

## Mineralizações sulfuretadas na Sequência Gabróica Bandada do Complexo Ígneo de Beja (Portugal)

### *Sulphide-mineralization types in the Layered Gabbroic Sequence of the Beja Igneous Complex (Portugal)*

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#### Abstract

Sulphide mineralization in LGS reflects different evolving steps of a discontinuous ore-forming process that is coeval with the gabbroic sequence development: (1) early stages involved mantle-derived S and metals, resulting from Ni-rich sulphide melt segregation at  $\approx 700^\circ\text{C}$  and 4 kbar; (2) these were followed by development of high sulphidation assemblages reflecting derivation from distinct mantle sources and/or different degrees of lower crustal magma contamination; at this stage,  $\approx 670\text{--}500^\circ\text{C}$ , the mineralization path approached  $a(\text{S}_2)$  *Po-Py* equilibrium; (3) late mineralization stages were influenced by crustal sources and the ore deposition was determined by admixing of Ni-poor,  $\text{Cu}\pm\text{Co}$ -rich immiscible sulphide melts with  $\text{H}_2\text{O}$ -rich fluids; a high sulphidation state was also achieved with  $a(\text{S}_2)$  buffered by *Po-Py* equilibrium from  $\approx 630^\circ\text{C}$  to  $\approx 450^\circ\text{C}$ .

**Keywords:** Sulphide mineralization, Gabbroic Sequence of the Beja Igneous Complex, Ossa-Morena Zone

#### Resumo

As mineralizações de sulfuretos na SGB reflectem diferentes estádios evolutivos de um processo mineralizante síncrono do desenvolvimento da sequência gabróica: (1) os estádios precoces, envolvendo S e metais de origem mantélica, resultaram da segregação de líquidos ricos em S e Ni a  $\approx 700^\circ\text{C}$  e 4 kbar; (2) um estado de sulfidização relativamente elevada foi atingido subsequentemente, sendo o conteúdo metalífero determinado por fontes mantélicas heterogéneas e/ou diferentes graus de contaminação do magma pela crosta inferior; entre  $\approx 670^\circ\text{C}$  e  $\approx 500^\circ\text{C}$ , o percurso mineralizante progrediu a  $a(\text{S}_2)$  próxima do equilíbrio *Po-Py*; (3) os estádios tardios foram fortemente condicionados por contaminação crustal e a deposição de sulfuretos regulada pela mistura de líquidos pobres em Ni, mas enriquecidos em S e  $\text{Cu}\pm\text{Co}$ , com fluidos aquosos; um estado de sulfidização relativamente elevada foi novamente atingido, evoluindo a  $a(\text{S}_2)$  em torno do equilíbrio *Po-Py* entre  $\approx 630^\circ\text{C}$  to  $\approx 450^\circ\text{C}$ .

**Palavras-chave:** Mineralizações sulfuretadas, Sequência Gabróica do Complexo Ígneo de Beja, Z. Ossa-Morena

## Introduction

The Layered Gabbroic Sequence (LGS) is a fundamental unit of the Beja Igneous Complex, located at the SW border of the Ossa-Morena Zone (e.g. Andrade, 1983; Santos *et al.*, 1990; Jesus *et al.*, 2007). LGS includes a broad range of gabbroic rocks rimmed by diorites that were emplaced during the early stages of the Variscan collisional magmatism (ca. 355-345 Ma, Jesus *et al.*, 2007). In the LGS western compartment (from W of Torrão to Beringel), five different Series of gabbroic rocks were distinguished (Jesus *et al.*, 2005b, 2006b), reflecting a complex evolution characterised by magma recycling (variable recharge / crystallization rates) and involving repeated influxes of primitive melts into the magma chamber(s). During some stages of the LGS evolution, distinct physical-chemical conditions were achieved, favouring the development of: (1) massive Fe-Ti-V oxides (*type I mineralization*); (2) intercumulus massive sulphides (*type III mineralization*); and (3) sulphide veins (*type II mineralization*) – Jesus *et al.* (2003a, b, 2005a, 2006a). The major goal of this work is to report and discuss the contrasting features showed by the sulphide mineralization types. Additionally, some critical issues concerning the genesis of these mineralizing systems will be addressed in order to characterise the main stages of a discontinuous ore-forming process that is coeval with the LGS development.

## Sulphide-mineralization types

*Type III mineralization* occurs in distinct portions of the gabbroic successions, outcropping in the Ferreira do Alentejo – Beringel sector (*Beringel I* and *II* Series). Two main occurrences of *type III mineralization* are worth noting: at the Serrabritas quarry (upper section of the Intermediate Group of *Beringel I*) and at the Figueirinha quarry (Lower Group of *Beringel II*). The best exposure of *type II mineralization* is at the Ventoso quarry, within the upper section of the *Odivelas III* Series. For a synthetic overview about the LGS western compartment see Jesus *et al.* (2005b, 2006b).

### Host rocks

Sulphide-bearing norites (*type III mineralization*) at Serrabritas quarry belong to an olivine leucogabbro sequence, representing the peak of a pyroxene/Ca-rich plagioclase cumulate stage. Sulphide-rich assemblages are rimmed by thick orthopyroxene (*Opx*) coronas, suggesting development of chemical reactions between different magma batches. *Opx-Cpx* equilibrium indicates temperatures of  $857 \pm 33^\circ\text{C}$ .

Massive intercumulus sulphides (*type III*) are hosted in pyroxenites at the Figueirinha quarry. These rocks comprise randomly oriented subhedral *Cpx* with a typical adcumulate texture. *Po* blebs with *Pn* and *Ccp* exsolutions occur as inclusions within coarser grains of *Cpx*, forming

graphic intergrowths. *Cpx* grains are disrupted with increasing mineral sulphide content, displaying abundant corrosion gulfs, but only mild retrograding effects. Rare plagioclase occurs interstitially or is included within the *Cpx*-sulphide framework (slightly altered to a fine-grained mixture of chlorite-prehnite). Minor magnetite (*Mgt*) and ilmenite (*Ilm*) coexist with sulphide blebs, suggesting late stage crystallization ( $\approx 620^\circ\text{C}$ )  $f\text{O}_2$  conditions close to the QFM buffer (Jesus *et al.*, 2005a, 2006a).

*Type II mineralization* at Ventoso comprises an irregular network of massive sulphide-veins hosted in metasomatic haloes that affected the gabbroic sequence and are related to pegmatoid dykes emplaced at  $342 \pm 9.1$  Ma (SHRIMP U-Pb age, Jesus *et al.*, 2007). Near the metasomatized domain, a rhythmic succession of well-layered olivine (leuco-)gabbro, pyroxenite and pyroxenic gabbro could be observed. Often, these rocks show pyrrhotite (*Po*) micro-blebs (including pentlandite flames – *Pn* – and rare chalcopyrite - *Ccp*) that are disseminated interstitially or included in the cumulus silicates. Single clinopyroxene (*Cpx*) thermobarometry on selected gabbroic rocks indicates primary crystallization conditions at  $1154 \pm 37^\circ\text{C}$  and  $4 \pm 1.5$  kbar (Jesus *et al.*, 2007). Hornblende-plagioclase bearing pegmatoid assemblages coeval with *type II mineralization* indicate conditions ranging between  $680^\circ\text{C}$  and  $500^\circ\text{C}$  (Jesus *et al.*, 2007).

### Ore microscopy

At the Serrabritas quarry (*type III*), massive sulphides form a mildly net-textured framework, locally coexisting with *Mgt*. Sulphide assemblages comprise coarse-grained *Po* displaying *Pn* lamellae and “flames”, besides minor *Ccp* exsolutions of variable geometry. Subhedral *Pn* can also be observed, coexisting with finer-grained *Po* aggregates. Minor (isolated) *Ccp* often develops millimetric and discontinuous fringes around *Po* without evident exsolutions. *Py* is rare and clearly limited to late depositional stage.

At the Figueirinha quarry, the intercumulus sulphides (*type III*) comprise *Po*, *Pn*, *Ccp*, *Py* and linnaeite group minerals. Early *Po* may coexist with *Mgt* and *Ilm*, although most of the times it encloses the oxide phases. Main *Po* aggregates, formed by coalescence of disseminated sulphide blebs, and show abundant *Pn* lamellae and “flames” coexisting with minor *Ccp* exsolutions. Linnaeite group minerals seal intra- and inter-granular zoned veinlets, recording late alteration stage of granular, *Pn* polycrystalline veinlets. *Py* is present as subhedral grains in the *Po* groundmass (occasionally developing textural relationships suggestive of phase equilibrium) or as fine-grained infillings of late-fractures; in linnaeite-bearing veinlets, *Py* is the latest phase. In general, *Ccp* fills up micro-fractures and replaces the pre-existing sulphides.

*Type II* sulphide veins comprise massive coarse-grained *Po*, associated with late-stage pyrite (*Py*) and *Ccp*; *Mgt* is preserved as inclusions within the rims of *Po*. The early development of *Ccp* seems to result from an incomplete replacement of *Po* grain boundaries subjected to strong (micro-) fracturing. Late *Ccp* deposition occurs along inter- and trans-granular fractures, leading to fine-grained aggregates including minor *Py*. Distribution of *Py* is also heterogeneous, the most significant contents comprising idiomorphic and zoned grains that seal late fractures. However, early *Py* grains develop equilibrium textures at the rims of *Po* masses. These mineralogical and textural features strongly contrast with the intercumulus character showed by sulphides in *type III mineralization*.

### Ore-mineral chemistry

Compositions of sulphide and oxide mineral phases were obtained with EPMA and MicroPIXE analyses.

Mineral phases forming *type III mineralization* in the two occurrences exhibit compositional differences. At Serrabritas, *Po* has  $N_{FeS}$  values from 0.946 and 0.985, and low Ni contents (0.04-0.23 wt%). *Pn* is relatively enriched in Co (11.62-17.72 wt%), displaying also traces of Cu ( $\leq 0.70$  wt%). Late alteration of *Pn* leads to linnaeite compositions containing 24.60 wt% Ni and 19.79 wt% Co, and traces of Cu ( $< 0.05$  wt%). At Figueirinha, *Po*  $N_{FeS}$  values range from 0.914 to 0.933, displaying low Ni (0.30-0.97 wt%) and Cd ( $\leq 0.11$  wt%). *Pn* lamellae are Co-rich (3.44-6.38 wt%). *Ccp* includes traces of Cd, Ni and Pd ( $\leq 0.13$ , 0.12 and 0.10 wt%, respectively). Most *Py* includes trace amounts of Ni ( $\leq 0.85$  wt%) and Zn ( $\leq 0.13$  wt%); however, *Py* in linnaeite-bearing veinlets is characterised by high Ni (1.76-4.99 wt%). Linnaeite veinlets show compositional zoning compatible with multiphase infilling and with early *Pn* alteration: core domains are typically Ni, Co-rich ( $\leq 29.05$  wt% Ni and  $\leq 7.39$  wt% Co) and strongly contrast with Co-poor late rims ( $\leq 0.70$  wt%). Patches of linnaeite in *Po* matrix have Co contents ranging from 3.63 to 7.87 wt%.

In *type II mineralization* (Ventoso), *Po* displays  $N_{FeS}$  values from 0.918 to 0.938 and includes minor amounts ( $\leq 0.23$  wt%) of Ni, Co and Ag; Cu contents are below 0.01 wt%. *Ccp* is stoichiometric, some whitish grains showing traces of Ag ( $\leq 0.12$  wt%). Co and Ni contents in *Py* vary between 0.40 and 0.60 wt%

### Ore geochemistry

Table 1 illustrates the sulphur and minor / trace metals concentrations of sulphide mineralization types.

Table 1 – Representative metal (ppm, except for Au, Pt and Pd in ppb) and S contents (%) in samples from Ventoso sulphides (CV) and Figueirinha (FG) whole-rock mineralization.

	CV20	CV26	CV30	FG6A	FG6B	FG6
S	22.99	21.76	24.26	6.17	8.22	8.23
Ti	200	200	200	1898	741	1592
V	12	14	11	85	43	66
Cr	52	57	51	210	121	171
Co	1240	2130	1220	413	1194	531
Ni	1480	1420	1526	3100	8900	4600
Cu	1774	1202	14060	9300	7100	9600
Zn	135	50	229	32	27	28
Se	20	17	23	16	27	18
Pd	<2	<2	<2	11	25	22
Pt	<5	<5	<5	31	41	71
Au	3.9	4	200	20	9	13

Metal contents reflect the chemical signature shown by the (i) sulphide mineralogy (mainly Ni, Cu, Co) and the (ii) accessory oxide assemblage (which incorporates minor or trace amounts of Cr, besides Fe, Ti and V). Nickel and copper contents (as well as those of Cr, Ti and V) are higher in *type III mineralization*; this feature is followed by the overall tendency for higher concentrations in Pd, Pt and Au. Cobalt contents are significant in both mineralization types. Trace amounts of other base metals, like Zn, are also preferentially incorporated in Cu-rich sulphide phases and *Po*; higher Zn contents characterise *type II mineralization*. Selenium is always quite low (just slightly above the detection limit of the analytical method used), being present mainly in *Pn*.

### Sulphide deposition

Some critical features controlling the early stages of sulphide deposition in both mineralization types can be addressed by means of mineral phase equilibrium, considering textural and compositional relationships displayed by ore minerals.

From the activity of  $S_2$  implied by the different *Po* compositions at 4 kbar (Toulmin and Barton, 1964; Scott and Kissin, 1973) it can be deduced that (fig. 1): (i) the main stage of *type III mineralization* development at Serrabritas took place under low-sulphidation conditions (never reaching the *Py* field) at  $650 \pm 50^\circ\text{C}$ ; (ii) the formation of *type III mineralization* at Figueirinha involved a higher sulphidation stage, approaching *Py-Po* equilibrium at temperature from  $\approx 670^\circ\text{C}$  to  $\approx 500^\circ\text{C}$  and  $\log a(S_2)$  values from -0.4 to -4; (iii) the development of *type II mineralization* at Ventoso also required a relatively high sulphidation with *Po-Py* equilibrium which was achieved from  $\approx 630^\circ\text{C}$  to  $\approx 450^\circ\text{C}$  under  $-4.6 \leq \log a(S_2) \leq -1.3$ .

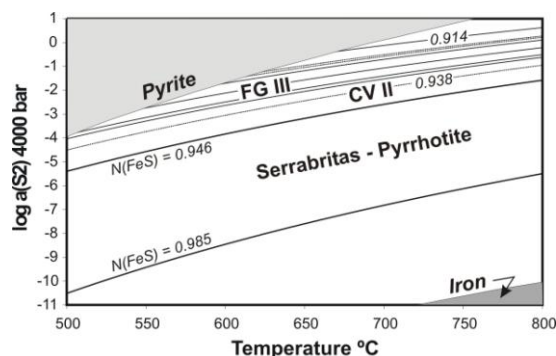


Fig. 1 – Diagram relating  $\log a(S_2)$  to  $Po$  composition at 4 kbar for the three sulphide occurrences.

$Po$ - $Mgt$  equilibrium at 4 kbar also indicates  $\log a(O_2)$  values from  $\approx -18$  at  $650^\circ C$  to  $\approx -22$  at  $450^\circ C$  (fig. 2), which is consistent with  $Mgt$ - $Ilm$  geothermobarometry ( $\approx 636^\circ C$  and  $\log fO_2 \approx -17.8 \pm 0.5$ ) for *type III mineralization*.

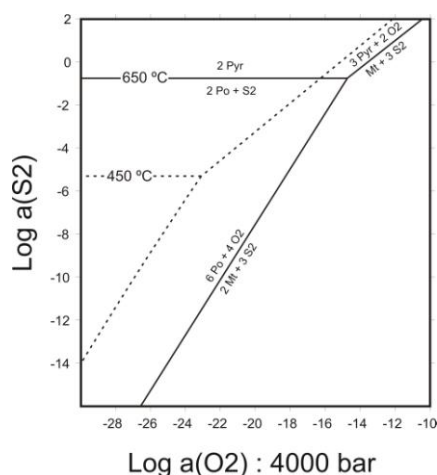


Fig. 2 –  $Po$ ,  $Mt$  and  $Py$ ,  $\log a(O_2)$  –  $\log a(S_2)$  equilibrium at 4 kbar, at  $650^\circ C$  and  $450^\circ C$  (thermodynamic data from Berman's TWQ vs 2.34, 2007).

### Sulphur and metal sources

In order to trace the main sources of sulphur and metals,  $Po$  and  $Cpy$  concentrates were analysed for  $^{34}S$  and  $Pb$  isotopes.

$\delta^{34}S$  values allow distinguishing between *type III* ( $-1.3$  to  $1.4$  ‰) and *type II mineralization* ( $6.1$  to  $6.3$  ‰). It is clear that mantle was the foremost source for S in the intercumulus mineralization at Serrabritas and Figueirinha, whereas a significant crustal component has to be evoked to explain the positive isotopic signature presented by the late sulphide veins at Ventoso.

$Pb$  isotopic data are heterogeneous and complex, differing for each sulphide mineral in both mineralization types. *Type III mineralization* shows  $18.029 \leq ^{206}Pb/^{204}Pb \leq 18.404$ ,  $15.553 \leq ^{207}Pb/^{204}Pb \leq 15.609$  and  $37.874 \leq ^{208}Pb/^{204}Pb \leq 38.105$ . *Type II mineralization* displays  $18.099 \leq ^{206}Pb/^{204}Pb \leq 18.121$ ,  $15.541 \leq ^{207}Pb/^{204}Pb \leq 15.560$  and  $37.918 \leq ^{208}Pb/^{204}Pb \leq 37.995$ . These values plot close to the orogenic field of

Zartman and Doe (1981) plumbotectonic diagrams and below the isotopic evolution curve of Stacey and Kramers (1975). It seems that  $Pb$  in both mineralization types resulted from heterogeneous mantle source(s) – that should have fed distinct magma pulses –, as well as different degrees of crustal contamination.

### Conclusions

The three main occurrences of sulphide mineralization so far recognised in LGS reflect different evolving steps of a discontinuous ore-forming process that is coeval with the gabbroic sequence development. In its early stages (*type III mineralization* - Serrabritas), this process involved mantle-derived S and metals, and resulted from Ni-rich sulphide melt segregation at  $\approx 700^\circ C$  and 4 kbar. Subsequently, a relatively high sulphidation state was achieved; S retained a mantle signature, but the origin of metals probably reflects distinct mantle sources and variable degrees of crustal contamination (*type III mineralization* – Figueirinha). Further evolving mineralization steps proceeded under  $a(S_2)$  conditions approaching the  $Po$ - $Py$  equilibrium from  $\approx 670^\circ C$  to  $\approx 500^\circ C$ . Late stages of the ore-forming process are represented by *type II mineralization* (Ventoso), where the influence of crustal contamination is clear. It is suggested that the formation of *type II mineralization* resulted from the admixing of Ni-poor,  $Cu \pm Co$ -rich immiscible sulphide melts with fluids related to the genesis of nearby pegmatoid dykes and metasomatic haloes. *Type II* sulphide deposition also required high sulphidation conditions, with  $a(S_2)$  close to the  $Po$ - $Py$  equilibrium from  $\approx 630^\circ C$  to  $\approx 450^\circ C$ . Sulphide ore-forming process should have evolved at  $\log a(O_2) \approx -18$  to  $-22$ , from  $650^\circ C$  to  $450^\circ C$ .

LGS and Aguablanca (Spain) sulphide mineralizations shares many common features. This is particularly evident for *type III mineralization*, as unravelled by the predominant mineral characteristics of sulphide ores and their isotopic signature (e.g. Tornos and Chiaradia, 2004; Piña et al., 2006; Tornos et al., 2006). The analogy is significant and strongly suggests an important metallogenic potential for the Variscan mafic-ultramafic belt formed at ca. 355 -345 Ma.

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