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Composition and textures of chromite and platinum-group minerals in chromitites of the western ophiolitic belt from Pampean Ranges of Córdoba, Argentina

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Abstract

Chromitite bodies hosted in the Neoproterozoic western ophiolitic belt of Pampean Ranges of Córdoba (Argentina) were studied at Los Congos and Los Guanacos ultramafic bodies, with regard to the composition and textures of the chromite and platinum group minerals. Primary chromite composition is only preserved in some massive chromitites from the Los Guanacos ultramafic body, and is similar to Al-rich ophiolitic chromitites, suggesting that they crystallized from melts with back arc basin basalts (BABB) affinity in the suprasubduction mantle. Subsequently, these chromitites underwent a prograde metamorphism. Chromites from chromitites and associated metamorphosed ultramafic rocks show complex replacement and exsolution textures. Mineral chemistry and texture indicate that the chromite composition records two main metamorphic trends. A first trend defined by chromite from massive chromitite, in which there is an enrichment in Fe^{3+} and Fe^{2+}, Cr remain relatively constant, and slightly depleted in Al, Mg. A second trend is defined by chromite from disseminated chromitite and metamorphosed dunite and harzburgite, in which a Fe-rich phase is replacing the Al-rich chromite. This alteration trend is characterized by enrichment in the total iron content ($Fe^{3+}+Fe^{2+}$) and a strong depletion in Al and Mg. The chemical composition of all analyzed spinels from Los Guanacos and Los Congos, as plotted on the ternary Fe^{3+}–Cr–Al diagram, correlates well with the Cr-spinels from the upper amphibolite to granulite-facies metamorphism.

Platinum group minerals (PGM) identified include native osmium, laurite, erlichmanite, irarsite, platinum and a number of inadequately identified phases such as an oxide or hydroxide of Ru, Pt and Ir–Ru, Pt telluride, Ir–Ru–As–Se and Ir–Ru–Ti compounds. Native osmium was the only PGM which remained unaltered; other PGM underwent mineralogical reworking during metamorphism. Although it is difficult to establish the extent of platinum group element mobilization based on mineralogical observation, our results suggest that the Ru–Os–Ir PGM in the Los Guanacos and Los Congos chromitites were modified *in situ*, producing re-distribution of these PGE on a small scale. The presence of rare Pt and PGE–As–Se minerals was possibly related to remobilization of Pt, As and Se by fluids during the alteration processes.

Keywords: Chromite; PGM; Ophiolite; Argentina; Los Guanacos; Los Congos

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1. Introduction

The potential of ophiolitic chromitites for platinum group elements (PGE) exploration has been recognized in the last decades (Gauthier et al., 1990; Kostantopoulou and Economou-Eliopoulos, 1991; Augé and Maurizot, 1995; Economou-Eliopoulos and Vacondios, 1995; Economou-Eliopoulos, 1996). The precious metals reside in specific trace minerals, the platinum group minerals (PGM), usually enchased in chromite crystals and more rarely located in the silicate matrix of the chromitites. It has been demonstrated that the chromite composition, as well as the PGE geochemistry and mineralogy of ophiolitic chromitites, can provide useful information about the petrological nature of their mantle source and geodynamic setting (Arai and Yurimoto, 1994; Melcher et al., 1997; Zhou et al., 1998; Proenza et al., 1999, 2004b; Gervilla et al., 2005; Uysal et al., 2005). Furthermore, these parameters can be used as petrogenetic indicators of the post-magmatic events that affected the ophiolitic chromitites and their host rocks (McElduff and Stumpfl, 1990; Nilsson, 1990;

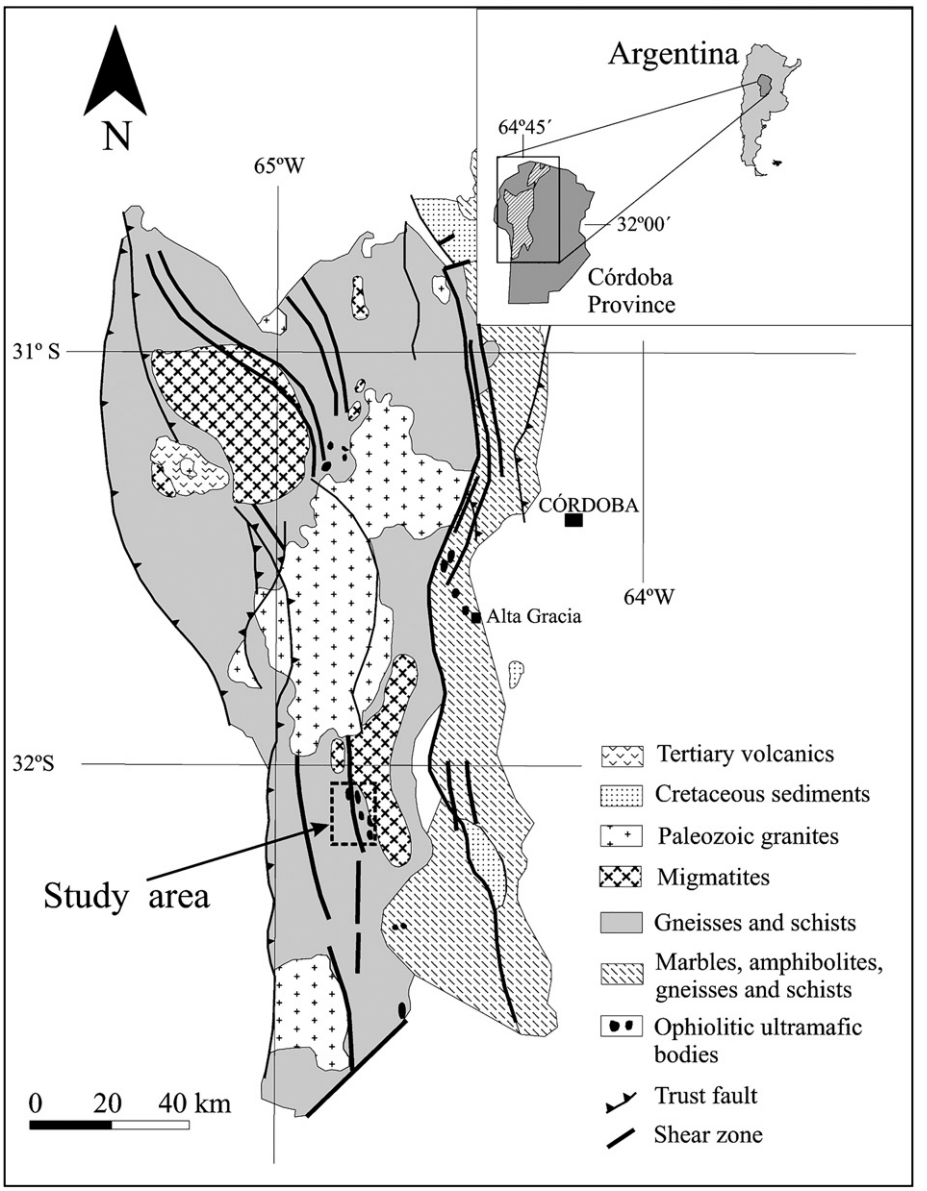

Fig. 1. Simplified geological map of Eastern Pampean Ranges, showing the location of the study area (after Kraemer et al., 1995; Rapela et al., 1998; Escayola et al., in press).

Thalhammer et al., 1990; Garuti and Zaccarini, 1997; Malitch et al., 2001; Zaccarini et al., 2005).

In this paper, we present the first description of PGM and their paragenesis, together with composition and textures of chromite in chromitites, hosted in a metamorphosed Neoproterozoic ophiolitic complex (640 Ma; Escayola et al., in press), located in the Pampean Ranges of Córdoba (Argentina). These chromitites represent one of the oldest ophiolitic chromitites recognized in Latin America and they had a protracted metamorphic evolution. The data are used to better understand the behavior of chromitites and the associated PGM during metamorphic processes.

2. Geological background

Neoproterozoic ophiolitic remnants crop out in Eastern Pampean Ranges of Córdoba, located in the Argentinian Central Andes (Kraemer et al., 1995; Escayola et al., 2004; Fig. 1). The Eastern Pampean Ranges are the easternmost exposures of the sialic basement of the central Andes, and represent a Neoproterozoic–Early Cambrian orogen which has been traditionally interpreted as developed at the SW paleo-Pacific margin of Gondwana (e.g., Ramos, 1988; Rapela et al., 1998). The Eastern Pampean orogen comprises metasedimentary–metaigneous rock units, consisting mainly of garnet–biotite gneiss and biotite schist intruded by metaluminous to peraluminous granitoid suites of Early Cambrian to Devonian age. These units were metamorphosed under P–T conditions transitional between medium- and upper-amphibolite facies. Hypersthene-bearing gneisses and amphibolites are also known in some localities, and indicate local granulite facies metamorphic conditions (Escayola et al., 1996; Rapela et al., 1998; Escayola et al., in press). Several migmatitic massifs have also been described (Gordillo, 1979, 1984). They comprise mainly stromatic migmatites with subordinate intercalations of cordierite- and garnet-bearing kinzigite containing amphibolite pods. The migmatites are intruded by a large number of granitic–granodioritic bodies as well as foliated tonalites. Cretaceous volcanic–sedimentary sequences and Tertiary volcanic rocks are recognized to the east and west respectively of the central part of the ranges (Gordillo and Lencinas, 1979).

The ultramafic rocks are arranged in two belts of NW–SE trend (Fig. 1), cropping out as boudin shape lenses in tectonic contacts with the migmatites and gneisses that surround them. The western ophiolitic belt,

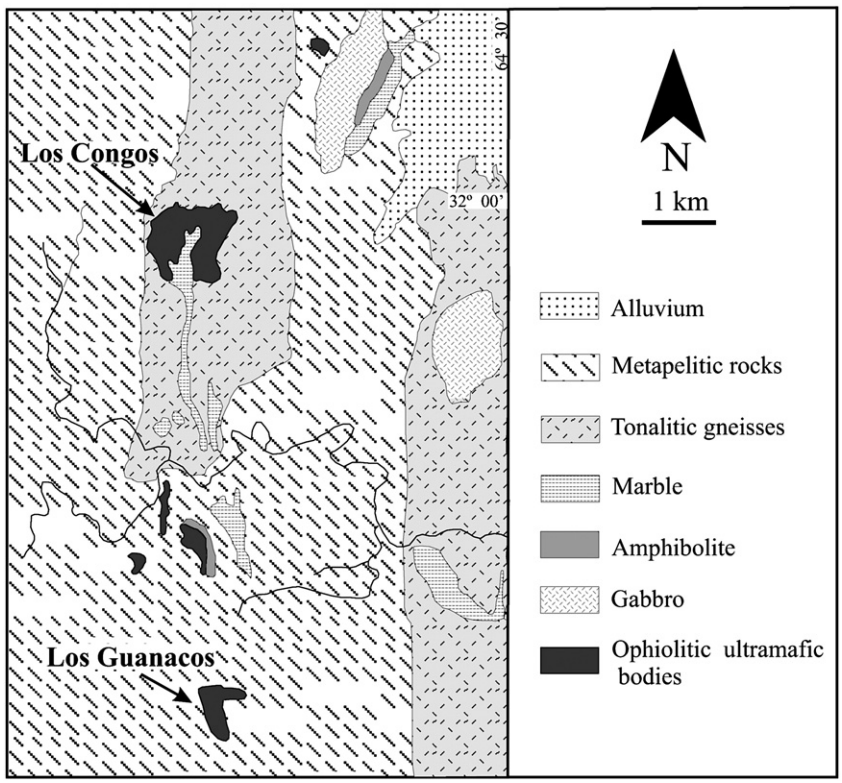

Fig. 2. Geological map of the Los Guanacos and Los Congos ultramafic bodies (after Escayola et al., 2004).

which is the matter of this study, is composed mainly of a metamorphosed suite of harzburgites and subordinated impregnated peridotites, intruded by dikes of dolerites and pyroxenites. Despite the metamorphic overprint, petrological, geochemical and isotopic data allowed Escayola et al. (1996, 2004, in press) to consider these ultramafic rocks as a mantle ophiolitic sequence represented by (i) the porphyroclastic harzburgite tectonites and (ii) the Moho Transition Zone (MTZ). The mafic–ultramafic rocks were emplaced into the upper crust in Neoproterozoic times during a collisional event between the Pampia terrane and the Rio de la Plata craton (Escayola et al., 2004).

According to the metamorphic evolution proposed by Escayola et al. (1996, 2004), the mafic–ultramafic bodies have recorded the following metamorphic events: (i) a first low grade metamorphism (Mx) related to a sea floor metamorphism, overprinted by (ii) a regional prograde metamorphic event (M1–M2, Rapela et al., 1998) related to a collisional event (540 to 530 Ma), (iii) retrograde metamorphism represented by anthophyllite and antigorite + brucite related to decompression and exhumation of the orogen, 514 Ma, (M3), and (iv) low grade metamorphism represented by veins of talc + chrysotile related to shearing and fluid circulation (M4).

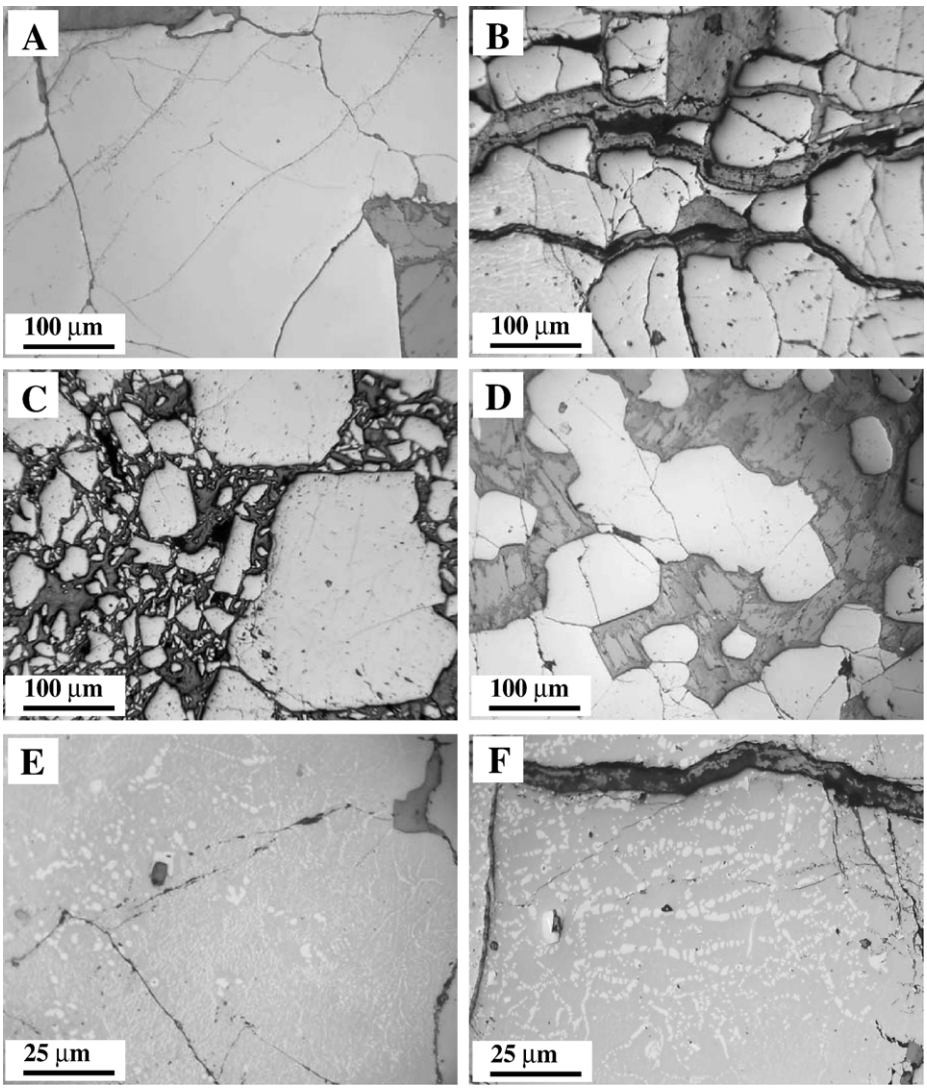

Fig. 3. Reflected light microscope images of the investigated chromitites, showing different textures. (A) and (B): massive and fractured, (C) brecciated, (D) lobate with relics of clinopyroxene (light grey mineral in the matrix), (E) and (F) exsolution of two spinels. The crack in Fig. 3F is filled with carbonates and chlorite.

Several chromitite bodies have been described in the entire Pampean Ranges. Some of these have been exploited in the past, despite their small size (Escayola et al., 2004 and references therein). Chromitite samples for this investigation were collected from the ultramafic bodies of Los Guanacos and Los Congos (Fig. 2).

3. Description of the chromitites and their host ultramafic rocks

3.1. Los Guanacos

The ultramafic body of Los Guanacos (1.5 km long and 0.6 km wide; Fig. 2) is in tectonic contact with metapelitic rocks (Mutti, 1994a,b; González-Chiozza, 2002; Escayola et al., 2004). The ultramafic rocks are predominantly depleted harzburgites accompanied by minor dunites and impregnated peridotites. Major and trace element characteristics indicate a residual origin, although they are strongly metasomatised (Escayola et al., 2004). The major mineral phases that occur in the serpentinized harzburgites are olivine (Fo_{91-92}), anthophyllite, antigorite, lizardite, brucite, talc and carbonates. The serpentinized impregnated peridotites are mainly composed of olivine, tremolite and antigorite. Several pyroxenite dykes, from 1 to 50 cm in width, up to several meters in length, and consisting mainly of olivine, spinel and anthophyllite, crosscut the ultramafic body. The ultramafic rocks of the Los Guanacos body have been considered to form part of a metamorphosed Moho Transition Zone from an ophiolitic sequence (Ramos et al., 2000; Escayola et al., 2004).

Small bodies of podiform chromitites occur in the area of Los Guanacos. They were exploited from 1940 to 1945, when several thousand tons of chromite ore were mined. The estimated production of chromite ore from a single body, Ume Pay, was about 50,000 tons. The old mine data indicate that the chromitite bodies rarely extended more than a few tens of meters in length, and were <5 m thick. Chromitite bodies are variable in size, have irregular to lenticular shapes in a dunite envelope and both rock types are hosted by harzburgites. The contact between chromitite and dunite is often along a zone of disseminated ore, although in some cases, the boundaries are relatively sharp. Pyroxenite dykes crosscut the chromitites and the host dunite and harzburgite.

3.2. Los Congos

Los Congos ultramafic body is located to the north of the Santa Rosa River (Fig. 2) and comprises several mining sites, known as Los Congos, Sol de Mayo and Los Coquitos (Escayola et al., 2004). This ultramafic body is one of the biggest of Córdoba Pampean Ranges being approximately 1300 m long and 700 m wide (Ramos et al., 2000; Escayola et al., 2004). The country rocks are mainly tonalitic gneisses, although marbles are the common lithologies to the south (Fig. 2). The ultramafic body is strongly serpentinized; lizardite, antigorite, tremolite, brucite, talc and magnetite were recognized. Whole rock geochemistry allows the serpentinized rocks to be classified as harzburgite (Escayola et al., 1996, 2004). According to these authors, the ultramafic body of the Los Congos is considered to be a portion of the mantle sequence of an ophiolite.

Several podiform chromitites were mined in this area, around 1940. Chromitite occurs as small pods of about 10 m long and 3 m wide, surrounded by variably

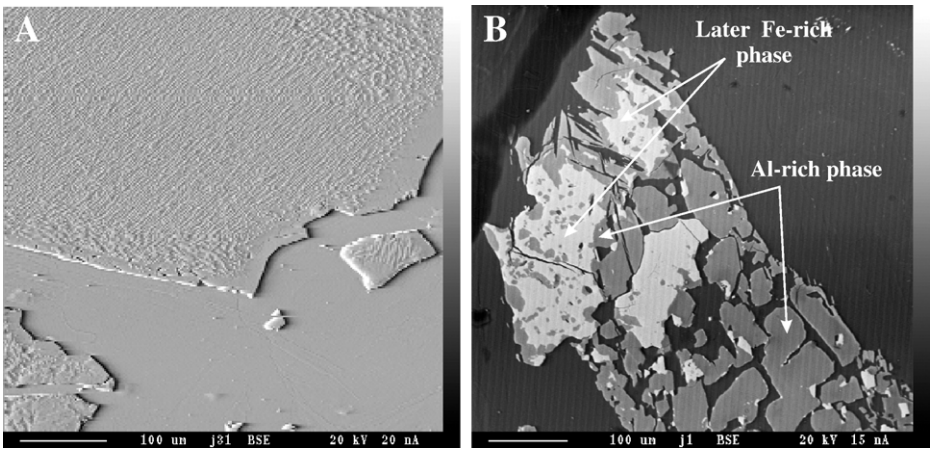

Fig. 4. Back-scattered electron images of a complex intergrowth consisting of Al-rich spinel and Fe-rich spinel in massive chromitite (A), and replacement texture in disseminated chromitite (B). Al-rich chromites appear dark (lower atomic number) while Fe-rich chromites appear light in this image (high atomic number).

thick dunite envelopes. Several pyroxenite dykes have been recognized and some of them crosscut the chromitite bodies.

4. Analytical techniques

Polished thin-sections were prepared from 15 chromitites and 10 metamorphosed ultramafic rocks from the Los Guanacos and Los Congos areas. They were studied under optical microscope, and by back-scattered electron imaging using a JEOL 360 scanning electron microscope at the Serveis Cientificotècnics (Universitat de Barcelona). Chemical analysis of chromite was carried out with a four-channel CAMECA SX50 electron microprobe at the same institution. Analytical conditions were 20 kV accelerating voltage, 20 nA beam current, 2 μm beam diameter, and count times of 10 s per element. Calibrations were performed using natural and synthetic reference materials: chromite (Cr, Al, Fe), periclase (Mg), rhodonite (Mn), rutile (Ti), NiO (Ni) and metallic V. The chemical data for Cr-spinels were stoichiometrically recalculated in order to distinguish FeO from Fe_2O_3 according to the procedure described by Carmichael (1967).

The PGM were first located in 31 polished sections, obtained from 12 massive chromitite samples from Los Congos and Los Guanacos, using a reflected light microscope at magnification between 250 and 800×. They were then examined *in situ* by SEM using a Philips 40 scanning electron microscope (SEM) at the Inter-department Instrumental Center (CIGS) of the University of Modena and Reggio Emilia with 20 to 30 kV accelerating voltage and 2 to 10 nA beam current. Subsequently, they were quantitatively analyzed with an ARL-SEMQ electron microprobe at the University of Modena and Reggio Emilia (Italy), operated at an accelerating voltage of 15 to 25 kV and a beam current of 15 to 20 nA, with a beam diameter of <1 μm. X-ray Kα lines were used for S, Cr, Fe, Ni, and Cu; Lα lines for Ir, Ru, Rh, Pt, Pd, and As; Mα line for Os. Count times of 20 s and 5 s for peak and background, respectively, were used in all analytical runs. Pure metals were used as standards for PGE, natural chromite for Cr and synthetic NiAs, FeS_2 and $CuFeS_2$ for Ni, Fe, Cu, S, and As. On-line ZAF data-reduction and automatic correction for the interferences Ru–Rh, Ir–Cu, and Rh–Pd were performed using the PROBE software package (version 1996) by J. Donovan. Selected analyses of PGM (wt.% and at.%) are presented in Table 3.

5. Chromitites of Los Guanacos and Los Congos

5.1. Texture of chromite

The textures of the chromitites have been investigated by reflected light and electron microscopy. The Los Congos and Los Guanacos chromitites display massive, lobate, brecciated and disseminate textures. Commonly, the chromite grains are highly fractured and mylonitized. Examples of the most common textures in the chromitites are illustrated in Figs. 3 and 4.

Few chromite crystals are homogeneous and most are in fact characterized by the presence of two

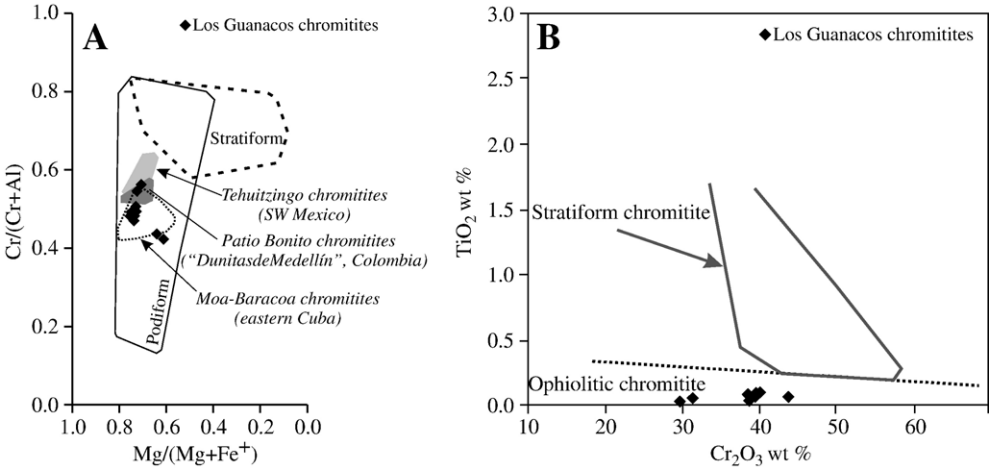

Fig. 5. (A) Primary compositions of chromite from Los Guanacos chromitite in terms of their Cr# [(Cr/(Cr+Al)] versus Mg# [(Mg/(Mg+Fe^{2+})]. Compositional fields of selected Al-rich ophiolitic chromitites of Latin America (Proenza et al., 1999, 2004a,b) are given for comparison. The podiform and stratiform fields are from Irvine (1967) and Leblanc and Nicolas (1992). (B) TiO_2 versus Cr_2O_3 contents of chromite from Los Guanacos chromitite, showing the distinct fields for ophiolitic and stratiform chromitites (after Ferrario and Garuti, 1988).

optically different, i.e., dark and light colored, phases (Figs. 3E,F and 4), that correspond compositionally to chromite and Fe-rich Cr-spinel, respectively. This texture is similar to the exsolution intergrown of two spinels reported by Garuti et al. (2003) from the Uktus Ural–Alaskan type chromitites (Urals) and to the symplectitic texture described in chromitites from the Iwanai-dake peridotite complex of Japan (Tamura and Arai, 2004, 2005).

Gangue minerals in the chromitites are mainly serpentine (antigorite) and chlorite (Cr-chlinoclore), which also are found as inclusions in chromite grains. In addition, inclusions of clinopyroxenes are present in some chromite grains. Relics of clinopyroxene have also been found as interstitial to chromite, especially in the chromitites with the lobate texture (Fig. 3D). Fractures in the chromitites are filled with serpentine, chlorite and, occasionally with carbonates, such as calcite and dolomite (Fig. 3F).

5.2. Chromite composition

Compositions of the various phases have been established by microprobe analysis. Some massive chromitite samples from Los Guanacos preserve primary chromite compositions in the grain cores. Their SiO_2 contents are invariably low (<0.2 wt.%) and unrelated to the contents of the other major oxides. This igneous chromite composition is also supported by the low Fe_2O_3 contents (<8.0 wt.%) and high MgO contents (> 15 wt.%), which are characteristics of ophiolitic primary chromite (e.g., Proenza et al., 1999). Only those analyses have been considered in the interpretation of the primary chromite, and used for petrogenetic indications.

Compositions of igneous (primary) chromite in Los Guanacos correspond to Al-rich chromite with Cr# [Cr/(Cr+Al)] <0.6 (Fig. 5A, Table 1). The Cr# varies from 0.48 to 0.56, and Mg# [Mg/(Mg+Fe^{2+})] from 0.61 to 0.75 (Fig. 5A). The Fe^{3+}# [Fe^{3+}/(Fe^{3+}+Cr+Al)] is lower than 0.08, and the TiO_2 contents are systematically low (<0.1 wt.%). These low TiO_2 values are typical of ophiolitic chromitites elsewhere (Fig. 5B). MnO contents ranges from 0.26 to 0.51 wt.%, ZnO between 0.1 to 0.3 wt.%, and V_2O_5 (≤0.1 wt.%) and NiO (<0.3 wt.%) are very low.

The diagram Cr# versus Mg# (Fig. 5A) indicates that all chromitite samples plot in the podiform (ophiolitic) chromitite field. This chemical composition is similar to other Latin American Al-rich ophiolitic chromitites, such as those in Tehuitzingo, SW Mexico (Proenza et al., 2004b; Zaccarini et al., 2005), Patio Bonito, Colombia (Proenza et al., 2004a, unpublished data) and Moa–Baracoa, eastern Cuba (Proenza et al., 1999).

In the Cr# versus TiO_2 plot (not shown), the Los Guanacos chromite compositions plot outside the field of boninites and mid-oceanic ridge basalts (MORB) as defined by Dick and Bullen (1984) and Arai (1992). However the compositions fall within the compositional range defined by the Al-rich chromitites from de Tehuitzingo (SW Mexico), Patio Bonito (Dunitas de Medellín, Colombia) and Moa-Baracoa (eastern Cuba). These have been interpreted as crystallized from melts

Table 1
Representative results of electron-microprobe analyses (wt.%) of chromite from Los Guanacos and Los Congos chromitites

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
	Los Guanacos								Los Congos							
SiO_2	0.06	0.02	0.05	0.06	0.01	0.04	0.04	0.07	0.14	0.26	0.18	0.27	0.14	0.26	0.06	0.08
TiO_2	0.03	0.06	0.07	0.09	0.05	0.09	0.12	0.20	0.08	0.16	0.08	0.08	0.08	0.16	0.22	0.17
Al_2O_3	27.44	29.06	27.17	28.03	24.19	15.84	12.34	8.69	25.24	23.78	21.35	20.98	25.24	23.78	17.80	14.42
V_2O_3	0.07	0.10	0.09	0.00	0.07	0.12	0.12	0.08	0.12	0.12	0.00	0.00	0.12	0.12	0.06	0.07
Cr_2O_3	38.75	39.54	38.69	39.66	32.00	35.13	32.46	21.83	34.91	35.42	40.41	39.96	34.91	35.42	35.15	36.87
Fe_2O_3	6.48	4.93	7.00	5.71	13.45	20.55	26.44	38.04	11.05	12.48	10.79	11.23	11.05	12.48	17.78	20.00
FeO	10.83	10.11	10.97	10.25	17.74	15.99	17.80	23.26	12.35	12.97	9.88	9.63	12.35	12.97	19.04	20.42
MgO	16.44	17.34	16.40	17.14	11.31	11.57	9.99	5.83	14.98	14.75	15.92	16.01	14.98	14.75	10.15	8.98
MnO	0.49	0.47	0.51	0.42	0.41	0.56	0.53	0.26	0.48	0.45	0.90	0.91	0.48	0.45	0.34	0.40
NiO	0.16	0.10	0.16	0.18	0.45	0.36	0.44	0.78	0.16	0.15	0.21	0.23	0.16	0.15	0.08	0.23
ZnO	0.17	0.16	0.06	0.08	0.33	0.12	0.12	0.16	0.08	0.24	0.24	0.25	0.08	0.24	0.18	0.06
Total	100.91	101.89	101.17	101.62	100.01	100.37	100.41	99.21	99.59	100.76	99.97	99.53	99.59	100.78	100.86	101.70
Cr#	0.49	0.48	0.49	0.49	0.47	0.60	0.64	0.63	0.48	0.50	0.56	0.56	0.48	0.50	0.57	0.63
Mg#	0.73	0.75	0.73	0.75	0.53	0.56	0.50	0.31	0.67	0.67	0.73	0.74	0.67	0.66	0.47	0.72
Fe^{3+}#	0.07	0.05	0.08	0.06	0.16	0.25	0.33	0.51	0.13	0.15	0.13	0.14	0.13	0.15	0.22	0.25

1–4: primary chromite in Los Guanacos massive chromitite. 5–8: altered chromite (Fe-rich Cr-spinel) in Los Guanacos chromitite. 9–16: altered chromite in Los Congos chromitite.

with back arc basin basalt (BABB) affinity (Proenza et al., 1999, 2004b).

In contrast, the most distinctive feature of chromite in the Los Guanacos and Los Congos chromitites is their complex alteration. In general, the primary chromite is mainly replaced by a more Fe-rich Cr-spinel. Chromite grains from Los Guanacos massive chromitites commonly display two main different compositional zones (Fig. 6A, Table 1). These are (i) Al-rich chromite zones that in some cases retained the primary chromite composition (Cr#: 0.34 to 0.66, Mg#: 0.67 to 0.75, Fe^{3+}# <0.08, <0.5 wt.% NiO, <0.3 wt.% ZnO, 0.26 to 0.6 wt.% MnO); and (ii) Fe-rich Cr-spinel (Cr#: 0.47 to 0.83, Mg#: 0.17 to 0.64, Fe^{3+}#: 0.25 to 0.68, 0.16 to 0.66 wt.% NiO, ≤0.33 wt.% ZnO, 0.48 to 0.60 wt.% MnO). The alteration to the Fe-rich phase is characterized by a progressive enrichment in Fe_2O_3 and FeO, and slight depletion in Al_2O_3 and MgO. This alteration trend does not show the strong depletion in Al and Mg that characterize most of the ferrian chromite observed elsewhere.

On the other hand, similar to massive chromitite from Los Guanacos, the chromite from Los Congos massive chromitites show replacement textures in which Al-rich chromite is replaced by a more Fe-rich Cr-spinel. However, in this case, Al-rich chromite is systematically enriched in Fe_2O_3 (Fig. 6B, Table 1), indicating that the

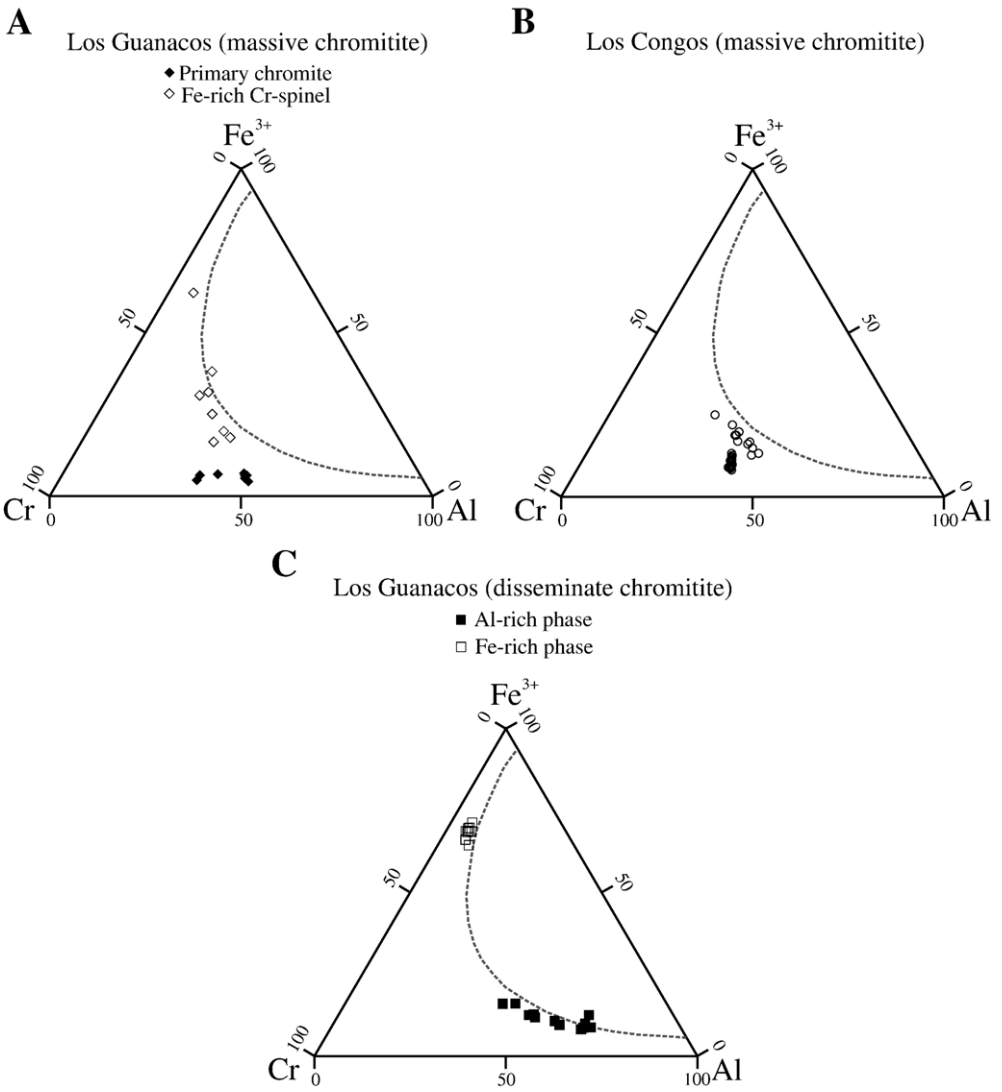

Fig. 6. Fe^{3+}–Cr–Al diagram of Cr-spinels from Pampean Ranges: (A) Los Guanacos massive chromitites, (B) Los Congos massive chromitite, and (C) Los Guanacos disseminated chromitite. The dashed line approximately represents the *solvus* curve for different metamorphic Cr-spinel phase (Purvis et al., 1972; Evans and Frost, 1975; Suita and Streider, 1996).

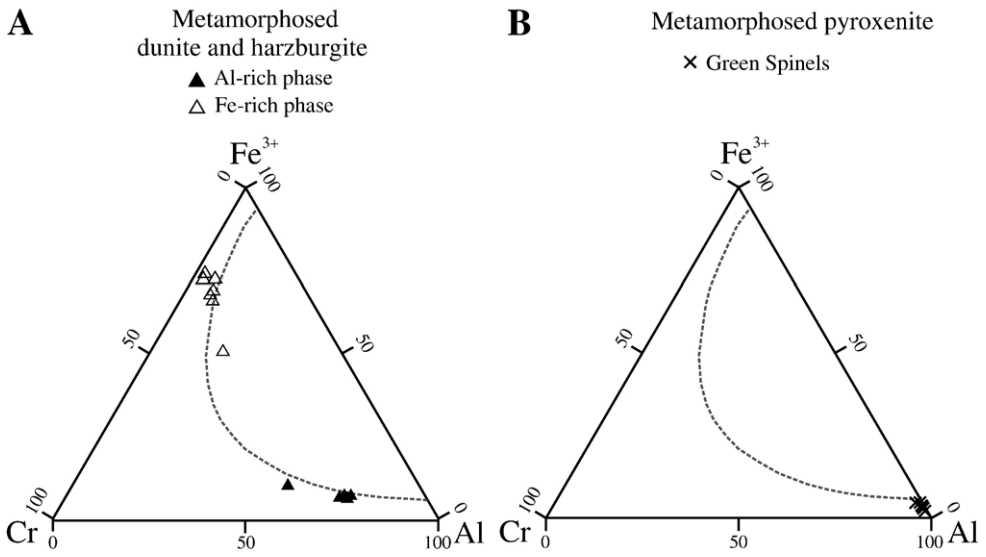

Fig. 7. Fe^{3+}–Cr–Al diagram of accessory spinels from Pampean Ranges metamorphosed dunite and harzburgite (A) and metamorphosed pyroxenite (B). The dashed line approximately represents the *solvus* curve for different metamorphic Cr-spinel phase (Purvis et al., 1972; Evans and Frost, 1975; Suita and Streider, 1996).

original magmatic Cr-spinel in any of studied samples from Los Congos did not survive the prograde metamorphism (up to granulitic facies; Escayola et al., 1996, 2004).

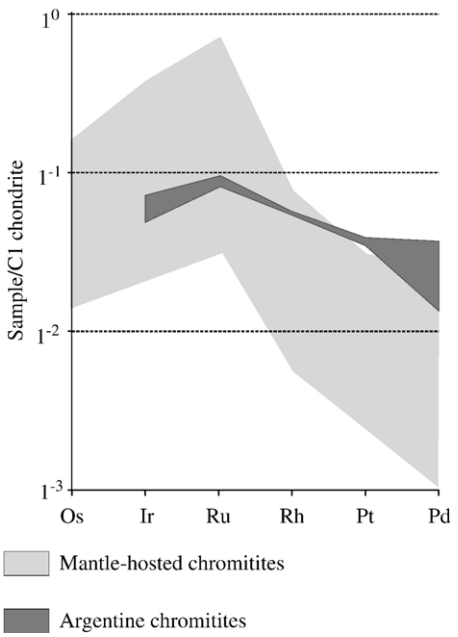

Fig. 8. Chondrite normalized (Naldrett and Duke, 1980) patterns of the investigated chromitites from Pampean Ranges of Córdoba (data from Escayola et al., 2004) and comparison with the chromitites hosted in the ophiolitic mantle (data from Gauthier et al., 1990; McElduff and Stumpfl, 1990; Economou-Eliopoulos, 1996; Kojonen et al., 2003; Proenza et al., 2004b).

In chromitites with disseminated texture, backscattered electron images show that predominantly Cr-spinel grains are composed of two zones (Figs. 4B and 6C): a Fe-rich phase (high average atomic number: light) and a Al-rich phase (lower average atomic number: dark). The Fe-rich phase (Cr#: 0.78 to 0.82, Mg#: ≤0.20, Fe^{3+}#: 0.65 to 0.71, 1.20 to 1.80 wt.% NiO, <0.17 wt.% ZnO, 0.30 to 0.60 wt.% MnO) replaces the Al-rich phase (Cr#: 0.26 to 0.51, Mg#: 0.6 to 0.75, Fe^{3+}#: <0.16, <0.50 wt.% NiO, 0.3 to 0.68 wt.% ZnO, 0.21 to 0.49 wt.% MnO).

In addition, in some chromite grains from chromitites, a complex intergrowth (exsolution?) consisting of Al-rich spinel and Fe-rich spinel is also visible (Figs. 3E,F and 4A). These complex exsolved intergrowths consist

Table 2
Mineralogy of the PGM from the Los Guanacos and Los Congos chromitites

PGM	Los Congos	Los Guanacos
Osmium	X	
Laurite		X
Erlichmanite		X
Irarsite		X
Platinum	X	X
Pt–Te	X	
Unnamed Ir–Ru–As–Se	X	
Unnamed Ir–Ru–Ti	X	
Unnamed Ru oxide or hydroxide		X
Unnamed Pt oxide or hydroxide	X	
Unnamed Ir–Ru oxide or hydroxide	X	

of an Al-rich phase, with similar levels of Cr_2O_3 and more Fe_2O_3 than the primary Al-rich chromite, and a Fe-rich phase, "chromian magnetite", with comparable contents of Cr_2O_3 to their host Al-rich phase. Similar Fe-rich spinel lamellae in Al-rich spinel from layered intrusions have been described by Eales et al. (1988).

6. Accessory chromites in metamorphosed dunite, harzburgite and pyroxenite

The accessory chromites in metamorphosed dunites and harzburgites are systematically altered to ferrian chromite and magnetite. Chromite grains show three different compositional zones: (i) Al-rich phase (Cr#: 0.21 to 0.38, Mg#: 0.66 to 0.70, Fe^{3+}#: <0.1), (ii) ferrian chromite zones (Cr#: 0.63 to 0.93, Mg#: <0.38, Fe^{3+}#: >0.51), and (iii) magnetite rims. The alteration to ferrian chromite in metamorphosed peridotites is characterized by enrichment in the total iron content ($Fe^{3+}+Fe^{2+}$) and a strong depletion in Al and Mg. There is a gap in chemical composition between the Al-rich zones and ferrian chromite zones (Fig. 7A). In addition, the ferrian chromite zones are enriched in Ni (up to 1.23 wt.% NiO) compared to the Al-rich phase (≤0.50 wt.% NiO).

Spinels in some pyroxenites correspond to green spinels related to coronites. On a Fe^{3+}–Cr–Al diagram, green spinel compositions plot in the Al_2O_3-rich corner (65.52 to 67.54 wt.% Al_2O_3, 21.89 to 23.50 wt.%

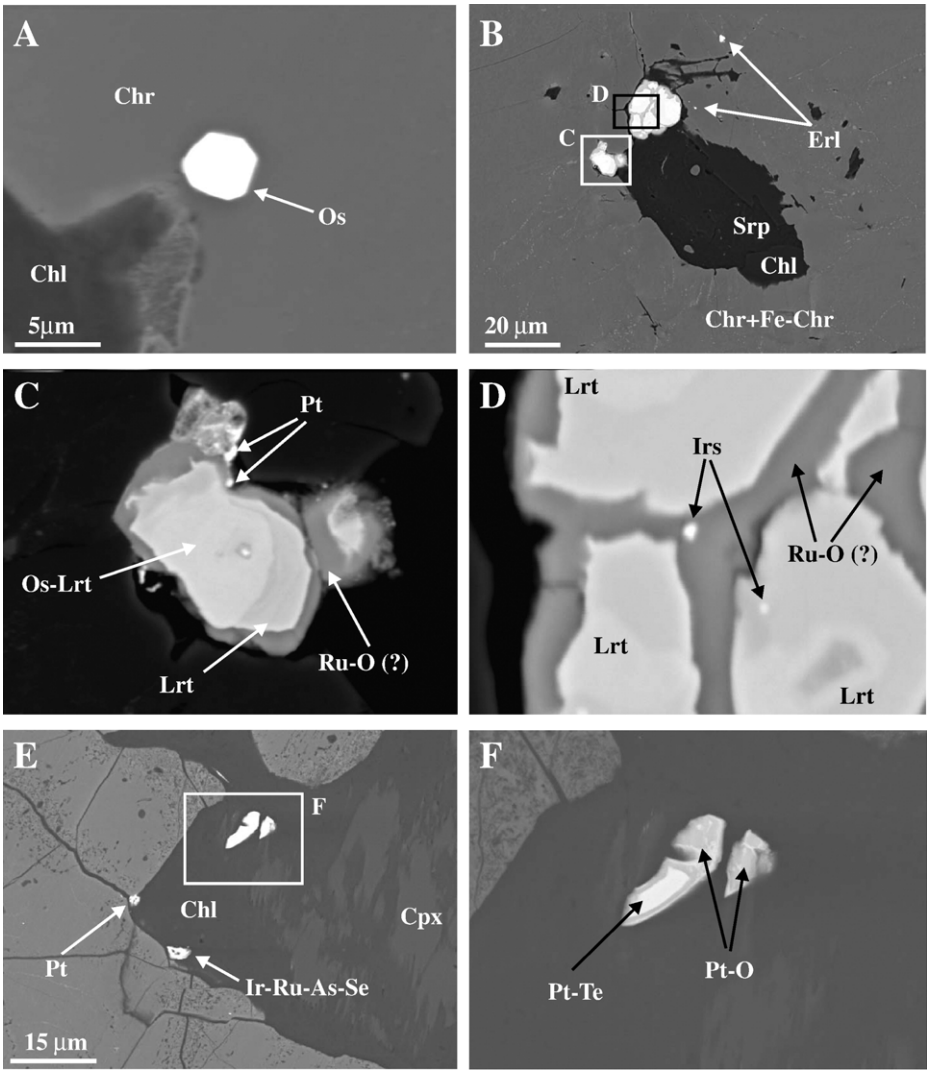

Fig. 9. Electron microscope images showing morphology, texture and mineral assemblages of PGM. Abbreviations (after Kretz, 1983): Os — osmium, Lrt — laurite, Erl — erlichmanite, Pt — platinum, Os-Lrt — Os-rich laurite, Ru–O (?) — Ru oxide or hydroxide, Irs — irarsite, Chr — chromite, Fe-Chr — ferrian chromite, Chl — chlorite, Srp — serpentine.

Table 3
Representative microprobe analyses of PGM from Los Congos and Los Guanacos chromitites

	Os	Ir	Ru	Rh	Pt	Pd	Fe	Ni	Cu	S	As	Total
D.L.	0.55	0.69	0.33	0.33	0.33	0.44	0.08	0.07	0.15	0.02	0.11	
Weight %												
Osmium												
N.1	69.18	26.23	3.56	n.d.	n.d.	n.d.	1.02	n.d.	n.d.	n.d.	n.d.	100.00
N.2	68.57	26.56	3.97	n.d.	n.d.	n.d.	1.00	n.d.	n.d.	n.d.	n.d.	100.42
N.3	65.15	22.20	4.19	0.53	0.79	n.d.	1.57	n.d.	n.d.	0.16	n.d.	94.62
N.4	68.42	25.37	3.86	n.d.	n.d.	n.d.	0.99	n.d.	n.d.	n.d.	n.d.	98.88
Laurite–erlichmanite												
N.1	17.02	7.75	39.56	0.94	n.d.	n.d.	0.22	n.d.	n.d.	35.36	1.10	101.98
N.2	16.01	4.21	44.39	0.57	n.d.	n.d.	0.24	n.d.	n.d.	36.64	0.18	102.30
N.3	16.07	5.65	43.21	0.42	n.d.	n.d.	0.52	n.d.	n.d.	36.09	0.26	102.24
N.4	15.70	6.30	41.58	0.53	n.d.	n.d.	0.29	0.07	n.d.	35.14	0.83	100.71
N.5	16.95	5.10	42.85	0.56	n.d.	n.d.	0.30	0.08	n.d.	35.40	0.12	101.35
N.6	16.17	6.93	39.95	0.69	n.d.	n.d.	0.50	n.d.	n.d.	34.25	0.80	99.48
N.7	15.33	4.18	42.95	0.56	n.d.	n.d.	0.35	0.06	n.d.	34.62	0.23	98.72
N.8	15.50	3.58	43.85	0.72	n.d.	n.d.	0.22	n.d.	n.d.	35.83	n.d.	99.79
N.9	15.63	5.87	41.68	0.44	n.d.	n.d.	0.26	n.d.	n.d.	34.98	0.61	99.48
N.10	14.02	5.70	42.27	0.61	n.d.	n.d.	0.67	n.d.	n.d.	35.75	0.54	99.62
N.11	11.79	4.38	46.25	0.47	n.d.	n.d.	0.65	0.13	n.d.	36.27	0.03	99.96
N.12	43.03	8.08	19.00	0.60	n.d.	n.d.	2.28	n.d.	0.26	31.44	0.92	105.66
N.13	17.85	7.77	39.99	0.55	n.d.	n.d.	0.62	n.d.	n.d.	35.27	0.91	102.98
Ru-oxide or hydroxide (?)												
N.1	n.d.	4.71	49.90	n.d.	n.d.	n.d.	0.57	1.20	1.00	0.87	n.d.	58.74
N.2	n.d.	5.75	51.06	1.05	n.d.	n.d.	0.21	1.25	1.22	3.00	n.d.	64.01
N.3	3.61	4.96	49.36	0.91	n.d.	n.d.	0.46	1.02	0.89	5.28	n.d.	66.49
N.4	1.19	4.70	50.35	0.41	n.d.	n.d.	0.73	1.26	0.88	5.17	n.d.	64.69
Atomic %												
Osmium												
N.1	65.67	24.64	6.36	–	–	–	3.30	–	–	–	–	
N.2	64.46	24.70	7.03	–	–	–	3.20	–	–	–	–	
N.3	63.17	21.30	7.65	0.95	0.75	–	5.17	–	–	0.91	–	
N.4	65.38	23.99	6.94	–	–	–	3.23	–	–	–	–	
Laurite–erlichmanite												
N.1	5.42	2.44	23.69	0.55	–	–	0.24	–	–	66.74	0.89	
N.2	4.95	1.29	25.82	0.33	–	–	0.25	–	–	67.18	0.14	
N.3	5.02	1.75	25.38	0.24	–	–	0.55	–	–	66.84	0.21	
N.4	5.01	1.99	24.97	0.31	–	–	0.32	0.07	–	66.51	0.67	
N.5	5.38	1.60	25.58	0.33	–	–	0.32	0.08	–	66.62	0.09	
N.6	5.27	2.23	24.50	0.41	–	–	0.56	–	–	66.22	0.66	
N.7	4.95	1.34	26.11	0.33	–	–	0.38	0.06	–	66.34	0.19	
N.8	4.90	1.12	26.08	0.42	–	–	0.24	–	–	67.17	–	
N.9	5.03	1.87	25.25	0.26	–	–	0.29	–	–	66.80	0.50	
N.10	4.43	1.78	25.15	0.35	–	–	0.72	–	–	67.06	0.44	
N.11	3.66	1.35	27.04	0.27	–	–	0.68	0.13	–	66.85	0.02	
N.12	15.07	2.80	12.53	0.39	–	–	2.72	–	0.28	65.34	0.82	
N.13	5.66	2.44	23.85	0.32	–	–	0.66	–	–	66.31	0.73	
Ru-oxide or hydroxide (?)												
N.1	–	4.11	82.88	–	–	–	1.71	3.42	2.67	4.55	–	
N.2	–	4.36	73.66	1.48	–	–	0.54	3.11	2.84	13.65	–	
N.3	2.54	3.46	65.43	1.18	–	–	1.10	2.32	1.91	22.05	–	
N.4	0.84	3.29	67.08	0.54	–	–	1.75	2.88	1.90	21.71	–	

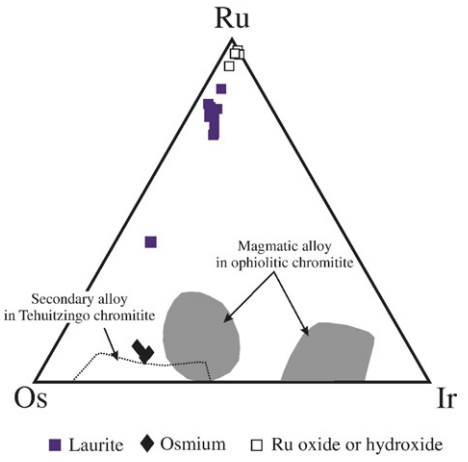

Fig. 10. Composition of the analyzed Ru–Os–Ir PGM from Argentine chromitites (at.%). The compositional field of the magmatic alloys from different ophiolitic chromitites and the composition of the secondary alloy from Tehuitzingo chromitites is plotted for comparison (data from Melcher et al., 1997; Garuti et al., 1999; Zaccarini et al., 2005 and unpublished data of the authors for chromitites from Albania, Greece, Egypt and Kempirsai).

MgO, 7.51 to 9.33 wt.% FeO, 2.71 to 4.10 wt.% Fe_2O_3, <0.6 wt.% Cr_2O_3; Fig. 7B). According to Evans and Frost (1975) these spinels are formed by metamorphic reaction at upper amphibolite- to granulite facies metamorphism.

7. Platinum-group minerals

The chondrite-normalized PGE-patterns (Fig. 8) show that the PGE concentrations in the investigated chromitites are very low. The general trend of the Argentine chromitites is characterized by a weak positive anomaly of IPGE relative to the PPGE when compared with chromitites from mantle ophiolites (Fig. 8). Despite the low PGE concentration, the following PGM have been found: native osmium, laurite, erlichmanite, irarsite, native platinum and a number of inadequately unidentified – and possibly unnamed – phases such as Ru–O, Pt–O, Pt–Te, Ir–Ru–As–Se and Ir–Ru–Ti compounds (Table 2). The PGM occur as small grains, <20 μm in size, as single- or polyphase grains consisting of two or three different PGM. Examples of the morphology, textural relations and paragenesis of the PGM are illustrated in Fig. 9.

Native osmium was found only in the Los Congos chromitites. It forms a polygonal single phase grain, enchased in a chromite crystal (Fig. 9A). The mineral is yellowish in color and displays a strong anisotropy, suggesting that it may be a hexagonal osmium. Based on its textural position and shape, the osmium has been classified as a magmatic PGM, i.e., formed at high temperature as pristine *liquidus* phase and mechanically collected in crystallizing chromite. Other PGM found in the Los Congos chromitites include inadequately unidentified phases such as a Pt and Ir–Ru oxide or hydroxide, Pt telluride and Ir–Ru–As–Se and Ir–Ru–Ti compounds (Fig. 9E,F). These PGM occur as irregular grains in the altered silicate matrix of chromitites. Only the Ir–Ru–Ti compound was found in the ferrian chromite. Similar PGM have been described by Jedwab (1995, 2004).

Most of the PGM found in the Los Guanacos chromitites (laurite, erlichmanite, irarsite, Ru oxide or hydroxide, native platinum) have been classified as secondary PGM, i.e., altered and modified after their

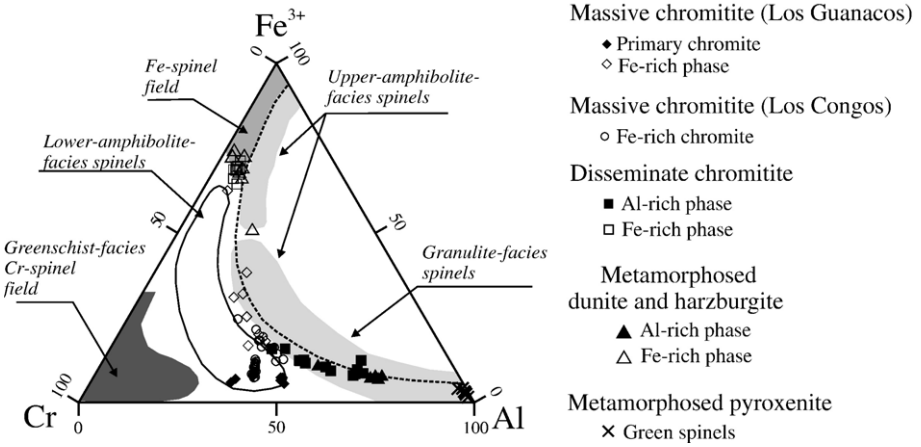

Fig. 11. Compositional changes in spinels from Los Guanacos and Los Congos (primary chromite and their alteration products) expressed in a triangular Fe^{3+}–Cr–Al plot. Spinel compositional fields from different metamorphic facies are from Purvis et al. (1972), Evans and Frost (1975), and Suita and Streider (1996).

magmatic formation. All these PGM occur totally embedded in the products of alteration such as ferrian chromite, serpentine and chlorite (Fig. 9B,C,D). Grains of laurite, up to 20 μm in size, have been found in the contact between chromite and altered silicate matrix. The observed laurite grains are characterized by a strong zonation and by an irregular shape (Fig. 9B–D). Most of them are rimmed by a grey-pinkish mineral characterized by a very low reflectance similar to those of the adjacent chromite, which has been tentatively classified as a Ru-oxide or hydroxide. Two small grains of erlichmanite (<5 μm in size) have been found associated with ferrian chromite (Fig. 9B). Irarsite has been identified only on the base of qualitatively composition, owing to the small size of the grains. The irarsite grains form small irregular blebs, ~1 to 2 μm in size, inside the zoned laurite and Ru-oxide or hydroxide. A few minute grains of an irregular PGM were only qualitatively identified because of their small size (~1 μm). The EDS spectra revealed that Pt was the only element present in the PGM. Furthermore, these PGM have a high electronic reflectance, therefore they must contain only heavy elements. As consequence, they can be tentatively considered as native platinum.

7.1. Electron microprobe composition of the Ru–Os–Ir minerals

The composition of the Ru–Os–Ir minerals (Table 3) has been plotted as at.% in the Ru–Os–Ir ternary diagram in Fig. 10. The PGM containing Os and Ir as the main PGE falls in the compositional field of osmium (Harris and Cabri, 1991). Comparison with the composition of magmatic Os–Ir alloys from ophiolitic chromitites and with the secondary Os–Ir alloys reported from Tehuitzingo chromitites, Mexico (Zaccarini et al., 2005), indicates that Os–Ir alloys from Los Congos chromitites are characterized by an intermediate composition between the magmatic and secondary Os–Ir alloys. Laurite displays a quite constant composition in terms of Ru–Os–Ir contents and contains minor Rh and Fe substituting for the main PGE, whereas Pt and Pd are absent. Very low As concentrations were detected in some grains. One grain has Os>Ru, reaching the composition of erlichmanite (Fig. 10).

Some grains of laurite show a compositional zonation characterized by the presence of a core of laurite enriched in Os, surrounded by a rim of Ru-rich laurite (Fig. 9C). A Ru-phase replacing laurite has been identified as Ru oxide or hydroxide. This conclusion is supported by the low analytical total and by the absence of any other elements than those analyzed. Furthermore, the Ru PGM has lower electronic reflectance than the associated laurite (Fig. 9C,D). It cannot therefore be a Ru alloy, but must contain light elements such as oxygen or hydrogen.

8. Discussion and conclusions

8.1. Primary chromite compositions and tectonic setting of the chromitites

The chemical composition of the primary chromites from the Los Guanacos chromitites is representative of Al-rich ophiolitic chromitites (Leblanc and Violette, 1983; Leblanc and Nicolas, 1992; Proenza et al., 1999; Zhou et al., 2001; Proenza et al., 2004b). In ophiolitic complexes containing important chromitite bodies, Al-rich chromitites tend to occur at the shallowest levels of the upper mantle, within the so-called Moho Transition Zone, very close to the lower layered-gabbro sequence (e.g., Leblanc and Violette, 1983; Leblanc and Nicolas, 1992; Proenza et al., 1999).

The genesis of mantle-hosted ophiolitic chromitites is still much debated, although they may have formed by melt-rock reaction in a suprasubduction mantle (Arai and Abe, 1994; Arai and Yurimoto, 1995; Zhou et al., 1998; Proenza et al., 1999). In addition, the presence of water in the melt is thought to be necessary for the crystallization of ophiolitic chromite (Edwards et al., 2000). Experimental results in water-oversaturated basalts (Matveev and Ballhaus, 2002) also suggest that ophiolitic chromitites would form only in the presence of primitive melts saturated in olivine–chromite and rich in water. Such conditions are most likely to occur in suprasubduction-zone environments.

According to Zhou et al. (1998), Al-rich chromitite forms in nascent spreading centers, such as back-arc basins. The likely tholeiitic affinity of the parental melts to the Pampean Range of Córdoba chromitites suggests formation from BABB-type melts in a back-arc basin tectonic setting. This tectonic scenery is consistent with the proposed tectonic evolution of the Pampean Ranges of Córdoba (Escayola et al., in press). According to these authors, the tectonic evolution of the Pampean Ranges of Córdoba includes, at ca. 700 to 650 Ma, the initiation of west-dipping subduction between the Pampia and Rio de La Plata blocks, with the development of an island arc and associated back arc basin (640 Ma). The back-arc basin must have closed sometime before the main metamorphic peak, around 540 to 530 Ma, promoting crustal thickening and overthrusting of the arc onto the Rio de La Plata Craton.

8.2. Metamorphic history

Compositions of Cr-spinels of the western ophiolitic belt from Pampean Ranges of Córdoba are mainly controlled by prograde metamorphism reactions, and are different from compositional trend for Cr-spinels altered at low temperatures, characterized by low Al contents (Roeder, 1994). The wide compositional range (Figs. 6 and 7) may reflect changes in their metamorphic evolution. Evans and Frost (1975) concluded that the Cr content of spinels increases with the increasing grade in the amphibolite facies. Abzalov (1998) demonstrated that the alteration induced by prograde metamorphism has a major control on the composition of Cr-spinels in the amphibolite metamorphic facies. In addition, Barnes (2000) concluded that chromite in lowest amphibolite facies (equilibrated below ~500 to 550 °C) retains the original igneous trivalent cation chemistry. However, metamorphism above 550 °C involves a substantial modification of the chromite compositions with surrounding silicate and infiltrating fluids.

The chemical compositions of all studied spinels (primary chromite and its alteration products) are displayed in the triangular Fe^{3+}–Cr–Al plot (Fig. 11). In this figure, the spinel compositional fields from different metamorphic facies (Evans and Frost, 1975; Suita and Streider, 1996; Barnes and Roeder, 2001) are also shown. The chemical compositions of all analyzed spinels from Los Guanacos and Los Congos plot mainly within the compositional fields of spinels from granulite facies (Fig. 11). The spinels have compositions that lie within the proposed *solvus* from prograde metamorphic rocks. We note, in particular, that the spinels (green spinels) from pyroxenite are rich in the $MgAl_2O_3$ component, and plot near the (Fe, Mg)Al_2O_3 corner. These Al-rich spinels are a product of the reaction of pre-existing Cr-spinel with Al-rich silicates during high grade metamorphism (Evans and Frost, 1975).

Cr-spinels from chromitites and associated metamorphosed ultramafic rocks show complex replacement and exsolution textures. These textures can be formed during magmatic conditions (Appel et al., 2002; Garuti et al., 2003; Tamura and Arai, 2005) or during metamorphism (Loferski and Lipin, 1983; Eales et al., 1988; Abzalov, 1998). The textures observed in Cr-spinel from the Pampean Ranges systematically indicate a metamorphic origin. In the case of unmixing textures (Figs. 3E,F and 4A), they indicate the solubility break between Al-rich Cr-spinels and ferric spinels. Estimated peak temperatures associated with regional metamorphism in the western ophiolitic belt from the Pampean Ranges of Córdoba are close to 600 to 700 °C, corresponding to upper amphibolite to granulite facies (Escayola et al., 2004), and probably represent the temperature at which exsolution in chromite began. However, exsolution in metamorphic spinels may occur only in rocks that have prolongated cooling histories.

In conclusion, the primary composition of Cr-spinels in metamorphosed peridotites, disseminated chromitites, and many chromitites from the western ophiolitic belt from Pampean Ranges of Córdoba were obliterated by prograde metamorphism up to granulitic facies. The use of their chemical composition as a petrogenetic and geotectonic indicator requires rigorous petrographic study.

8.3. Conditions of PGM formation and post-magmatic evolution

It is commonly believed that PGM enclosed in chromite crystals crystallized before and during the precipitation of the host chromite, and are magmatic in origin. Textural and paragenetic relationships and theoretical predictions deduced from relative stability of the PGM indicate that, in most ophiolitic chromitites, the order of the magmatic crystallization of PGM is the following: Ru–Os–Ir alloys → laurite → erlichmanite. This order of crystallization implies that the PGM, in the magmatic stage, formed under increasing fS_2 with decreasing temperature (Augé and Johan, 1988). The presence of osmium as inclusions in the chromite of the Los Congos (Fig. 9A) suggests that this PGM was probably one of the first to precipitate at very low sulfur activity. In contrast, the presence of laurite and erlichmanite, although altered, in the Los Guanacos chromitites is indicative of a higher sulfur fugacity during their crystallization.

Recent investigations have demonstrated that PGM can be altered or modified at a relatively low temperature. Stockman and Hlava (1984) argued that Ru-rich alloys in chromitites of southwestern Oregon were formed during serpentinization by alteration of magmatic laurite. Formation of these secondary PGM, as a result of low temperature modification, was then reported from several ophiolitic chromitites (McElduff and Stumpfl, 1990; Nilsson, 1990; Thalhammer et al., 1990; Garuti and Zaccarini, 1997). One common PGM alteration process in ophiolitic chromitites is the formation of Ru–Os–Ir–Fe oxides by *in situ* desulfurization of laurite–erlichmanite during serpentinization, followed by oxidation of the desulfurized PGM (Garuti and Zaccarini, 1997). Some zoned laurites in the Los Guanacos chromitites show relics of a core composed of erlichmanite rimmed by laurite which in turn is overgrown by Ru oxide or

hydroxide (Fig. 9C,D). Since the Os-content of laurite crystallized from a silicate melt is a direct function of fS_2 increase with decreasing temperature (Augé and Johan, 1988), the observed zoning ($OsS_2 \rightarrow RuS_2$) clearly is not consistent with a magmatic crystallization of the laurite grains. This observation, and the presence of the Ru oxide or hydroxide, strongly suggests that these laurite grains were altered and reworked *in situ*, after their magmatic formation during the metamorphism. Although it is difficult to establish the extent of platinum group element mobilization based on mineralogical observation, our data indicate that the *in situ* alteration process that affected the PGM of Ru–Os–Ir in the Los Guanacos and Los Congos chromitites caused redistribution of these PGE on a small scale.

A typical feature of ophiolitic chromitites is the presence of abundant PGM of Ru–Os–Ir and the scarcity of Pt–Pd–Rh phases. The occurrence of abundant Pt–Pd–Rh minerals has been documented, in detail, only from the ophiolitic chromitites of New Caledonia (Augé and Maurizot, 1995) and Kraubath, Austria (Malitch et al., 2003). Augé and Maurizot (1995) suggested that the magmatic Pt-minerals associated with the chromitites of New Caledonia precipitated directly from a new magma characterized by low fugacity of S and injected in the crustal cumulate pile of the ophiolitic sequence. The New Caledonia chromitites show a typical cumulus texture and are enrichment in Ti and Fe^{3+} due to the precipitation from an evolved magma.

The chromitites of Kraubath are enriched in Pd–Pt–Rh minerals and have been interpreted to be hosted in the transition zone of an ophiolite, closely above the mantle section, rather than being representative of the crustal cumulate pile (Malitch et al., 2003). The formation of abundant Pd–Pt–Rh minerals in these mantle chromitites was ascribed to remobilization of PGE and other elements such as Hg, As, Sb, Te and Au by hydrothermal processes during polyphase regional metamorphism (Malitch et al., 2001).

Similar to those of Kraubath, the Los Guanacos and Los Congos chromitites are believed to be hosted in the mantle portion close to the transition zone of an ophiolite that was affected by a strong metamorphism, and not in the crustal cumulate pile as those of the New Caledonia ophiolite. Therefore, the presence of rare Pt PGM, including tellurides, oxides or hydroxides and unusual PGE–As–Se compounds associated with the altered silicate of the chromite matrix (Fig. 9E,F) in the Los Congos chromitites, could be explained in the same way as proposed by Malitch et al. (2001) for the formation of PGE mineralization in the Kraubath chromitites, i.e., hydrothermal processes during regional metamorphism.

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