicate for the same P-T conditions; 3) fluid/rock ratios seem to be determinant in talc or lizardite formation in metasomatised carbonate rocks via interaction with siliceous fluids, provided that conditions exist for significant Ca leaching.

Results of mass balance calculations, although controversial in some aspects due to the difficulty of find an actual protolith for many of the metasomatic rocks, are consistent with the afore-mentioned mineral transformations, suggesting that many of the chemical elements were indeed mobilised during metasomatic and hydrothermal alteration processes and that notable volume variations have occurred (Martins, 2003). The most outstanding mass balance results were found for carbonate rocks and MV2 metavolcanics. In the former lithologies, gains in silica and water (up to 53% and 35%, respectively) along with Ca losses (up to 25%) occurred under a general volume decrease (from 19 to 25%). In MV2 metavolcanics, a common tendency exists for SiO_2, K_2O and Na_2O losses (up to 19%, 2% and 7%, respectively) together with Mg and Ca enrichments (up to 22% and 5%, respectively), always under a volume increase (up to 14%). Mass balance calculations also show that metals and related elements were considerably redistributed and/or added during metasomatic and hydrothermal alteration processes, the maximum values obtained per 100 g of rock being 9212 ppm Zn, 1243 ppm Pb, 170 ppm As and 0.6 ppm Ag in carbonate rocks, and 347 ppm As, 82 ppm Zn, 3.7 ppm Ag in MV2 metavolcanics.

The great variety of mineralogical-textural transformations shown by rocks hosting Zn-Pb(-Ag-Sb-Au) ores at Enfermarias reflect largely post-metamorphic, structural and metasomatic to hydrothermal processes. Accordingly, pre-Variscan sulphide ores were much reworked, mislaying their fundamental primary features; this means that effects of Variscan and Late-Variscan processes cannot be easily discarded whatever is the metallogenic model conceived to explain the development of these ores.

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