

# CHONDRITE-NORMALISED PGE PATTERNS OF DEFORMED AND METAMORPHOSED PERIDOTITES FROM PORTUGAL

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## Abstract

The PGE contents of peridotites/chromitites from the Continental Allochthonous Terrane of the Bragança Nappe Complex and of peridotites belonging to the Beja-Acebuches Ophiolite Complex are examined. Variable fractionation between IPGE and PPGE can be inferred on the basis of the obtained (Pt+Pd)/IPGE<sub>N</sub> ratios and chondrite-normalised PGE patterns. When a primary sulphide phase is lacking, negatively fractionated PGE assemblages are generated; conversely, positive fractionation trends indicate that PPGE are mainly incorporated in disseminated sulphide aggregates usually comprising pentlandite ± pyrrhotite as major phases. The PGE distribution is somewhat modified during rock deformation, mostly under amphibolite facies conditions.

**Key-words:** Peridotites; Bragança Nappe Complex; Beja-Acebuches Ophiolite Complex; Chondrite-normalised PGE patterns.

## 1. Introduction

Relatively large masses of deformed and metamorphosed peridotites can be found in several places of Portugal, particularly in the Continental Allochthonous Terrane (CAT) of the Bragança Nappe Complex (*e.g.* Marques *et al.*, 1996 and references therein) and in the Beja-Acebuches Ophiolite Complex (BAOC – *e.g.* Quesada *et al.*, 1994 and references therein). In CAT, peridotites belong to a set of lower-crust mafic-ultramafic rocks (comprising also metagabbros and metapyroxenites) that intrude mafic granulites and paragneisses, and were variably retrogressed in amphibolite facies conditions during later, Variscan, blastomylonitisation events. In BAOC, peridotites represent the deep crustal section of the ophiolite sequence and, together with the gabbroic rocks, experienced syntectonic recrystallisation under high temperature conditions (during ophiolite emplacement), and were subsequently subjected to Variscan metamorphism under amphibolite facies conditions.

The peridotites of CAT are usually affected by serpentinisation of variable intensity (*e.g.* Portugal Ferreira, 1965; Figueiredo, 1998), the most strongly altered rocks having been converted to a mesh-textured lizarditic serpentinite locally enriched in Cr-clinochlore and including also abundant magnetite and remnants of Cr-spinels (that invariably reveal more or less distinct reaction rims composed of ferritchromite ± magnetite); late serpentine corridors may also contain pyrite ± bravoite. Harzburgites prevail (*e.g.* Bridges, 1992; Figueiredo, 1998) and comprise abundant relics of enstatite, Fo<sub>91-94</sub> olivine (with average NiO contents around 0.4 wt%) and Cr-spinels (displaying  $\#Fe = Fe^{2+}/(Mg+Fe^{2+})$  and  $\#Cr = Cr/(Al+Cr)$  ratios ranging from 0.55 to 0.98 and from 0.53 to 0.89, respectively); average whole-rock Cr, Ni, Co and Cu contents are, respectively, 3055, 2215, 117 and 4 ppm, being the sulphur and arsenic concentration less than 133 and 5 ppm, respectively. The presence of variably amphibolitised diopside grains alongside relatively well-preserved enstatite strongly suggests, however, a former lherzolitic nature for some peridotites of CAT; in these rocks, Fo<sub>89-90</sub> olivine displays average NiO contents near 0.3 wt% and the composition of the preserved Cr-spinels is  $0.62 \leq \#Fe \leq 0.73$  and  $0.77 \leq \#Cr \leq 0.86$ . Samples representing earlier dunites (see also Bridges, 1992; Figueiredo, 1998) show usually relics of Cr-spinels (chemically characterised by  $0.61 \leq \#Fe \leq 0.89$  and  $0.76 \leq \#Cr \leq 0.91$ ) and of Fo<sub>93-95</sub> olivine (with average NiO contents near 0.5 wt%); the obtained average whole-rock contents in Cr, Ni, Co are, respectively, 3650, 2333 and 100 ppm, being those in S, Cu and As below 250, 135 and 47 ppm, respectively. Chromitites can also be recognised in CAT and are commonly hosted by harzburgitic and dunitic rocks (*e.g.* Bridges *et al.*, 1995 and references therein). These rocks, containing mostly Cr-spinels ( $0.32 \leq \#Fe \leq 0.65$  and  $0.62 \leq \#Cr \leq 0.85$ ) and interstitial Fo<sub>93-95</sub> olivine, comprise also PGE minerals (*e.g.* Coteló Neiva, 1946, 1947, 1948; Jedwab *et al.*, 1989; Bridges *et al.*, 1993, 1995); the average whole-rock contents in Ni and Co are 2360 and 102 ppm, respectively, the S, As and Cu concentrations being quite variable and below 400, 26 and 1790 ppm, respectively.

In the peridotites of BAOC (mainly harzburgites and clinopyroxene peridotites), serpentinisation is ubiquitous and 80% or more complete (*e.g.* Mateus *et al.*, 1998). In general, only altered cores of Cr-spinel ( $0.40 \leq \#Fe \leq 0.50$  and  $0.35 \leq \#Cr \leq 0.45$ ) and enstatite (sometimes enstatite ± diopside) remain and these are enveloped by serpentine aggregates of lizarditic nature; the scarce relics of Fo<sub>83-86</sub> olivine display average NiO contents near 0.24 wt%. Mesh textures are well developed and consist of lizardite and bastite pseudomorphs after both olivine and orthopyroxene. Magnetite generated by iron liberated from olivine and orthopyroxene form finely disseminated rims around some primary silicate grains. Individual mesh textural units are outlined by ribbonous lizardite which generally parallels the foliation, accentuating the tectonic fabric of the strongly deformed ultramafic cumulates. Micrometric sulphide grains and alloy particles are wide-

spread but of difficult optical characterisation, although qualitative microprobe analyses revealed a predominant Ni-Fe composition. It is also noteworthy that these samples display average Cr, Ni and Co contents around 2253, 1440 and 113 ppm, respectively; sulphur concentrations and Ni/Cu ratios are quite variable, ranging respectively between 330 and 1550 ppm and between 20 and 242.

## 2. PGE abundances and chondrite-normalised patterns

Representative chemical analyses of peridotites and chromitites from CAT and BAOC are listed on Table 1, as well as the Chondrite C2 values that were used as normalisation standards of PGE (Charmichael, 1990) and the respective (Pt+Pd)/IPGE<sub>N</sub> ratio applied as an index for fractionation between PPGE (Rh, Pt, Pd) and IPGE (Os, Ir, Ru) – see, *e.g.*, Naldrett & Von Gruenewaldt (1989) for details.

The PGE contents of chromitites, although low, are significantly higher than those presented by peridotites, but in both cases compatible with the PGE abundances found in many ultramafic complexes, irrespective of their age and geodynamic setting (ophiolite sequences and stratiform complexes – see, *e.g.*, Talkington & Watkinson, 1986, and references therein). Strongly strained peridotites (where a mylonitic fabric is sometimes developed) exhibit always PGE contents lower than those presented by similar rocks but not affected by an intense non-coaxial deformation; depletion in IPGE seems to be more significant, although all PGE show relative (and variable) losses.

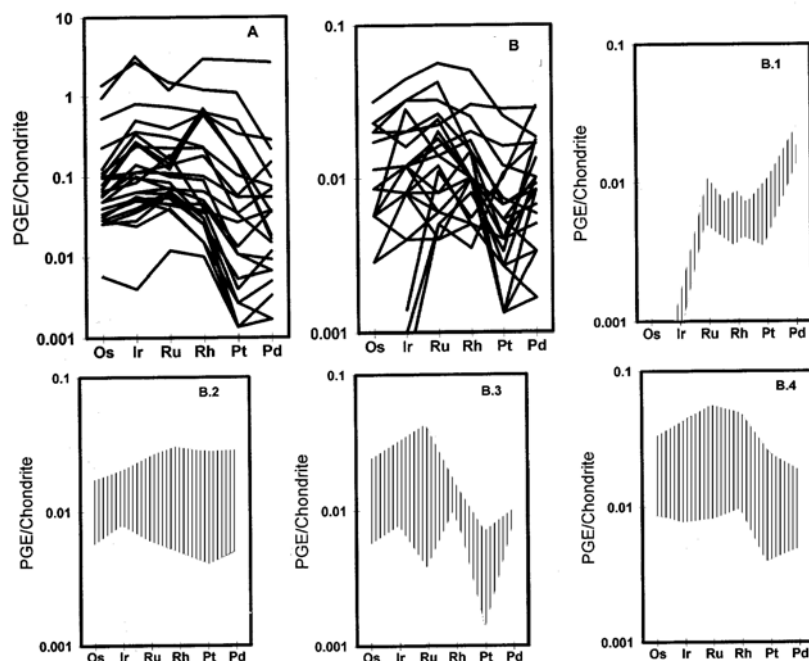
**Table 1**  
Bulk-rock PGE, Ni and Cu contents in representative samples of peridotites/ chromitites belonging to CAT (Prichard *et al.*, 1991; Figueiredo, 1998) and in peridotites from BAOC (Mateus *et al.*, 1998)

	Os ppb	Ir ppb	Ru ppb	Rh ppb	Pt ppb	Pd ppb	(Pt+Pd)/IPGE <sub>N</sub>	Ni ppm	Cu ppm	Source data
<b>PERIDOTITES</b>										
FA1-9	Bdl	0.5	5	1.6	5	21	2.40	1691	7	Mateus <i>et al.</i> 1998
FA1-13	Bdl	0.3	5	0.7	16	20	3.39	1217	62	Mateus <i>et al.</i> 1998
FA1-14	Bdl	0.7	11	1.1	15	35	2.24	1413	38	Mateus <i>et al.</i> 1998
FAB-4	4	4	8	3	11	7	0.30	2150	1	Figueiredo, 1998
FS-2a	14	10	22	6	42	34	0.47	2500	7	Figueiredo, 1998
FC-3	12	10	26	3	6	10	0.10	2400	Bdl	Figueiredo, 1998
FALS-1	8	10	32	2	Bdl	4	0.03	2000	22	Figueiredo, 1998
BRAG623	14	16	32	5	18	12	0.13	Nd	Bdl	Prichard <i>et al.</i> , 1991
BRAG43	22	22	56	10	32	22	0.17	Nd	Bdl	Prichard <i>et al.</i> , 1991
<b>CHROMITITES</b>										
BRG142	960	1350	1500	240	1650	260	0.10	755	Bdl	Prichard <i>et al.</i> , 1991
BRG145	370	400	740	125	740	116	0.13	915	Bdl	Prichard <i>et al.</i> , 1991
BRAG64	70	56	140	36	86	180	0.32	9778	1793	Prichard <i>et al.</i> , 1991
BRG45	78	118	225	45	155	90	0.15	2057	26	Prichard <i>et al.</i> , 1991
BRAG56	28	26	38	3	2	4	0.02	2646	16	Prichard <i>et al.</i> , 1991
BRAG39	34	32	72	10	20	44	0.15	1608	87	Prichard <i>et al.</i> , 1991
Chondrite C2	700	500	1000	200	1500	1200				Charmichael, 1990

Bdl = below detection limit of the analytical procedure used; Nd = not determined

The obtained (Pt+Pd)/IPGE<sub>N</sub> ratios suggest that a variable fractionation between the two PGE subgroups exists independently of the rock type, corroborating the graphical trends shown by the chondrite-normalised plots in fig.1. In chromitites (fig.1-A), the general slope varies from flat or moderately negative to steeply negative, being worth noting the: (i) development of marked peaks at Ir and Rh in some patterns; (ii) distinct upturns at Ru and Pd exhibited by other profiles; and (iii) slight peaks at Ru and Pd. All these features are compatible with the relative abundance and the chemical composition displayed by the identified PGE minerals in these rocks (see references quoted above). The chondrite-normalised PGE patterns obtained for peridotites (fig.1-B) are apparently less consistent, but a systematic examination of the available data reveals that: (i) peridotites containing significant accessory amounts of sulphides (pentlandite + pyrrhotite) show positively fractionated PGE normalised-patterns (fig.1-B.1 – this is particularly evident for BAOC peridotites); (ii) sulphide-free peridotites show minimal fractionation between IPGE and PPGE, the slight depletions in PPGE or in IPGE being mainly ascribable to the presence of micrometric PGE alloys (fig.1-B.2); and that (iii) the PGE normalised patterns displayed by peridotites relatively enriched in Cr-spinels are quite similar to those exhibited by chromitites (fig.1-B.3 and B.4).

**Fig.1** – Chondrite-normalised PGE patterns for chromitites (A) and peridotites (B) belonging to CAT and BAOC. Diagrams from B.1 to B.4 illustrate the general trends exhibited by peridotites with distinct primary mineral assemblages (see text for discussion).



## 4. Discussion

### 4.1. Theoretical and experimental constraints

In magmatic systems, the PGE distribution changes during magmatic processes and is mainly controlled by physico-chemical conditions, such as  $fS_2$ ,  $fO_2$  and T, and by crystallising phases (oxides, silicates and/or sulphides). Besides these primary features, it is noteworthy that PGE abundances may be strongly modified during several metasomatic processes, particularly those developed during greenschist to amphibolite metamorphism in highly deformed areas. The significance of late- and postmagmatic fluids for PGE enrichments has indeed been stressed by Stumpfl (1986); details on the behaviour of PPGE under temperatures below 450°C

and experimentally controlled  $fS_2$  and  $fH_2$  were comprehensively examined by Gammons (1995) and Ballhaus & Ulmer (1995).

Common peridotites show usually flat PGE patterns, suggesting that the PGE distributions in these rocks are not controlled by silicate phases; often, slight depletions in PPGE are documented and mainly ascribable to the presence of IPGE metals or alloys and/or to the greater partition coefficient between sulphide and silicate for PPGE (4950 for Pd, Fleet *et al.*, 1991) than for IPGE (3180 for Ir, Crockett *et al.*, 1992, quoted by Yan *et al.*, 1995). Significant Cr-spinel crystallisation would, however, influence the PGE distribution, because the high and low chromite/melt partition coefficients for IPGE and PPGE, respectively (22 or 25 for Ru, and  $< 0.02$  for Pd, respectively; Capobianco & Drake, 1990) imply a preferential removal of IPGE from the melt, resulting in a PGE pattern with a negative slope. Additionally, the very facts that the solubility of metallic Pt in melts is much higher than that of Ir, and that Ir solubility decreases faster than that of Pt as  $fO_2$  increases, suggest that IPGE may be extracted from the magma as alloys or metals, whereas PPGE would require an immiscible sulphide liquid as a collector (*e.g.* Peck & Keays, 1990; Peach *et al.*, 1994 and references therein); IPGE alloys would then crystallise under a favourable combination of  $fO_2$  and  $fS_2$  at high temperatures before sulphur saturation is achieved (*e.g.* Amossè *et al.*, 1990). Therefore, after the crystallisation of Cr-spinels, but before the precipitation of olivine and Cr-spinel cumulates, the magma would be characterised by (Pt+Pd)/IPGE<sub>N</sub> ratios above 1. An increase of  $fS_2$  is further required for the establishment of suitable conditions for magmatic fractionation of IPGE from PPGE, resulting in the relative enrichment of the latter group of metals.

### 4.2. Data interpretation

From the above comments one may conclude that the shape of PGE chondrite-normalised pattern for non-sulphide bearing rocks would be flat or have a negative to slightly convex upward slope, denoting the lack of PGE fractionation or the presence of IPGE alloys (as intercumulus particules and/or as discrete inclusions in Cr-spinel). In sulphide bearing rocks, conversely, a positively sloped PGE normalised-pattern is usually achieved, indicating the presence of intercumulus sulphides (mostly pentlandite and pyrrhotite) and/or PPGE-bearing arsenides. These expected patterns are indeed observed both in CAT (peridotites/chromitites) and in BAOC (peridotites), although the original PGE distributions may be somewhat affected during later significant rock deformation/hydration under amphibolite facies conditions. Such a strong mineralogical dependence (that can be used as an additional guide for high-T sulphide mineralisations)

prevents the use of PGE normalised-patterns as a reliable indicator of particular geodynamic settings, precluding thus any attempt of distinguishing ophiolite peridotites from continental peridotites on their basis.

From the available data it seems also that the PGE distributions may be somewhat affected by the physical and chemical conditions under which tectonic deformation of peridotites took place, but not severely modified by serpentinisation, since the PGE contents in strongly strained rocks are usually lower than those in rocks with almost similar degrees of serpentinisation but not affected by an intense non-coaxial deformation. This is not in conformity with the conclusions reported by Bridges *et al.* (1995), who interpret many features concerning PGE abundances in chromitites of CAT simply as a result of several chemical remobilisation processes of these metals during whole-rock serpentinisation.

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