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**Gabriela Ferracutti, Ernesto Bjerg &
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Petrology, geochemistry and mineralization of the Las Águilas and Virorco mafic–ultramafic bodies, San Luis Province, Argentina

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Abstract The layered mafic–ultramafic rocks in the Sierras de San Luis, Argentina (Las Águilas, Las Higueras and Virorco), constitute a 3–5-km-wide belt that extends over 100 km from NE to SW. They carry a sulphide mineralization consisting of pyrrhotite, pentlandite and chalcopyrite, in veins and as disseminated to massive ore. Disseminated spinels are frequently associated with the sulphide minerals as well as platinum group minerals. A strong correlation between S, Ni, Co, Cu, Cr, Pt and Pd indicates the presence of one to three levels of mineralization within the ultramafic units. The maximum concentration of these elements coincides with the units containing platinum group minerals (PGM) and spinel group minerals. This clear relationship constitutes a good prospecting guide in the search for layers with high-grade ore, probably associated with deeper stratigraphic levels where ultramafic rocks are dominant. The bulk rock chemistry and concentrations of metals and platinum group elements as well as textural evidence suggest that the parental magma was mafic with tholeiitic affinities and MgO rich. The Las Águilas layered mafic–ultramafic body and the remaining bodies in the area bear similar characteristics to well-known stratified complexes developed in extensional tectonic regimes, as it is the case of Jinchuan (China), Kabanga (Tanzania) and Fiambala (Argentina).

Keywords Layered · Mafic–ultramafic · Geochemistry · PGE · Argentina

Introduction

The belt of mafic–ultramafic rocks in San Luis province, Argentina, trends NE–SW and extends for 100 km on the eastern slope of the Sierra Grande of San Luis (Fig. 1). The southernmost outcrops are located at 35 km to the NE of San Luis city and comprise the Las Águilas, Las Higueras and Virorco mafic–ultramafic bodies.

In addition to the mafic–ultramafic rocks, in this part of the Sierras de San Luis, there are outcrops of metavolcanic and metasedimentary rocks of Precambrian–Paleozoic age, all belonging to the Sierras Pampeanas morphostructural unit.

The mafic–ultramafic rocks consist mainly of: (1) orthopyroxene (opx) + amphibole (amph) + plagioclase (pl) ± clinopyroxene (cpx) ± biotite (bi) ± spinel (spl) ± sulphides ± platinum group minerals (PGM) and (2) olivine (ol) + spl + sulphides ± PGM (Mogessie et al. 1994, 1995; Hauzenberger et al. 1997a, b; Felfernig et al. 1997). Several studies have been carried out on the mafic–ultramafic bodies of San Luis, among others by Villar (1975); Kilmurray and Villar (1981); Sabalúa et al. (1981); Sabalúa (1986); Gervilla et al. (1993, 1997); Malvicini and Brogioni (1992, 1993, 1996); Brogioni (1994, 2001a, b); Ferracutti et al. (2004) and Delpino et al. (2007).

This contribution documents the petrological, geochemical and mineralization significance of the mafic–ultramafic rocks present between the Las Águilas and Los Manantiales rivers. To accomplish these objectives, detailed field work was performed covering the

G. Ferracutti (✉) · E. Bjerg
Departamento de Geología, INGEOSUR (CONICET-UNS),
Universidad Nacional del Sur, San Juan 670, B8000ICN Bahía
Blanca, Argentina
e-mail: gferrac@uns.edu.ar

A. Mogessie
Department of Mineralogy and Petrology, Institute of Earth
Sciences, University of Graz, Universitaetsplatz 2, 8010 Graz,
Austria

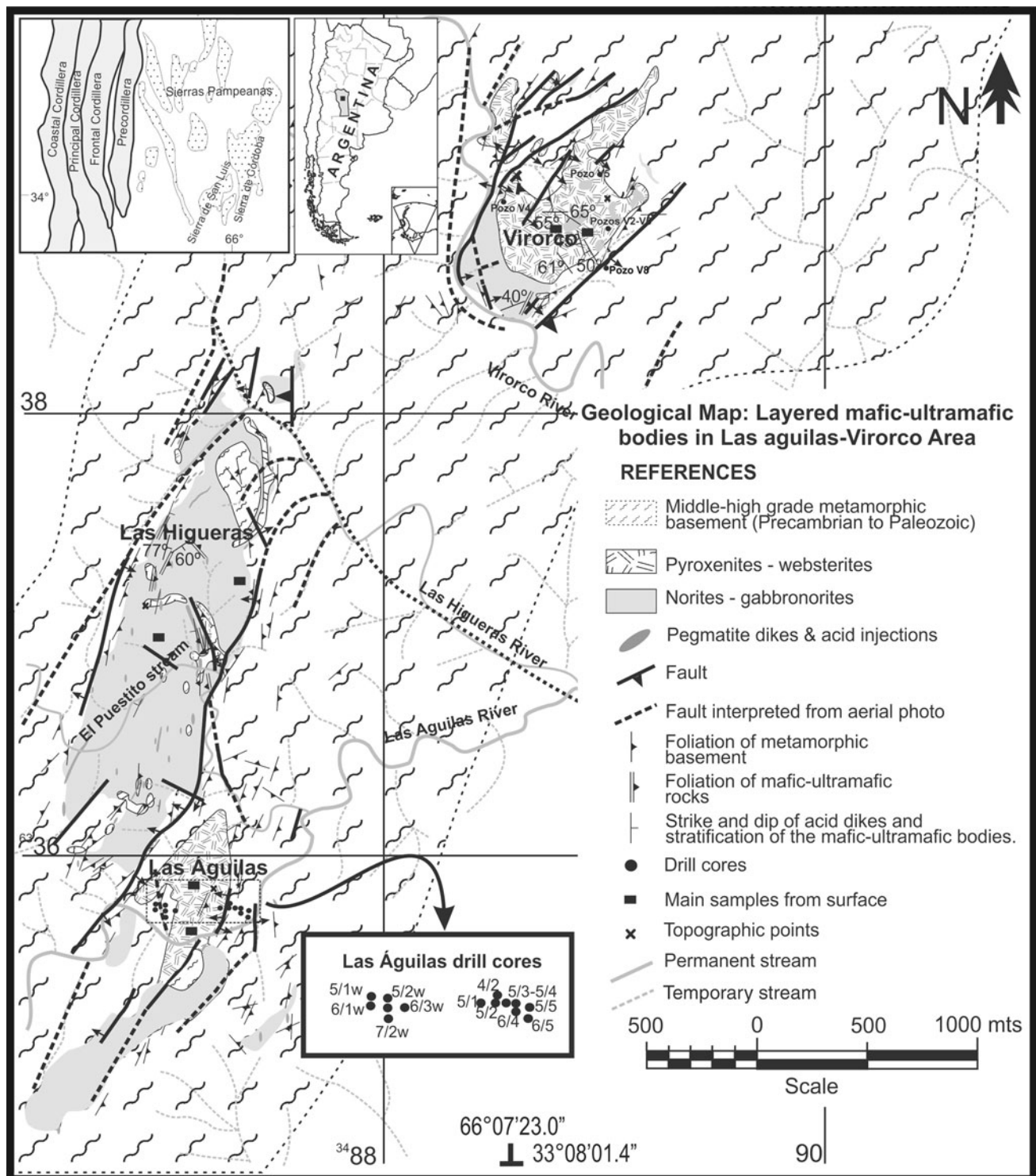


Fig. 1 Geological map of the Las Águilas, Las Higueras and Virorco area, San Luis province, Argentina

mafic-ultramafic units and the metamorphic basement rocks. Petrographic and geochemical studies were conducted on the mafic-ultramafic rocks present in the area, and their relation with mineralization was analysed in

order to establish the composition of the primitive magma.

Based on the concentrations of platinum group elements (PGE) and Cu-Ni-Au, the geotectonic setting was defined

and compared with other worldwide occurrences of similar rock types.

Geological setting

In the Sierra Grande of San Luis, rocks occurring between the Las Águilas and Los Manantiales rivers (Fig. 1) comprise Precambrian to Paleozoic mafic–ultramafic and basement (metasediments and metavolcanics) rocks (Hauzenberger et al. 1997b; Rapela et al. 1998; Sims et al. 1998; Von Gosen et al. 2002).

The mafic–ultramafic rocks are associated with high-grade metamorphic rocks such as gneisses, amphibolites and granulites. The intrusives consist of norites (the dominant rock type in the outcrops), gabbro-norites, pyroxenites and peridotites with an associated base metal sulphide mineralization (Ni–Cu–Co). Based on the geological and geophysical mapping of the Sierras Pampeanas, including an extensive programme of SHRIMP and Ar–Ar geochronology, Sims et al. (1997) concluded that the mineralized Las Águilas mafic–ultramafic rocks are Ordovician. More recently, Sato et al. (2002) established an Early Mesoproterozoic ($1,502 \pm 95$ Ma) age for these rocks based on a Sm–Nd isochrone for the komatiites and amphibolites located at the westernmost part of the Sierra Grande of San Luis.

The mafic–ultramafic bodies show geochemical patterns similar to those of layered complexes (Mogessie et al. 2000; Hauzenberger et al. 1997a). Based on petrological and geochemical evidences, these rocks were emplaced in an extensional back-arc basin during the Late Proterozoic (Ramos 1988).

The spinel group minerals provide important information regarding the tectonic setting and magmatic conditions at the time of initial crystallization. In the Las Águilas mafic–ultramafic complex, spinels have been studied by Gervilla et al. (1993), Malvicini and Brogioni (1992) and Mogessie et al. (2000). Spinel compositions allowed Ferracutti et al. (2004, 2006a) to classify the mafic–ultramafic body as a layered mafic–ultramafic intrusive. Ferracutti et al. (2006a) reported the existence of two groups of spinels (Type I and II), both with chromium–aluminium-rich cores whose magmatic origin is supported by the following facts: (a) on the Al–Cr–Fe³⁺ they plot along a trend which does not intercept the solvus line typical of spinel formed under high-grade metamorphic conditions, (b) there is no Fe²⁺–Mg exchange between the silicates (orthopyroxene and olivine) and spinels after the crystallization, and (c) spinels are hosted by ultramafic rocks still retaining primary magmatic features. They are not the result of corona-forming reactions which would lead to the formation of

aluminous green spinel as it occurs with the chromites hosted in ultramafic rocks from the Cordoba Ophiolite (Proenza et al. 2008). According to Ferracutti et al. (2006a) there is a close similarity between Las Águilas spinels and the “brown spinels” type from the Americano and Mangabal I and II complexes from Brazil (Candia and Gaspar 1997). The chemical compositions of these interstitial “brown spinels” are considered as the result of their reaction with the intercumulus liquid during the postcumulus stage.

Analytical methods

More than 150 thin sections of mafic and ultramafic rocks from outcrops and drill cores were studied using a combination of reflected light microscopy, electron microprobe and scanning electron microscopy (SEM). The analyses were made at the Institute of Mineralogy and Petrology, Karl Franzens University Graz, Austria, with a JEOL 6310 SEM microprobe.

Standard analytical conditions were set to an accelerating voltage of 15 kV and 5 nA sample current for silicate minerals and 20 kV for sulphides and PGM. Matrix corrections were made using the ZAF procedure for EDX and WDS analyses. The following mineral standards were used: Si, K, Adularia; Al, Andalusite; Fe, Mg, Garnet or Olivine; Ca, Ti, Titanite; Mn, Tephroite; Zn, Gahnite; Cr, synthetic Mg–Chromite; Cl, Atacamite; F, F–Apatite; Na, Jadeite and pure sulphides and PGM. Practical detection limits in these routine analyses vary from 0.05 to 0.1 wt% for the MICROSPEC wavelength dispersive system (F and Na) and 0.1–0.5 wt% for the LINK ISIS energy dispersive system (for the rest of the elements analysed).

Bulk rock chemical analyses for major, trace, rare earth (REE) and platinum group elements (PGE) were done with X-ray fluorescence (XRF) for major oxides and ICP-MS and INAA for trace elements and PGE at Activation Laboratories, Canada. The detection limits for PGE were 1 ppb for Ir, Rh, Re, Ru, Pd and Pt and 2 ppb for Os.

Petrography of mafic–ultramafic rocks

The mafic rocks are norites, gabbro-norites, norite mylonites and gabbro-norite pegmatites. The ultramafic rocks comprise dunites, harzburgites, orthopyroxenites and websterites.

Changes in mineralogy, texture and mineral composition documented in the Las Higueras and Virorco bodies indicate primary magmatic layered textures (Winter 2001). These are non-uniform (mineralogically heterogeneous)

with a different modal composition and an intermittent regularity. Figure 2a–e shows outcrops from Viorco with a significant repetitive layering with different modal compositions between $\text{opx} \pm \text{cpx} + \text{Mg hbl} \pm \text{pl}$ and $\text{Mg hbl} + \text{Tsch hbl} + \text{Ath}$ (Fig. 2c–e). Although some thin fine-grained pyroxenite layers have a sharp contact, the general sequence shows transitional contacts.

Figure 2b shows an outcrop displaying colloform layering or banding, similar to the structures described for the Marginal Border Group of the Skaergaard Intrusion by McBirney and Noyes (1979), Irvine (1982), Shelley (1993) and Andersen (2002). This structure is the result of progressive magma cooling at the external border of the intrusion and very probably represents in situ crystallization of magma (Irvine 1982). The domal layers face towards the centre of the intrusion and are separated by sharp cusps that point towards the walls (Shelley 1993).

Mineralization

Platinum group minerals (PGM) are associated with the mafic–ultramafic rocks of Las Águilas and Viorco bodies, as indicated by Sabalúa et al. (1981), Sabalúa (1986), Malvicini and Brogioni (1992, 1993, 1996), Gervilla et al. (1993, 1997), Mogessie et al. (1995, 2000), Felfernig et al. (1997), Hauzenberger et al. (1997a), Ferracutti and Bjerg (2002) and Ferracutti et al. (2006b, 2007). According to these authors, the mineralization varies from massive to disseminated and comprises pyrrhotite, pentlandite and chalcopyrite with minor amounts of pyrite, PGM (palladium bismuthotellurides, platinum arsenides and iridium–rhodium sulpharsenides), molybdenite, bravoite, violarite, mackinawite, cubanite, ilmenite, magnetite and graphite constituting accessory phases.

According to Ferracutti et al. (2007), the base metal and PGM mineralization in the Las Águilas and Viorco bodies

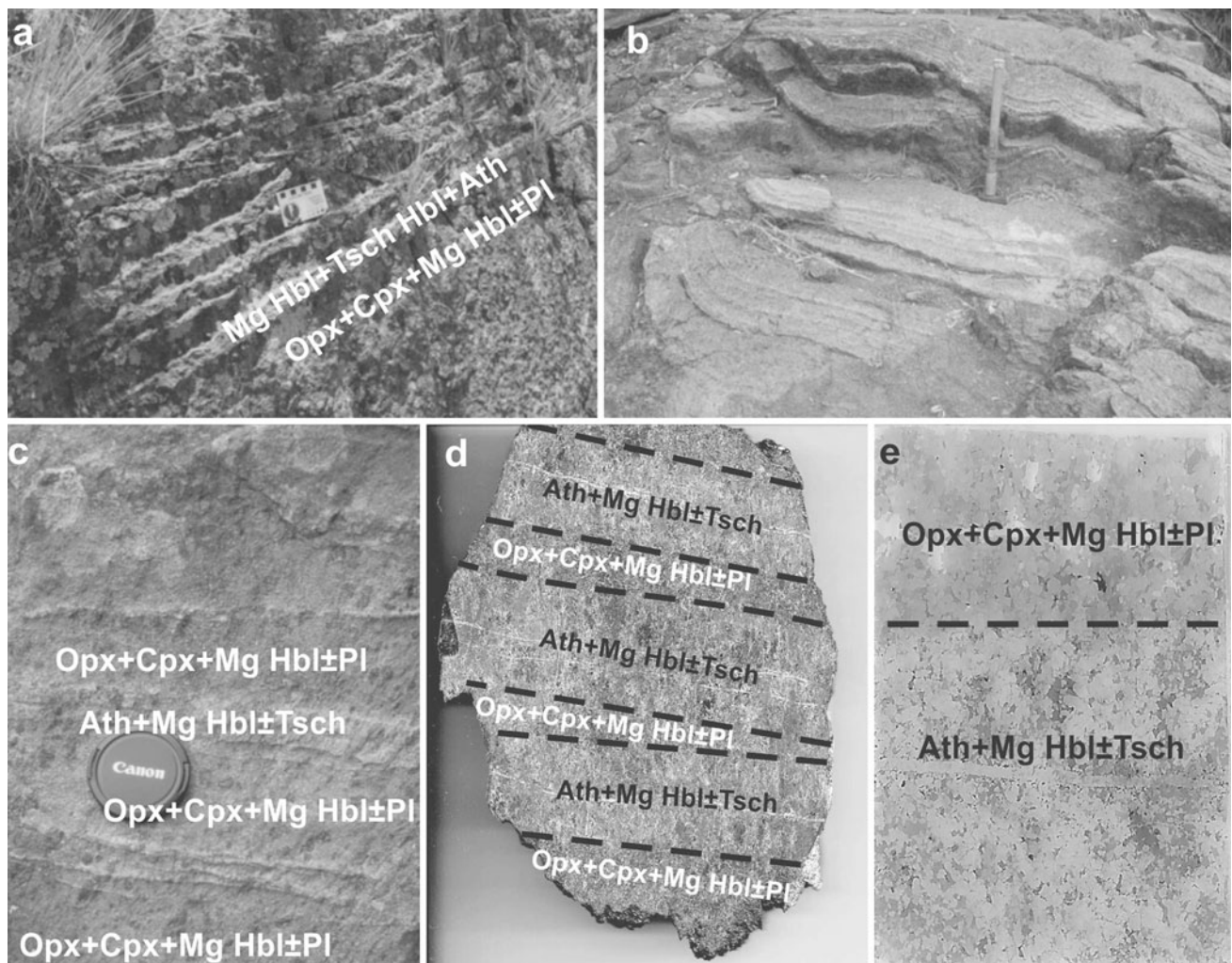


Fig. 2 Outcrops of layered mafic–ultramafic rocks with repetitive layering (a, c, d, e) and colloform layering (b). Abbreviations Opx (orthopyroxene), Cpx (clinopyroxene), Pl (plagioclase), Mg Hbl (magnesio-hornblende), Ath (anthophyllite) and Tsch (tschermakite)

Table 1 Whole-rock composition of drill core samples from Las Águilas deposit and outcrop samples from the study area

Sample	SL-68	RF 3	RF 9	5/3-66.8	5/4-84.8	E43	4/2-55.7	5/5-163.1	7/4-158.6	SL-95	SL-97	4/2-42.7	5/5-141.5	6/4-125.2
Rock	Gab	Gab	Gab	Gab	Gab	CM	Sulph-rich dun	Pyrox	Pyrox	Pyrox	Pyrox	Sulph-rich harzb	Harzb	Sulph-rich dun
	Outcrop	Outcrop	Outcrop	Drill core	Drill core	Outcrop	Drill core	Drill core	Drill core	Outcrop	Outcrop	Drill core	Drill core	Drill core
	LA	Vi	LH	LA	LA	Vi	LA	LA	LA	Vi	Vi	LA	LA	LA
SiO ₂	55.51	48.57	48.83	47.35	48.47	48.76	35.88	48.92	43.45	52.05	52.44	29.62	33.98	25.87
TiO ₂	0.55	0.7	0.35	0.13	0.17	0.54	0.15	0.18	0.21	0.35	0.37	0.05	0.05	0.03
Al ₂ O ₃	16.59	9.63	20.03	12.57	10.43	14.37	3.45	4.61	4.4	4.38	5.59	1.45	1.18	0.61
FeO	9.31	13.12	8.26	13.68	14.77	10.83	29.8	13.25	19.48	11.36	12.63	24.96	18.7	27.99
MnO	0.22	0.21	0.16	0.28	0.19	0.21	0.29	0.23	0.28	0.23	0.25	0.17	0.22	0.16
MgO	8.04	18.33	8.35	13.35	16.57	13.55	17.22	24.96	21.03	21.92	23.21	26.54	33.03	26.55
CaO	6.88	5.45	10.83	6.7	4.96	8.85	1.6	4.91	2.24	8.19	4.27	0.59	1.57	0.3
Na ₂ O	1.16	0.62	1.16	0.83	0.45	0.92	0.17	0.18	0.26	0.31	0.36	0.06	0.06	0.03
K ₂ O	1.15	0.87	0.31	0.35	0.4	0.47	0.3	0.06	0.51	0.11	0.17	0.07	0.03	0.04
P ₂ O ₅	0.1	0.04	0.02	0.36	0.21	0.03	0.02	0.01	0.02	0.01	0.01	0.02	0.02	0.02
LOI	0.06	0.43	0.82	1.66	<0.36	0.37	4.56	1	2.51	0.23	0.19	10.52	6.36	8.8
S	n.a.	n.a.	n.a.	n.a	n.a	n.a.	7.1	1.32	3.96	n.a.	n.a.	6.57	2.85	9.8
Total	100.55	99.43	100.03	98.76	97.9	100.1	100.54	99.63	98.35	100.18	100.71	100.62	98.05	100.2
#mg	0.46	0.58	0.50	0.49	0.53	0.56	0.37	0.65	0.52	0.66	0.65	0.52	0.64	0.49
Sc	30	48	28	30.2	33	41	26	40	36	67	48	4	9	4
Cr	142	1220	40	737	1 330	480	4 850	2 549	3 973	1626	1267	3 870	3 446	2 122
Co	42	69	44	152	183	56	642.1	113.2	149.3	76	101	218.5	131.4	453.5
Ni	73	253	20	2 507	1 058	190	11 942	704	1 606	217	273	3 531	1 681	9 135
Zn	27	110	64	237	107	100	199	129	124	9	8	167	240	77
Rb	63	32	6	16	30	8	12	2	21	3	4	4	2	2
Sr	143	60	273	114	181	180	9	26	10	22	44	11	11	6
Y	14	18	11	16	22	17	4	5	5	10	10	2	2	1
Zr	68	47	19	30	27	24	9	9	11	17	22	8	7	4
Nb	5	2	3	n.a	n.a	2	2	1	2	1	2	1	1	1
Ba	218	118	59	84	105	47	23	11	31	40	77	10	10	5
V	164	264	181	n.a	158	188	171	179	204	222	235	55	62	35
La	8.38	6.17	8.20	n.a	17.20	5.37	1.65	0.81	2.32	1.70	2.72	0.95	0.89	0.30
Ce	19.95	18.11	18.13	n.a	36.00	15.3	5.08	2.23	6.69	5.52	7.03	2.08	2.23	0.56
Pr	2.33	2.76	2.31	n.a	n.a	1.95	0.68	0.32	0.78	0.82	0.91	0.24	0.26	0.06
Nd	11.48	13.20	10.06	n.a	18.00	9.54	3.30	1.80	3.31	4.95	5.15	1.10	1.19	0.26
Sm	2.44	3.40	2.45	n.a	4.50	2.65	0.81	0.58	0.80	1.38	1.31	0.27	0.29	0.04

Table 1 continued

Sample	SL-68	RF 3	RF 9	5/3-66.8	5/4-84.8	E43	4/2-55.7	5/5-163.1	7/4-158.6	SL-95	SL-97	4/2-42.7	5/5-141.5	6/4-125.2
Rock	Gab	Gab	Gab	Gab	Gab	CM	Sulph-rich dun	Pyrox	Pyrox	Pyrox	Pyrox	Sulph-rich harzb	Harzb	Sulph-rich dun
	Outcrop	Outcrop	Outcrop	Drill core	Drill core	Outcrop	Drill core	Drill core	Drill core	Outcrop	Outcrop	Drill core	Drill core	Drill core
	LA	Vi	LH	LA	LA	Vi	LA	LA	LA	Vi	Vi	LA	LA	LA
Eu	0.67	0.59	0.70	n.a	0.91	0.72	0.17	0.15	0.19	0.34	0.35	0.05	0.06	0.01
Gd	2.19	3.55	2.29	n.a	n.a	2.93	0.75	0.67	0.76	1.62	1.51	0.26	0.27	0.05
Tb	0.39	0.60	0.39	n.a	0.60	0.52	0.13	0.13	0.14	0.28	0.26	0.04	0.04	<0.01
Dy	2.43	3.24	2.25	n.a	n.a	2.95	0.78	0.80	0.82	1.84	1.62	0.26	0.27	0.05
Ho	0.49	0.62	0.45	n.a	n.a	0.6	0.15	0.18	0.18	0.37	0.35	0.04	0.06	0.01
Er	1.58	1.76	1.37	n.a	n.a	1.83	0.44	0.53	0.50	1.15	1.08	0.14	0.15	0.05
Tm	0.23	0.23	0.20	n.a	n.a	0.27	0.07	0.08	0.08	0.17	0.16	0.02	0.02	0.01
Yb	1.59	1.45	1.19	1.15	1.94	1.68	0.48	0.57	0.55	1.10	1.08	0.14	0.15	0.05
Lu	0.26	0.23	0.18	0.16	0.28	0.25	0.07	0.08	0.09	0.17	0.16	0.02	0.02	0.01
Rh	n.a	n.a	n.a	1	n.a	n.a	12	2	5	n.a	n.a	35	24	45
Pd	n.a	n.a	n.a	150	n.a	n.a	347	65	180	n.a	n.a	719	450	1 420
Ir	n.a	n.a	n.a	<1	<2	n.a	7	1	2	n.a	n.a	11	8.3	24
Pt	n.a	n.a	n.a	22	n.a	n.a	5	28	104	n.a	n.a	247	180	84
La/Yb	5.27	4.26	6.90	–	8.87	2.29	3.44	1.42	4.22	1.55	2.52	6.79	5.93	6
Eu* = [(Sm × Gd) _N] ^{1/2}	13.04	19.59	13.34	–	–	15.71	4.4	3.52	4.4	8.43	7.93	1.49	1.58	0.25

Eu* is the value of Eu anomaly obtained by interpolating the normalized values of Sm and Gd

Major elements (wt%), trace elements (ppm) and platinum group elements (ppb). The nearest values to the parental magma are in bold (see text for details). n.a. not analysed. LA: Las Águilas, LH: Las Higueras and Vi: Viorco

Gab gabbroid, *CM* chilled margin, *Pyrox* pyroxenite, *Sulph-rich harzb* sulphide-rich harzburgite, *Harzb* harzburgite, *Sulph-rich dun* sulphide-rich dunite

is mainly restricted to ultramafic layers which have associated spinel minerals. This mineralization comprises two mineral associations: (a) primary magmatic mineralization composed of $Po1 + Ccp1 + Pn \pm PGM \pm Cub$ which is present with net or interstitial and nodular textures and (b) the mineralization of $Po2 + Ccp2 + Pn \pm PGM \pm Py \pm Mck$ associated with remobilization and present in disseminated texture and filling massive fractures. The PGM are mainly associated with the second one.

Bulk rock geochemistry

Major elements

The results of the analyses of outcrop samples from Las Águilas, Las Higueras, Virorco and Las Águilas drill cores are given in Table 1 and plotted in Fig. 3.

The MgO content ranges from 5 to 16 wt% in mafic rocks and from 16 to 37 wt% in ultramafic rocks (Fig. 3) and shows a positive correlation with FeO_{total} and other major oxides. In mafic rocks FeO_{total} is below 15 wt% and

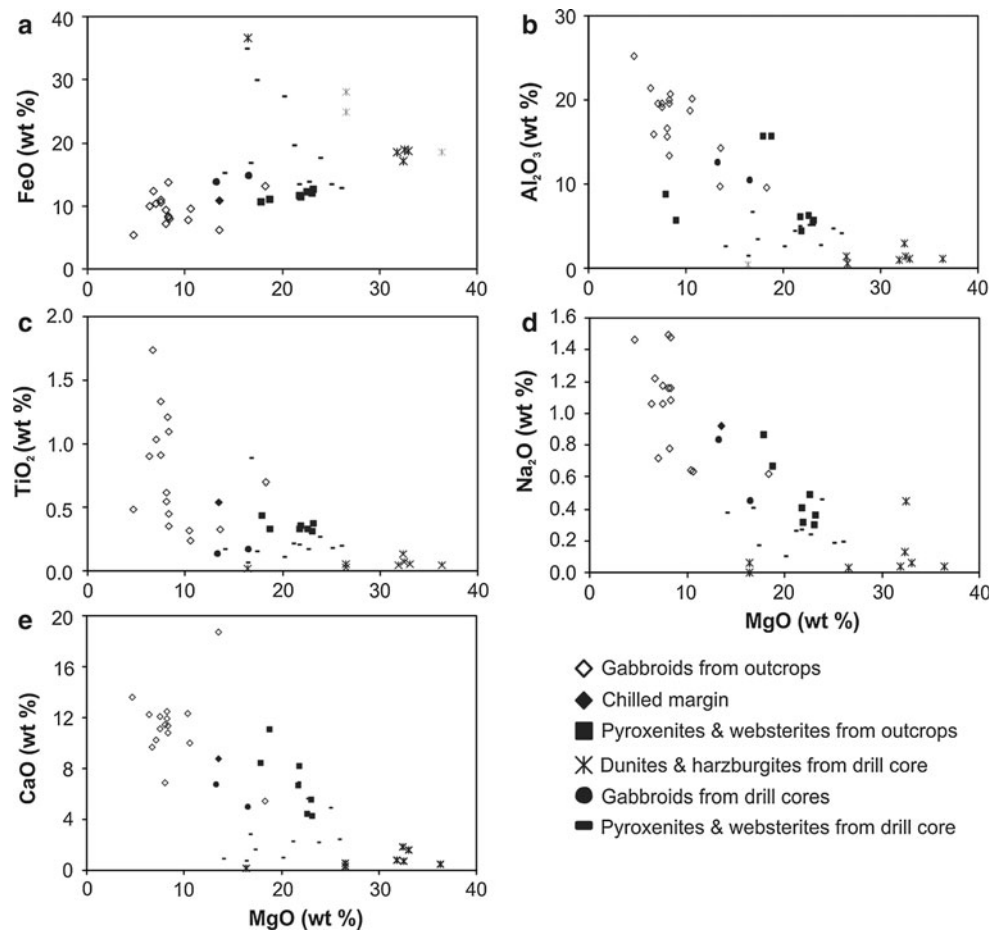
varies from 11 to 37 wt% in ultramafic samples. Ultramafic rocks with FeO_{total} values between 25 and 37 wt% have significant sulphide mineralization.

Al_2O_3 , TiO_2 , Na_2O and CaO show a negative correlation with MgO (Fig. 3b–e). In mafic rocks the TiO_2 content ranges from 0.25 to 1 wt%, while in ultramafic samples, it is below 0.4 wt%. The Al_2O_3 content ranges from 9.6 to 25 wt% and 0.43–16 wt% in mafic and ultramafic rocks, respectively. In mafic rocks the CaO content varies between 5 and 19 wt% and 0.16 and 11 wt% in ultramafic rocks, while Na_2O is below 1.5 and 0.9 wt%, respectively.

Trace elements and transition metals

Plots of Zr, Ta, Y, Hf, Nb, V, Sr, Sc versus MgO (Fig. 4) show clear differences between the most primitive and the most differentiated rocks. The ultramafic rocks have contents of incompatible elements similar to primitive mantle values (PM, Taylor and McLennan 1985). According to Pearce (1983), during metamorphism and due to the influx of meteoric fluids, Hf and Zr behave as moderately incompatible elements, while Nb and Ta are incompatible

Fig. 3 MgO versus FeO (total), Al_2O_3 , TiO_2 , Na_2O and CaO



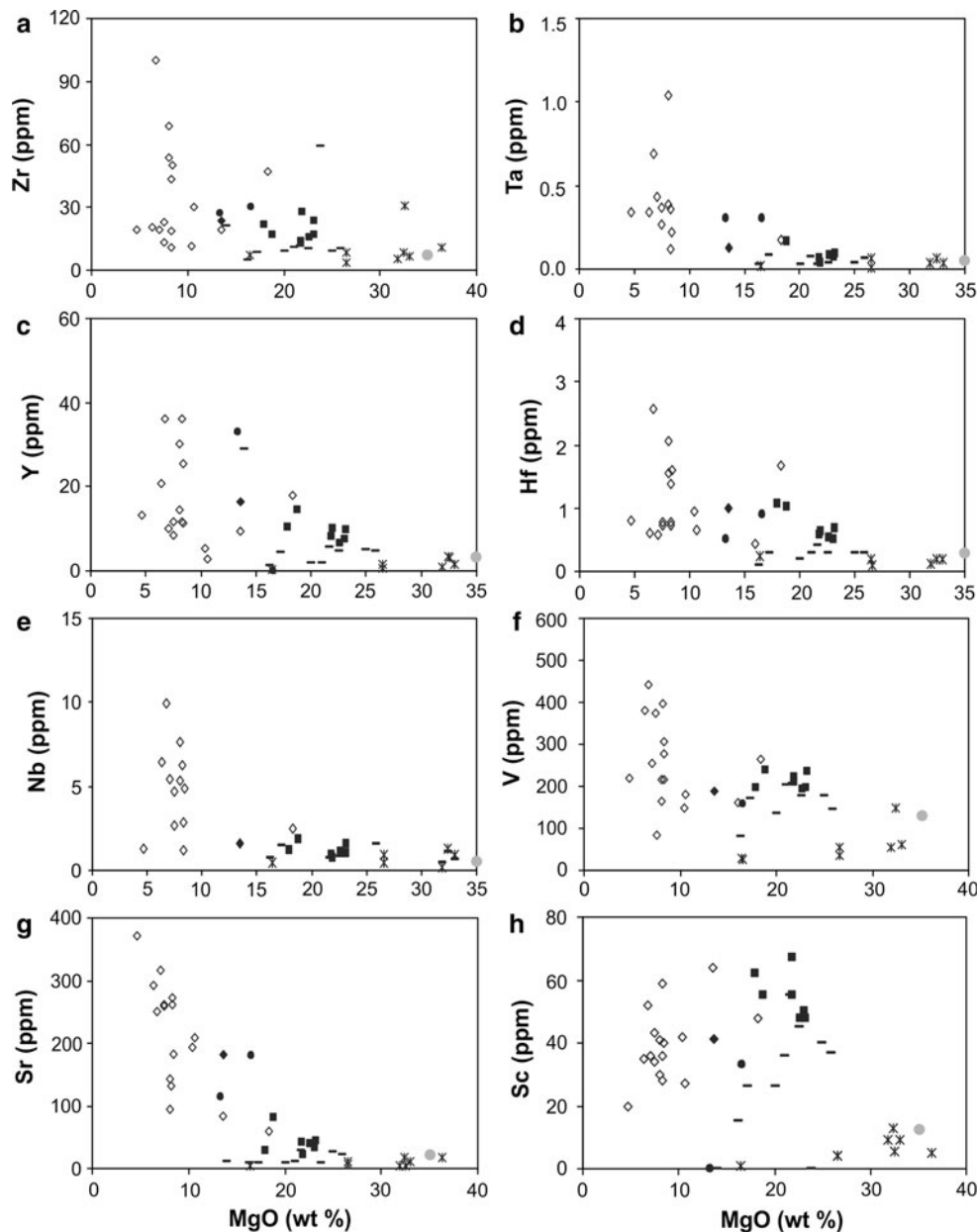


Fig. 4 MgO versus trace elements. Symbols as in Fig. 3, grey circle is the value for Primitive Mantle (after Taylor and McLennan 1985)

and immobile. Zr is a good indicator of igneous fractionation (Saunders and Tarney 1979), and the Zr and Hf versus MgO diagrams reflect this process.

Compatible elements like Co, Cr and Ni plotted against MgO (Fig. 5a–c) display a positive correlation. However, the Co and Cr versus MgO diagrams show a group of ultramafic rocks more enriched in these elements than the other rocks. These enriched samples have abundant ore minerals (30–70 %) and higher modal amounts of spinel compared to the rest of the plotted samples. The concentrations of Pt and Pd range from 5 to 17,800 and 1420 ppb, respectively (Table 2). Pt and MgO display a positive correlation (Fig. 5d).

Sr, which is compatible in plagioclase, shows a negative correlation with MgO but a clearly positive one against Al_2O_3 (Fig. 5e).

Rare earth elements (REE)

Pyroxenites and websterites

Pyroxenites and websterites (Fig. 6a) display a chondrite-normalized REE pattern with LREE enrichment and La_N/Yb_N ranging from 4.7 to 1.1. In general, a characteristic feature of these groups of rocks is the negative Eu anomaly.

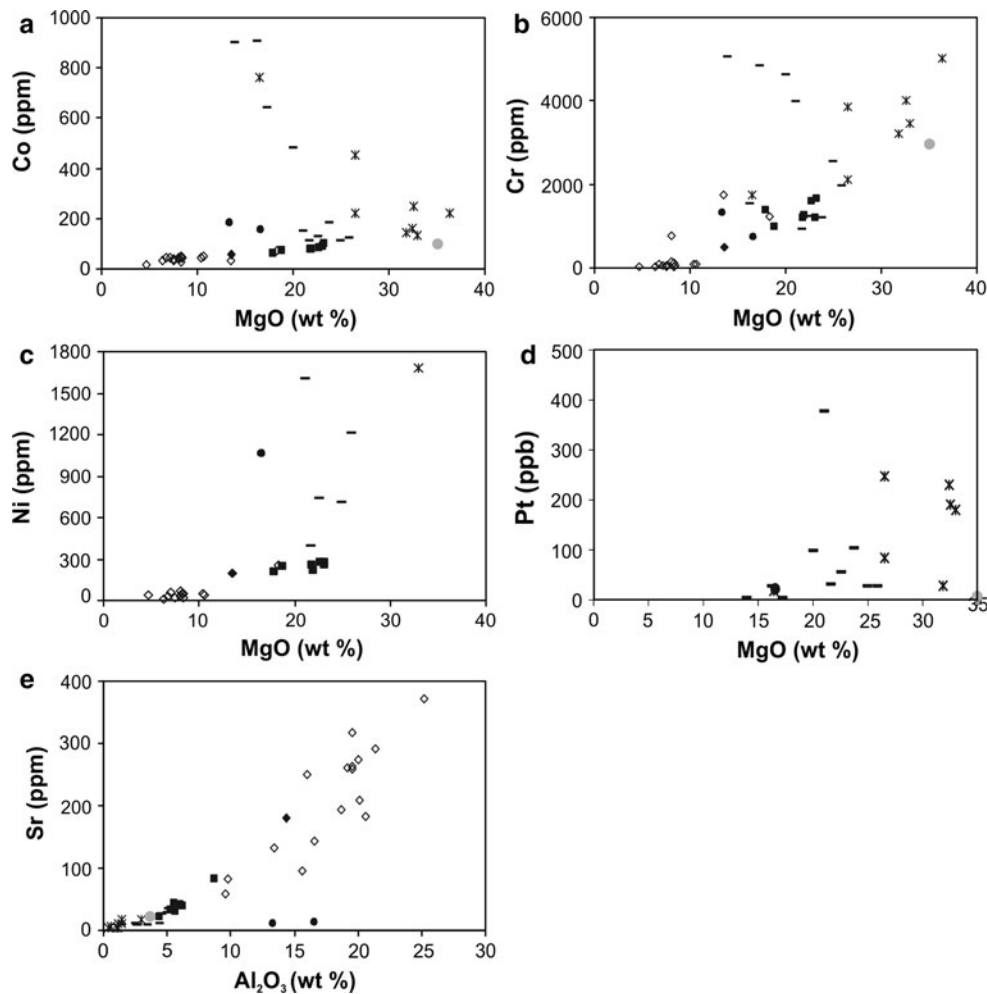


Fig. 5 MgO (wt%) versus trace elements (ppm; Pt in ppb) and Al₂O₃ (wt%) versus Sr (ppm). Symbols as in Fig. 3

Two groups of pyroxenites–websterites can be distinguished (Fig. 6a). One of them shows HREE and MREE values similar to chondrite (Sun and McDonough 1989), a moderate enrichment of LREE (samples 7/4–137.4 and 7/4–106, Fig. 6a), significant sulphide mineralization and no evidence of alteration. The other group of rocks, which has a more or less flat, unfractionated REE pattern, comprises samples that are altered and do not carry significant amounts of sulphide minerals.

Dunites and harzburgites

Normalized REE patterns (Fig. 6b) are very similar to those of pyroxenites–websterites, with occasional negative Eu anomalies and LREE enrichment. The La_N/Yb_N varies from 2.6 to 4.9 in drill core samples and from 1.6 to 1.9 in outcrop samples (RG 32–3 and RG 32–6).

Two samples (6/4–125.2 and 4/2–36.5), which carry 20–60 modal per cent sulphides, are depleted compared to chondrite.

Gabbroids

The chondrite-normalized REE plots of outcrop and drill core gabbroid samples are plotted in Fig. 6c. These rocks are characterized by an enrichment of LREE (La_N/Yb_N between 1.3 and 5.0) and a negative Eu anomaly.

Base metal mineralization and platinum group elements

In order to evaluate the possible relationships between sulphide mineralization, Pt–Pd contents and bulk rock geochemistry, a series of plots are presented in Figs. 7a, b, 8. The geochemical data from drill cores 6/4 and 5/3 are from samples that cover an interval of 3 m each, including rocks with and without mineralization. There is a positive correlation among S, Ni, Cu, Co, Pt and Pd, indicating the presence of one to three levels of mineralization within the ultramafic unit (Fig. 7a, b). The maximum concentration of these elements is coincident with the mineralized ultramafic units containing platinum

Table 2 Representative analyses of platinum group elements (PGE), Ni and Cu

Sample	Ni	Os	Ir	Ru	Rh	Pt	Pd	Au	Cu
Detection limit	2	0.1	5	0.2	5	2	0.5		
	(ppm)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)	(ppm)
SL-96 (pyroxenite)	25	1	7	1	5	6	1	252	19
SL-142 (gabbroid)	7	2	1	5	1	5	2	1	18
4/2-35.2 (sulphide-rich dunite)	2,420	20	49	39	89	5	485	17	930
4/2-36.5 (sulphide-rich dunite)	1,540	22	71	27	176	18	1,130	55	745
4/2-42.7 (sulphide-rich harzburgite)	353	44	11	86	34.8	247	719	61	1,497
4/2-55.7 (sulphide-rich dunite)	1,194	2	6.6	70	12.1	5	347	100	328
4/2-98.8 (sulphide-rich dunite)	74	2	1	5	5.6	56	284	26	100
4/2-115.0 (gabbroid)	39	2	0.5	5	1.3	32	23	12	33
5/3 66.80 (gabbroid)	251	2	1	17	1.3	22	150	11	251
5/3 80.00 (dunite)	572	2	1	11	3.3	190	650	160	202
5/3 91.6 (pyroxenite)	850	2	5.6	5	10	42	192	25	510
5/3 98.40 (pyroxenite)	239	2	1	12	2	30	67	1	112
5/3 103.0 (pyroxenite)	1,270	2	15.6	43	71	75	8	43	540
5/3 116.60 (sulphide-rich pyroxenite)	1,653	42	10	60	29	17,800	330	330	4,762
5/3 116.0 (pyroxenite)	50	2	0.1	5	0.2	5	2	19	550
5/3 116.5 (pyroxenite)	50	2	0.1	5	0.8	5	8	7.7	60
5/4 94.4 (sulphide-rich harzburgite)	2,200	22	45	35	96	83	295	43	450
5/5-136.5 (harzburgite)	116	2	0.1	5	0.5	5	2	4.9	57
5/5-141.5 (harzburgite)	168	2	8.3	5	23.6	180	450	32	89
5/5-148.1 (Sulphide-rich dunite)	434	6	21	22	40	28	413	11	279
5/5-163.1 (pyroxenite)	70	2	0.7	5	2.4	28	65	18	43
6/4-125.2 (sulphide-rich dunite)	914	26	24	90	45.3	84	1,420	56	1,019
7/4-116.7 (pyroxenite)	121	2	0.5	5	0.7	378	305	29	123
7/4-137.4 (sulphide-rich pyroxenite)	831	2	6.5	61	13.4	5	476	19	696
7/4 143.4 (pyroxenite)	113	2	7.8	12	17	24	280	47	81
LAW 6/1 97.4 (gabbroid)	484	2	3.6	5	10.6	136	232	180	569
Primitive mantle	Ni	Os	Ir	Ru	Rh	Pt	Pd	Au	Cu
Barnes et al. (1987)	200	4.2	4.4	5.6	1.6	8.3	4.4	1.2	2.8
Chondrites		Os	Ir	Ru	Rh	Pt	Pd	Au	
Naldrett and Duke (1980)		514	540	690	200	1,020.0	545	152	

group minerals, base metal sulphides and spinels (Table 2).

Correlations among S, Ni–Cu and Pd–Pt are positive (Fig. 8). The linear relationship between Ni, Cu, Pd, Pt and S reflects the association of PGE and base metals with sulphide.

Geochemistry of platinum group elements and metals

Due to the wide range of PGE values (Table 2), only PM-normalized patterns of samples with the highest and lowest PGE contents are plotted in Fig. 9. Samples 4/2 36.5 and 5/3 116.6, which have the highest PGE content, are enriched in sulphides (50 modal per cent), and their patterns define a positive trend from the Ir group elements (IPGE)

to the Pt group elements (PPGE). However, sample 4/2 36.5 displays significant negative anomalies for Pt and Au, whereas sample 5/3 116.6 shows a positive Pt anomaly.

Samples with low PGE content (5/3 116.5, 4/2 115.0 and SL 142) also display positive correlations from IPGE to PPGE, all of them showing negative Ir and Ni anomalies. These are samples with a very low proportion of sulphide mineralization (<5 modal per cent).

Cu/Pd versus Pd and Ni/Pd versus Cu/Pt

The PGE concentration in a deposit is a function of: (a) amount of sulphides in the rocks and (b) the metal content (e.g. Cu, Ni) in the sulphides (Barnes et al. 1993). The first of these functions is called the R factor which is

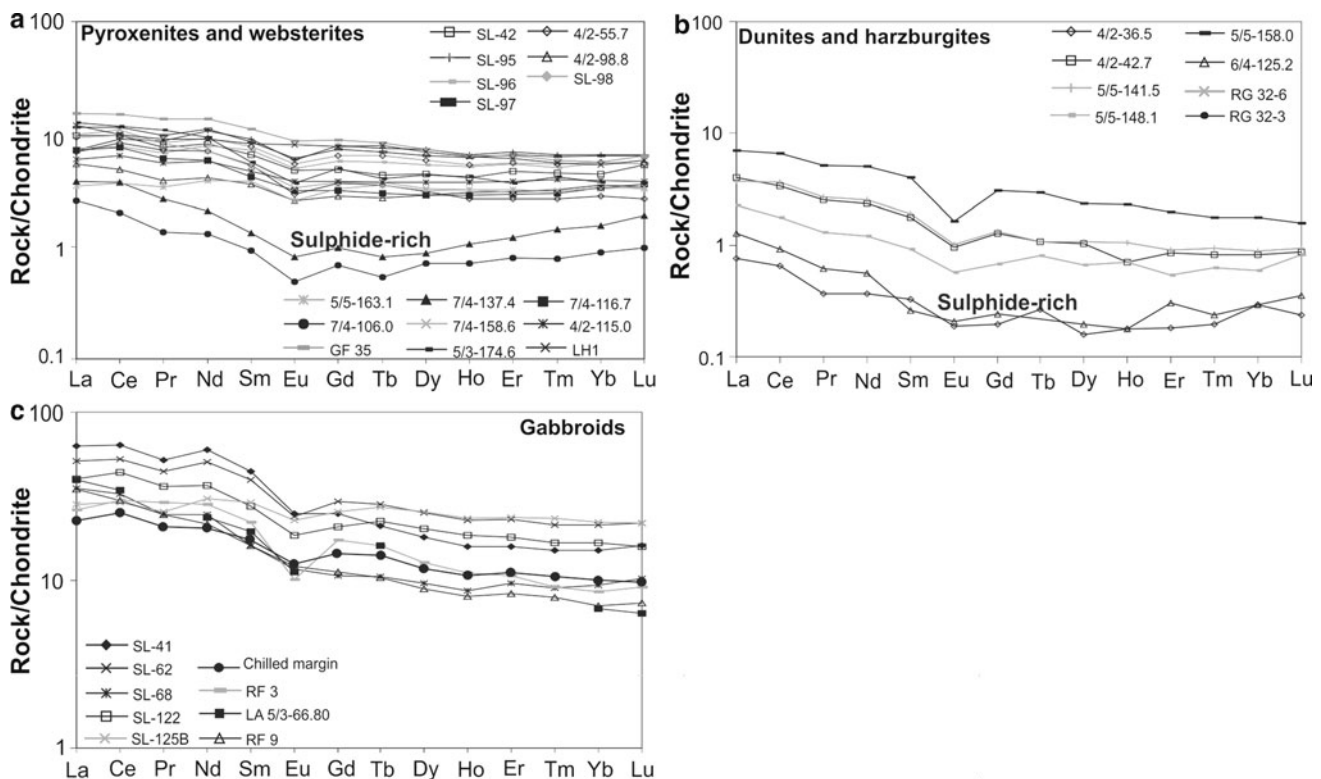


Fig. 6 REE normalized to chondrites (Sun and McDonough 1989). **a** Pyroxenites and websterites, **b** dunites and harzburgites and **c** mafic rocks (gabbroids)

the mass relation between silicate and sulphide liquids (Campbell and Naldrett 1979).

In Fig. 10a, the solid lines relate the silicate liquid and sulphides in equilibrium with this liquid at different R factors (from 0.001 to 100,000 after Campbell and Naldrett 1979). The grey points on each line show the composition of rocks containing 0.1, 1, 10 and 100 % sulphides.

The Cu/Pd versus Pd plot (Fig. 10a) can be divided into three parts: the upper part (PGE depleted) where samples have a Cu/Pd ratio greater than the mantle, a central part corresponding to samples with contents similar to the mantle and finally a lower part grouping rocks that are PGE enriched with a Cu/Pd ratio lower than the mantle (PGE enrichment). Most of the samples from drill cores and outcrops (Fig. 10a) have a Cu/Pd ratio that plot inside the fields delimited by rocks with PGE contents similar to the mantle or PGE depleted. The first ones (PGE mantle values) have R values ranging from 100 to 10,000 and approximately between 1 and 70 % of sulphides (Fig. 10a). Samples corresponding to the second group (PGE depleted) have very high Cu/Pd ratio, similar to those of La Force (f) and Sudbury (Sud) deposits (Barnes et al. 1993). This suggests removal of Pd (Barnes et al. 1993) due to early sulphide segregation, a process that is also evidenced by the Ni/Pd versus Cu/Pt diagram (Fig. 10b) which can be applied to elucidate the effects of partial melting and

sulphide segregation (Theriault et al. 2000), with the Las Águilas samples plotting in the areas corresponding to contents similar to the mantle and PGE depleted (Fig. 10b).

Composition of the primitive magma

Chai and Naldrett (1992b) and DeBari (1994) used indirect methods to calculate the primitive magma composition. One of these estimates the value of MgO/FeO in the magmatic liquid based on the composition of olivine (Roeder and Emslei 1970). They considered the partition coefficient (K_D) between Fe–Mg and proposed the equation $K_D = (\text{FeO/MgO})_{\text{ol}}/(\text{FeO/MgO})_{\text{liq}} = 0.3 \pm 0.03$.

However, as a result of re-equilibration with the intercumulus liquid, the magnesium content of olivine is lower compared with the content in the liquid during crystallization. Olivine is mainly present in the mineralized ultramafic rocks of Las Águilas body (Fig. 11a). Due to their occurrence with sulphide phases, they did not react with the interstitial silicate liquid; thus, it is possible to assume that their composition is close to the primitive magma.

Table 3 shows the most magnesium-rich olivines (Fo 83.8–82.31) from Las Águilas drill core samples with up to 50 modal per cent sulphides. The FeO content of the primitive magma can be assumed to be equivalent to the

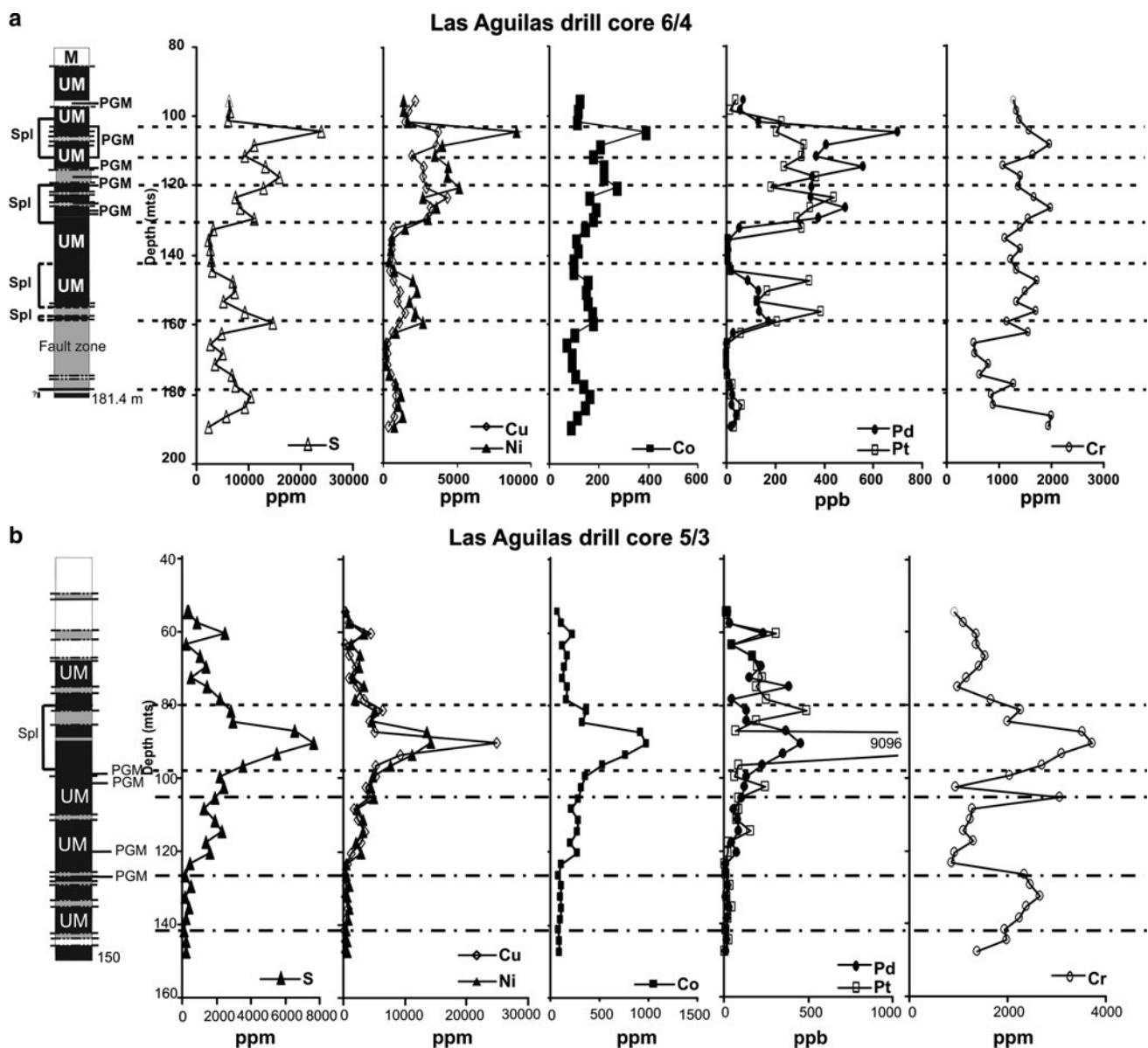


Fig. 7 Variation of the contents of S, Ni, Cu, Cr, Pt and Pd with depth. Drill cores **a** 6/4 and **b** 5/3. Samples taken at 3-m interval

FeO content in the MgO-rich olivine (sample 6/4 109.6, FeO = 15.56 wt%). Considering the above K_D coefficient value and equation, the values of $MgO/(MgO + FeO)$ in the parental liquid were in the range 0.61–0.57, and the value of MgO in the magma was 13.68 wt%.

Another method to calculate the composition of the primitive magma is to define a trend between FeO and MgO (Fig. 11b) considering samples with less than 2 modal per cent of sulphides. As the line defined by the $MgO/(MgO + FeO)$ ratio is different from the trend defined by the regression line ($y = 0.413x + 3.487$), the intersection between both lines corresponds to the MgO (15.45 wt%) and FeO (9.81 wt%) contents of the primitive magma.

The first method assumes that the FeO value was constant (15.56 wt%), but does not consider the exchange of Fe–Ni between olivine and sulphides. Therefore, the second method is considered valid to establish the composition of the primitive magma because it is applied to samples with very low contents of mineralization.

The third method to calculate the parental magma composition is based on the wt% average oxides composition of those rocks without significant sulphide mineralization. With this method we obtained a MgO value of 14.68 wt% and FeO = 11.04 wt% (Table 3).

The results suggest that (a) the rocks which most closely approach the composition of the parental magma are samples [5/3-66.80] (FeO = 13.68 wt%, MgO = 13.65 wt%) and

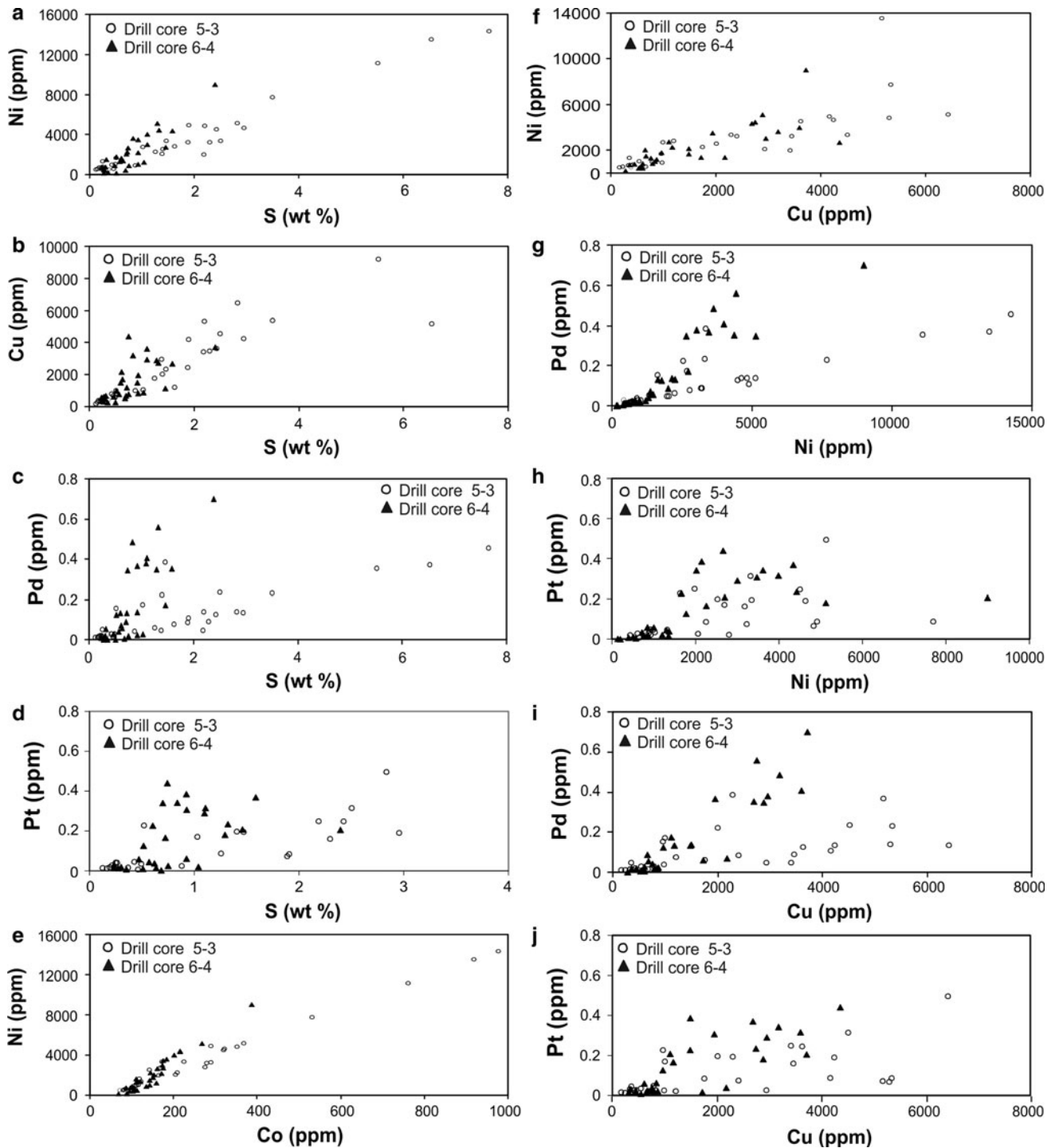


Fig. 8 Bivariate diagrams of S, Cu, Co, Ni, Pt and Pd

[5/4–84.80] (FeO = 14.77 wt%, MgO = 16.57 wt%), and (b) the parental magma of the Las Águilas rocks was mafic. According to Chai and Naldrett (1992b), the MgO content for ultramafic magmas should be >30 wt%.

It can be assumed that the composition of a sample from the chilled margin (Sample E43, Table 1) is equivalent to the composition of the primitive magma and therefore the values of MgO, FeO and mg# in the primitive magma were

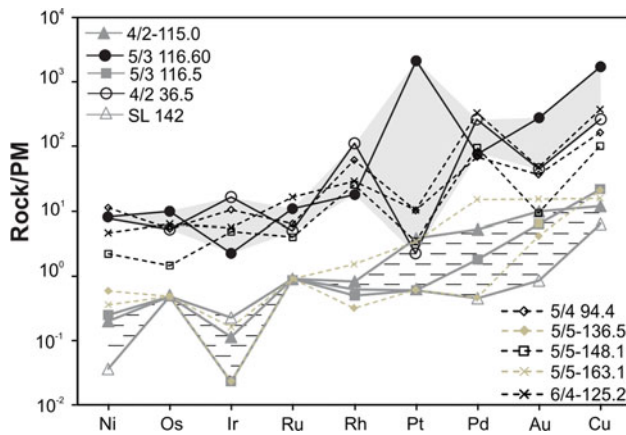


Fig. 9 Ni, Au, Cu and PGE normalized to Primitive Mantle (PM, Barnes et al. 1987). The diagram includes the most enriched and depleted samples from outcrops and drill cores from Las Águilas

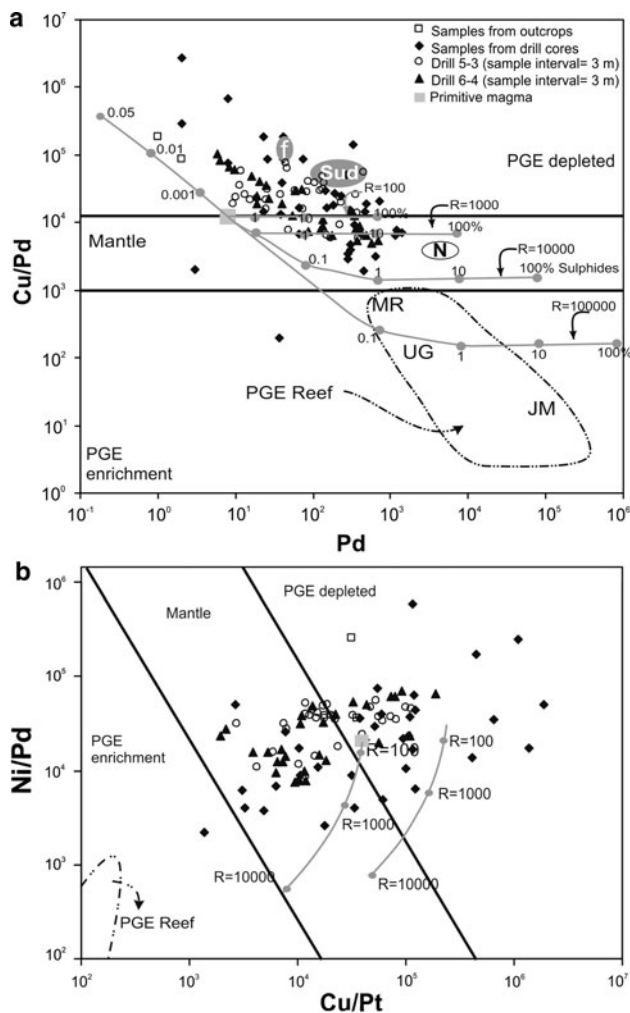


Fig. 10 **a** Cu/Pd versus Pd diagram (after Barnes et al. 1993). N = Noril'sk; Sud = Sudbury; JM = JM Reef; UG = UG Reef; MR = Merensky Reef and f = La Force. **b** Ni/Pd versus Cu/Pt for Las Águilas samples (after Theriault et al. 2000)

13.55, 10.83 and 0.56 wt%, respectively. These values are broadly similar to those obtained by the three indirect methods described above.

Pd/Ir versus Ni/Cu and Ni/Pd versus Cu/Ir

The Pd/Ir ratio increases as the magma suite becomes more evolved, while the Ni/Cu ratio decreases. Therefore, a plot of Pd/Ir versus Ni/Cu ratios allows the differentiation of magma suites (Barnes et al. 1987; Fig. 12a, b). Figure 12a shows that drill core samples from the Las Águilas body lie inside the field of “layered intrusives” and in particular in the field defined for high MgO-rich basalts. A similar situation was reported by Chai and Naldrett (1992a) from the Jinchuan deposit (China).

The Cu/Ir versus Ni/Pd diagram (Fig. 12b) is useful because Ni and Cu have very similar partition coefficients into the sulphide liquid (Rajamani and Naldrett 1978), and therefore, a sulphide liquid segregation from a silicate magma has effect neither on the Ni/Cu ratio of the remaining silica magma nor on the cumulates which carry sulphides (Barnes et al. 1987). As partial melting increases, the Cu/Ir ratio increases and Ni/Pd decreases (Barnes et al. 1987). Outcrop and drill core samples from the study area plot in the field of layered igneous bodies and above the high MgO-rich basalt field.

Tectonic setting

According to Brogioni (2001b), the Virorco and El Fierro mafic-ultramafic bodies have tholeiitic affinity and were generated in a back-arc basin, while Sims et al. (1997) and Ramos et al. (2000) based on geochronological and geophysical data consider they have a back arc or frontal island arc signature.

The maximum and minimum REE contents of the mafic-ultramafic rocks from Las Águilas normalized to chondrite are compared with rocks from different tectonic environments (Fig. 13). This diagram shows that the San Luis mafic-ultramafic bodies are very similar to well-known deposits like Jinchuan (continental rift with MgO = 12 wt%, Chai and Naldrett 1992b), Kabanga (intraplate with MgO from 12 to 15 wt%, Evans et al. 2000), Fiambalá (island arc with MgO = 11 wt%, DeBari 1994) and Belleterre-Angliers Belt (island arc, Barnes et al. 1993). There is no similarity with the patterns from ophiolites, which are often LREE depleted.

The PGE patterns of rocks from different tectonic environments are unique (Barnes et al. 1985) when normalized to Primitive Mantle or Chondrite. Regarding the Las Águilas body, Mogessie et al. (2000) concluded that the PGE patterns are similar to those of layered intrusions.

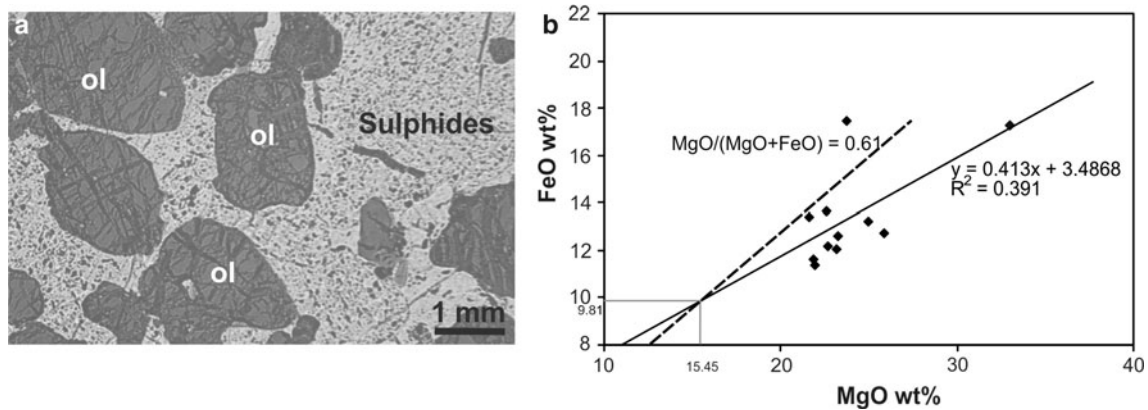


Fig. 11 **a** Dunite containing sulphides and olivine crystals. The composition of olivine is used to estimate the composition of the primitive magma applying indirect methods. **b** Extrapolation of the

primary magma composition of Las Águilas and other mafic-ultramafic bodies from San Luis

Table 3 Determination of primitive magma

Samples	6/4 109.6 Ol	6/4 120-3 Ol	6/4 120-8 Ol	4/2 34,3 3 Ol	4/2 36.5 Ol	7/4 108.3 Ol	7/4 108.3 Ol				
SiO ₂	38.87	39.29	39.68	39.80	39.66	41.04	40.84				
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00				
Al ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00				
Cr ₂ O ₃	0.01	0.00	0.00	0.00	0.27	0.00	0.00				
FeO	15.56	16.23	16.38	16.02	16.40	15.64	15.39				
MnO	0.20	0.23	0.18	0.23	0.20	0.25	0.26				
NiO	0.15	0.00	0.00	n.a	n.a	0.00	0.00				
ZnO	0.19	0.00	0.00	0.01	0.00	0.00	0.00				
MgO	45.61	44.43	45.35	45.39	42.82	44.24	44.64				
CaO	0.06	0.00	0.00	0.02	0.00	0.00	0.00				
Na ₂ O	0.01	0.04	0.00	0.00	0.00	0.00	0.03				
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00				
Total	100.66	100.22	101.59	101.52	99.35	101.17	101.15				
Fo	83.76	82.73	82.99	83.47	82.31	83.22	83.56				
Fa	16.24	17.27	17.01	16.53	17.69	16.78	16.44				
#mg = [(MgO/40,30)×100/((MgO/40,30) + (FeO/71,85))]	83.94	83	83.15	83.48	82.32	83.45	83.8				
(FeO/MgO)ol	0.34	0.37	0.36	0.35	0.38	0.35	0.34				
Kd = 0.3 (Roeder and Emslei 1970) Kd = (FeO/MgO)ol/(FeO/MgO)liq = 0.3											
(FeO/MgO) liq	1.14	1.22	1.2	1.18	1.28	1.18	1.15				
Considering for the determinations FeO = 15.56 (sample 6/4 109.6)											
MgO wt% primitive magma	13.68	12.75	12.97	13.19	12.16	13.19	13.54				
#mg liq	61.06	58.4	58.45	59.55	56.59	60.08	61.07				
Average values among samples without significant mineralization	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Total	
	49.1	0.53	12.38	11.04	0.2	14.68	8.74	0.75	0.35	99.06	

Bold italic values are calculated for the parental magma (see text for details)

n.a. not analysed

mg of primitive magma in samples without mineralization = [(MgO/40.30) × 100 / ((MgO/40.30) + (FeO/71.85))] = **70.33**

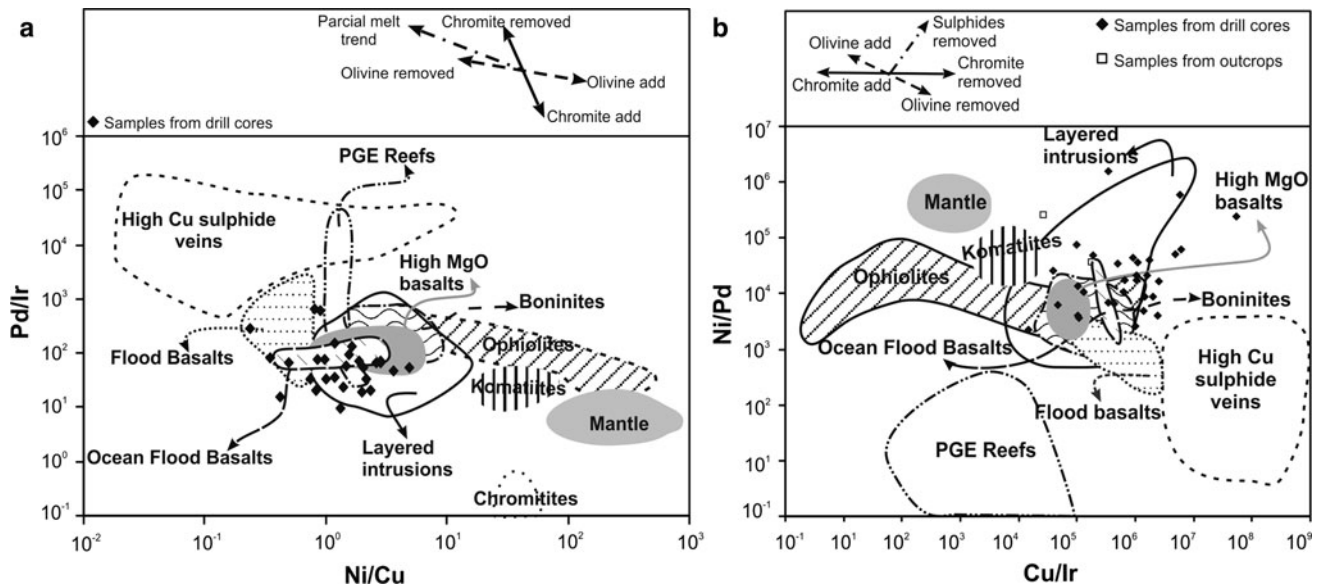


Fig. 12 Las Águilas samples plotted on **a** Pd/Ir versus Cu/Ni diagram and **b** Ni/Pd versus Cu/Ir diagram (after Barnes et al. 1987)

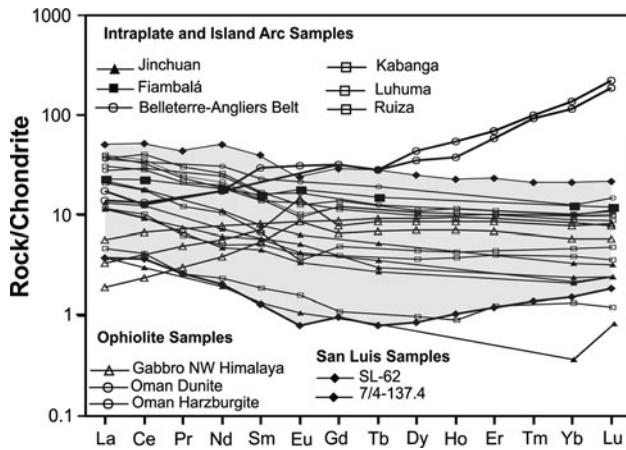


Fig. 13 REE normalized to chondrite (after Sun and McDonough 1989) showing mafic–ultramafic rocks from San Luis (shaded area) and samples from Kabanga–Ruiza–Luhuma Intraplate intrusive (Evans et al. 2000), Belleterre–Angliers Belt Arc Island (Barnes et al. 1993), Jinchuan Continental Rift (Chai y Naldrett 1992b), Oman Ophiolite (Godard et al. 2000) and Nidar South Ladakh Ophiolite—NW of Himalaya gabbros (Mahéo et al. 2004)

The Las Águilas PGE–Ni–Cu average contents (PM normalized) from both outcrop and drill core samples (Fig. 14a) display similar patterns to those of high MgO-rich basalts, which according to Barnes et al. (1987) comprise rocks derived from magmas with 12–18 wt% of MgO (komatiitic basalts, tholeiites and high MgO-rich basalts). Figure 14b, c shows that patterns of average PGE contents (chondrite normalized) from Las Águilas are similar to those associated with continental tholeiites and patterns from worldwide layered deposits (Naldrett and Duke 1980). From Fig. 14c it is obvious that average PGE

patterns of ophiolitic bodies (such as Oman and New Caledonia) are enriched in the IPGE, while those from Las Águilas are enriched in PPGE.

Discussions

Whole-rock geochemistry

The relationships between FeO, Al₂O₃, TiO₂, Na₂O, CaO and MgO (Fig. 3) probably indicate that the mafic–ultramafic rock suite developed by fractional crystallization processes. The subsequent crystallization of plagioclase and amphibole in the gabbroic rocks is reflected by a progressive enrichment of CaO, Al₂O₃ and TiO₂.

At Las Águilas, the contents of the REE are lower in rocks carrying significant sulphide mineralization, present as interstitial phases between olivine and orthopyroxene, than in rocks devoid of sulphides. This feature and the fact that the REE patterns are similar to the Jinchuan deposit (Chai and Naldrett 1992b) suggest that at Las Águilas the differentiation process was controlled by the crystallization of olivine and orthopyroxene, because REE are incompatible in these two minerals (Cox et al. 1979). This is also supported by a positive correlation between TiO₂, some REE, Y and V.

Platinum group elements and minerals

The PM-normalized PGE patterns (Fig. 9) of the San Luis mafic–ultramafic bodies allow the distinction of two groups

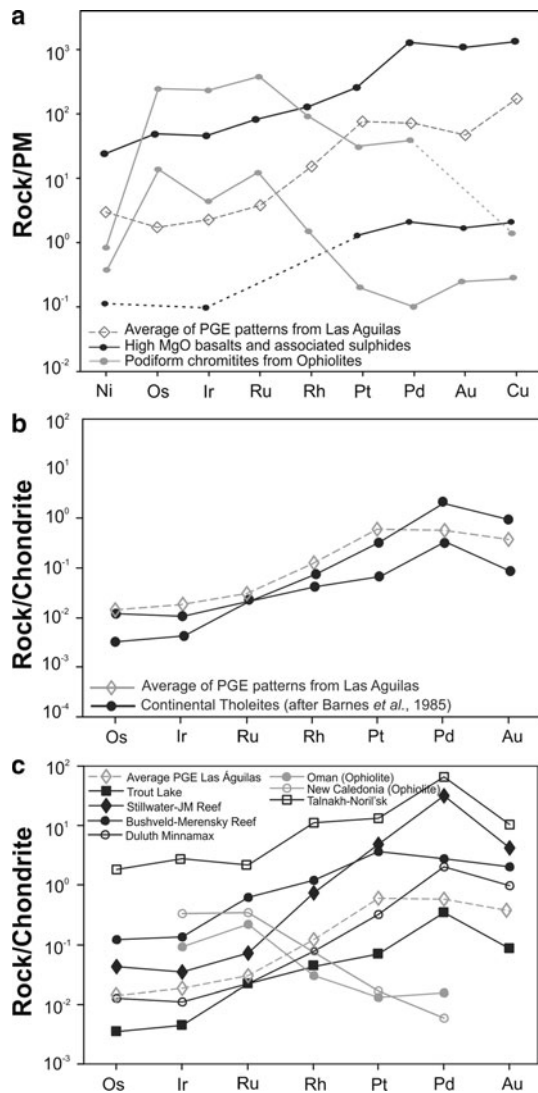


Fig. 14 Average of PGE from drill core and outcrop samples from Las Águilas in comparison with patterns from: **a** high MgO basalts and podiform chromitites from ophiolites (PM, Barnes et al. 1987); **b**, **c** with continental tholeiites (**b**) and ophiolites and layered intrusive deposits (**c**) (chondrite values of Naldrett and Duke 1980)

with the same positive trend from IPGE to PPGE, but with very different total PGE contents.

The presence of sulphides influences PGE patterns because they are extracted by sulphur and base metal-rich liquids (Barnes et al. 1987). In the studied units, an early sulphide liquid segregation took place during the evolution of the mafic–ultramafic bodies, extracting PGE and particularly IPGE, which resulted in PGE-depleted rocks (Fig. 9). The negative Ni anomaly and the scarce mineralization in these rocks are considered as additional evidence of this process. Rocks with significant ore mineral concentrations have the highest PGE contents (Table 2).

Ultramafic rocks related to Ni deposits usually show depleted and flat PGE patterns, while mafic rocks show

enrichments of Pt, Pd and Au (Naldrett and von Gruenevaldt 1989). This characteristic is coincident with the PGE patterns of Las Águilas samples and with the primitive mafic magma composition discussed in the foregoing sections. Similar patterns were described for the Noril'sk-Talnakh district (Zientek et al. 1994; Barnes et al. 1997), Dunka Road in Duluth Complex (Theriault et al. 2000) and Stillwater Complex (Zientek et al. 1994).

Cu/Pd versus Pd relation

The PGE-depleted samples (Fig. 10a) indicate that the magma source was PGE depleted and therefore, the exposed units are not good exploration targets. However, it is possible that PGE and sulphide-enriched layers are present at deeper stratigraphic levels with lower Cu/Pd ratios (Fig. 10a).

Theriault et al. (2000), based on the study of the source of the Cu–Ni–PGE sulphide mineralization in the Partridge intrusion of the Duluth Complex, concluded that the magma from which the sulphides segregated had a high Cu/Pd ratio, as is the case of Las Águilas and the other mafic–ultramafic bodies in San Luis province. In this area the magma segregated sulphides at depth, and therefore, the upper levels became depleted in Pd with respect to Cu. Samples with Cu/Pd ratios similar to mantle values can lead to the formation of Cu–Ni deposits from which PGE can be recovered as accessory products or as PGE reefs (Barnes et al. 1993).

Ni/Pd versus Cu/Pt

The influence of magmatic sulphide segregation processes on the composition of the mineralization is clearly reflected by this relationship (Fig. 10b). Rocks from San Luis display a positive correlation between Cu/Pt and Ni/Pd, with approximately 50 % of the samples plotting in the PGE-depleted field and the other 50 % in the field representing rocks with PGE values similar to the mantle (Fig. 10b). Samples with Cu/Pt and Ni/Pd above 10^5 and 10^4 , respectively, are enriched in Cu and Ni and PGE depleted, indicative of an early sulphide segregation process, which incorporated the PGE and resulted in a relative base metal enrichment. This process is also reflected by the Cu/Pd versus Pd ratios (Fig. 10a), indicating that in the studied area, rocks with higher PGE concentrations are probably present at deeper stratigraphic levels.

In the Las Águilas mafic–ultramafic rocks, there is no evidence of high metal concentrations in the host rocks, as is the case for the Duluth Complex, where magmatic rocks intrude Proterozoic metasedimentary rocks of the Virginia Formation, whose argillaceous horizons are sulphide

bearing with up to 15 % laminated pyrrhotite (Theriault et al. 2000).

Magma type and Ni/Pd versus Cu/Ir ratio

The San Luis mafic–ultramafic bodies plot in the field of layered intrusives and particularly in the field defined by high MgO basalts. However, in the Cu/Ir versus Ni/Pd diagram (Fig. 12b) Las Águilas samples plot outside this field, as it occurs in the Seiland intrusions in northern Norway (Barnes et al. 1987). According to these authors, a combination of high Ni/Pd and high Cu/Ir ratios indicates that the noble metals were extracted from the magma, probably due to sulphide segregation during an earlier period of magma evolution.

Conclusions

While mafic rocks (norites and gabbro-norites) are the dominant rock types cropping out in the San Luis area, the ultramafic rocks (pyroxenites, websterites, dunites and harzburgites) occur mainly at depth, as demonstrated by samples from drill cores.

Considering the primary layered magmatic textures recognized in outcrops from Las Higueras and Virorco and the relationship between Pd/Ir versus Ni/Cu and Ni/Pd versus Cu/Ir displayed by drill core samples from Las Águilas, it is concluded that the mafic–ultramafic bodies in the studied area belong to the “layered intrusive” type.

Ultramafic rocks from drill cores have contents of trace elements, transition elements and MgO close to primitive magma, while mafic rocks represent the more differentiated units. The same feature is shown by the REE patterns normalized to chondrite. The positive correlation between TiO₂, some REE and immobile trace elements indicates that magmatic crystallization was controlled by the formation of olivine and orthopyroxene.

In the studied ultramafic rocks, there is a very clear relationship among zones with mineralization of base metals (Ni, Cu, Co) and the presence of spinel, platinum group minerals and contents of platinum group elements. Based on the relationships between Cu/Pd versus Pd and Cu/Pt versus Ni/Pd, it is possible to differentiate two groups of rocks, one with ratios that are typical of mantle rocks and the other depleted in PGE. The last one is the result of an earlier sulphide segregation which removed Pt and Pd from the magma.

The close positive relationship between rocks, metals and minerals discussed above is a good prospection tool in the search for units with high-grade ore. It is suggested that they are most probably associated with the stratigraphic

levels where ultramafic rocks are dominant, levels that are also expected to carry chromitites.

The parental magma of the mafic–ultramafic rocks had tholeiitic affinity and was a Mg-rich mafic magma. This conclusion is based on whole-rock chemistry, PGE, metal contents, textural evidences and comparisons with deposits from other parts of the world.

Las Águilas and the other mafic–ultramafic bodies in the area share many characteristics with large and well-studied layered complexes associated with extensional tectonic environments such as Jinchuan (China), Kabanga (Tanzania) and Fiambalá (Argentina).

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