

# PLATINUM-GROUP MINERALS IN ALTERED CHROMITITES OF THE CAMPO FORMOSO LAYERED INTRUSION (BRAZIL): EVIDENCE FOR REMOBILIZATION OF PLATINUM-GROUP ELEMENTS AT LOW TEMPERATURE

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## INTRODUCTION

The platinum group elements (PGE) are commonly believed to be inert and practically immobile under hydrothermal conditions, being mainly transported and concentrated during magmatic processes. Recent investigations, however, indicate that the mineral carriers of the PGE (the platinum-group minerals, PGM) may become unstable during alteration of the host rocks, providing the source material for deposition of secondary PGM at temperatures much lower than magmatic (i.e.: Stumpf, 1974; Stockman and Hlava, 1984; Garuti and Zaccarini, 1997). Although bulk-rock PGE ratios remain unchanged in most cases, indicating migration of the PGE over short distance, the primary PGM assemblage can be drastically transformed by reaction with cool hydrous solutions, giving rise to new PGM, whose mineralogical nature depends on physical-chemical conditions of alteration (Garuti et al., 1997; Garuti and Zaccarini, 1997)

The chromite-PGE deposits in the Proterozoic Campo Formoso layered intrusion of Brazil (Figure 1) provide a useful example for studying these low temperature processes.

They consist of 7 chromitite layers hosted in ultramafic rocks deeply altered into a serpentine-chlorite-carbonate-talc assemblage by reaction with hydrothermal fluids. This paper reports on the mineralogy, texture and paragenesis of secondary PGM closely associated with the chlorite matrix of the chromitites.

## LOW TEMPERATURE ALTERATION OF THE CHROMITITES

According to Boukili et al. (1983; 1984), low-grade regional metamorphism transformed the ultramafic rocks of Campo Formoso into a lizardite-chrysotile-magnetite-bastite assemblage (serpentinization stage). Due to subsequent reaction with fluids emanating from the

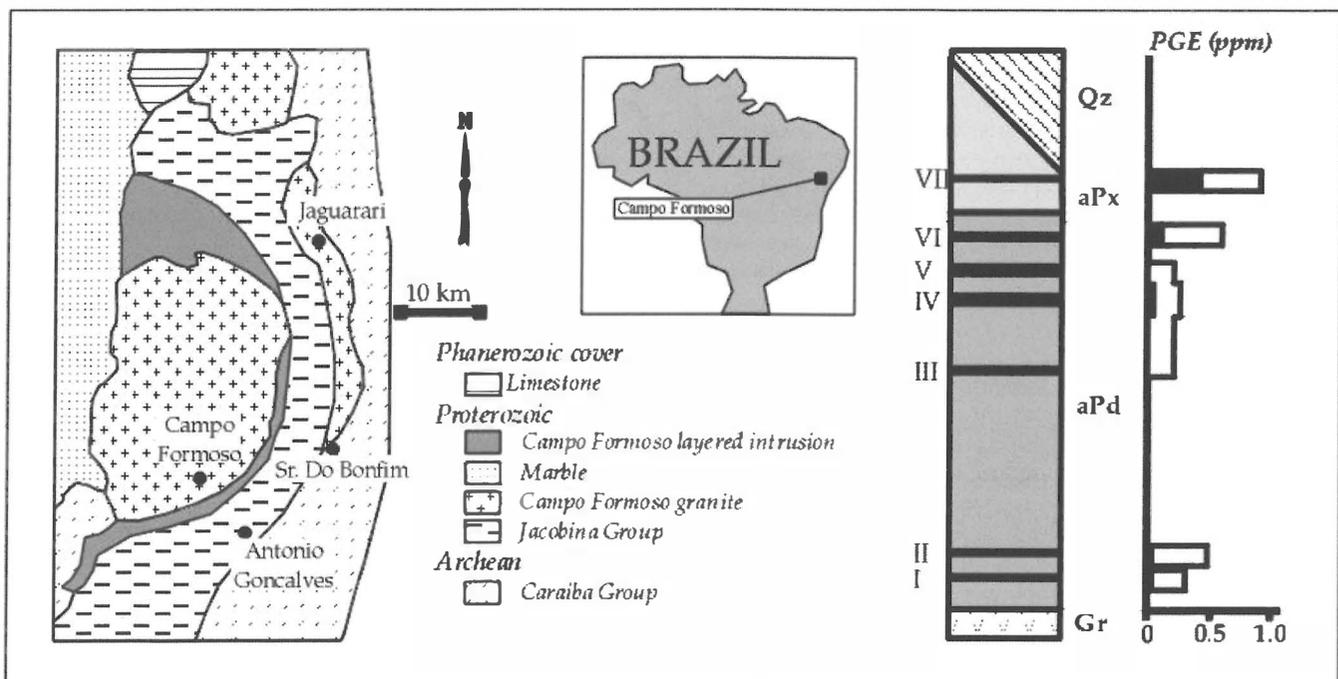


Figure 1: Simplified geology of the Campo Formoso layered intrusion (after de Deus et al., 1982) and idealized stratigraphy of chromitite layers, with total PEG contents (ppm) and relative proportions of PPGE (black) vs. IPGE (white). Qz = quartzite, aPx = altered pyroxenite, aPd = altered peridotite, Gr = granulite.

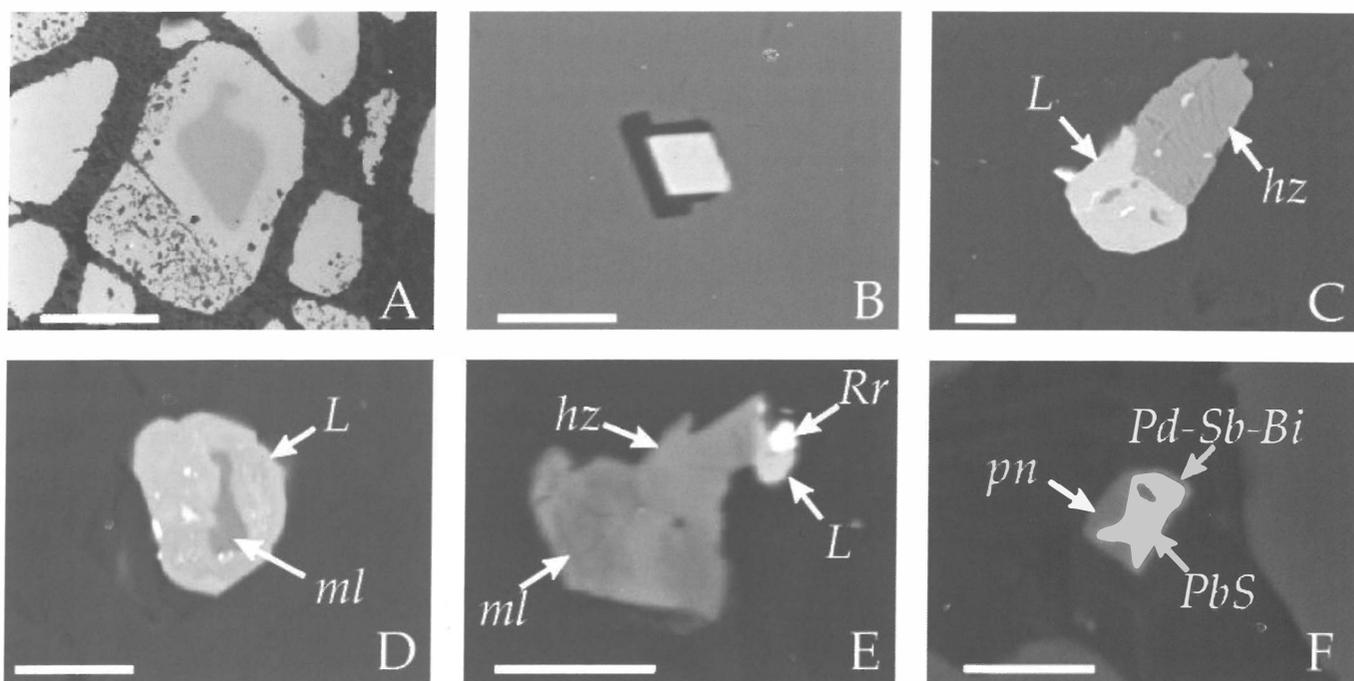


Figure 2: A) Three-phase zoning of chromite grains. B) Primary laurite-silicate inclusion in fresh chromite. C) Laurite-heazlewoodite association in chlorite; white spots are irarsite. D) Millerite replaced by laurite with spots of irarsite, in chlorite. E) Laurite + ruarsite with millerite + heazlewoodite, in chlorite. F) Pd-Sb-Bi compound associated with pentlandite and galena, in chlorite. L = laurite, Rr = ruarsite, hz = heazlewoodite, ml = millerite, pn = pentlandite. Scale bar: A) = 0.3 mm; B) to F) = 10 microns.

adjacent granite (Boukili et al. 1983; 1984; Zaccarini et al., 2005) this assemblage was replaced by various generations of chromian clinocllore and antigorite (chloritization stage). A third stage followed, characterized by carbonatization, steatitization and silicification, by which the chlorite-assemblage is replaced by magnesite, talc, dolomite, calcite, quartz and rare Cr-bearing hydroxycarbonates. Chromite is little affected during serpentinization, but alters into ferrian-chromite during the chloritization stage. This reaction involves transfer of Mg, Al and minor Cr to chlorite, with a relative increase of Fe<sup>2+</sup> and Fe<sup>3+</sup> in the ferrian-chromite rims (Beeson & Jackson, 1969). With proceeding alteration to the carbonatization stage, ferrian chromite becomes unstable and dissolves, being replaced by calcite, dolomite and Cr hydroxycarbonates. The chloritization-carbonatization event produces the spectacular zoning of chromite grains, consisting of an unaltered core, replaced by a solid rim of ferrian-chromite which, in turn, grades outward into a porous aggregate of ferrian-chromite, chlorite and carbonates (Figure 2A).

## SECONDARY PGM AND RELATED MINERALS

The polyphase, penetrative hydrothermal metasomatism did not substantially modify the composition of chromite cores (Figure 2A) and distribution of the PGE which still are consistent with magmatic fractionation processes (Lord et al., 2004; Garuti et al., 2006) emphasized by enrichment in Rh, Pt and Pd (PPGE) with respect to Os, Ir and Ru (IPGE) in the highest chromitite layers VI and VII (Figure 1). However, two genetically different populations of PGM have been identified in the chromitites (Table 1).

The primary PGM (Ru-Os-Ir sulfides and alloys) occur as euhedral crystals included in the unaltered chromite cores (Figure 2B). They are considered to be early liquidus

crystals entrapped in chromite at high temperature (e.g.: Garuti et al., 1999; Zaccarini et al., 2002). In contrast, a secondary assemblage of PGM sulfides, sulfarsenides and antimonides, typically anhedral in shape, occur systematically in the intergranular chlorite matrix. They form composite grains with Ni-rich sulfides pentlandite, heazlewoodite, and millerite (Figure 2C to F). Laurite may replace, grow over, or exsolve from the Ni-sulfides and contains spot-sized exsolutions of irarsite. The Pd-Sb phases occur independent of laurite, forming composite grains with pentlandite and galena.

## GENETIC CONSIDERATIONS

Paragenetic association is indicative of co-crystallization of the secondary PGM with the Ni-sulfides. The Ni-rich bulk composition of these sulfides is not consistent with equilibration of a magmatic sulfide liquid, neither does it reflect in situ alteration of an intercumulus sulfide phase. They are part of a complex association of Fe-Ni sulfides that initially originated as a by-product of the alteration of mafic silicates (Eckstrand, 1975) and was subsequently remobilized during the chloritization-carbonatization stages. The whole assemblage comprises the Ni-sulfides (pentlandite, heazlewoodite, millerite) characterized by S/Me atomic ratios equal to or less than unity, thus reflecting low fO<sub>2</sub> and fS<sub>2</sub>, and Fe-Ni sulfides with S/Me > 1 (pyrite, polydymite, violarite) indicators of relatively high fS<sub>2</sub> and fO<sub>2</sub>. Noteworthy, the S-poor sulfide associate systematically with PGM in the chlorite groundmass. In contrast, the S-rich sulfides occur exclusively in the carbonate assemblage and conspicuously they do not associate with PGM.

The chloritization-carbonatization paragenetic assemblages indicate that the infiltrating solution carried H<sub>2</sub>O and CO<sub>2</sub>. It was probably moderately to strongly

Mineral	type-composition	habit	mineral in contact
1) Primary PGM included in the unaltered core of chromite grains			
Laurite 1	(Ru,Os,Ir)S <sub>2</sub>	euhedral	Pentlandite, Un. Cu-sulfides, rutile, silicate
Osmium	(Os,Ir,Ru)	"	silicate
Erlichmanite 1	(Os,Ru,Ir)S <sub>2</sub>	"	laurite, silicate
2) Secondary PGM situated in the chlorite matrix			
Laurite 2	(Ru,Os) (S,As) <sub>2</sub>	anhedral	Ni-sulfides, PGM sulfide-sulfarsenides
Erlichmanite 2	OsS <sub>2</sub>	"	Laurite 2, Ni-sulfides
Irarsite	(Ir,Rh)AsS	exsolved blebs	Laurite 2, Ni-sulfides
in:			
Hollingworthit	(Rh,Pt,Ir)AsS	anhedral	Ni-sulfides
e			
Ruarsite	(Ru,Pt,Rh)AsS	"	Laurite 2, Ni-sulfides
Sudburyite	PdSb	"	single-phase
Unk. Pd-Sb 1	Pd <sub>4</sub> Sb <sub>3</sub>	"	bismuthinite
Unk. Pd-Sb-Bi	Pd(Sb,Bi)	"	Pentlandite, galena, Un.Pb-Sb
Un. Pd-Sb	?	"	Pentlandite, galena, Un.Pb-Sb
Un. Pt-Te	?	"	heazlewoodite

Table 1: Texture and paragenesis of 200 Platinum-Group Mineral grains from the Campo Formoso chromitites

acidic, and was therefore capable to chemically attack the assemblage of base metal sulfides and PGM occurring interstitial to chromite. Presumably, PGE and base metals, mainly Ni, were dissolved forming bisulfide or chloride complexes (Pan and Wood, 1994; Xiong and Wood, 2000). We suggest that they were redeposited together with the Ni-sulfides soon after because of a sudden reduction of the redox conditions. Reducing conditions are expected to occur in the surroundings of altered chromite grains as a consequence of chromite oxidation. In fact, the breakdown of chromite into ferrian chromite requires that water is reduced by extraction of O to oxidize Fe<sup>2+</sup> (in chromite) to Fe<sup>3+</sup> (in ferrian-chromite), thereby H<sub>2</sub> is

released in the system causing reducing conditions. The process leads to the precipitation of metals (PGE, Ni, Fe, Pb etc.) as sulfides, sulfarsenides, antimonides, depending on the activity of the single ligands. Conditions for the precipitation of the PGM-sulfide assemblage in terms of fO<sub>2</sub>, fS<sub>2</sub> and T°C are depicted in Figure 3.

An increase of the CO<sub>2</sub>/H<sub>2</sub>O activity ratio marks the transition to «carbonatization». Ferrian chromite of the first generation becomes unstable and is transformed into a porous aggregate of ferrian chromite intermixed with dolomite, magnesite and chlorite. Electron microprobe analysis indicates a decrease of total FeO that is

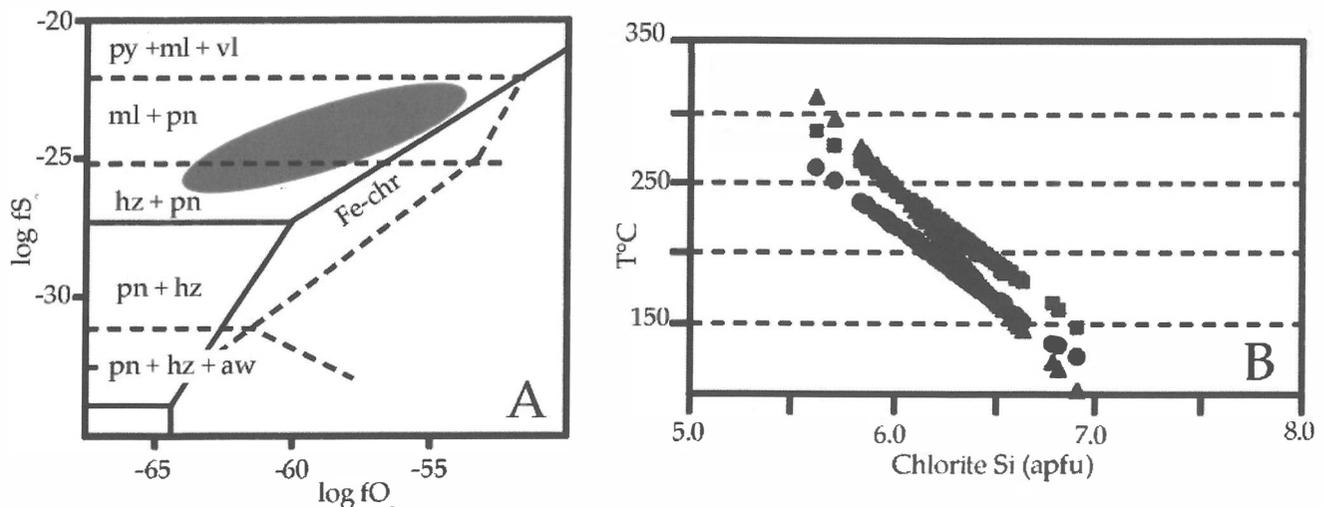


Figure 3: Sulfur-oxygen fugacity (grey field in A) and Temperature conditions (B) for the precipitation of the secondary PGM, inferred from the Ni-sulfide paragenesis and the chlorite geothermometry according to three different equations. Py = pyrite, pn = pentlandite, ml = millerite, hz = heazlewoodite, aw = Ni-Fealloys, vl = violarite.

preferentially dissolved with respect to Al, Mg, and Cr, with concomitant change of the oxidation state of iron from Fe<sup>3+</sup> to Fe<sup>2+</sup>. This reaction liberates O<sub>2</sub>, and drives the redox to oxidizing conditions again. The newly formed PGM appear to be absent in the carbonatization assemblages, suggesting that they may become unstable, and dissolve in the CO<sub>2</sub>-rich solution. However, this process does not seem to have substantially affected the secondary PGM associated with the chlorite matrix of the chromitites.

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