# CARBONATIZATION OF B.A.O.C.'S BASIC AND ULTRABASIC ROCKS (GUADIANA VALLEY): STRUCTURAL CONTROL AND METALLOGENETIC POTENTIAL

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#### **Abstract**

At the Guadiana Valley, the original basic and ultrabasic rocks included in the Beja-Acebuches Ophiolitic Complex, were metamorphosed in the granulite facies and then retrograded with deposition of amphiboles, phogopite, large amounts of serpentine and minor chlorite and carbonate, as the rocks reequilibrated with ever lower temperatures. However,  $D_2$  and  $D_3$  shear zones acted as conduits for the circulation of large amounts of fluids, responsible for very intense deposition of carbonates and subordinate quartz. The presence of high temperature sulphides and of strongly carbonatized ultramafic rocks (listwaenites) make BAOC and associated rocks an interesting target for mineral exploration.

#### 1. Introduction

The examined basic and ultrabasic rocks belong to the Barranco da Gravia and Vau de Baixo Units, respectively, and represent the main basal lithologies of the tectonically dismembered Southern Variscan geological unit known as the Beja - Acebuches Ophiolitic Complex (B.A.O.C.; e.g. Quesada et al., 1994). The emplacement of this unit by obduction (D<sub>1</sub> deformation phase) occurred under high temperature and low pressure conditions - granulite facies - and originated several microand mesostructures where kinematic criteria reveal transport mainly to the North (e.g., Fonseca, 1995 and references therein). At the Guadiana Valley (fig. 1), the B.A.O.C.'s present North and South limits are tectonic, but according to the available data it is not clear whether these limits were originally tectonic or not, nor whether the Beja Igneous Complex is the original geological unit adjoining the B.A.O.C. to the North. As a matter of fact, an increasing amount of field and microstructural evidence reveals that the main WNW-ESE shear zones now present in B.A.O.C. and limiting it to the North and to the South were generated during the D<sub>2</sub> variscan deformation phase and were later repeatedly reactivated, particularly during the D<sub>3</sub> deformation

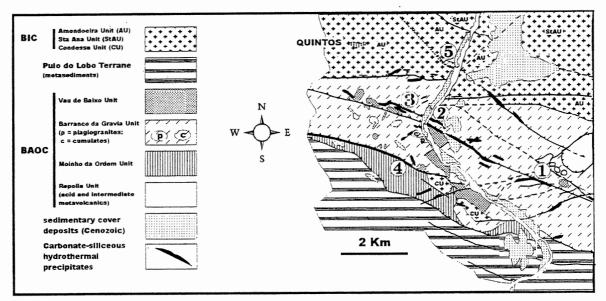


Fig. 1. Simplified geological map of the Guadiana Valley with indication of the studied sectores (1 - Melrinas; 2 - Moinho dos Machadinhos; 3 - Sete Pés; 4 - Telheirinho; 5 - Mina da Palmeira). Adapted from Fronseca (1995).

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phase. Detailed mapping at the 1:5000, 1:100 and 1:10 scales (e.g. Gonçalves et al., 1997) confirms this interpretation, as it shows that these regional shears have irregular geometry, sometimes numerous branches, and comprise different structural corridors developed under distinct deformation regimes: left-lateral N140-145 subvertical shears represent the main family of earlier, sin-D<sub>2</sub>, structural corridors generated under a semi-ductile - semi-brittle transition regime and ubiquitous thrust left-lateral N110-120 shears with strong dip (> 75°) towards NNE were formed under a progressive deformation regime under semi-brittle and brittle conditions during tectonic events ascribable to the D<sub>3</sub> deformation phase; subsidiary structures of these late structural corridors are also present and are usually related either to late coalescence of en échelon minor shears or to the waving trace shown by several segments of the major shears.

## 2. Metasomatic processes;

# structural control, relative chronology, typical textures and mineral record

There are several worthnoting common features which are independent of the type, tectonic style and lateral continuity of the shear zones: (1) presence of hydrothermal polyphasic carbonate aggregates (usually silicified) and/or of quartz precipitates within some domains of the shear corridors wherein relics of dynamically incorporated fragments of the adjoining altered host rocks can also be recognized; (2) development of alteration halos with variable extension and intensity along the tectonic accidents, leading to pronounced carbonatization and silicification of gabbros and/or serpentinites; this altered rocks sometimes underline earlier shears and/or apparently non-tectonic syn-D<sub>2</sub> narrow metasomatic corridors; and (3) establishment of complex late brittle deformation patterns, which, in some locations, are clearly ascribable to hydraulic brecciation processes. Taking these features as a whole, it seems plausible to infer that the D<sub>2</sub>/D<sub>3</sub> shears served as main conduits to the syn-deformational fluid flows responsible for large-scale and repeated CO2 and SiO<sub>2</sub> introduction into the system. Dehydration and degassing reactions induced at depth by the development and advance of thrust complexes by obduction, are an appropriate source of the required amount of fluids chemically adequate for the observed metasomatism. The earliest metassomatic events (the most important of which is the hydration and alkali-earth metasomatism responsible for the amphibolitic assemblages particularly abundant in many of the B.A.O.C.'s intermediate to upper units), developed under a semi-ductile - semi-brittle transition deformation regime (e.g. Gonçalves et al., 1997), and are correlative of the late-D<sub>1</sub> and D<sub>2</sub> variscan deformation phases. A deformation continuum at all scales between D<sub>1</sub> and D<sub>2</sub> should therefore exist, and the apparent predominance of syn-D<sub>2</sub> structures results mainly from: (1) the difficulty of preserving the earlier structures, expressed in minerals chemically unstable under the new conditions; (2) the strong heterogeneity of syn-D<sub>1</sub> deformation, particularly notorious in representative (less retrograded) domains of the allochthonous oceanic rock units and in continental portions not far away from the orogenic suture, now outcropping out of the Guadiana Valley.

### 2.1. Basic rocks

Basic rocks are well represented in all of the studied sectors, but their accurate classification is often difficult, given the multiple deformation and retrogradation of the primary minerals. The mineral parageneses observed in relatively unaltered samples reveal, however, that these rocks mostly comprise variable amounts of calcium plagioclase and pyroxene (mainly orthopyroxene, although some samples exhibit roughly equal amounts of ortho- and clinopyroxene), and should be classified as gabbros and gabbronorites. There are, however, three worthnoting exceptions: 1) in some of the samples collected at Moinho dos Machadinhos sector, the calcium plagioclase crystals (sometimes strongly zoned) predominate largely over pyroxenes, giving the rock an anorthositic character; 2) several examined specimens belonging to Moinho dos Machadinhos and Sete Pés sectors contain significant amounts of (serpentinized) olivine, along with plagioclase and pyroxene, allowing their dubious classification as troctolites; 3) the relative abundance of plagioclase + altered olivine in some representative samples of the Mina da Palmeira sector suggests that troctolite rocks may coexist with strongly altered wehrlites (?) (see below). Finally, it should be pointed out that in the Melrinas sector, the outcropping gabbroic rocks often host retrograded pyroxene cumulates and/or plagioclase-bearing hornblende pyroxenites.

Minor and variable amounts of vanadium enriched ( $V_2O_3$  values ranging from 1 to 3 wt%) ilmenite and/or magnetite, sometimes accompanied by sparse ulvöspinel crystals, represent the main accessory mineral phases of the dominant gabbroic rocks, wherein subordinate, although ubiquitous, amounts of primary, interstitial, micrometric sulphide grains (mainly pyrrhotite, pyrite and sparse chalcopyrite) can also be recognized.

As mentioned above, and previously discussed by Gonçalves et al. (1997), the examined gabbroic rocks usually display mineralogical and textural transformations ascribable to earlier ductile deformation (syn-D<sub>1</sub>) and metasomatic (late-D<sub>1</sub>) events. The former are responsible for general plastic yielding of most of the primary minerals under temperature conditions of granulite facies metamorphism; textural and microstructural features due to these deformation events are preserved only in domains far from the D<sub>2</sub>/D<sub>3</sub> shear zones. Late-D<sub>1</sub> metasomatism is mainly shown by late plagioclase zoning and by variable bulk silicification of the rock. Heterogeneous plastic yielding of quartz aggregates, intra- and intergranular fracturing of plagioclase and pyroxene, as well as their partial or total alteration (via saussuritization and amphibolitization processes, respectively), took place afterwards, and so are coeval of the D2 variscan deformation phase. Subsequent fluid inflow through the above mentioned shear zones led to late polyphasic metasomatism, particularly notorious in rock domains close to that tectonic accidents, as documented by the development of micrometric aggregates of siderite (sometimes Mg, Mn enriched) ± dolomite + microcrystalline quartz ± relics of different types of sheet silicates (chlorite ± Cr-sericite). In these strongly metasomatized rock domains, magnetite remains apparently unaltered and coexists with corroded ulvöspinel and ilmenite grains. Carbonatized gabbros in the Moinho dos Machadinhos sector show, however, abundant relics of high Ti oxide minerals with intriguing V contents ( $V_2O_3$  values ranging from 1 to 4.5 wt%), whose presence may be ascribed either to primary pseudobrookite or to a complex alteration path of the primary vanadium enriched ilmenite grains; work in progress should bring some light to this problem.

Another interesting feature of the studied gabbroic rocks concerns the sulphide paragenesis and its heterogeneous distribution. The ubiquitous presence of primary interstitial sulphide aggregates was already referred; nevertheless, it should be emphasized that in some of the non-carbonatized gabbros (of prevailing troctolitic nature) outcropping in the Sete Pés and Mina da Palmeira sectors, the relative abundance of coarser aggregates of chalcopyrite + pyrrhotite + pentlandite + pyrite may represent a valuable indicator for primary Cu-Ni(-Co) mineralizations related to some of the B.A.O.C.'s gabbroic facies. This is especially obvious at Mina da Palmeira, where slightly deformed troctolites, as well as ultrabasic rocks (of probable wehrlitic composition), are preserved in a megaboudin settled along an early, subvertical, syn-D<sub>2</sub> shear (known as Monte Peixoto-Monte do Gago shear) that does not display evidence for important late reactivation during late-D<sub>2</sub> and/or D<sub>3</sub> times.

Primary paragenesis of the Mina da Palmeira troctolites comprise mainly calcium plagioclase, Ni-free olivine, orthopyroxene, and minor amounts of clinopyroxene; the major accessory mineral phases are represented by heterogeneously disseminated grains of Cr-spinels and of high-temperature sulphides. Pyroxenes are usually rimmed by amphibole (hornblende) and/or phlogopite (sometimes Cr enriched) crystals. Phlogopite also displays an interstitial development and represents the last mineral formed during the retrograding sequence of reactions that occurred under conditions of amphibolite facies metamorphism. These rocks were serpentinized in two main stages: the first one is responsible for strong olivine alteration, whose expansion gives rise to a characteristic brittle deformation pattern in adjoining plagioclase and amphibolitized pyroxenes crystals; the second event of serpentinization allowed the development of antigoritic (?) precipitates inside late, intergranular fractures, wherein aggregates of clinochlore (sometimes Cr-enriched) also occur. In all the observed samples, chloritization postdates serpentinization and represents the last stage of a late metasomatic process that, in general, led to intense alteration of amphibole and phlogopite crystals, to the destruction of plagioclase and pyroxene relics, to local deposition of magnesite + dolomite ± Mg-siderite and to the genesis, around olivine pseudomorphs, Cr-spinel crystals and sulphide aggregates of dark green-coloured fringes composed of late serpentine, Cr-bearing chlorite, and probable Ni-tochilinite and/or Cr-valleriite. Locally, in close association with some of the Cr-clinochlore + magnesite/dolomite aggregates, a Cr-K mica (fuchsite type) was recognized. Cr-spinel crystals are fine grained and display almost always subsolidus reequilibration rims mainly formed by ferritchromite and ferritchromite ± magnetite. The latter oxide forms also micrometric rods or lenticular aggregates that occur mainly along corridors of strong serpentinization together with probable awaruite and in open cleavage fractures of pyroxene and phlogopite.

Sulphide aggregates are especially common in rock domains impoverished in Cr-spinels and, according to the available petrographic data, four main types can be distinguished: 1) Co-pentlandite (and/or bravoite) ± pyrrhotite ± heazlewoodite aggregates within the magnetite fringes that surround altered Cr-spinels; 2) randomly disseminated irregular millimetric globules of Co-pentlandite (and/or bravoite) + pyrrhotite + chalcopyrite ± mackinawite; 3) fine aggregates of bravoite dispersed within weakly serpentinized rock domains, possibly resulting from pentlandite alteration; and 4) late disseminated awaruite ± pirite. Taking together all these petrographic information, it is possible to infer that the bulk of serpentinization took place under high Mg chemical potential values and temperatures ranging most probably from 400 to 500°C, before stable pyrite deposition could be achieved.

#### 2.2. Ultrabasic rocks

In the studied B.A.O.C.'s domains, strongly serpentinized ultrabasic rocks form discontinuous outcropping spots whose contacts with the adjoining gabbroic lithologies are usually tectonic. The scarce relics of primary mineral assemblages (namely the preservation of ortho- and/or clinopyroxene corroded crystals) indicates a predominant harzburgitic nature for these rocks, although the presence of Iherzolites and wehrlites can not be discarded for sectors like Sete Pés and Mina da Palmeira, respectively; in the latter sector, detailed field work is needed to establish the precise nature of the contact between the ultrabasic rocks and the prevailing troctolites.

When present, pyroxene relics are usually rimmed by amphibole, which displays also an interstitial development and represents the first steps of the retrograding process under conditions of amphibolite facies metamorphism. Serpentinization is most of the times relatively intense, postdating talc formation in some specimens, and giving rise to a characteristic mesh texture, typical of lizardite aggregates. As in the gabbroic rocks, late serpentinization events allowed the development of antigoritic (?) precipitates along irregular veinlets, wherein micrometric aggregates of clinochlore (sometimes Cr-enriched) and scarce carbonates (mostly magnesite and dolomite) also occur.

Besides serpentine and relics of primary silicate minerals (olivine and pyroxenes), micrometric grains of more or less altered Al- or Cr-spinel, pyrrhotite (sometimes Ni-enriched), Co-pyrite, and pentlandite and its alteration products are disseminated in all the ultrabasic rock types, independently of their degree of alteration. As in the gabbroic rocks, chromite and Cr-spinel crystals display almost always rims of subsolidus reequilibration mainly formed by ferritchromite and ferritchromite  $\pm$  magnetite. Dispersed decimillimetric rods of this latter oxide, sometimes accompanied by centimillimetric crystals of awaruite and heazlewoodite (?) (representing products of primary sulphides alteration), are also common within strongly serpentinized rock domains. These petrographic data are very important in the interpretation of the mineral-textural transformations having occurred in domains near  $D_2/D_3$  shears, since opaque minerals may represent the only relics of the primary parageneses still

extant there. In fact, in these domains, the ultrabasic rocks are almost completely replaced by fine-grained carbonate aggregates of variable composition (dolomite + magnesite ± Mg-siderite) that often contain altered masses of serpentine ± Mg (Cr)-chlorite and show notorious late silica enrichment, as documented by the presence of microcrystalline quartz aggregates in the altered rock matrix and within millimetric interstitial vugs. An interesting feature of the metasomatized ultrabasic rocks is given by the more or less evident corrosion of primary spinels and their particular chemical signature, being Zn enriched (ZnO wt% values between 6.5 and 13%) and loosing all of its original Al and Mg contents; in the presence of these "chemically anomalous" spinels, matrix carbonates coexist always with late sulphides (mostly pyrite) suggesting that Zn incorporation in spinel is mainly ascribable to hydrothermal processes that involve the circulation of metal-sulphur rich fluids.

# 2.3. Listwaenites and hydrothermal quartz-carbonates fillings

Irrespective of the mineralogical nature of the basic and ultrabasic rocks, metasomatism effects in the vicinity of D<sub>2</sub>/D<sub>3</sub> shears are invariably intense, leading to the genesis of strongly metasomatized lithologies, like listwaenites (carbonatized ultrabasic rock types), where a complete destruction of the primary textures and parageneses may occur. These fine- to medium-grained, often silicified, Mg-Fe-Ca carbonate aggregates, comprising variable amounts of primary mineral relics and/or of more or less preserved products of serpentinization, were subject to repeated chemical and tectonic reworking, usually giving rise to a complex network of brittle structures whose relative chronology is sometimes impossible to establish. According to the available data, however, and from a general point of view, it seems possible to conclude that the earlier structures are filled up by coarse hydrothermal precipitates of dolomite (sometimes Fe-enriched), comprising quite often randomly distributed aggregates of pyrite ± chacopyrite and chlorite, whereas the later structures, consisting of different vein types with variable orientations, are sealed up by dolomite-ankerite, ankerite-microcrystalline quartz and siderite-pyrite-microcrystalline quartz. Late veins/veinlets of microcrystalline quartz and coarse calcite aggregates represent the final steps of hydrothermal fluid circulation in this geochemical system. Although convincing data is presently lacking, a simple comparison of this general picture with similar mineralogical/structural settings in world famous obducted ophiolites, justify the work currently in progress in order to evaluate the metallogenetic potential of these hydrothermal precipitates for precious metals (especially gold).

### 3. Conclusions

According to the present state of knowledge, and from a general point of view, the carbonatization-silicification metasomatism shown by the B.A.O.C.'s rock types at the Guadiana Valley postdates the establishment of retrograde syn-D<sub>2</sub> mineral assemblages typical of amphibolite facies metamorphism (500-600°C), and is mainly ascribable to late-D<sub>2</sub> and D<sub>3</sub> fluid circulation along thrust - left-lateral N110-120

shear zones. In gabbroic rocks, the earlier metamorphic retrograde reactions led mainly to widespread hornblende development; in ultrabasic specimens, talc, wherever present, precedes serpentine formation. Subsequent circulation of large volumes of  $CO_2$ -Si $O_2$  rich fluids, generated as a result of chemical rearrangements in the OMZ autochthonous formations overthrusted by the B.A.O.C. slices (including extensive decarbonation of impure marbles), enabled the development of intense carbonatization/silicification metasomatism under temperatures below 400°C, creating also a favourable geochemical environment for gold precipitation. It should also be noted that the nature and heterogeneous distribution of primary oxide and sulphide assemblages in non-altered and carbonatized gabbroic rocks, indicate that troctolitic and gabbronoritic/noritic rock types, may include, respectively, Cu + Ni ( $\pm$  Co) and Ti - V anomalies of potential economic interest. The real importance of the mineralogical/chemical data so far obtained for exploration activities is currently under investigation.

#### **Acknowledgements**

The authors acknowledge financial support from JNICT through the Research Project MIZOMOR - PBICT/P/CTA/2112/95 and wish to express their appreciation to A. Ribeiro for fruitful discussions on problems related to B.A.O.C. emplacement/deformation.

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