

GEOCHEMISTRY OF THE POLYPHASE METASOMATISM RECORDED BY VOLCANIC-SEDIMENTARY ROCKS ADJOINING BASE METAL ORES AT THE ENFERMARIAS PROSPECT (MOURA, PORTUGAL)

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Abstract

In the Moura-Ficalho area, rocks of the Lower Cambrian *Dolomitic Formation* record significant mineralogical, textural and chemical transformations due to metasomatism and hydrothermal alteration that occurred after the Variscan metamorphic peak. The acid H₂O-CO₂ fluids involved in these transformations were generated by metamorphic degassing. As temperature decreases and fluid/rock ratios increase, carbonate rocks change their bulk chemistry by earth-alkaline metasomatism, decarbonation, silication and hydration reactions, with large volume decreases and gains in SiO₂, mainly balanced by CaO loss. In metavolcanic rocks the advance of hydrolysis, hydration, and alkali – earth-alkali metasomatism caused volume increase coupled with MgO and CaO gains chiefly balanced by SiO₂, K₂O and Na₂O loss. The resulting secondary mineral assemblages are mostly enriched in Ca and Mg-hydrous silicates. These processes remobilised pre-existing massive sulphide ores and introduced some metals not previously present.

Introduction

In the Moura-Ficalho area (Ossa-Morena Zone - OMZ), the Lower Cambrian *Dolomitic Formation* is chiefly composed of metadolostones with metavolcanic intercalations at the base (*e.g.* Oliveira & Matos, 1992 and Martins, 2003). At Enfermarias (Moura), there are massive lenses of pre-metamorphic Pb-Zn sulphides associated to the intermediate-mafic horizons (Oliveira & Matos, 1992; Barroso, 2002; Martins, 2003). After the Variscan metamorphic peak, intense metasomatism and/or hydrothermal alteration took place predominantly along any structural discontinuity that happen to be active at each development stage of the system, sometimes leading to total obliteration of the original textural and mineralogical relationships. A detailed characterisation of these processes can be found in Martins (2003). In this extended abstract we present the main geochemical features of these processes as recorded in the *Dolomitic Formation*.

Sampling and methods

A group of 322 samples were collected in 3 boreholes and examined under a stereomicroscope; 29 samples were selected for whole-rock chemical analysis by ICP at the certified Activation Laboratories (Ancaster, Ontario, Canada). Secondary phyllosilicates were identified by X-ray diffraction (Philips PW 1710 with a PW 1820/00 goniometer); 74 polished thin sections were examined by petrographic microscopy and electron microprobe analyses (JEOL 733) were made on 41 of them at the Centro de Geologia da Universidade de Lisboa. Mass balance calculations were made according to the Gresens equation, but lack of unaltered protoliths at Enfermarias impart some uncertainty to the results, which must be used semi-quantitatively as an indication of the ease of mobilisation of the elements during metasomatism and hydrothermal alteration. Whenever the original lithology of the altered rock is still identifiable, the least altered sample of that type was used as protolith, otherwise, the best approximation to the protolith has been chosen among those rocks which have similar normalized REE and incompatible elements patterns.

Results

Table I and figures 1 and 2 summarize all relevant data pertaining to the *Dolomitic Formation* at Enfermarias. The bimodal character reported for volcanic rocks of the same lithostratigraphical setting in many places of the OMZ (for details, see Martins, 2003) is clearly present at Enfermarias, since the

metavolcanic sequences MV1 and MV3 are felsic whereas MV2 is intermediate-mafic. The carbonate rocks are mainly dolomitic marbles (DM), but calcite marbles (CM) and banded calcite/dolomite marbles (BCDM) also occur. Fluid circulation along tectonic accidents may also give rise to extremely metasomatised rocks, which may be either mainly composed of Ca-amphiboles or massive chloritites. These metasomatic rocks seem to result from extreme transformation of the marbles as they retain normalised REE and incompatible elements patterns similar to the those of the marbles ($(La/Yb)_{\text{marbles}} = [3.53-5.28]$; $(La/Yb)_{\text{mts}} = [2.11-4.72]$; $Zr/Nb_{\text{marbles}} = [0.96-1.93]$; $Zr/Nb_{\text{mts}} = [0.29 - 4.5]$, Fig. 1 and 2). The results of mass balance calculations show that several elements very often immobile in common geological systems, were effectively mobilised at Enfermarias.

Discussion and conclusions

Relics of the metamorphic mineral assemblage in the MV2 metavolcanics indicate the chemical equilibrium $Mg\text{-}Amph + Ca\text{-}Plg \Leftrightarrow Ab + Ep + Ca\text{-}Amph + Chl$, positioning the P-T conditions of the Variscan metamorphic peak in the greenschist – amphibolite facies transition ($450 \pm 50^\circ\text{C}$). Under these conditions, metamorphic degassing of the volcanic-carbonate sequence results in the development and subsequent diffuse circulation of acid $\text{H}_2\text{O-CO}_2$ fluids, causing marble decarbonation and/or dedolomitisation and Mg ($\pm\text{Ca}$) fluid enrichment. In the felsic metavolcanic rocks, this fluid percolation leads to hydrolysis and hydration of the primary mineral assemblages (with abundant precipitation of micas) and to some Si, K and Al removal, due to the low pH of the fluids. Hydrolysis and hydration also affect the intermediate-mafic metavolcanics. The presence of Fe^{3+} in some minerals (e.g. phengite and talc), as well as deposition of magnetite and pyrite, indicate $f\text{O}_2$ values along *mgt-py* boundary for the earlier stages of retrograde metamorphism. Intense metasomatism, with mineral assemblages indicating temperatures ($300\text{-}400^\circ\text{C}$) lower than those of the metamorphic peak, can be seen along shear zones and contacts between carbonate and metavolcanic rocks and is interpreted as resulting from a gradual fluid flow focusing to mechanical or lithological discontinuities, which characterises the subsequent metasomatic/hydrothermal stages of the system. Depending on temperature, water/rock ratios, and Ca and/or Mg saturation, any of the minerals tremolite/actinolite, lizardite or talc may precipitate from the fluids first flowing along the discontinuities. High water/rock ratios at $300\text{-}200^\circ\text{C}$ result in a strong chloritization of the rocks and in the deposition of sulphides and sulphosalts (see gains in metals in Table I, details in Barroso, 2002), indicating that the system entered the *py* stability field, with the corresponding lower $f\text{O}_2$ and higher $f\text{S}_2$ conditions.

The above results suggest that the fluids correlative of these transformations have a regional derivation (because they advect metals not previously present at Enfermarias) but were extensively reequilibrated with the *Dolomitic Formation* (or equivalent rocks) before their documented metasomatic action. This explains the carbonatisation (with K loss and Mg and Ca introduction) of the metavolcanic rocks and the silication (and Ca loss) of the carbonate ones.

These metasomatic processes also reworked the pre-existing massive sulphide ores, with partial dissolution and redeposition of its metals, along with introduction of metals not previously present. This new metal precipitation generated new mineralisation types (mainly disseminations and fracture infillings) spatially superposed on the older ones.

Acknowledgements

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References

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Table I – General characteristics of the *Dolomitic Formation* intersected by drill hole SDM-3 (*oxides and LOI in weight per cent, other elements in ppm).

		Texture	Mineral assemblages	Major distinctive lithogeochemical characteristics *	Mass balance results (maximum values)
Metavolcanic	MV3	Blast-aphanitic (relict)	primary : K-feldspar + albite + phengite secondary: quartz + phengitic muscovite (sericitisation) disseminations: pyrite + sphalerite late veins: phengite + quartz + pyrite + sphalerite ± biotite ± calcite	10.77 < K ₂ O < 12.50 0.89 < MgO < 1.60 0.50 < CaO < 0.81 139.90 < ΣREE < 144.96 0.88 < (Eu/Sm) < 0.95	Volume variation + 14% Gains: MgO: 22% CaO: 5% Zn: 83ppm As: 347ppm Ag: 3.7ppm LOI: 12% Loss: SiO ₂ : 19% Al ₂ O ₃ : 2% K ₂ O: 7% Na ₂ O: 2% Zr: 25.6ppm Sr: 208ppm
	MV2	Blast-aphanitic porphyritic (relict)	primary: Mg-hornblende (± diopside) + albite secondary: epidote + albite + muscovite + quartz (saussuritisation) + tremolite/actinolite + chlorite disseminations: pyrite + sphalerite late veins: phengite + quartz + pyrite + sphalerite ± biotite ± calcite ± chlorite	3.34 < K ₂ O < 6.71 7.41 < MgO < 11.33 3.82 < CaO < 12.72 240.48 < ΣREE < 248.95 0.91 < (Eu/Sm) < 0.98	
	MV1	Blast-aphanitic porphyritic (relict)	primary: K-feldspar + albite + phengite secondary: quartz + phengitic muscovite (sericitisation) disseminations: pyrite + sphalerite late veins: phengite + quartz + pyrite + sphalerite ± biotite ± calcite	K ₂ O = 5.68 MgO = 1.51 CaO = 0.31 ΣREE = 244.99 (Eu/Sm) = 0.35	
Marbles	DM/CM	granoblastic	calcite/dolomite ± Mg-chlorite	As = 0; ΣREE = 43.56; (Eu/Sm) = 0.88	Volume variation – 25% Gain: SiO ₂ : 53% MgO: 9% Zn + Pb: 10445ppm As: 170ppm Ag: 0.6ppm Loss: CaO: 25% MnO: 4% Sr: 62ppm LOI: 35%
	BCDM	Grano-lepidoblastic	calcite + dolomite + Mg-chlorite + pyrite + sphalerite ± tetrahedrite ± realgar ± tremolite/actinolite ± talc	744 < As < 4660; 14.42 < ΣREE < 37.44; 0.66 < (Eu/Sm) < 1.53	
	MDB	granoblastic dolomitic clastic	dolomite ± calcite ± Mg-chlorite ± biotite ± pyrite ± magnetite	As = 0 ΣREE = 25.11 (Eu/Sm) = 0.80	
Metasomatic Rocks	Amphibolic	grano-lepidoblastic	tremolite/actinolite + calcite ± chlorite ± talc ± pyrite ± sphalerite	MgO = 27.34 ; SiO ₂ = 58.15	
	Chloritic	massive	Mg-chlorite ± lizardite ± talc ± magnetite ± pyrite	31.86 < MgO < 4.51; 29.71 < SiO ₂ < 29.78	

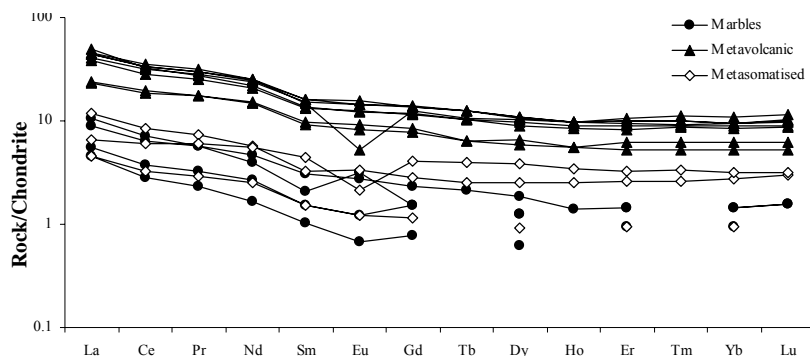


Figure 1 – REE normalised patterns of the rocks included in table I (values normalized to C1 chondrite from Boynton, 1994)

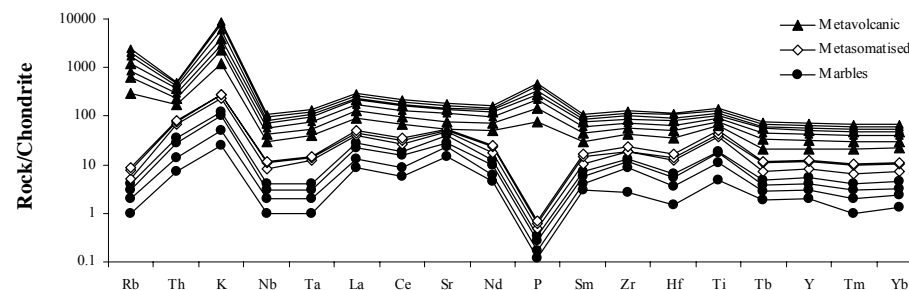


Figure 2 – Spider Diagram patterns of the rocks included in table I (values normalized to C1 chondrite from Boynton, 1994)