Paper published in *Comunicações do Instituto Geológico e Mineiro*, vol **84**, nº 1, p. B-87 - B90

Origin, chemical reactivity and circulation regimes of the CO_2-(SiO_2) fluids responsible for the polyphasic metasomatism at the Beja-Acebuches Ophiolite Complex[(1)]

GONÇALVES M.A.[*], MATEUS A.[*], FIGUEIRAS J.[*] & FONSECA P.[*]

Palavras-Chave: Complexo Ofiolítico de Beja-Acebuches; processos de carbonatização; origem e circulação de fluidos CO_2-(SiO_2)

Resumo: Na vizinhança das zonas de cisalhamento regional WNW-ESE, as rochas máficas e ultramáficas do BAOC exibem metassomatismo polifásico pronunciado (carbonatização, em especial). Um simples conjunto de cálculos revela ser pouco plausível atribuir a génese dos fluidos CO_2-(SiO_2) à instalação a quente do complexo ofiolítico. Deste modo, a origem dos fluidos CO_2-(SiO_2) afigura-se preferencialmente atribuível a mecanismos de desgaseificação das unidades autóctones de natureza carbonatada/xistenta ocorridos durante o metamorfismo varisco e a intrusão do Complexo Ígneo de Beja.

Key-words: Beja-Acebuches Ophiolite Complex; carbonatization processes; origin and circulation of CO_2-(SiO_2) fluids.

Abstract: Near the regional WNW-ESE shear zones, the mafic and ultramafic rocks of BAOC display strong polyphasic metasomatism (mostly carbonatization). A set of simple calculations shows the CO_2-(SiO_2) fluid genesis during the ophiolite complex hot emplacement to be very unlikely. Therefore, the origin of CO_2-(SiO_2) fluids should be mainly related to degassing of the autochthonous carbonate/schist units during variscan metamorphism and the Beja Igneous Complex intrusion.

INTRODUCTION

The origin and chemical reactivity of the CO_2-SiO_2 fluids is a major problem of the polyphasic metasomatism of the mafic-ultramafic rocks of the Beja – Acebuches Ophiolite Complex (BAOC) adjoining the regional WNW-ESE shear zones. Since relics of the Ossa-Morena Zone (OMZ) autochthon terrane within the Beja Igneous Complex (BIC) comprise rocks relatively rich in carbonate rocks, two main simple solutions may be envisaged. The first one involves the generation of fluids during thrusting of the young oceanic crust over the stretched continental margin; this will favour a prograde metamorphism of the continental terrane and its dehydration and/or decarbonation, promoting fluid flow across the overthrust plate during thrusting. The heat given off by the obducted rocks triggers the circulation of the required volumes of CO_2-(SiO_2) fluids, progressively channelized as BAOC emplacement is completed and suitable conditions for shear zone development is achieved. The second solution mainly considers the chemical changes of the autochthonous metasediments during variscan metamorphism and BIC intrusion/cooling; here, the main fluid flow should be coeval of the above mentioned shear zones, *i.e.*, of the final steps of the collisional stage (late-D_2 and D_3 variscan deformation phases; QUESADA *et al.*, 1994). Both solutions will be examined and discussed in detail.

GEOLOGICAL BACKGROUND

Within BIC, there are several strongly deformed metasedimentary relics of the Autochthon Terrane of the OMZ; from SE to NW: the Serpa - Brinches, Ventosa - Sra das Neves - S.Brissos, Vidigueira - Vila de Frades and Alvito - Viana do Alentejo units. The deformation evolution of these metasedimentary units is still under investigation, and no comprehensive study of their mineral parageneses and textures enables a complete understanding of their metamorphic path. However, in all these elongated units, three main litho-stratigraphic sub-units and an internal imbricated structure, with older rocks on top of progressively younger ones may be recognized (FONSECA, 1995 and references therein): 1) a dolomitic and/or calcitic marble sequence of Lower Paleozoic (Cambrian?) age; 2) an intermediate sequence mainly composed of amphibole-bearing gneisses, (Upper Proterozoic?); and 3) an heterogeneous sequence of carbonate rocks, amphibolites and biotite micaschists interbedded with lidites and black quartzites, presumably a lateral equivalent of the Série Negra.

---

[*] Departamento de Geologia da Faculdade de Ciências da Universidade de Lisboa, Edifício C2, Piso 5, Campo Grande, 1700 Lisboa.

(1) This work was financed by the *Fundação para a Ciência e Tecnologia* through the project PBICT/CTA/2112/95 - MIZOMOR.

In these marbles, calcite and forsterite ± diopside ± amphibole (tremolite/actinolite) ± phlogopite predominate in the southeastern units, whereas calcite ± dolomite ± ankerite + wollastonite + diopside ± garnet appear to prevail in the northwestern units. This suggests the establishment of temperatures (from near 450 to 600ºC) suitable for the development of decarbonation reactions under variable $X\mathrm{CO}_2$ (probably reflecting the progress of coeval dehydration processes, such as amphibole breakdown to give diopside and garnet) and unknown pressures, due to lack of mineral chemistry data. Large volumes of CO_2 would be liberated during decarbonation, and the most probable reaction $CaCO_3 \Leftrightarrow CaO + CO_2$ suggests that carbonate bodies should have shrinked significantly, particularly at their contacts with the quartz-feldspatic rocks. The liberated CO_2 would hardly migrate directly into the country rocks at the site of genesis, and metasomatic reaction zones should be an usual feature of marble-gneiss contacts. Accepting this general interpretation, the development of particular mineral parageneses may reflect both mineral stabilities at high CaO activities, and the variable H_2O/CO_2 ratios of the border domains of the carbonate horizons. For instance, the stable Ca-garnet + calcite association (without wollastonite and quartz) should record mainly the local H_2O-rich conditions near the limits with non-graphitic country rocks; conversely, the absence of epidote (clinozoisite) and the coexistence of calcite + (calcic) plagioclase in marbles in the Ventosa - Sra das Neves - S.Brissos unit, should reflect higher temperatures and lower water pressures than in sites where epidote (clinozoisite) occurs in diopside-bearing horizons.

EARLY THERMAL EVOLUTION OF THE COUPLE BAOC – AUTOCHTHONOUS METASEDIMENTS

BAOC corresponds to an obducted oceanic sequence with back-arc affinities over a stretched continental margin (*e.g.* Quesada *et. al.*, 1994). The thrust footwall was probably at a very high temperature (≈ 800-900ºC) since most metagabbroic rocks show evidence of mineral recrystallization under an anisotropic stress field induced by the emplacement of BAOC. Even though several metamorphic facies can be observed in the areas over which BAOC rocks were obducted, usually ranging from amphibolite to greenschist facies conditions, these can not be the result of the thermal input provided by the obduction. Petrographic studies support this assertion, and so these metamorphic events should be a consequence of the variscan cycle, whose metamorphic peak is correlative of D_2 deformation phase. A set of simple calculations in order to model the thermal evolution of such a system was performed.

Model description and parameters

In order to model the above mentioned scenario, a 5 Km thick allochthonous sequence representing BAOC was put upon a 20 Km thick stretched continental crust (mostly of granite-like properties); its upper 500 m were assumed to be marbles and the next 3000 m correspond to schists. The thermal gradients for both crustal blocks were calculated according to the equation (Turcotte & Schubert, 1982)

$$T = T_s + \frac{q_m z}{k} + \frac{\rho H_s h_r^2}{k}\left(1 - e^{-z/h_r}\right)$$

where T is the calculated temperature for a given block of rock at a depth z with mean thermal conductivity k and mean density ρ, assuming a surface temperature T_s, a heat flux q_m from its base, and a rate of heat release H_s due to radioactive decay of elements in the crustal block, whose concentration decrease exponentially downwards with a characteristic distance h_r. The heat fluxes considered were adjusted so that both a basal temperature of 900ºC for BAOC and an approximate geothermal gradient in the range 10-20ºC.Km^{-1} for the autochthonous crustal rocks were obtained; low geothermal gradients are expected in subduction zone environments. The mean thermal conductivities of the continental crust and of the ophiolite suite were calculated using data given in Turcotte & Schubert (1982) for the rock types involved, and weighted according to the volumes of each rock type in the crustal block. Mean densities were calculated in the same way for both blocks and the values used for the heat rate release due to radioactive elements (H_s) were determined as a function of their mean concentration in the upper continental and oceanic crusts. The characteristic distance used for both blocks was 10 Km in agreement with the general knowledge on radioactive element concentration in the crust. Surface temperature was arbitrarily set to zero. Both these data values (densities and radioactive heat rate release) can be found in Carmichael (1989).

The initial conditions assume an instantaneous thickening of the crust with no heat loss, which is somewhat unrealistic given the minimum 2 m/year convergence rate needed for this to occur (Peacock, 1989). However, such assumption is not crucial as will be seen below. The model calculates one-dimensional temperature variations of the crustal column with time, by solving numerically the heat conduction equation

$$\frac{\partial T}{\partial t} = -\kappa \frac{\partial^2 T}{\partial x^2} + \frac{A}{\rho C},$$

where $\kappa = k/(\rho C)$ is the thermal diffusivity, A is the volumetric heat production due to radioactive decay (equivalent to ρH_s), and C is the heat capacity. The boundary conditions for the base of the crustal section admits a constant heat flux of 0.03 W.m^{-2}, which sets a constant thermal gradient of about 13 ºC/Km at the base of the crust, according to the equation (Fourier law)

$$q_m = k \frac{dT}{dz}.$$

This gives rise to a Neumman boundary condition for the base of the crustal section, being the derivative, in this case, normal to the boundary. The top of the crustal section is kept at 0ºC. The model does not calculate any heat loss mechanism other than conduction. This may be a limitation, since the presence of crustal fluids should account for a significant convective heat loss as well, which may turn the calculations rather conservative. However, it will be seen that such limitation is not significant for the purpose of the calculations. The high temperatures involved also suggest a rather ductile regime and fluid circulation in such conditions is very ill-known. Fluid involvement is expected to be more important in the later cooling stages of the crustal section.

Results and discussion

The above equations were solved for a maximum time period of 1 million years, in order to see the evolution of the thermal profile and its deviation from the equilibrium geotherm at the end of this period. The runs show that the inverted temperature gradient due to the thrust of the BAOC is short-lived. At 1 Ma the geotherm is almost equilibrated, but temperatures at the base of the crust are lower than expected for such depths and geothermal gradients. A second set of runs was also performed, assuming that the basal 2 Km of BAOC had a constant temperature of 900ºC (as would be expected if it was a very hot magmatic chamber, immediately below *solidus*). This is a limiting case and was considered to find out if it would cause a much slower thermal re-equilibration, and therefore explain some of the features mentioned in the introductory part.

In the more realistic scenario, it is seen, with different time-steps, that at the thrust plane the temperature drops significantly, to around 470ºC after 10000 years (or 550ºC for 1000 years). The thermal anomaly propagates through the base rocks to as far as 4.5 Km in 1 Ma, but at this depth the temperature remains below 200ºC. Temperatures above 400ºC are reached only in the upper 150 m of marbles, but all marbles reach temperatures above 300ºC with a peak at approximately 50000 years. Within the marble column, maximum temperatures occur at 4000 years (432ºC) in the upper 100 meters, and decrease very slowly until 10000 years and more abruptly afterwards. The second model gives similar results: the marble column reaches higher temperatures, but only slightly higher than 500ºC at the top after 10000 years; the base stays below 400ºC (peak at 384ºC after 70000 years). As in the previous model, the thermal anomaly reaches a 9.5 Km depth, but with a temperature of 200ºC after 1 Ma.

According to these results, it seems very unlikely that BAOC hot emplacement (D_1 phase of deformation) could account for the several carbonate (and silica) hydrothermal precipitates along the major WNW-ESE shear zones, because the above thermal modelling shows that temperatures high enough to promote degassing of the autochthonous carbonate sequence cannot be maintained for the time interval spanning the D_1-D_2 gap, and the available data strongly suggest that the hydrothermal precipitates are mainly developed during the final stages of D_2 and during D_3. Since fluid circulation accelerates the cooling rate of the crustal section due to convective heat transfer, these calculations may be regarded as conservative, which reinforces the above considerations. However, it is important to stress that maintaining a hydrothermal system for some time, maybe for a period of 200,000 years after BAOC emplacement, is possible according to this kind of models. Such hydrothermal systems need a permeable media to promote mass and heat transfer in the system, and the question is: had BAOC rocks the required permeability at these stages, since no important fracture network is to be expected at the high temperatures prevailing? If such fluid circulation had occurred, evidences of early pervasive hydrothermal events should have been observed.

Finally, these calculations definitely rule out the possibility of the late amphibolite to greenshist facies metamorphism (observed in BAOC and in the autochthonous sequence) as an expression of the ophiolite post-emplacement cooling stages.

Paper published in *Comunicações do Instituto Geológico e Mineiro*, vol **84**, nº 1, p. B-87 - B90

CHEMICAL EFFECTS OF VARISCAN METAMORPHISM AND BIC INTRUSION

Fom the above results it appears that the metasomatic processes recorded by the mafic/ultramafic rocks of BAOC and the hydrothermal mineral deposition along the regional WNW-ESE shear zones, are mainly related to degassing mechanisms of the autochthonous carbonate/schist units accomplished during the variscan metamorphism and the BIC intrusion (whose initial steps are also coeval of the D_2 phase of deformation). Indeed, the most widely studied mechanisms for liberating CO_2 is through discontinuous reactions involving calcite and silicates in carbonate rocks (*e.g.* GLASSLEY, 1983). Substantial volumes of CO_2 can be released via several reactions, such as the following

$$\text{Tremolite} + 3\ \text{Calcite} + 2\ \text{Quartz} \Rightarrow 5\ \text{Diopside} + 3\ CO_2 + H_2O$$
$$\text{Tremolite} + 11\ \text{Dolomite} \Rightarrow 8\ \text{Forsterite} + \text{Calcite} + 9\ CO_2 + H_2O$$
$$\text{Calcite} + \text{Quartz} \Rightarrow \text{Wollastonite} + CO_2 + H_2O,$$

if the silicate volume is sufficient to allow most of the carbonate to be consumed. This means that the genesis of silicate-bearing marbles involves the loss as CO_2 of 20 to 40% of the original carbonates, if intermediate P-T conditions are assumed. In these circumstances, fluid pressures are similar to lithostatic pressures and close to the sum of partial pressures of H_2O and CO_2 ($\pm CH_4$). Under the temperature range inferred from the mineral parageneses observed in marbles, PH_2O is expected to be much greater than PCO_2, and so CO_2 would not become a major volatile species. This temperature range coincide with the one deduced for the paroxysmal variscan metamorphism; therefore, the genesis and the circulation of large volumes of H_2O-CO_2 fluids can be inferred to be intimately connected to the variscan metamorphic processes and to the intrusion/cooling of BIC rocks, which are closely related in space and time. This may also lead to local fracturing if $P_{\text{fluid}} > P_{\text{lithostatic}}$; high P_{fluid} would also favour the development of more or less complex arrays of tensional fractures at the tips of propagating shear zones and of their subsidiary structures.

During circulation through mafic/ultramafic rocks of BAOC, the H_2O-CO_2 fluids move upwards and will precipitate carbonates via wall-rock alteration (until virtually all CO_2 is removed) if equilibrium conditions with Ca-Fe-Mg-silicates are attained (*e.g.* FYFE *et al.*, 1978; TURNER, 1981) and/or if significant reduction of H^+ concentration in fluid is achieved during silicate hydrolysis (causing an increase in CO_3^{2-} concentration for a given total-carbon-species concentration).

The late H_2O-CO_2 fluid flows are also responsible for the deposition of significant amouts of quartz, besides calcite. Since carbonate solubilities decrease with temperature, their deposition from cooling solutions means that suitable conditions for system depressurization existed, probably related to the seismic activity associated with the reactivation/ propagation of WNW-ESE shear zones during D_3 and late-D_3 phases of variscan deformation.

REFERENCES

CARMICHAEL R.S. (1989) - *Practical Handbook of Physical Properties of Rocks and Minerals*. C.R.C. Press Boston, 741 p.

FYFE W.S., PRICE N.J. & THOMPSON A.B. (1978) - *Fluids in the Earth's Crust*. Elsevier Publishing Co., Amsterdam: 393 p.

FONSECA P. (1995) - Estudo da Sutura Varisca no SW Ibérico, nas regiões de Serpa-Beja-Torrão e Alvito-Viana do Alentejo. Dissertação de candidatura ao grau de Doutor, Fac. Ciências da Univ. Lisboa: 325 p., 2 mapas.

GLASSLEY W. (1983) - Deep crustal carbonates as CO_2 fluid sources: evidence from metasomatic reaction zones. *Contrib. Mineral. Petrol.*, 84: pp. 15-24.

PEACOCK S.M. (1989) - Thermal modelling of metamorphic pressure-temperature-time paths: a forward approach. *Short Course in Geology: Volume 7*, American Geophysical Union: pp. 57-102.

QUESADA C., FONSECA P., MUNHÁ J., OLIVEIRA J. T. & RIBEIRO A. (1994) - The Beja-Acebuches Ophiolite (Southern Iberian Variscan fold belt): Geologic characterization and geodynamic significance. *Boletín Geológico y Minero*, 105-1: pp. 3-44.

TURCOTTE D.L. & SCHUBERT G. (1982) - *Geodynamics. Application of Continuum Physics to Geological Problems*. John Wiley & Sons, New York. 450 p.

TURNER F.J. (1981) - *Metamorphic Petrology*. McGraw-Hill, New York, 524 p.