CARBONATE DISSOLUTION AND PRECIPITATION DURING HYDROTHERMAL PROCESSES IN PALAEOZOIC MARBLES OF THE MOURA REGION AND ITS RELATION TO THE "OWL-EYE" FACIES DEVELOPMENT

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Abstract

Metadolostones and calcitic marbles included both in the *Dolomitic Formation* and the *Volcanic-Sedimentary Complex of Moura-Ficalho* often show evidence of late carbonate dissolution-precipitation along different structural discontinuities. These chemical processes are envisaged as a result of incipient hydrothermal activity triggered by fracturing mechanisms at 150º≤T≤300ºC that, in its essence, is equivalent to the waning evolving stages recorded by some long-lived ore-forming systems occurring in the Moura area. According to the available data, the development of "owl-eye" marbles in the *Volcanic-Sedimentary Complex of Moura-Ficalho* can indeed be ascribed to hydrothermal processes.

Introduction

The Palaeozoic metavolcanic-metasedimentary sequences outcropping in the Moura region comprise different types of carbonate rocks, usually grouped into two main suites (Oliveira et al., 1991): 1) metadolostones, locally showing metric intercalations of silicate-bearing marbles of calcitic and/or dolomitic nature, that form a thick and monotonous succession belonging to the *Dolomitic Fm.* (Lower Cambrian); and 2) calcitic marbles, sometimes banded and silicate enriched, that include metric to decametric strata, belonging to the *Volcanic-Sedimentary Complex of Moura-Ficalho* (Middle Cambrian? – Ordovician). In both cases, the effects of the Variscan metamorphic recrystallisation under transitional greenschist-amphibolite facies conditions are evident. However, these effects can be partly or totally obliterated by metasomatic products generated during metamorphic retrogradation and/or hydrothermal alteration related to the (re-)deposition of sulphides and sulphosalts in some long-lived ore-forming systems, such as those known as Enfermarias and S^{to} André (Oliveira & Matos, 1992; Barroso, 2002; Martins, 2003). According to the present state of knowledge, the post-metamorphic transformations preserved in carbonate rocks of the *Dolomitic Fm.* at Enfermarias were mostly caused by earth-alkali metasomatism, dedolomitisation, decarbonation, silication and hydration reactions. At S^{to} André, a strong replacement of marbles of the *Volcanic-Sedimentary Complex* by massive coarse-grained siderite (with abundant disseminated sulphides) was drilled for *ca.* 30 m. In the Moura region, other evidences for late carbonate replacements both in metadolostones and marbles can be observed, far from any ore-forming system but always along structural discontinuities of various natures, geometries and lateral extensions (macroscopic veins and veinlets, mesoscopic fracture networks, fault zones, *etc.*). When developed in calcitic marbles and controlled by fracturing processes, these late mineral-textural transformations often lead to macroscopic features very similar to those that characterise the "owl-eye" marble facies, very familiar to people working in quarries of the Ossa-Morena Zone (because it degrades significantly the rock quality for commercial purposes). The issue to be addressed in this extended abstract is therefore double: on one hand, the eventual correlation between processes responsible for carbonate replacements in mineralised and non-mineralised settings is examined, and its geological meaning discussed; on the other hand, the possibility of some "owl-eye" marble facies be due to hydrothermal processes is explored. It should be noted that the development of this facies is commonly ascribed to supergene alteration caused by intense downward flow of superficial waters.

Sampling and methods

Five non-weathered outcrops were selected for study because of their particular macroscopic features and a total of 17 samples were picked up. After careful examination of each sample with a high-magnitude stereomicroscope, five of them were taken for detailed investigation and further subdivided in portions with distinct mineralogical-textural characteristics (see below). All these portions (totalling 19) were then finely crushed and prepared for X-ray diffraction (XRD). The fine powders, spread on a silicon plate Philips PW1817/32, were used to obtain XRD patterns with a Philips PW1710 powder diffractometer, using Cu Kα radiation, a curved graphite crystal monochromator and a PW1820 Bragg-Brentano goniometer; subsequent phase identification was based on the Mineral Powder Diffraction File Databook (Bayliss et al. 1993).

Mineralogy and textural relationships

The five samples chosen for detailed analysis represent quite well all the observed changes displayed by metadolostones and calcitic marbles adjoining different structural discontinuities. The EO-2A sample was collected near Moura (on the road to Safara) and characterise the usual marble of the *Volcanic-Sedimentary Complex*; in this outcrop, the millimetric rhythmic banding (260º,40ºN) of the marble is disrupted by fractures of variable orientation (300º,60ºNE; 130º,30ºSE and 120º,50ºNNE) filled with late carbonate brownish aggregates (EO-2BI); the latter are very similar to those found in irregular masses typical of the “owl-eye” facies observed in the western domain of the outcrop (EO-2BII). In another outcrop (S of Fábrica do Visconde), these marbles are massively replaced by late coarse-grained carbonate aggregates displaying different tints (pinkish – EO-3A, and brownish-white – EO-3B), including locally significant amounts of a clearly green phyllosilicate (EO-3C); very late transformations are confined to narrow bands adjoining discrete fractures and result in the development of fine-grained, white (calcitic) aggregates variably enriched in quartz (?) and pale-green phyllosilicates (EO-3D). In the Monte de Enfermarias, marbles (EO-4A) of this *Complex* also show many features ascribable to late carbonate dissolution and precipitation: 1) growth of coarse-grained brownish aggregates (EO-4B) along mesoscopic fractures oriented 55º,65ºNNW; 2) growth of massive, brown to brown-reddish, fine-grained carbonated infillings (EO-4C1 and EO-4C2) of sub-vertical, NE-SW veins; and 3) growth of pinkish, fine to medium-grained aggregates somewhat enriched in very fine-grained quartz and with disseminated green phyllosilicates (EO-4E; the portion EO-4D corresponds to a concentrate of these phyllosilicates). Metadolostones of the *Dolomitic Formation* can be observed in several outcrops mostly scattered in a NNW-SSE-trending girdle from Moura to Herdade dos Machados. The EC-14 sample documents a typical massive, fine-grained metadolostone (EC-14B) that is replaced, near a sub-vertical, N-S trending strike-slip fault, by brownish, coarse-grained carbonate aggregates (EC-14A). The EC-17 sample represents the most common product resulting from the tectonic fragmentation of the metadolostones when affected by major, N-S to NE-SW sub-vertical fault zones; in this breccia, the portion corresponding to the reddish and very fine-grained siliceous cement was labelled EC-17A, while the portion mainly composed of heterometric carbonate fragments (sometimes clearly corroded) was termed EC-17B.

The XRD results obtained for the afore-mentioned five samples are as follows (mineral phases by decreasing order of their relative abundance):

SAMPLE Nº	*Portion reference*	*MINERAL PHASES IDENTIFIED*
EO-2	EO-2A	Calcite
	EO-2BI	Dolomite and/or Minrecordite + vestigial Calcite
	EO-2BII	Dolomite ± Calcite + Quartz
EO-3	EO-3A	Dolomite and/or Minrecordite ± Muscovite 2*MI*
	EO-3B	Dolomite and/or Minrecordite + Quartz + Muscovite 2*MI*
	EO-3C	Muscovite 2*MI*
	EO-3D	Calcite + Muscovite 2*MI* ± Quartz
EO-4	EO-4A	Calcite + Muscovite 2*MI*
	EO-4B	Dolomite + Calcite
	EO-4C1	Ankerite + Dolomite (and/or Minrecordite?) ± Calcite + Quartz
	EO-4C2	Dolomite and/or Minrecordite + Ankerite ± Calcite

	EO-4D	Muscovite 2*MI*
	EO-4E	Quartz + Calcite ± Dolomite and/or Minrecordite + Muscovite 2*MI*
EC-14	EC-14A	Dolomite ± Muscovite 2*MI*
	EC-14B	Dolomite
EC-17	EC-17A	Quartz + Dolomite (+ non or poorly crystallised Fe-oxides or hydroxides)
	EC-17B	Dolomite ± Quartz

Minrecordite is the zincian analogue of dolomite. Two different parts of EO-4D and EO-3C portions were independently X-rayed given exactly the same results.

Discussion and conclusions

From the results obtained it is clear that the late carbonate aggregates are mostly composed of (Zn-bearing) dolomite, sometimes along with calcite and ankerite. This carbonate assemblage, chemically distinct from the pre-existing one in the metadolostones and marbles, may also include accessory amounts of quartz and muscovite, thus suggesting that its development results from hydrothermal activity involving aqueous-carbonic fluids variably enriched in Fe (Zn, Mn), Mg and Ca. If so, the analogy with the late stages of the Enfermarias and S^{to} André mineralising systems is plausible, since both provide evidence for (repeated) circulation of large volumes of fluids significantly metal enriched and/or for rather efficient fluid flow focusing (along complex arrays of repeatedly opened fractures within or around major fault zones). The available data also shows that episodic flow of metal-poor hydrothermal fluids in variably fractured calcitic marbles can promote considerable carbonate dissolution-precipitation and substantial volume variation, leading to mineral-textural features indistinguishable from those of the classical "owl-eye" marble facies (in general, characterised by strong dolomitisation). This means that hydrothermal processes can indeed play an important role in the genesis of "owl-eye"-like marbles commonly observed in many places of the Ossa-Morena Zone, and that these rock types may be found at depth, far from any influence of supergene chemical alteration.

In order to better understand the mechanisms involved in the genesis of these late carbonate assemblages, carbonate dissolution and precipitation in hydrothermal systems must be examined, particularly their dependence on CO_2 partial pressure and fluid salinity. With 150º≤T≤300ºC, calcite solubility is quite high in the presence of solutions with moderate to high salinity, thus favouring the development of extensive sideritic and/or ankeritic haloes (like those in S^{to} André), provided that Fe and Mg (± Mn) are available and suitable conditions for large-scale deposition of new carbonates are achieved. For the same T conditions, very limited carbonate dissolution rates are expected to occur in the presence of low salinity fluids, which is compatible with mineral replacements limited to narrow bands bordering the prevailing fluid pathways. The precipitation of hydrothermal carbonates can occur as a consequence of different processes, the most important being CO_2 degassing and pH increase. System depressurisation (triggered by repeated seismic activity, for instance) may easily cause CO_2 removal from hydrothermal solutions causing their pH to increase, thus explaining the usual association of these late carbonate assemblages to structural features due to fracturing mechanisms.

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