

## Sulphide dissemination in metatroctolites of the Beja - Acebuches Ophiolite Complex; their genesis and geological meaning

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*Palavras-Chave:* Complexo Ofiolítico de Beja-Acebuches; rochas metagabroicas; sulfuretos de Fe+Ni(±Cu) disseminados; origem do S.

*Resumo:* A abundância relativa de agregados de sulfuretos de Fe+Ni(±Cu) nos metatroctolitos da Palmeira (Vale do Guadiana, Serpa) deverá reflectir fundamentalmente a pré-existência de uma fonte mantélica de composição adequada e de graus favoráveis da sua fusão parcial, para além de subsequentes misturas magmáticas. A distribuição global das gotículas de sulfuretos, bem como a redistribuição dos metais por difusão em função dos gradientes térmicos, não deverá ser alheia aos fenómenos estabelecidos durante os estádios iniciais de recristalização síncronos da instalação do complexo ofiolítico sob condições de temperatura elevada, nem aos que se desenrolam durante o subsequente percurso de arefhecimento.

*Key-words:* Beja-Acebuches Ophiolite Complex; metagabbroic rocks; Fe+Ni(±Cu) sulphide dissemination; S origin.

*Abstract:* The relative abundance of Fe+Ni(±Cu) sulphide aggregates in the metatroctolites of Palmeira (Guadiana Valley, Serpa) should chiefly represent a fruitful combination of a suitable mantle source and adequate degrees of its partial melting, besides subsequent magma mixing. The whole-rock distribution of sulphide goticules, as well as the redistribution of metals by diffusion in response to thermal gradients, may further be accomplished during the initial stages of the high-T recrystallization experienced by the host rocks during ophiolite emplacement, and its subsequent cooling path.

### INTRODUCTION

Metagabbroic rocks (mostly gabbros and gabbronorites) belonging to the Beja – Acebuches Ophiolite Complex (BAOC - *e.g.* QUESADA *et al.*, 1994) comprise most of the times accessory amounts of sulphides. These form usually microscopic and randomly distributed aggregates of irregular morphology dominated by pyrrhotite + pyrite ± chalcopyrite. There is a general relationship between ilmenite composition and the main sulphide phases, ilmenite being iron-enriched (submicroscopic hematite exsolutions?) when pyrite is the main sulphide present. Nevertheless, millimetric and somewhat rounded aggregates of chalcopyrite + pyrrhotite + pentlandite ± pyrite appear to be characteristic of ilmenite-free rocks of gabbroic affinity, namely the metatroctolite rocks found at Palmeira, in the Guadiana Valley. Although the simple identification of this sulphide paragenesis does not by itself prove the existence of primary Cu-Ni(-Co) mineralizations in BAOC, the fact remains that the mineralogical/chemical data so far obtained may represent a valuable tool for the evaluation of its metallogenic potential. This is the major goal of the present work.

### GEOLOGICAL SETTING

The metatroctolite/metawehrlite rocks of Palmeira are slightly deformed and do not have extensive hydrothermal alteration. They are preserved in a megaboudin settled along the western extension of the Monte Peixoto - Monte do Gago shear, that brings them to contact with the olivine-gabbros of the Beja Igneous Complex. The existing outcrops at Palmeira do not allow the observation of the contact between the metawehrlite rocks and the prevailing metatroctolites, although the former seem to predominate within the south - southeastern domain of the referred to megaboudin.

The Monte Peixoto – Monte do Gago shear zone is an early WNW-ESE Variscan left-lateral structure generated during the D<sub>2</sub> phase of deformation. It bends gradually towards NW, cutting the Torrejão – Serpa accident, which commonly marks the northern boundary of the Beja – Acebuches belt in the Guadiana area. Field evidence for late reactivation of the Monte Peixoto – Monte do Gago shear zone during D<sub>3</sub> and/or late-D<sub>3</sub> times is restricted to domains far from Palmeira, and concerns mainly structural and mineralogical/textural features related polyphasic silicified carbonate infillings and to prominent metasomatic transformations in the adjoining metagabbroic rocks.

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## PETROGRAPHY AND MINERAL CHEMISTRY

Besides serpentine and relics of primary silicate minerals (mostly olivine and amphibolitized orthopyroxene), disseminated grains of more or less altered Cr-spinel and mixed globules of pyrrhotite-pentlandite can be easily recognized in the metawehrlite rocks; Cr-spinel crystals has most of the times rims of subsolidus reequilibration mainly of ferritchromite and ferritchromite  $\pm$  magnetite; dispersed decimillimetric rods of magnetite, sometimes with centimillimetric crystals of awaruite and heazlewoodite, are also common within strongly serpentinized domains. Primary paragenesis of metatroctolites comprise mainly weakly zoned An<sub>58-77</sub> plagioclase, low-Ni (< 0.23 wt% NiO) Fo<sub>83-86</sub> olivine, clinopyroxene (of diopsidic nature), and (apparently?) subordinate amounts of orthopyroxene (of prevailing enstatite composition). The major accessory minerals are heterogeneously scattered grains of zoned spinels and of magnetite, and sulphide blebs (pentlandite  $\pm$  bravoite + pyrrhorite  $\pm$  heazlewoodite  $\pm$  chalcopyrite  $\pm$  mackinawite ) or disseminated awaruite  $\pm$  pyrite.

Ortho- and clinopyroxenes do not display optical and chemical zonation and have average *mg*-numbers ( $[\text{Mg}/(\text{Mg}+\text{Fe}^{\text{tot}})]\times 100$ ) close to 85; slight Fe enrichments can, however, be found in some clinopyroxene edges adjacent to plagioclase crystals. Al<sub>2</sub>O<sub>3</sub> values of these silicates range between 1.2 and 2.3 wt%; CaO generally increases around 2 wt% from core to rim.

Pyroxenes are usually rimmed by amphibole (Mg-hornblende) and/or phlogopite. Hornblende composition is, in general, very similar to the one found in the normal metagabbros of BAOC, having *mg*-numbers ranging from 73 to 97 (although typically between 81 and 83). Phlogopite has an interstitial development and seems to be the last mineral formed during retrograding amphibolite facies conditions. *mg*-numbers for phlogopite vary from 89, in core domains, to 87 in crystal rims; the mineral also has significant amounts of TiO<sub>2</sub> (0.7 to 2.4 wt%), Na<sub>2</sub>O (1.7 to 2.2 wt%) and Cr<sub>2</sub>O<sub>3</sub> (0.6 to 0.9 wt%).

Plagioclase has average compositions near An<sub>71</sub>. Crystal zoning is optically weak, but chemically significant, ranging from An<sub>76</sub> in cores, to An<sub>66</sub>, in rims; external rims may occasionally show An<sub>64-58</sub> compositions.

Serpentinization took place in two main stages. The first one strongly alters olivine, leading to lizarditic mesh-textured aggregates, and to brittle deformation of the adjoining plagioclase and amphibolitized pyroxene crystals, due to local rock expansion. The second event produced antigoritic (?) precipitates inside late, intergranular fractures, wherein aggregates of clinocllore (with *mg*-numbers scattered between 79 to 86) also occur.

Chloritization postdates serpentinization and represents the last metasomatic event. It is particularly well documented in some metatroctolite specimens and is, in general, responsible for: 1) intense alteration of amphibole and phlogopite; 2) destruction of plagioclase and pyroxene relics; 3) local deposition of magnesite  $\pm$  dolomite; and 4) genesis of dark green-coloured fringes composed of late serpentine, chlorite, and probable Ni-tochilinite and/or Cr-valleriite, around olivine pseudomorphs, spinel crystals and sulphide aggregates. Locally, closely associated to some of the late chlorite + magnesite/dolomite aggregates, a Cr-K mica (fuchsita type) is found. Late chlorite is predominantly clinocllore with trace amounts of Cr<sub>2</sub>O<sub>3</sub> (<0.057 wt%) somewhat enriched in iron (average *mg*-number: 76). It was not possible to confirm quantitatively the identity of Ni-tochilinite and/or Cr-valleriite.

Cr-spinel is fine grained and has a relatively continuous trend of chemical compositions that can be correlated with primary differentiation processes. This trend is clearly distinct from the one due to late reequilibration of Cr-spinels during serpentinization, usually recorded by conspicuous irregular rims of ferritchromite or ferritchromite  $\pm$  magnetite. Magnetite also forms micrometric rods or lenticular aggregates occurring mainly along strong serpentinization corridors together with probable awaruite and in open cleavage fractures of preserved pyroxene and phlogopite.

Sulphides are especially common wherever Cr-spinel is impoverished; they occur: 1) as randomly disseminated irregular millimetric globules of pentlandite (and/or bravoite) + pyrrhotite  $\pm$  chalcopyrite  $\pm$  mackinawite; 2) as pentlandite (and/or bravoite) + pyrrhorite  $\pm$  heazlewoodite aggregates within magnetite fringes surrounding altered spinels; and 3) as fine aggregates of bravoite within weakly disseminated awaruite  $\pm$  pyrite.

Sometimes, pentlandite and pyrrhotite appear to occur as thin lamellar intergrowths, pyrrhotite being the matrix. Generally, however, the sulphide phases are more coarsely segregated, with pyrrhotite concentrated in the core area and pentlandite  $\pm$  chalcopyrite at the margin. The analysed sulphides are generally stoichiometric, except for pyrrhotite, which is commonly between Fe<sub>7</sub>S<sub>8</sub> and Fe<sub>8</sub>S<sub>9</sub>. Ni concentrations in pyrrhotite is low ( $\leq$  0.17 wt%) but quite variable from globule to globule; the same happens with Cu, Zn and As whose concentrations may reach 0.22, 0.18 and 0.11 wt%, respectively. Pentlandite is almost ideal (Fe, Ni, Co)<sub>9</sub>S<sub>8</sub>, being relatively Co-enriched (up to 1.40 wt%) and having trace amounts of Zn, Cu and As (below 0.11, 0.08, 0.04 wt%, respectively).

Droplet and lamellar exsolutions of Co-bearing chalcopentlandite and/or mackinawite (FeS) exist within pyrrhotite. Exsolutions of mackinawite seem to be usual in coarser crystals of pentlandite, and those of mackinawite/pyrrhotite and of cubanite (very close to ideal  $\text{CuFe}_2\text{S}_3$ ) occur within scarce anhedral chalcopyrite crystals; the latter is approximately  $\text{CuFeS}_2$ , and has, most of the times, some Ni ( $\leq 0.93$  wt%) and traces ( $\leq 0.10$  wt%) of Zn, As and Au.

The presence of pentlandite (and/or bravoite) + pyrrhotite  $\pm$  heazlewoodite within magnetite fringes surrounding altered spinels is a good evidence for primary sulphide precipitation around Cr-spinels. Therefore, bravoite ( $(\text{Ni,Fe,Co})\text{S}_2$ ) and heazlewoodite (near  $\text{Ni}_3\text{S}_2$ ) should be secondary and related to the alteration of pentlandite during serpentinization. Further desulphurization will lead to the genesis of awaruite (FeNi, with Ni:Fe close to 2:1), the liberated sulphur forming the late and micrometric crystals of pyrite within domains of strong serpentinization.

## DISCUSSION

Estimated (following the procedure of WELLS, 1977) equilibrium temperatures for coexisting ortho- and clinopyroxenes of these rocks range approximately from 800 to 880°C. These thermal conditions, compatible with those deduced by QUESADA *et al.* (1994), reflect mainly the chemical re-homogenization experienced by ortho- and clinopyroxene during their syntectonic recrystallization, and thus record the initial steps of ophiolite emplacement under pressures not exceeding 2-3 kbar. Under these conditions, plagioclase would also recrystallize and tend to homogenize. The notable homogeneity of the primary silicates contrasts with the extensive chemical variation of Cr-spinels and prevents the use of mineral chemistry to infer early petrogenetic features, especially those usually deduced from clinopyroxene-plagioclase and pyroxene-spinel equilibria.

Variscan metamorphism temperatures can be estimated from amphibole and plagioclase-rim compositions. Its maximum value is 600-620°C (amphibolite facies). Later minerals (including phlogopite) and textures are due to subsequent cooling. The bulk of serpentinization took place under high Mg-chemical potential values (non-widespread deposition of Ni-tochilinite and/or Cr-valleriite – see, *e.g.*, VAN DE VUSSE & POWELL, 1983) and temperatures ranging most probably from 400 to 500°C, before stable pyrite deposition could be achieved. Further hydration gives rise to heterogeneous chloritization under lower temperature conditions, usually associated to the breakdown of Mg-hornblende, phlogopite, plagioclase, and of the remaining pyroxene relics. These transformations are commonly correlative of late serpentine – Fe-enriched chlorite aggregates, locally accompanied by magnesite  $\pm$  dolomite ( $\pm$  Cr-K mica).

Two contrasting, but complementary, processes can be envisaged for sulphide deposition in metatroctolite rocks. A non-hydrothermal precipitation is suggested by the rounded shape of the major sulphide aggregates and by the predominance of Fe-Ni sulphides over chalcopyrite. Features such as lamellar texture, typical exsolutions, mineralogy and relative constant bulk compositions, also favour a high-temperature ( $\approx 650$ -600°C) for sulphide differentiation and deposition (*e.g.* CRAIG, 1990). The predominance of pyrrhotite and pentlandite, and the lack of pyrite, millerite, and other common secondary sulphides do not favour a hydrothermal origin, suggesting an origin as droplets of immiscible sulphide liquid separated from silicate melt.

Hydrothermal alteration may cause significant modifications of the primary signature of sulphides, leading to considerable metal redistribution. In fact, sulphide blebs are relatively unstable during rock hydration, and the development of bravoite and heazlewoodite (with probable Ni-tochilinite) reveals that the major sulphides predate serpentinization and chloritization, being either igneous or correlative of the early recrystallization processes of the metatroctolites. Wherever strong (and polyphasic) hydration is present, subsequent desulphurization enabled the growth of awaruite and pyrite disseminated within the late bands of serpentine/chlorite, coexisting with magnetite.

All the above mineralogical features are compatible with the whole-rock chemistry of these rocks: 1) relatively high Cr contents (2180-2430 ppm); 2) Cu+Co+Ni+Zn abundances  $\approx 952$ -1200 ppm, with Ni predominating, followed by Co; 3) sulphur concentrations of 0.037-0.058 wt%; and 4) low V contents (34-58 ppm). An important question, of significance for all the rocks belonging to the lower section of BAOC, concerning sulphur and its origin, remains, since these rocks have sulphur contents ranging from 0.010 to 0.050 wt%, being  $\approx 0.155$  and 0.113 wt% in some ultrabasic and metagabbroic samples, respectively.

Three major mechanisms may explain such relative sulphur enrichments. The first one is the assimilation of some crustal rocks (mainly Iberian Terrane margin rocks) during the hot ophiolite emplacement. Obduction and incorporation of country rocks causes cooling (of the semi-molten, S-undersaturated, ultramafic cumulates and gabbroic rocks) and assimilation of S and, possibly  $\text{CO}_2$  and  $\text{SiO}_2$ . This modifies the recrystallization process, leading to local sulphur saturation and thus to immiscible sulphide droplets. Sulphide deposition would to some extent be coeval of the earlier syntectonic recrystallization of the lower section of BAOC, and its abundance should mainly reflect both the availability of metals (liberated during silicate recrystallization and/or formerly present as disseminated Fe-Ni alloys) and the sulphur

contribution from the country rocks. The relatively high cooling-rate estimated for BAOC during its emplacement suggests, however, that the high-T recrystallization of the lower ophiolite section was relatively brief, preventing the required dispersion of crustal rock elements during obduction (even assuming extremely efficient diffusion paths for sulphur migration in semi-molten igneous rocks).

The second mechanism for sulphur rise in BAOC, is the evolution of “first-stage” S-saturated melts, like MORBs, which contain average S concentrations of 800 ppm (e.g. SEITZ & KEAYS, 1997). This implies low to moderate degrees of partial melting of an undepleted mantle and, therefore, the genesis of a “refractory upper residue” relatively enriched in immiscible PGE-bearing sulphide, not proved for BAOC. Accepting this hypothesis, the formation of immiscible monosulphide (*mss*) blebs during magmatic fractionation is induced by local  $fS_2$  increase due to  $Fe^{2+}$  extraction. This latter event, probably coeval with the late steps of Cr-spinel precipitation, may provide enough sulphur to convert high-temperature Fe-Ni (and/or PGE) alloys to an *mss* phase, whose further evolution (during system cooling) leads to the observed disseminated sulphide goticules. This implies a relatively wide period of slow crystallization that should be recorded at least by Cr-spinel and olivine (since the remaining primary silicates did experienced syntectonic recrystallization under high-T conditions). However, there is no evidence for crystal chemical zonation of both minerals, despite the fact that an extensive trend of Cr-spinel compositions is obtained for the metatroctolites.

The third possibility, somewhat similar to the latter one, involves the evolution of basaltic magmas generated after moderately to highly degrees of partial mantle melting, which seems to be a common feature of island arc/back-arc basin systems (e.g. DICK & BULLEN, 1984). The relatively high sulphur content of BAOC can then be related to the input of new magma pulses and subsequent mixing with the resident evolved melt, causing the segregation of *mss*. This hypothesis, compatible both with the geochemical signature of the analysed rocks (including the ultramafic cumulates) and to the compositional trend exhibited by Cr-spinels (particularly those in metatroctolite rocks), also explains the occurrence of a rhythmic enrichment in Cr-spinel in the ultramafic cumulate sequence intersected by the FA2 borehole at Ferreira do Alentejo. Sulphides are thus truly magmatic and their relative abundance should chiefly represent a fruitful combination of a former mantle source with an adequate composition and suitable degree of partial melting, besides magma mixing. The whole-rock distribution of sulphide droplets, as well as the redistribution of metals by diffusion due to thermal gradients, may be further accomplished during the initial stages of the high-T recrystallization experienced by metatroctolites during ophiolite emplacement, and the subsequent cooling path. If this hypothesis is valid, the occurrence of sub-economic Ni(-Co-PPGE) sulphide mineralizations would be expected, since major Cu-Ni(-Co-PGE) deposits are typically related to a selected group of magmas that were S-undersaturated at the time of magma generation and emplacement (e.g. SEITZ & KEAYS, 1997).

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