

## **The origin of different types of magmatic mineralizations from small-volume melts in the lherzolite massifs of the Serranía de Ronda (Málaga, Spain).**

### **Origen de los diferentes tipos de mineralizaciones magmáticas a partir de pequeños volúmenes de fundido en los macizos lherzolíticos de la Serranía de Ronda (Málaga, España).**

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**Abstract:** The ultramafic massifs of the Serranía de Ronda are portions of an old (Proterozoic), subcontinental lithospheric mantle that suffered partial melting and infiltration of asthenospheric melts, just before their tectonic emplacement in the continental crust, probably during the early Miocene. This resulted in the development of a recrystallization front that separates the rests of the ancient protolith, called the spinel tectonite domain (located above the front) from the underlying granular peridotites which re-equilibrated with the partial melts and infiltrated melts. The crustal emplacement of the massifs is recorded by the development of the plagioclase tectonites, mainly superimposed on the granular domain.

The peridotite massifs contain three types of mineralizations spatially distributed according to the zoning of the massifs: 1) veins composed of chromite and Ni arsenides (Cr-Ni ores) associated with orthopyroxenites and cordierite rocks. These ores are rich in noble metals (up to 1.79 ppm PGE and 15 ppm Au) and are mainly located above the recrystallization front. 2) Irregular bodies of sulfides (pyrrhotite, pentlandite, chalcopyrite and cubanite) containing chromite and graphite (S-G ores) in fracture and fault zones. These ores are poor in noble metals (contain 218-800 ppb PGE and 13-230 ppb Au) and occur above the recrystallization front. 3) Chromitites (Cr ores) that form podiform bodies, lenses, entwined veins or schlierens associated with clinopyroxenites, orthopyroxenites or dunites. These ores contain variable noble metals contents (up to 9 ppb Au and 2 ppm PGE with a high (Os+Ir+Ru)/PGE ratio) and always occur in layered, refractory peridotites within the plagioclase tectonite domain.

The different types of mineralizations formed from residual magmatic liquids, rich in As, S, noble metals and volatiles, generated by the fractionation of small-volume melts that migrated above the recrystallization front. The early segregation of immiscible arsenide liquids (collecting most noble metals) coeval with the crystallization of Al-rich chromite gave rise to the formation of Cr-Ni ores. The S saturation in the residual liquids led to the segregation of noble metals-depleted sulfide melts (locally containing droplets of the earlier immiscible arsenide melts) which formed the S-G ores. As the peridotite bodies cooled, the small-volume melt mass decreases and the composition of the melts

became richer in Cr and Mg, and poorer in S, As and chalcophile elements. These were the parental melts of Cr-Ni ores located at and below the recrystallization front. The latest melts were restricted to dunitite bodies where they reacted with the host rocks forming chromitites, just before or during the crustal emplacement of the massifs.

**Key words:** Chromite - Ni arsenide ores, Ni-Cu sulfide ores, chromite ores, lherzolite massifs.

**Resumen:** Los macizos ultramáficos de la Serranía de Ronda constituyen porciones de un antiguo (Proterozoico) manto litosférico subcontinental que sufrieron procesos de fusión parcial y de infiltración de fundidos astenosféricos justo antes de su emplazamiento tectónico en la corteza continental, probablemente durante el Mioceno Inferior. Estos procesos dieron lugar, como resultado, al desarrollo de un frente de recrystalización que separa los restos del protolito antiguo, llamado dominio de tectonitas con espinela (localizado por encima del frente), de las peridotitas granulares subyacentes, las cuales se reequilibraron (y aumentaron de tamaño de grano) con los fundidos parciales generados y con los de procedencia astenosférica. El emplazamiento cortical de los macizos ha quedado registrado en las tectonitas con plagioclasa, cuya fábrica oblitera la textura magmática de las peridotitas granulares.

Los macizos de peridotitas contienen tres tipos de mineralizaciones distribuidas espacialmente de acuerdo con la zonalidad de los macizos: 1) filones compuestos por cromita y arseniuros de Ni (mineralizaciones tipo Cr-Ni) asociados a ortopiroxenitas y cordierititas. Estas mineralizaciones son ricas en metales nobles (hasta 1,79 ppm de EGP y 15 ppm de Au) y se localizan, principalmente, por encima del frente de recrystalización. 2) Cuerpos irregulares de sulfuros (pirrotina, pentlandita, calcopirita y cubanita) con cromita y grafito (mineralizaciones tipo S-G), encajados en zonas de fractura o falla. Estas mineralizaciones son pobres en metales nobles (contienen 218-800 ppb de EGP y 13-230 ppb de Au) y se localizan por encima del frente de recrystalización. 3) Cuerpos de cromititas (mineralizaciones tipo Cr) con diversas morfologías (podiformes, lenticulares, schlierens o filoncillos entrelazados), asociados a clinopiroxenitas, ortopiroxenitas y/o dunitas. Estas mineralizaciones muestran contenidos variables en metales nobles (hasta 9 ppb de Au y 2 ppm de EGP con elevadas relaciones (Os+Ir+Ru)/EGP) y siempre encajan en peridotitas bandeadas refractarias dentro del dominio de tectonitas con plagioclasa.

Los diferentes tipos de mineralizaciones se formaron a partir de líquidos magmáticos residuales, ricos en As, S, metales nobles y volátiles, generados por la fraccionación de pequeños volúmenes de fundido que migraron por encima del frente de recrystalización. La segregación temprana de los líquidos arseniurados inmiscibles (concentrando la mayor parte de los metales nobles), junto con la cristalización de cromita rica en Al, dio lugar a la formación de las mineralizaciones tipo Cr-Ni. La saturación en S de los líquidos residuales condujo a la segregación de líquidos sulfurados empobrecidos en metales nobles (localmente contienen gotas de los líquidos arseniurados más anteriores), los cuales formaron las mineralizaciones tipo S-G. Conforme los cuerpos de peridotitas se enfriaron, la masa de los pequeños volúmenes de fundido descendió y la composición de los fundidos se hizo más rica en Cr y Mg y se empobreció en S, As y, de una forma general, en elementos calcófilos. Estos constituyeron los fundidos parentales de las mineralizaciones tipo Cr-Ni localizadas en y por debajo del frente de recrystalización. Los últimos fundidos quedaron restringidos a los cuerpos de dunitas donde reaccionaron con las rocas encajantes, formando cromititas, justo antes, o durante, el emplazamiento crustal de los macizos.

**Palabras clave:** Mineralizaciones de cromita-arseniuros de Ni, mineralizaciones de sulfuros de Ni-Cu, mineralizaciones de cromita, macizos lherzólíticos.

## Introduction

From a metallogenic point of view, the orogenic lherzolite massifs of the Serranía de Ronda in south Spain, and the Beni Bousera massif in north Morocco, are characterized, by the occurrence of different types of

magmatic Cr, Ni, Cu and PGE mineralizations (Oen, 1973; Oen et al., 1979; Gervilla et al., 1988; Gervilla, 1990; Gervilla and Leblanc, 1990; Gervilla et al., 1996; Gutiérrez-Narbona, 1999). Most of them were explored or mined in the past but, to day are not of economic interest. Gervilla (1990) and Gervilla and

Leblanc (1990) distinguish three main types of mineralizations spatially distributed according to the zoning of the peridotite massifs (Fig. 1): Chromite-Ni arsenide ores (Cr-Ni type), Fe-Ni-Cu sulfide-graphite ores (S-G type) and chromite ores (Cr type). Gervilla (1990) and Gervilla and Leblanc (1990) clearly show the magmatic nature of the different ores studied. Their genetic interpretation consider that the different types of mineralizations formed by the fractionation of melts that migrated from the core to the rim of a rising diapir. This model assumed the ideas of Obata (1980), Frey et al. (1985) and Suen and Frey (1987) who considered the Ronda peridotite as a portion of a mantle diapir, formerly made up of garnet lherzolites, that melted around 30 kb with a higher fusion rate in the core than at the rim of the diapir (Frey et al., 1985) and equilibrated at 20 to 25 kb and 1,100 to 1,200°C (the "primary conditions" of Obata, 1980). Nevertheless, the pressure conditions estimated for the formation of the different magmatic ores (10 kb) are not in agreement with those assumed for the crystallization of the melts generated in the above partial melting event in the form of mafic layers (>20 kb; Suen and Frey, 1987), nor with the subsolidus evolution of the peridotite body during its adiabatic upwelling from the "primary conditions" (Obata, 1980). These inconsistencies were already noted by Gervilla and Leblanc (1990) who claimed for a more recent partial melting event at moderate to low pressure conditions, as the source of the parental melts of the mineralizations.

The aim of this paper is to review the mineralogical and chemical features of the mineralizations (they have been mostly published since 1988), in order to built up a new genetic model, consistent with the zoning pattern proposed by Van der Wal and Vissers (1993) and based on: 1) the fractionation of small-volume melts segregated from the melts generated during the low pressure, partial melting and melt percolation event

documented by Van der Wal and Bodinier (1996), Garrido and Bodinier (1999) and Lenoir et al. (2001); 2) the fast upwelling of the peridotite bodies (0.4 cm/year; Platt et al., 1998) just before their tectonic emplacement in the continental crust; 3) the existence of arsenide liquids which segregated earlier than sulfide liquids from the parental silicate melts (see. Merkle, 1992) and which were immiscible from both the silicate and sulfide liquids (Gervilla et al., 1996); 4) the high affinity of nickel and noble metals (platinum-group elements - PGE- and gold) for arsenide liquids together with the high capacity of nickel arsenides to dissolve PGE (Gervilla et al., 1994), and 5) the formation of chromitite by the replacement of the host peridotite and pyroxenite by highly fractionated silicate melts under relatively oxidizing conditions (Gutiérrez-Narbona, 1999).

#### **The ultramafic massifs of the Serranía de Ronda**

The ultramafic massifs of the Serranía de Ronda crop out in the westernmost part of the Internal Zones of the alpine Betic Chain (Fig. 1) and represent portions of the subcontinental lithospheric mantle emplaced tectonically in the crust during the early Miocene (Zindler et al., 1983; Zeck, et al., 1989; Monié et al., 1994; Platt et al. 1998). The ultramafic rocks occur sandwiched between an upper, thick (up to 7 km) metapelitic sequence made up (from the contact with the peridotite upward) of acid granulites (kinzigites), gneisses and migmatites, schists, phyllites and, locally, marbles (Loomis, 1972; Torres-Roldán, 1981; Tubía, 1985), and a lower carbonate-rich metasedimentary unit which contain relatively abundant amphibolite bodies (Mollat, 1968; Tubía, 1985).

The peridotite massifs mainly consist of lherzolites and harzburgites with minor dunites and pyroxenite layers (mafic layers). According to Obata (1980), the Ronda massif

exhibits an incomplete mineral facies zoning from the upper contact inward: there is a zone of garnet-lherzolite facies, followed by zones of Arieigite subfacies of the spinel-lherzolite facies, Seiland subfacies of the spinel-lherzolite facies and plagioclase-lherzolite facies. This pattern of zoning was also recognized in the Ojén (Gervilla, 1990; Targuisti, 1994) and Carratraca (Soto and Gervilla, 1991) massifs, and was interpreted in terms of progressive subsolidus re-

equilibration of a mantle diapir during its adiabatic upwelling from around 80 km deep (Obata, 1980). Nevertheless, recent structural, petrological and geochemical data (Van der Wal and Vissers, 1993, 1996; Gervilla and Remaïdi, 1993; Remaïdi, 1993; Van der Wal and Bodinier, 1996; Garrido and Bodinier, 1999 and Lenoir et al., 2001) have led to a new interpretation that consider the Ronda massif as a portion of a 1.3 Ga old (Reisberg and Lorand, 1995), subcontinental lithospheric

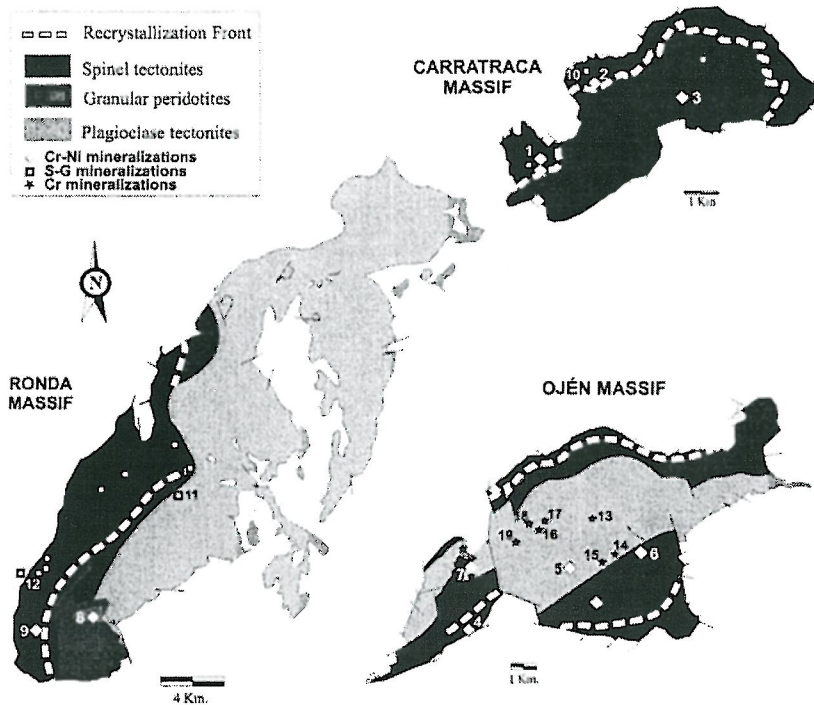


Fig. 1: Zoning of the ultramafic massifs of the Serranía de Ronda and distribution of the studied mineralizations. 1: Los Jarales district; 2: San Agustín; 3: El Sapo; 4: La Gallega; 5: El Lentisco; 6: El Nebral; 7: Mina Baeza; 8: Arroyo de la Cala; 9: Majada Redonda; 10: El Gallego; 11: Mina Marbella; 12: Arroyo de la Cueva; 13: Cerro del Águila (CDA); 14: Pista (Pis); 15: Cañada del Lentisco (L); 16: Arroyo de los Caballos (CAB); 17: Arroyo de los Caballos (ARC); 18: Arroyo de los Caballos (ACA); 19: Cantera de dunitas (CD).

Fig. 1: Zonación de los macizos ultramáficos de la Serranía de Ronda y distribución de las mineralizaciones estudiadas. 1: Distrito de Los Jarales; 2: San Agustín; 3: El Sapo; 4: La Gallega; 5: El Lentisco; 6: El Nebral; 7: Mina Baeza; 8: Arroyo de la Cala; 9: Majada Redonda; 10: El Gallego; 11: Mina Marbella; 12: Arroyo de la Cueva; 13: Cerro del Águila (CDA); 14: Pista (Pis); 15: Cañada del Lentisco (L); 16: Arroyo de los Caballos (CAB); 17: Arroyo de los Caballos (ARC); 18: Arroyo de los Caballos (ACA); 19: Cantera de dunitas (CD).

mantle, thermally and chemically eroded just before its crustal emplacement. This new interpretation is based on the presence of a recrystallization front [corresponds to the transition between Ariegite and Seiland subfacies of spinel-lherzolite facies in Obata's (1980) pattern of zoning] which separates an upper spinel tectonite domain, representing the ancient proterozoic, subcontinental mantle protolith (Van der Wal and Bodinier, 1996; Garrido and Bodinier, 1999), from the lower granular domain which develops at expenses of the preexisting spinel tectonites by upward, prograding partial melting (Lenoir et al., 2001) (Fig. 1). Partial melts extracted from the granular peridotites cooled when crossed the recrystallization front due to the existence of smooth thermal gradient along the front (from 1200°C downward; Lenoir et al., 2001). Under these conditions, partial melts reacted with the host peridotite, forming clinopyroxene+spinel at expenses of orthopyroxene (or olivine), and segregating residual, volatile-rich small-volume melts that infiltrated the upper spinel tectonites (Van der Wal and Bodinier, 1996). According to the latter authors, below the recrystallization front, the granular domain can be subdivided into three subdomains from the recrystallization front downward (towards the south and east): 1) the coarse-granular subdomain, mainly composed of coarse-grained, olivine-rich lherzolites and harzburgites; 2) the fine-granular subdomain, characterized by the presence of strongly corroded orthopyroxene, and secondary clinopyroxene and spinel which produced re-fertilized lherzolites, and 3) the layered-granular subdomain, characterized by symmetrically zoned bodies of olivine-rich lherzolites, grading to harzburgites and dunites (all containing, locally, secondary clinopyroxene and spinel) in their center, and alternating with fertile plagioclase lherzolites. Whereas in the coarse-granular peridotites melt/rock interaction mainly led to the coarsening of the constituent minerals (Van der Wal and Bodinier, 1996; Lenoir et al., 2001; Vauchez

and Garrido, 2001), downward from the recrystallization front (in the fine-granular and layered-granular subdomains), melt/rock reactions gave rise to pyroxene dissolution and olivine crystallization at increasing melt mass, followed by the partial dissolution of olivine and the crystallization of secondary clinopyroxene and spinel, at decreasing melt mass and temperature (Van der Wal and Bodinier, 1996). The plagioclase-tectonite domain superimposed to the preexisting subdomains by the development of a shear deformation that overprinted most of the magmatic features described. This deformation generated along discrete shear zones related with the tectonic emplacement of the peridotite massifs in the continental crust.

The melts generated during the partial melting and melt/rock reactions described, also modified the composition and distribution of the mafic layers (Garrido and Bodinier, 1999). Thus, in the spinel tectonite domain most mafic layers conserve their ancient garnet-bearing mineral assemblages (some of them also contain corundum and sapphirine; Morishita *et al.*, 2001) and their major and trace elements composition (type A of Garrido and Bodinier, 1999). However, some small-volume melts migrating above the recrystallization front were trapped in cracks, crystallizing in the form of discordant dykes of chromium-rich websterites. Mafic layers located along the recrystallization front reacted with percolating melts at increasing melt mass, giving rise to spinel websterites and rare spinel-garnet websterites (type B of Garrido and Bodinier, 1999). Similarly, in the granular domain, partial melts and melts infiltrated from the asthenospheric mantle reacted with the preexisting, garnet-bearing pyroxenites, forming chromium-rich websterites, clinopyroxenites and orthopyroxenites (type D of Garrido and Bodinier, 1999) and locally, accumulated and reacted with the host peridotite, forming Ti-rich spinel pyroxenites (Type C of Garrido and Bodinier, 1999). The

latter often reacted with late, residual melts at decreasing melt mass and temperature and were replaced by chromium-rich, type D pyroxenites.

## Mineralizations

### *Chromite-Ni arsenide ores*

These ores are made up of chromite and nickel arsenides associated to orthopyroxene or cordierite, or both, and represent a rather unique example of magmatic ores in mantle rocks. In the different localities, the ores occurs as veins or layers discordant to the foliation of the host peridotites, always showing sharp contacts. Their lateral extend varies from 15 to 50 m, but locally they can reach up to 100 m. Their thickness is variable too, ranging between 5 and 70 cm. The orebodies consist of banded ores comprising layers of massive chromite and nickel arsenides alternating with layers of pyroxenite or cordierite rocks (>90% cordierite).

Unaltered massive ore layers consist of chromite crystals (60-98 vol.%) with intergranular nickel arsenides [mainly nickeline (NiAs) but also nickeliferous löllingite ((Fe,Ni,Co)As<sub>2</sub>)] and, locally (in the nickel arsenide-rich ores), minor ilmenite and rutile. Chromite grain size varies from 0.005 to 0.6 mm and its crystal habit is a function of the modal proportion of nickel arsenides. In nickel arsenide-poor ores (<10 vol.% Ni arsenides) chromite grains develops a polygonal pattern having nickeline as blebs located in the triple joints. In contrast, in nickel arsenide-rich ores (20-40 vol.% Ni arsenides) chromite grains tend to be euhedral to rounded or show dissolved grain boundaries within a nickeline (>90 vol.%) matrix. This nickeline is associated with nickeliferous löllingite and often shows rounded, irregular or lamella-like exsolutions [following the (0001) planes of the host nickeline] of pyrrhotite, pentlandite, chalcopyrite, cubanite and, rarely, native gold,

undefined Au-Ag-Cu compounds and undetermined Au-Cu-Bi, Bi and BiPb tellurides. Chromite grains also show variable single to poly-phased, rounded inclusions consisting of orthopyroxene, phlogopite, wonesite, magnesian chlorite, quartz, nickeline, nickeliferous löllingite, pararammelsbergite (NiAs<sub>2</sub>), pyrite, pyrrhotite and chalcopyrite, as well as lamella-like exsolutions of ilmenite or rutile. Orebodies affected by late tectonic deformation (and fracturing) or hydrothermal alteration show an arsenide assemblage characterized by the partial replacement of nickeline for maucherite [Ni<sub>11</sub>As<sub>8</sub>, locally associated to westerveldite ((Fe,Ni,Co)As)], by a decrease of the modal proportions of nickeliferous löllingite and by the crystallization of Fe- and Co-rich gersdorffite [(Ni,Fe,Co)AsS] (Gervilla et al., 1990, 1993; Gervilla and Rønsbo, 1992).

Massive ore layers grade to the alternating orthopyroxenite and cordierite rocks, developing disseminated chromite-Ni arsenide ores with orthocumulate textures (disperse subidiomorphic silicate crystals in a chromite-Ni arsenide matrix) that evolve to adcumulate textures formed by large (1-10 mm), subidiomorphic crystals of orthopyroxene or cordierite with intercumulus chromite and nickeline. The latter ore minerals are often abundant at the borders of the cumulus silicates. Orthopyroxenite exhibits pnematoblastic texture with elongated prismatic crystals and small polygonal neoblasts. Similarly, cordierite rocks are formed by ganoblastic aggregates of large cordierite crystals (0.5-1 cm) that grade to fine-grained (< 1mm), polygonally-textured rocks. In the occurrences located above the recrystallization front, where Cr-Ni ores coexist with orthopyroxenite and cordierite rocks, there are intermediate silicate assemblages consisting of prismatic orthopyroxene crystals within a polygonally-textured cordierite matrix.

Cr-Ni ores are rich in gold (up to 15 ppm Au) and show platinum-group element (PGE) abundances (up to 1 ppm Pt+Pd) that approach

the C1 chondritic values (Leblanc et al., 1990). Nevertheless these noble metals contents are very variable as they depend on the modal proportions of nickel arsenides in the ore. The PGE- and Au-poorest ores, those from the northern vein of Mina Baeza (Ojén massif)<sup>1</sup>, contain 304 ppb PGE and 48 ppb Au (Fig. 2). In contrast, the Cr-Ni ores from the San Juan mine in Los Jarales district (Carratraca massif), the richest in nickel arsenides (30 vol.% on average) contain up to 1.79 ppm PGE and 15 ppm Au. The Cr-Ni ores described in the Beni Bousera massif are even richer in noble metals (containing up to 3 ppm Pt+Pd and 18 ppm Au), as they show higher molar proportions of nickel arsenides (up to 50 vol.%) (Leblanc et al., 1990). In spite of the high, whole-rock PGE abundances, Cr-Ni ores are devoid of platinum-group minerals (PGM) (Leblanc et al., 1990) since PGE are hidden in solid solution in the nickel arsenides (Gervilla et al., 1994, 2000). Recent micro-pixe results have detected variable Ru contents in nickeline (up to 4 ppm) and in nickeliferous löllingite (up to 19 ppm), as well as Pd in nickeline (up to 7 ppm), in nickeliferous löllingite (up to 30 ppm) and, mainly, in maucherite (up to 64 ppm) (Gervilla et al., 2000). Although micro-pixe analysis of Pt on nickel arsenides is affected by important errors due to strong interference with Bi, the

obtained results seems to indicate that this element tend to concentrate in nickeliferous löllingite and gersdorffite.

The mineralogy, the mineral chemistry and, as a consequence, the bulk chemical composition of the Cr-Ni mineralizations vary according to the spatial distribution of the different occurrences in the mantle section (Fig. 1). Thus, those located well above the recrystallization front (e.g. Mina La Gallega, which occur in the uppermost garnet lherzolites of the Ojén massif) are characterized by a mineral assemblage made up of Al-, Fe-, V- and Zn-rich chromite (up to 40%  $\text{Al}_2\text{O}_3$ , 31% FeO, 2.6%  $\text{V}_2\text{O}_5$  and 1% ZnO) (Fig. 3) and nickel arsenides (up to 30 vol. %), with minor ilmenite, rutile and base-metal sulfides. These ores are associated with orthopyroxenite containing Al-rich bronzite ( $\text{En}_{75-69}$  with 3.0-4.49 wt.%  $\text{Al}_2\text{O}_3$ ) or cordierite rocks (formed by magnesian cordierite), or both (Gervilla and Leblanc, 1990). In contrast, the mineral assemblage of Cr-Ni ores located below the recrystallization front contains chromite progressively impoverished in Al, Fe, V and Zn (enriched in Cr and Mg) as the occurrence is located farther from the front (e.g. in Mina Baeza, which is located in plagioclase tectonites,  $\text{Al}_2\text{O}_3$ , FeO,  $\text{V}_2\text{O}_5$  and ZnO contents of chromite are as low as 16 wt.%, 14 wt.%, 0.13 wt.% and 0 wt.%, respectively) (Fig. 3). These chemical variations in chromite correlate positively with a strong decrease in the modal proportions of nickel arsenides (down to 2 vol.%) and, consequently, in the bulk noble metals (PGE and Au) contents (Fig. 2). The chemical composition of the associated orthopyroxene also changes toward Fe- and Al- poor compositions (e.g. in Mina Baeza the orthopyroxene is  $\text{En}_{95}$  with 1.25 wt.%  $\text{Al}_2\text{O}_3$ ) (Gervilla and Leblanc, 1990). These ores do not contain Ti oxides nor occur associated to cordierite.

#### *Fe-Ni-Cu sulfides-graphite ores*

These mineralizations occur as veins, irregular masses of massive to disseminated ores

<sup>1</sup> The northern vein of Mina Baeza and the ores located in the Arroyo de la Cala in the Ronda massif, were ascribed to the Cr type by Gervilla (1990) and Gervilla and Leblanc (1990). However, their textural relations with the associated orthopyroxenites, the abundance of interstitial nickel arsenides and the mineralogical and chemical features of most Cr-type occurrences (now well characterized by Gutiérrez-Narbona, 1999) suggest a more proper ascription of these occurrences to the Cr-Ni type. We consider that both occurrences are intermediate between Cr-Ni and Cr types and represent transitional examples. In fact, in Mina Baeza district coexist a chromite vein containing at least 2 vol.% nickel arsenides, associated to orthopyroxenite (the northern occurrence) and disseminated, small (centimeter-thick), entwined chromite veins in dunite (the southern occurrence) showing most features of Cr-type ores.

and stockworks, always associated to late fault zones within the spinel-tectonite domain (above the recrystallization front) or in the coarse-granular subdomain (Fig. 1). Frequently they contain xenoliths of the host rocks (peridotites and pyroxenites) and, rarely, exhibit brecciated textures. The contact between S-G-type orebodies and their wall-rock is either sharp or is traced along a variably-thick (tens of centimeter), hydrothermally-altered zone. The latter is observed only in the different occurrences of the Arroyo de la Cueva area where the hydrothermal aureole consist of serpentine, talc and chlorite (Hem, 1998; Hem et al., 2001). The size of S-G-type orebodies is

very variable too. It ranges between centimeter-scale, narrow veins to irregular masses tens of meters long and few meters thick. It is possible that some old exploited deposits (e.g. Mina Marbella) were larger considering the abundance and size of the works.

In most occurrences these ores are strongly altered and consist of earthy masses of Fe oxides and hydroxides containing spheroidal to lenticular bodies of graphite (these contain disperse chromite grains which show corrosion structures). Nevertheless, the primary mineral assemblage is preserved in some occurrences where it is made up of Fe-Ni-Cu sulfides (pyrrhotite, pentlandite, chalcopyrite

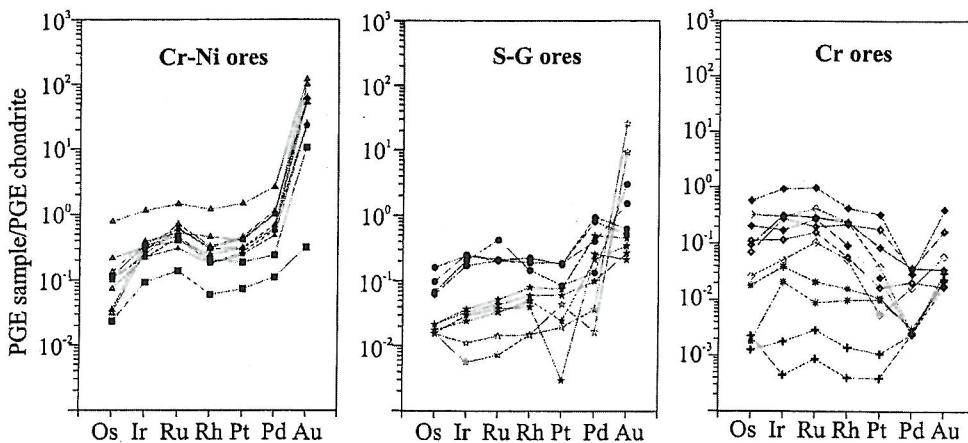


Fig. 2: C1 chondrite-normalized PGE patterns of representative studied samples from the different types of mineralizations. Cr-Ni ores: Thick-open triangles: samples from occurrences located above the recrystallization front; black squares: samples from Arroyo de la Cala and Mina Baeza, located below the recrystallization front. S-G ores: Black circles: samples from transitional S-G ores containing arsenide globules; black stars: samples from occurrences without arsenide globules; open stars: samples from the Arroyo de la Cueva. Cr ores: Black diamonds: samples from CAB, Thick-open diamonds: samples from CDA; open diamonds: samples from ACA and ARC; cross-star: samples from L; crosses: samples from CD. Fig. 2: Espectros de los EGP normalizados a los valores de las condritas C1, representativos de las muestras estudiadas de los diferentes tipos de mineralizaciones. Mineralizaciones tipo Cr-Ni: Triángulos gruesos vacíos: muestras de indicios localizados por encima del frente de recrystalización; cuadrados negros: muestras del Arroyo de la Cala y Mina Baeza, localizados por debajo del frente de recrystalización. Mineralizaciones tipo S-G: Círculos negros: muestras de mineralizaciones tipo S-G transicionales que contienen glóbulos de arseniuros; estrellas negras: muestras de indicios sin glóbulos de arseniuros; estrellas vacías: muestras del área del Arroyo de la Cueva. Mineralizaciones tipo Cr: Rombos negros: muestras de CAB, rombos gruesos vacíos: muestras de CDA; rombos vacíos: muestras de ACA y ARC; cruces+estrellas: muestras de L; cruces: muestras de CD.



and cubanite) with minor amounts of nickel arsenides (nickeline and maucherite), westerveldite, löllingite ( $\text{FeAs}_2$ ), cobaltite (cubic  $\text{CoAsS}$ ), alloclasite (orthorhombic  $\text{CoAsS}$ ), rutile, ilmenite, magnetite, pyrite, molybdenite and/or sphalerite, as well as rare tellurides [melonite ( $\text{NiTe}_2$ ), altaite ( $\text{PbTe}$ )...]. The associated silicates are, mainly, phlogopite, pyroxenes and plagioclase.

Pyrrhotite is the most abundant sulfide and frequently shows rectilinear grain boundaries and triple joints developing a

mosaic texture. Nevertheless these recrystallized grains, often show folded cleavage (0001) planes that records a previous deformation history. Pyrrhotite also contains flame-like exsolutions of pentlandite and, in most samples, is partly altered to Fe oxides and hydroxides along cleavage planes. Most pentlandite occurs as intergranular aggregates variably altered to violarite. Chalcopyrite and, less frequently, cubanite occur filling intergranular spaces and fractures. When associated, the latter minerals form lamellar

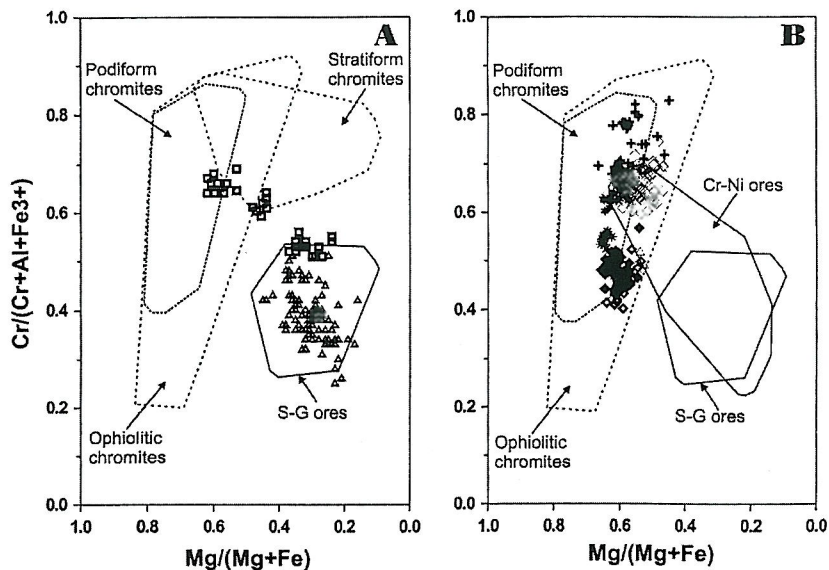


Fig. 3: Composition of chromite from different occurrences compared with the composition of chromite from ophiolitic and stratiform complexes. A: Thick-open triangles: cromite from Cr-Ni ores located above the recrystallization front; thick-open squares: chromite from Cr-Ni ores located below the recrystallization front (Note that the compositional field of chromite from S-G ores overlap that of the Cr-Ni occurrences located above the recrystallization front). B: Composition of chromite from Cr ores. Symbols as in figure 2 and, in addition: open triangles: samples from the southern occurrence of Mina Baeza; thick-stars: samples from La Pista.

Fig. 3: Composición de la cromita de diferentes indicios comparada con la composición de la cromita de complejos ofiolíticos y estratiformes. A: Triángulos gruesos abiertos: cromita de las mineralizaciones tipo Cr-Ni localizadas por encima del frente de recrystalización; cuadrados gruesos abiertos: Cromita de las mineralizaciones de Cr-Ni localizadas por debajo del frente de recrystalización (se observa como el campo composicional de la cromita de las mineralizaciones tipo S-G se solapa con el de las cromitas de las mineralizaciones tipo Cr-Ni localizadas por encima del frente de recrystalización). B: Composición de la cromita de las mineralizaciones tipo Cr. Símbolos como en la figura 2 y, además: triángulos abiertos: muestras del indicio sur de Mina Baeza; estrellas gruesas: muestras de La Pista.

intergrowths parallel to the (111) planes of chalcopyrite. Graphite distribution and texture depend on the alteration degree of the ore. Thus, in strongly altered mineralizations graphite forms centimeter-sized, nodular aggregates or lenticular bodies with variable lateral extent (from tens of centimeter to tens of meters), included in limonitic masses which rarely preserve evidences of the pre-existing sulfides. In fresh sulfide masses, graphite occurs as disseminated tabular crystals with an average size of 0.4 to 0.04 mm (often included in chromite) or forming millimeter-size nodular aggregates. Proportion of chromite in sulfide ores is very variable. Although in some deposits it can reach 20 vol.%, in the Cu sulfide-rich ores of the Arroyo de la Cueva area it is absent. These proportions also vary within single sulfide bodies where it is possible to observe polygonally-textured chromite aggregates containing as low as 30 vol.% intergranular sulfides that evolve laterally to a dissemination of small (0.2 mm on average) chromite grains in sulfides. The latter grains exhibit rounded to irregular grain-shapes. In addition, irregular chromite crystals with clear corrosion structures, occur within plagioclase and phlogopite, and disseminated in the graphite-rich bodies of the altered part of the ore.

The S-G ores have one tenth of the noble metals content of the Cr-Ni ores (Fig. 2). They contain 218-800 ppb PGE and 13-230 ppb Au, excluding the hydrothermal, Cu sulfide-rich ores of the Arroyo de la Cueva area which have lower PGE (703 ppb) but much higher Au (2.61.2 ppm) contents (Leblanc et al., 1990). PGE occur both hidden in solid solution in nickel arsenides (up to 70 ppm Pd and 58 ppm Pt have been detected, respectively, by micro-PIXE, in nickeline and in maucherite; Gervilla et al., 2000) and forming rare, dispersed platinum-group minerals: kotulskite, froodite and palladian melonite.

As in the Cr-Ni ores, the mineralogical composition of the different S-G-type occurrences vary as a function of their spatial

distribution with respect the recrystallization front. These variations are defined by the decrease in the modal proportion of chromite and nickel arsenides (and, as a consequence, in the bulk PGE abundances) and by the increase in Cu sulfides and hydrous minerals with the distance to the recrystallization front. In addition, those orebodies located close to the recrystallization front show magmatic textures and not altered wall-rock peridotites whereas those located far away the front exhibit hydrothermal alteration in the wall rock. In fact, some occurrences (e.g. Los Pobres) located close to the recrystallization front, show mineralogical and chemical features which are transitional with those of Cr-Ni. In these occurrences, Fe-Ni-Cu sulfide ores contain different types of arsenide globules: 1) globules of nickeline, 2) globules of maucherite, 3) globules of nickeline surrounded by radially fractured maucherite with westerveldite aggregates along the fractures and, often, with a variably thick, discontinuous corona of Co- and Fe-rich gersdorffite, 4) globules of nickeliferous löllingite, maucherite, nickeline, pyrrhotite and native gold (Gervilla et al., 1996). These authors interpret the arsenide globules as droplets of immiscible arsenide melt trapped in the crystallizing sulfide melt. Chromite in these arsenide-rich S-G ores contain abundant composite silicate inclusions made up of quartz, albite and phlogopite which bulk composition resembles that of dioritic melts (Leblanc and Gervilla, 1995). On the other hand, the sulfide ores of the Arroyo de la Cueva, located far away from the recrystallization front, at the contact between the ultramafic rocks and the overlying acid granulites (at La Herrumbrosa Mine the sulfide ore is hosted by granulites; Fig. 1), do not contain chromite, are very rich in chalcopyrite and cubanite, and, as noted above, are rich in gold. In addition, they are poor in nickel as evidence the Fe- and Co-rich nature of the scarce arsenides (löllingite) and sulfarsenides

(alloy, cobaltite and arsenopyrite), and the Co-rich composition of pentlandite (Hem, 1998; Hem et al., 2001). In these occurrences, the orebodies exhibit hydrothermally-altered wall rocks mainly composed of serpentine, chlorite and talc.

#### *Chromite ores*

Chromite ores are always located in layered-granular peridotites within the plagioclase-tectonite domain (Fig. 1). Thus the primary magmatic textures are mostly obliterated by the deformation that generated the tectonite structure. The chromite bodies show morphological and chemical characteristics similar to those of the chromitites from the ophiolitic complexes although they are much smaller. They occur as podiform bodies, lenses, irregular and entwined veins or schlierens associated to clinopyroxenites or orthopyroxenites within variably-thick dunite bodies, or to dunites. The contact between chromitite and its host rock is either sharp or gradual, defined by a zone of disseminated ore. Most orebodies are elongated parallel to the foliation of the host lherzolites. Nevertheless some irregular veins cut such foliation and the contact between the host pyroxenite and the enveloping dunite. The lateral extent of the chromitite bodies varies between 1 and 5 meters and the thickness between <1 and 30 centimeters.

The most common texture of the chromitite is massive, with chromite grain size from 0.2 to 6 millimeters. Chromite grains contain abundant primary solid inclusions varying in size from one to hundred microns. They can be single or composite and consist of silicates, base-metal sulfides, nickel arsenides and sulfarsenides, alloys and platinum-group minerals (PGM). The abundance, size and mineralogy of the inclusions is variable, and partly depend on the lithology of the host rock and the nature of the minerals interstitial to chromite (Gutiérrez-Narbona, 1999); thus: 1) the most

abundant anhydrous silicate included in chromite is clinopyroxene (frequently associated to small, irregular orthopyroxene grains and scarce olivine) in the chromitite associated to clinopyroxenite of the Cerro del Aguila (CDA); 2) in the three occurrences located in the Arroyo de los Caballos (in CAB and, mainly, in ACA and ARC where chromitite replace and cut orthopyroxenite veins) the most abundant anhydrous silicate inclusion is orthopyroxene (up to 81% of the silicate inclusions in ACA); 3) clinopyroxene and olivine predominates in the anhydrous silicate assemblage included in chromite from the Cañada del Lentisco (L), where the host rock is strongly serpentized; 4) olivine is the most abundant anhydrous silicate included in chromite in the Cantera de Dunitas (CD), where the chromitite is only associated to dunite; 5) in the southern chromitite outcrop of Mina Baeza (MB, associated to dunite and scarce orthopyroxenite veins), chromite includes mainly olivine and scarce orthopyroxene; 6) chromite from the chromitite outcrop at La Pista (Pis) does not include anhydrous silicates because it is very fractured and altered. Most of these inclusions contain variable amounts of pargasite or brown mica, or both (hydrous silicates are more abundant than anhydrous ones) which are rich in fluorine and chlorine. The composition of brown mica varies from the phlogopite to the wonesite end-members (Torres-Ruiz et al., 1993; Garuti et al., 1994; Gutiérrez-Narbona, 1999).

Other minerals included in chromite are: pentlandite, millerite (NiS), parkerite  $[\text{Ni}_3(\text{Bi,Pb})_2\text{S}]$ , heazlewoodite  $(\text{Ni}_3\text{S}_2)$ , godlevskite  $[(\text{Ni,Fe})_7\text{S}_6]$ , chalcopyrite, maucherite, nickeline, orcelite  $(\text{Ni}_5\text{As}_2)$ , westerveldite and gersdorffite. These minerals usually occur associated with PGM (except in the CD occurrence where only few, tiny laurite and irarsite grains have been observed) and to hydrous silicates: pargasite and mica. The most abundant primary PGM are laurite  $(\text{RuS}_2)$ , rich in Os and Ir) and PGE sulfarsenides with

compositions intermediate between the irarsite (IrAsS), ruarsite (RuAsS), osarsite (OsAsS) and hollingworthite (RhAsS) end-members (Torres-Ruiz, 1996, Gutiérrez-Narbona, 1999). Other primary PGM described are sperrylite (PtAs<sub>2</sub>), malanite [Cu(Pt,Ir)<sub>2</sub>S<sub>4</sub>], Pt-Fe alloys, stibiopaladinite and some unknown (and undefined) phases: (Ni,Fe,Cu)<sub>2</sub>(Ir,Rh)S<sub>3</sub>, (Pt, Rh, Ir, Cu) sulfide, (Pd, Ni)As, PdS and PdBi (Torres-Ruiz, 1996, Garuti et al., 1995; Gervilla et al., 1999; Gutiérrez-Narbona, 1999). These primary PGM occur as single or composite assemblages mainly included in chromite far from fractures. Pull-apart fracturing of the chromite and serpentinization promoted the alteration of the primary parageneses giving rise to secondary, S- and As-poor assemblages containing pentlandite, millerite, heazlewoodite, parkerite, maucherite and/or, orcelite, as well as native Ru or Pt-Fe alloys. These phases occur in fractures or interstitial to the chromite grains (Torres-Ruiz et al. 1996; Gutiérrez-Narbona, 1999).

The chemical composition of chromite is very variable and, like the anhydrous silicate assemblage observed as inclusions in chromite, it broadly correlates with the nature of the host rock (Fig. 3). Thus, Cr<sub>2</sub>O<sub>3</sub> increases and, at lesser extent, TiO<sub>2</sub> decreases from chromitites associated to clinopyroxenites (e.g. CDA), to chromitites associated to orthopyroxenites (e.g. ACA and ARC) and to chromitites associated to dunites (CD). As a whole, the Cr# [Cr/(Cr+Al)] of chromite varies from 0.4 to 0.83 and TiO<sub>2</sub> proportions vary from 0.19 wt.% to 0.89 wt.%. In contrast, the Mg# [Mg/(Mg+Fe)] of chromite from different occurrences is very similar ranging from 0.46 to 0.66. The compositional field of these chromitites in the Cr# versus Mg# diagram partially overlap that of podiform chromitites from ophiolite complexes described in the literature. Nevertheless chromite from Cr ores of the Ojén Massif is richer in Fe.

Noble metals abundance in the different chromitite occurrences does not correlate with

the chemical composition of chromite (Fig. 2). Most chromitites show similar chondrite-normalized PGE patterns with a nearly flat, or convex-upward segment from Os to Rh (between 0.1 and 1 times the chondritic values), and a variable depletion in Pt and Pd. Lower PGE contents have been measured in the analyzed samples from L (around 0.01 times the chondritic values) and, mainly in those from CD where PGE values drop down to 0.001 times the chondritic values. These two chromite occurrences are the richer in modal Ni arsenides. Most analyzed samples show comparable Au contents (between 0.01 and 0.1 times the chondritic values) and Au/Pd ratio higher than unity.

#### Origin of the different ore types

According to Gervilla and Leblanc (1990) and Gervilla et al. (1996), Cr-Ni and S-G ores formed from mantle-derived, highly fractionated melts and can be genetically related assuming the segregation of two immiscible arsenide and sulfide melts from a preexisting As- and S-rich parental melt. The earlier As saturation of the parental melt (e.g. Merkle, 1992) collected most Ni and noble metals and concentrated them, along with chromite, in the Cr-Ni ores. The subsequent S saturation promoted the segregation of an immiscible, noble metals-poor sulfide melt that produced the S-G ores. This sulfide melt locally carried small amounts of immiscible arsenide melt which gave rise to the transitional S-G ores (e.g. Los Pobres). But, how this peculiar As-, S- and volatile-rich melt could be generated? This question can be answered by discussing a possible genetic model of the different types of mineralizations based on the fractionation of small-volume melts generated after melt/peridotite reactions at decreasing melt volume and temperature. These small volume melts were rich in volatiles and carried the most incompatible

elements (Al, Ti, As, S, PGE, C...), which were progressively concentrated in the residual, volatile-, As- and S-rich melt, as the fractionation proceeded away from the recrystallization front.

The Cenozoic evolution of the Alboran sea basin is characterized by a thermal event (heating) associated to the thinning of the lithosphere caused by the removal of the lithospheric mantle beneath the center of the basin (see Van der Wal and Vissers, 1993; Platt et al., 1998; Comas et al., 1999; Torné et al., 2000). Delamination of the lithospheric root promoted pervasive partial melting of the thinned lithospheric mantle along with km-scale, asthenospheric-derived melt infiltration (Van der Wal and Bodinier, 1996; Garrido and Bodinier, 1999; Lenoir et al., 2001) (Fig. 4A). Nevertheless the rapid ascent of the peridotites (upwelling rates of 0.4 cm/year have been calculated by Platt et al. 1998) caused the cooling of the shallowest mantle preventing the upward progression of the partial melting and melt migration front (the recrystallization front; Lenoir et al., 2001). Thus, the recrystallization front represents an isotherm close to the dry peridotite solidus (1200C) (Lenoir et al., 2001). Thus, as cited above, when upward migrating partial melts crossed the front, reacted with the host peridotite forming clinopyroxene+spinel at expenses of orthopyroxene (or olivine), and segregating residual, volatile-rich small-volume melts. These small-volume melts were channeled above the recrystallization front through refractory peridotites and partially fractionated by the crystallization of interstitial clinopyroxene on cooling, or were trapped into open fractures forming intrusive, Cr-rich pyroxenite dykes (Garrido, 1995; Garrido and Bodinier, 1999). The residual melts generated by these processes became richer in  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$  and  $\text{FeO}$ , and concentrated the volatile components ( $\text{H}_2\text{O}$ , F, Cl and C) as well as S, As and chalcophile elements (including PGE), constituting the parental melts of the

Cr-Ni and S-G ores (Fig. 4B). Since the first melts that reached the recrystallization front were generated by partial melting (and melt/rock reactions) of relatively fertile peridotites, and pyroxenites rich in nickel arsenides (Lorand, 1983) and graphite (originally diamonds; Pearson et al., 1989; Davies et al. 1993), the first small-volume melts that migrate upward the recrystallization front were the more effective to form arsenide- and sulfide-rich mineralizations.

As the peridotite rose up, it cooled down, promoting the crystallization of the interstitial melt below the recrystallization front, thus moving this partial melting and melt migration front to deeper horizons in the mantle (Fig. 4C). Under these conditions, the amount of small-volume melts that crossed upward the new front were progressively smaller. In addition, they came from melts generated by partial melting (and melt/rock reactions) of early melted peridotites and, as a consequence, these small-volume melts were impoverished in  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{FeO}$ , As, S and chalcophile elements, and contained higher amounts of Cr and Mg. This explain the mineralogical and chemical features of Cr-Ni ores located close to or below the recrystallization front (e.g. El Lentisco and El Nebral) which do not contain cordierite and consist of chromite and minor nickel arsenides (<10 vol.%) associated to Mg-rich orthopyroxenite.

Further uplift and cooling of the lithospheric mantle gave rise to new downward displacement of the front and restricted melt percolation to dunitic channels forming the layered granular peridotites (Remaïdi, 1993; Van der Wal and Bodinier, 1996) (Fig. 4D). In this context formed the Ni arsenide-poorest Cr-Ni ores (Arroyo de la Cala and the northern vein of Mina Baeza) which also contain the Cr-and Mg-richest chromite. The latest small-volume melts were very rich in  $\text{H}_2\text{O}$  and percolated through dunite bodies (sometimes containing pyroxenite layers). On cooling, these melts reacted with the host rocks to

produce the Cr-type ores. Because of the high upwelling rates, these late small-volume melts were isolated interacting with limited peridotite volumes under non-equilibrium conditions, giving rise to the great variety of chromite composition observed in this type of ores. Thus the parental melt of CDA chromitite generated by limited melt/peridotite reaction which produced a narrow dunite body within lherzolite. As a consequence the melt contained a high  $\text{Al}_2\text{O}_3/\text{Cr}_2\text{O}_3$  ratio, by the preferential dissolution of pyroxenes (Zhou et al., 1994; Arai, 1997). This limited melt/rock reaction also produced S-poor melts, which is in agreement with the predominance of laurite inclusions in chromite with respect

to irarsite (only one grain of irarsite was observed by Torres-Ruiz et al. 1996) as laurite can be formed from S-undersaturated melts, under  $f\text{S}_2$  as low as  $-2$  (below 1275°C; Brenan and Andrews, 2001). On the contrary, the parental melt of CD chromitite formed after partial melting and melt/rock reactions involving larger volumes of refractory peridotite. The melts produced had lower  $\text{Al}_2\text{O}_3/\text{Cr}_2\text{O}_3$  ratio and lower  $f\text{O}_2$  but, surprisingly, they were relatively rich in As. This could be explained by considering that the scarcity and heterogeneous distribution of arsenide phases in fertile peridotites of the Serranía de Ronda massifs required melt extraction from large volumes of rocks to ensure significant As

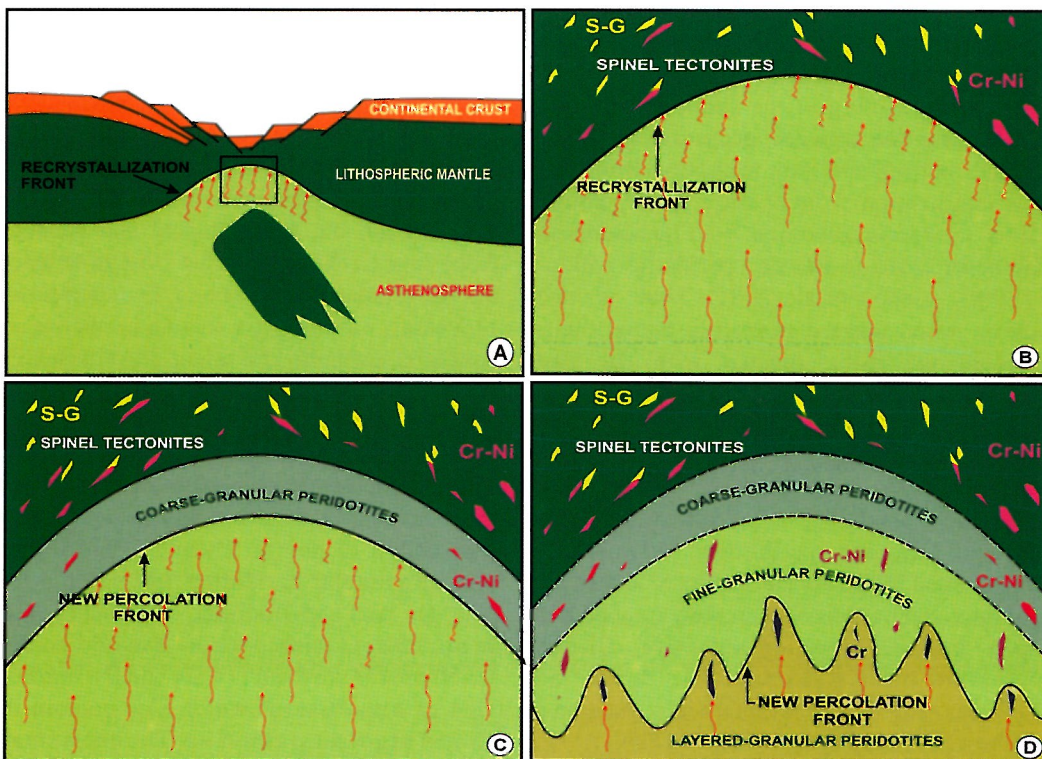


Fig. 4: Skematic interpretation of the genesis of the different types of mineralizations with the mantle evolution of the peridotite massif during the Cenozoic.

Fig. 4: Interpretación esquemática de la génesis de los diferentes tipos de mineralizaciones durante la evolución mantélica de los macizos peridotíticos en el Cenozoico.

contents in the melt. However, the low PGE contents of CD chromitites is a question that remain unanswered.

The conditions for the crystallization of chromite instead silicates (and replacing silicates) could be attained by relative increase in the oxygen fugacity (to enter the chromite liquidus field in the P-T-fO<sub>2</sub> space, Hill and Roeder, 1974) as the consequence of infiltration of fluids. In fact around the mineralized zones there are frequent late, discordant millimeter-thick veins of amphibolites. Another possible explanation for the crystallization of chromite (not tested experimentally) can be related with the unmixing of the fluid component (mainly H<sub>2</sub>O) of the small-volume melt during its fractionation coeval with the strong cooling and decompression. The decrease in water content in the melt produce a drop in the solubility of Cr<sup>3+</sup> and consequently the crystallization of chromite instead of silicates (Edwards et al. 2000). In this model, the late discordant amphibolite veins can be regarded as the products of reaction between the unmixed fluid component and the host peridotites along the walls of narrow cracks.

This model consider that the different types of mineralizations formed during the final uplift of the peridotite bodies, just before or, even coeval, with their crustal emplacement. In fact, in the Arroyo de la Cala occurrence, the unconsolidated chromite-(nickeline) ore was deformed by a shear zone genetically related with those responsible of the development of the plagioclase-tectonite domain and of the crustal emplacement of the peridotite bodies.

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