

# **Contemporaneous Segregation of PGE- and BM-Rich Sulfide Melts and Chromite Crystallization: The Caridad Chromite Deposit, Mayarí-Baracoa Ophiolitic Belt (Eastern Cuba)**

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**ABSTRACT.** An immiscible sulfide melt rich in platinum group elements (PGE) and base metals (BM) appears to have segregated contemporaneously with the crystallization of chromite during the formation of an ophiolitic chromitite body (Caridad deposit) in the Sagua de Tánamo mining district (eastern Cuba). Evidence includes: 1) droplet-like inclusions of BM sulfides in laurite (often oriented along growth planes); and 2) PGE- and BM-rich sulfide mineralogy now found as solid inclusions in the chromite. The segregation of immiscible sulfide melts coeval with chromite crystallization is explained in terms of chromitite formation by turbulent mixing/mingling of melts in open conduits in the upper sub-oceanic mantle.

## **1 INTRODUCTION**

Despite great progress in the study of magmatic processes in mafic-ultramafic ore systems, many geological, petrological and geochemical aspects of the PGE enrichment shown by ophiolitic chromitites are still not fully understood. In particular, sulfide immiscibility, an effective mechanism for PGE concentration in many magmatic mafic-ultramafic ore systems, seems to have a minor role in concentrating PGEs during the formation of ophiolitic chromitites. In fact, only a few examples of segregation of PGE-rich sulfide melts during crystallization of chromitites are known in ophiolitic complexes. In such cases, the segregation of sulfide melt was interpreted as a consequence of large degrees of fractional crystallization (Prichard et al. 2008) or as the result of segregation of sulfur from volatile-oversaturated melts (Ferrario and Garuti 1990; Torres-Ruiz et al. 1996; Gutierrez-Narbona et al. 2003).

In this contribution we report an example of a chromitite body, the Caridad deposit, in the Mayarí-Baracoa Ophiolitic Belt (eastern Cuba), which records evidence of segregation of PGE- and BM-rich sulfide melt coeval with the crystallization of chromite at early magmatic stages.

## 2 REGIONAL GEOLOGY AND ENVIRONMENT OF FORMATION OF THE CARIDAD CHROMITITE DEPOSIT

The Caridad deposit is one of the 10 Cr-rich chromite ore bodies in the Sagua de Tánamo mining district, which lies almost in the centre of the Mayarí-Baracoa Ophiolitic Belt (MBOB) in eastern Cuba (Murashko and Lavandero 1989; Proenza et al. 1999; Gervilla et al. 2005). The MBOB constitutes a strongly deformed and faulted mafic-ultramafic thrust overriding a Cretaceous volcanic arc. The ophiolite bodies show suprasubduction geochemical signature (Proenza et al. 1999, 2006; Marchesi et al. 2006, 2007).

Chromite deposits in the MBOB can be subdivided into three mining districts according to chromite composition: 1) the Moa-Baracoa district, with Al-rich chromitite ( $\text{Cr\#} = 0.43\text{--}0.54$ ); 2) the Mayarí district, with Cr-rich chromitite ( $\text{Cr\#} > 0.69$ ); and the Sagua de Tánamo district, with both Al-rich and Cr-rich chromitite ( $\text{Cr\#} = 0.46\text{--}0.71$ ; Proenza et al. 1999). According to the above described geological setting for the formation of the ophiolite bodies, Cr-rich chromitites from the Mayarí District formed from boninitic-type melts generated on the axis of the arc, whereas Al-rich chromitites from the Moa-Baracoa District were generated below the back-arc basin from MORB-type melts. A transitional spatial/temporal stage is represented by the Sagua de Tánamo District, where Cr- and Al-rich chromitites coexist (Proenza et al. 1999; Gervilla et al. 2005).

## 3 SULFIDES AND ASSOCIATED MINERALS

Platinum-group minerals (PGM), base-metal sulfides (BMS) and associated minerals were found within chromite crystals and, to a lesser extent, in fractures and in the serpentinized silicate matrix. Grains show variable morphology; most of those in chromite are euhedral, but they are partially corroded to anhedral when found in fractures and in the serpentinized silicate matrix. Grains can be single crystals or form composite aggregates. As a general rule, grain size is less than 10  $\mu\text{m}$  but some larger grains, up to 60  $\mu\text{m}$  across, were also recognized.

PGE-sulfides include laurite ( $\text{RuS}_2$ ), cuproiridisite ( $\text{CuPt}_2\text{S}_4$ ), ruthenian-rich pentlandite [ $\text{Ru}(\text{NiFe})_8\text{S}_8$ ] and a mineral with a composition close to a monosulfide solid solution (mss) rich in PGE ( $\text{IrNiCuFeRhPtS}$ ). In contrast, BMS are mainly millerite, heazlewoodite and pentlandite with minor amounts of chalcopyrite, bornite, chalcocite and pyrite. Other minerals accompanying the sulfides are PGE and/or BM alloys [ $\text{Ru-Os-Ir-(Pt-Rh)}$  alloys and awaruite ( $\text{Ni}_3\text{Fe}$ )], irarsite ( $\text{IrAsS}$ ) and native Cu.

Single isolated grains within chromite are mainly euhedral laurite, millerite and, more rarely, heazlewoodite, pentlandite, bornite and Ru-Os-Ir alloys. Composite inclusions consist of various PGM or BMS alone or, more commonly, of PGM with BMS. PGM aggregates always contain a large laurite grain, with which may be associated either one of the Ir-Rh-Pt-(Ni-Fe-Cu)-sulfides or, much less frequently, Ru-Os-Ir alloys or irarsite. BMS inclusions consist of two-phase aggregates of millerite with chalcopyrite or bornite, or three-phase aggregates of pentlandite and chalcopyrite with bornite or millerite. Assemblages consisting of PGM and BMS include: 1) two-phase grains of laurite and chalcocite; 2) PGE-rich mss with pentlandite, millerite, bornite or chalcopyrite; and 3) Ru-Os-Ir-(Pt-Rh) alloys as blebs or lath-shaped inclusions in pentlandite or chalcopyrite. It is remarkable that laurite grains (some of them showing variable patterns of zoning) host subhedral to anhedral, drop-like inclusions of BMS (mainly millerite, chalcocite and pentlandite). Commonly, these inclusions align along crystal growth faces of laurite grains (González-Jiménez et al. 2009a).

Grains in fractures and in the silicate matrix are similar to those described in chromite. However, some characteristic distinctive features are the presence of large pentlandite grains replaced by heazlewoodite (in some grains the replacement contact is marked by the presence of Ir-Pt alloy spherules less than 1  $\mu\text{m}$  in diameter). Awaruite crystals with spongy textures replace pentlandite and native Cu as a by-product of alteration of Cu-Fe sulfides.

## 4 DISCUSSION

The predominantly euhedral shapes of the sulfides and their associated minerals in chromite suggest their crystallization from melts before or coeval with chromite (e.g., Stockman and Hlava 1984; Augé 1985; Melcher et al. 1997; Gervilla et al. 2005; González-Jiménez et al. 2009a,b). In contrast, the corroded outlines and/or anhedral morphology of grains located in open fractures or in the serpentinized silicate matrix indicate that they were primary grains that interacted with fluids related with serpentinization (Stockman and Hlava 1984; Thalhhammer et al. 1990; Garuti and Zaccarini 1997; González-Jiménez et al. 2009b).

Early-crystallized laurite indicates sulfide undersaturation in the parental melt at high temperature (Brenan and Andrews 2001). However, the presence of BMS as inclusions in some of these grains (frequently zoned), suggests that an immiscible sulfide melt segregated contemporaneously with growing laurite when  $fS_2$  fluctuated in the melt (González-Jiménez et al. 2009a). Moreover, the Ir-Rh-Pt-(Ni-Fe-Cu)-sulfides such as cuproiridisite, and the PGE-rich mss often coexisting with laurite, may be interpreted as crystallized from the segregated PGE- and BM-rich sulfide melt. The formation of PGE-free BMS can be interpreted as recording PGE-poor BM-rich sulfide melts generated at lower temperature. Upon cooling (below 500°C), and as a consequence of the low solubility of PGE in BMS (Makovicky et al. 1986), these noble metals were expelled from the BMS. The released PGE clustered, forming the PGE alloys now found as inclusions or laths at the margins of the BMS. Likewise, some re-mobilization of PGEs initially dissolved in BMS (mainly Ir and Pt) also took place when the primary sulfide mineralogy equilibrated with serpentinization related fluids (e.g., Garuti and Zaccarini 1997).

Estimations by Proenza et al. (1999) and Gervilla et al. (2005) suggest that the podiform chromitite of the Caridad deposit precipitated in equilibrium with PGE-rich boninitic-type basaltic melts, which typically are S-undersaturated (Hamlyn et al. 1985). This is consistent with sulfur saturation being reached as a result of “instantaneous” increases of  $fS_2$ . These changes in the physico-chemical properties of the melt can be accounted for by a mechanism of chromite crystallization during turbulent mixing/mingling of variably-differentiated basaltic melts in open conduits in the upper mantle (Gervilla et al. 2005; González-Jiménez et al. 2009a). As S solubility in mafic-ultramafic melts mainly depends on removal of FeO, a complete subtraction of FeO could be reached by crystallization of chromite in the hybrid melt (Ballhaus 1998). This will allow the segregation (as small droplets) of small volumes of immiscible sulfide melts.

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