Mineralogy and Petrology (2000) 68: 85–114

Mineralogy
and Petrology

Genesis of platinum-group minerals in the Las Aguilas mafic-ultramafic rocks, San Luis Province, Argentina: textural, chemical and mineralogical evidence

A. Mogessie[1], **Ch. A. Hauzenberger**[1], **G. Hoinkes**[1], **A. Felfernig**[1], **E. F. Stumpfl**[2], **E. A. Bjerg**[3], and **J. Kostadinoff**[3]

[1]Institute of Mineralogy – Crystallography and Petrology, University of Graz, Austria
[2]Institute of Geosciences, Mining University of Leoben, Austria
[3]Departmento de Geologia, Universidad Nacional del Sur-CONICET, Bahia Blanca, Argentina

With 10 Figures

Received September 15, 1998;
revised version accepted July 21, 1999

Summary

Palladium bismuthotellurides (merenskyite-michenerite-moncheite-melonite) of variable composition and platinum arsenides (sperrylite) are documented in several drill cores of the Las Aguilas mafic-ultramafic intrusion, San Luis province, central Argentina. The mafic-ultramafic rocks ranging in composition from harzburgite to dunite, lherzolite, norite, and gabbro, intruded an amphibolite facies basement causing locally granulite facies metamorphism. The platinum – group minerals (PGM) identified in these rocks occur in (1) unaltered orthopyroxene-rich, plagioclase- and spinel-bearing rocks which carry abundant base-metal sulphides (BMS), such as chalcopyrite, pentlandite, and pyrrhotite; and in (2) serpentinized olivine-rich zones along cracks, but always associated with BMS, spinel, serpentine, and secondary magnetite. Textural evidence suggests a primary magmatic origin as well as late-stage hydrothermal remobilization, transport, and deposition of the PGM. Geophysical exploration and geological field work have delineated the extent of the Cu-Ni sulphide mineralization in the mafic-ultramafic intrusion underlain by a crystalline basement of Ordovician age. It is estimated that platinum-group-element (PGE) – enriched zones of several meters thickness could be present at depth in the mafic-ultramafic intrusion. Chondrite – normalised plots reveal that the ultramafic rocks have a similar PGE fractionation trend as the Bushveld and Stillwater layered complexes. This contrasts with the ophiolite-

type ultramafic associations of the Sierras Pampeanas in Cordoba Province, which occur about 400 km to the northeast of the study area.

Zusammenfassung

Die Genese von Platingruppenmineralen in mafisch-ultramafischen Gesteinen von Las Aguilas, Provinz San Luis, Argentinien: Texturelle, chemische und mineralogische Befunde

Palladium-Bismuthtelluride (Merenskyit-Michenerit-Moncheit-Melonit) unterschiedlicher Zusammensetzung und Platin-Arsenide (Sperrylit) wurden in mehreren Bohrkernen der mafisch-ultramafischen Intrusion von Las Aguilas, Provinz San Luis, Argentinien, dokumentiert. Die mafisch-ultramafischen Gesteine, die hauptsächlich aus Harzburgiten, Duniten, Lherzoliten, Noriten und Gabbros bestehen, intrudierten ein amphibolitfazielles Grundgebirge, das in den Randbereichen der Intrusion eine granulitfazielle Überprägung zeigt. Platingruppenminerale (PGM) kommen in folgenden Gesteinen vor: (1) in nicht alterierten, Orthopyroxenreichen, Plagioklas- und Spinellführenden Gesteinen, die noch zusätzlich angereichert an Buntmetallsulfiden, wie Chalkopyrit, Pentlandit und Pyrrhotin sind; und (2) entlang von Rissen in serpentinisierten, Olivinreichen Gesteinen, jedoch immer assoziiert mit Buntmetallsulfiden, Spinell, Serpentin und sekundärem Magnetit. Texturelle Beobachtungen zeigen, daß die PGM sowohl primär-magmatisch gebildet als auch in einem hydrothermalen Prozeß remobilisiert, transportiert und wieder auskristallisiert wurden. Mittels geophysikalischer Explorationsmethoden und Geländebeobachtungen konnte die Größe der Cu-Ni-Sulfidmineralisation in der mafisch-ultramafischen Intrusion, die ein ordovizisches Basement überlagert, abgeschätzt werden. Man nimmt an, daß mehrere Meter mächtige Platingruppenelement (PGE) – führende Zonen in bestimmten Tiefen der Intrusion vorkommen. Chondritnormalisierte Diagramme von Gesamtgesteinen zeigen, daß die ultramafischen Gesteine einen ähnlichen PGE Fraktionierungstrend aufweisen wie die lagigen Intrusionen von Bushveld und Stillwater. Dies ist gegensätzlich zu den Ophiolitvorkommen in den Sierras Pampeanas, Provinz Cordoba, die ca. 400 km nordöstlich von unserem Arbeitsgebiet vorkommen.

Introduction

The regional geology and tectonic evolution of the Andean and Pampean Ranges have been discussed extensively by *Ramos* (1988a,b, and references therein). Geochronological studies have been conducted on hundreds of samples by *Caminos* et al. (1982, and references therein). *Gordillo* and *Lancinas* (1979) have documented the geology and petrology of the Sierra Pampeanas in Cordoba and San Luis provinces. Recently, *Sims* et al. (1997) have made extensive mapping of the Sierras Pampeanas and discussed the tectonic and metallogenic evolution of the region. Based on geological and geophysical mapping together with an extensive program of SHRIMP (ion probe U-Pb and Th-Pb) and Ar-Ar geochronology, these authors suggest three distinct tectonic and two metallogenic stages in the Paleozoic history of the southern Sierras Pampeanas. Accordingly orogeny in the Sierras Pampeanas occured during the Paleozoic rather than the Proterozoic, and comprised three major events – in the Cambrian (Pampean), Ordovician (Famatinian), and Devonian (Achalian). The mineralized mafic-ultramafic rocks considered in the present investigation are dated to be of Ordovician age.

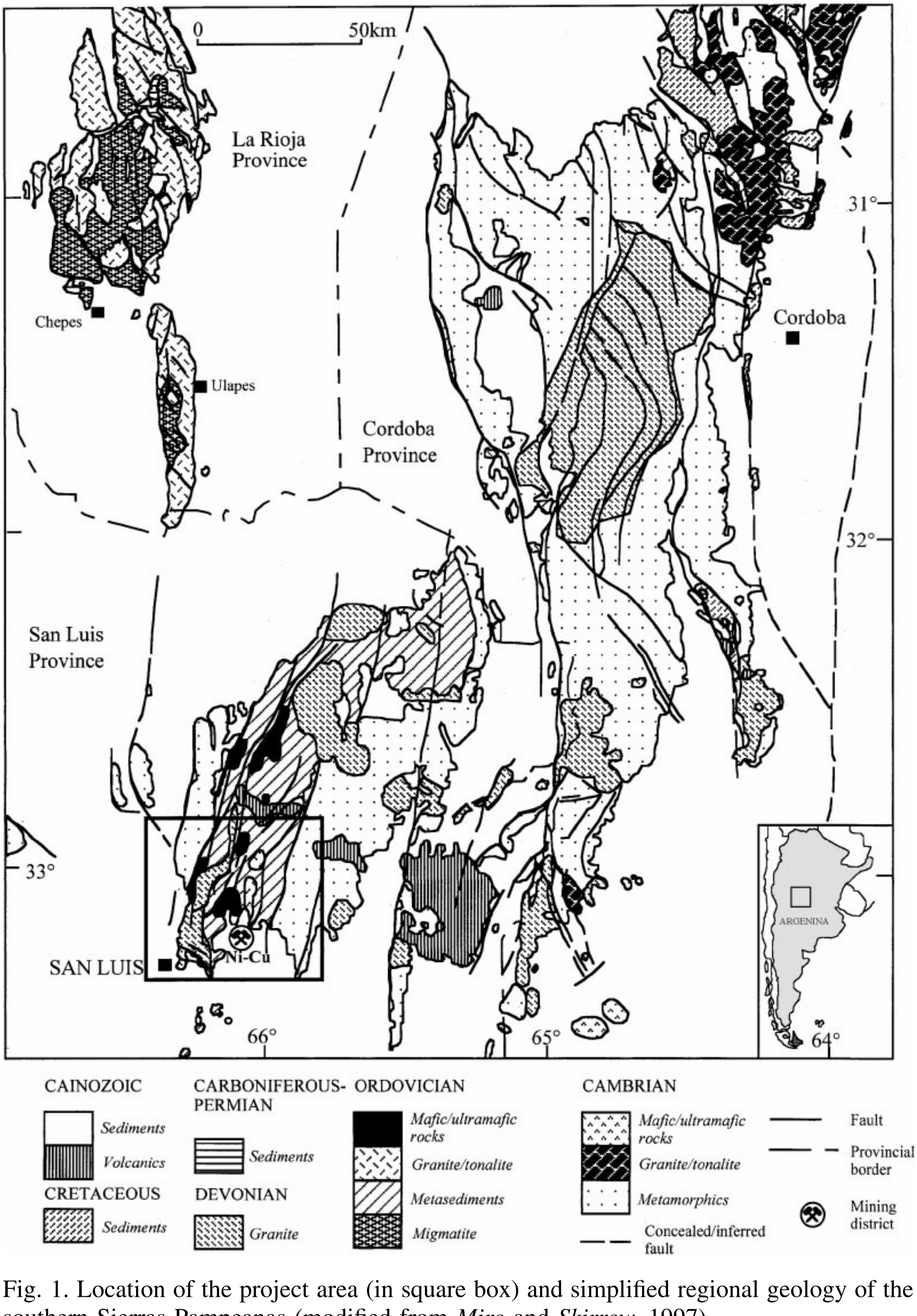


Fig. 1. Location of the project area (in square box) and simplified regional geology of the southern Sierras Pampeanas (modified from *Miro* and *Skirrow*, 1997)

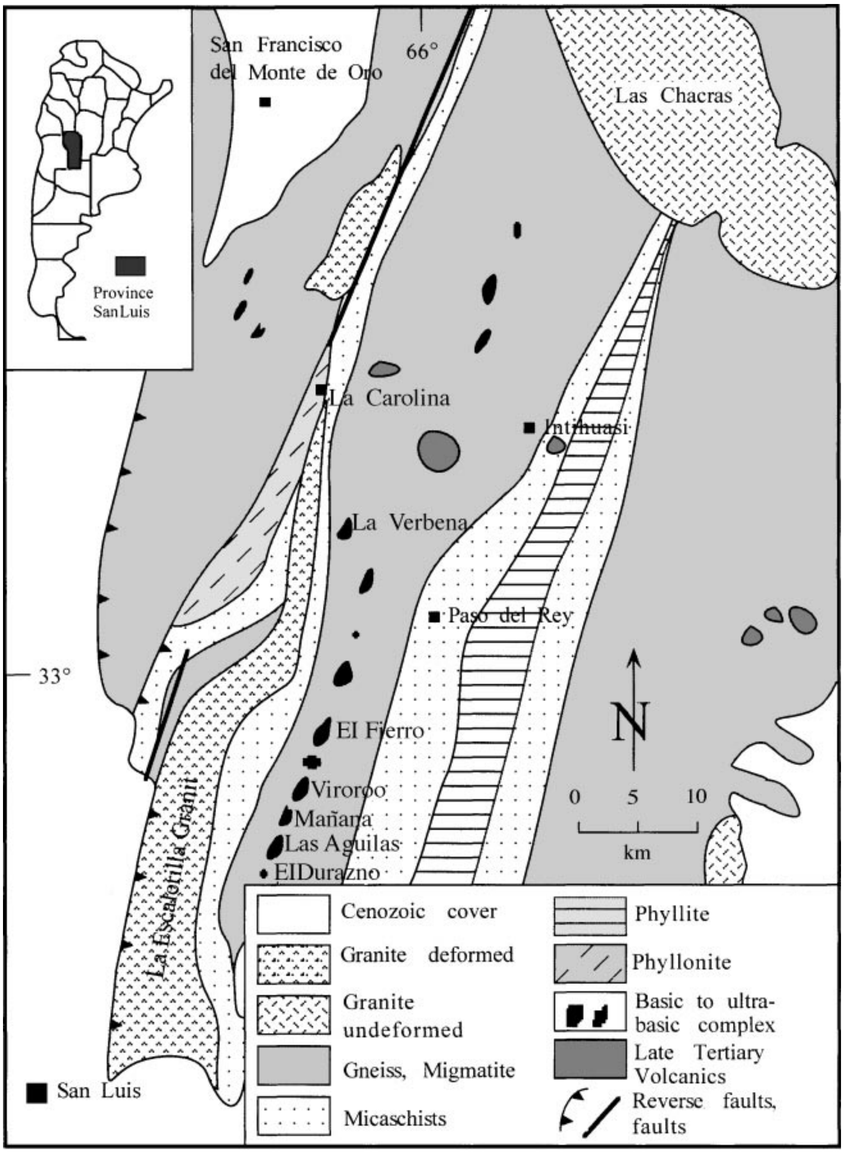


Fig. 2. The geology of the study area in San Luis province and the location of the exposed mafic-ultramafic intrusions (dark lenses). Modified from *Suarez* et al. (1992)

The Sierras Pampeanas of the San Luis area (Figs. 1, 2) consist of a crystalline basement of Upper Precambrian to Lower-Middle Paleozoic metamorphic rocks (gneisses, schists, phyllites, amphibolites, migmatites, and granulites), granites, pegmatites, as well as mafic and ultramafic rocks. There are several fault blocks in the area bounded by high angle northerly to north-northeasterly striking lineaments marking regional extension in Plio-Pleistocene times.

The mafic-ultramafic rocks of the San Luis Province investigated in this study are enclosed within a north-northeasterly trending Precambrian basement with a strike length of 100 km (*Brogioni*, 1992, 1994; *Malvicini* and *Brogioni*, 1992;

Gervilla et al., 1993; *Mogessie* et al., 1994, 1995, 1996). They comprise lenticular gabbros, norites, pyroxenites, and dunites. Accompanying these mafic-ultramafic rocks are quartz feldspar and tourmaline rich pegmatite veins striking in the same NNE direction. Recent studies of the mineralized Las Aguilas mafic-ultramafic rocks in the San Luis province are those of *Malvicini* and *Brogioni* (1992); *Gervilla* et al. (1993, 1995); and *Mogessie* et al. (1994, 1995, 1996). Geological and geophysical studies have indicated that the lenses of mafic-ultramafic rocks in outcrop actually represent parts of a large mafic-ultramafic complex intruding the Precambrian basement. These mafic-ultramafic lenses are exposed in a northerly trending tectonic lineament near El Durazno, Las Aguilas, Virorco, El Fierro, and Las Verbenas (Fig. 2).

Exploration for platinum-group elements (PGE) was conducted by the Argentine Government in the 1970s (*Sabalua* et al., 1981; *Sabalua*, 1986) where 59 holes with a combined length of 9000 m were drilled into the Las Aguilas body (Fig. 3). According to the resulting assays the sulfide mineralizations carried a maximum of 0.75 g/tonne Pd and 2 g/tonne Pt as well as 2.20 Mt 0.51 wt.% Ni, 0.50wt.% Cu, 0.035wt.% Co (*Sabalua*, 1986).

Detailed petrological, geochemical, geophysical and economic geology studies of the mineralized Las Aguilas mafic-ultramafic rocks and the surrounding high-grade metamorphic basement in San Luis province are presently lacking. In this paper we present a detailed study of PGM from the BMS and spinel-enriched zone of the Las Aguilas mafic-ultramafic rocks. We also present geochemical and geophysical data pertinent to the mafic-ultramafic lithologies in the San Luis area.

Methods

Polished sections were made from several hundred drill core and surface samples of mafic-ultramafic rocks. PGM and associated minerals were identified using a combination of reflected light microscopy and scanning electron microscope (SEM) analysis at the Institute of Mineralogy, University of Graz.

Silicate mineral analyses were carried out with an electron microprobe (ARL-SEMQ) operated at 15 kV accelerating voltage, 0.02 μA sample current, and 20 seconds counting time. The sulphides and the PGM have been analysed using a JEOL- 6310 SEM with an attached link energy dispersive system (EDX) and a microspec wavelength dispersive system (WDS) using 20 kV accelerating voltage and counting time of 100 sec calibrated on cobalt. In all cases the standards used were natural minerals: spinel, chromite, tephroite, kaersutite, tremolite, jadeite, garnet, and adularia. In addition, sulphide and PGM standards as well as pure metals were used for the calibration and analyses of the ore minerals. Matrix effects were corrected according to *Bence* and *Albee* (1968) for the microprobe analyses and ZAF for the EDX and WDS analyses. The structural formulae of the minerals were calculated with HYPER-FORM (*Bjerg* et al., 1992); amphibole nomenclature was established using EMP-AMPH (*Mogessie* et al., 1990).

The PGE and other major, trace and rare earth elements were analysed by Don Mills Laboratories, Ontario, Canada and Actlabs (Activation Laboratories), Canada. The PGE were analysed using Inductively Coupled Plasma-mass Spectrometer (ICP-MS) after a nickel sulfide fire assay concentration of 25 g

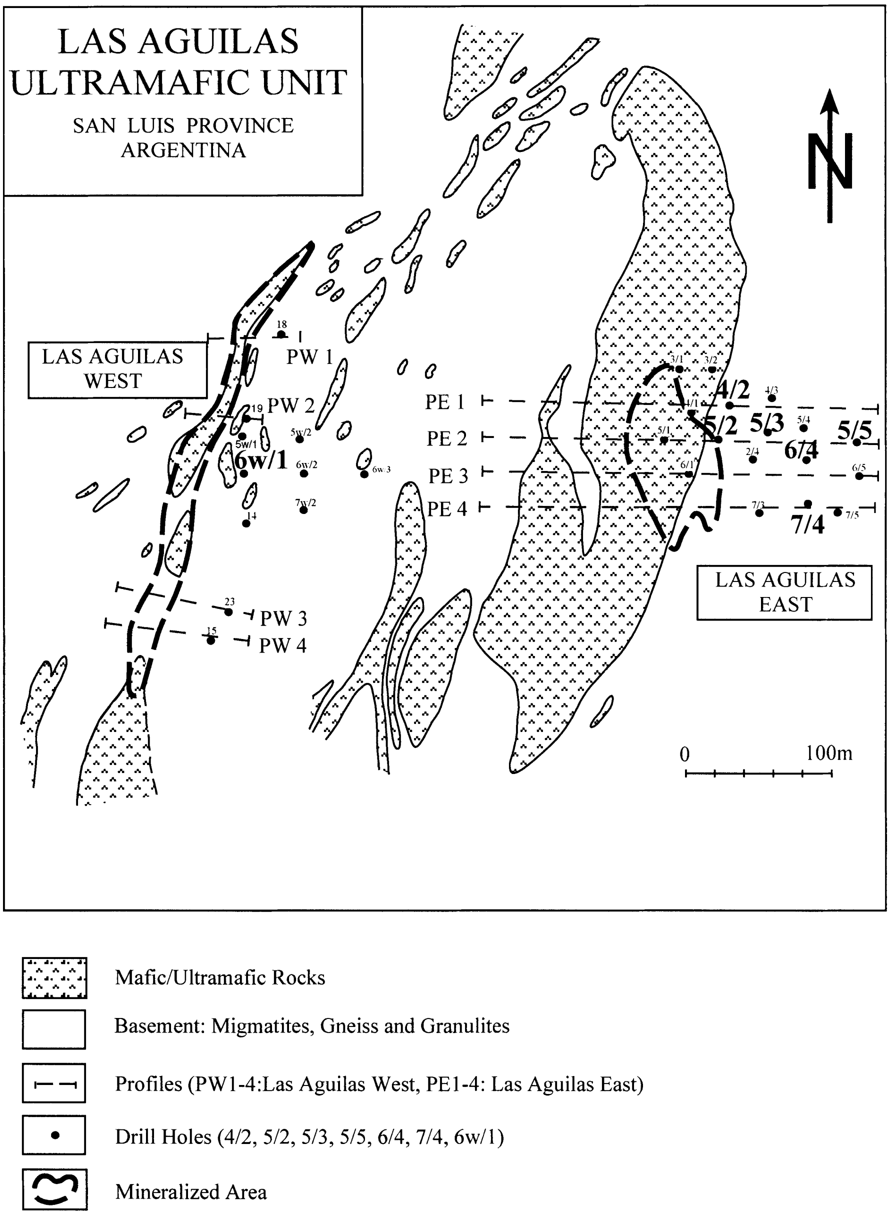


Fig. 3. The Las Aguilas mafic/ultramafic intrusion, embedded in migmatites and granulites, and the location of the drill holes. Those drill holes indicated in bold (e.g. 4/2, 6w/1...) were sampled in this study. Modified after *Sabalua* (1986)

samples. The detection limits were 1 ppb for Ir, Rh, Re, Ru, Pd, Pt, and 2 ppb for Os.

Geological setting of the PGM-bearing mafic-ultramafic rocks

The mafic-ultramafic intrusive rocks occur in outcrop as lenses and xenoliths within granulite facies basement rocks. According to *Sabalua* (1986) the igneous

rocks at the Las Aguilas east body (Fig. 3) are suggested to be zoned horizontally from east to west with a thin pyroxenite margin; dunite; alternating pyroxenite and dunite units; pyroxenite; norite with minor pyroxenite. This compositional zonation lead *Sims* et al. (1997) to suggest that the eastern contact may be close to the original base of the intrusion. Generally the mineralogy of the interlayered harzburgites, dunites and lherzolites can be represented by the assemblage pyroxene (opx + cpx) + olivine + chrome spinel + BMS ± amphibole ± plagioclase ± phlogopite ± PGM and accessories such as apatite. Most mafic rocks are norites with the characteristic mineral assemblage orthopyroxene + plagioclase. Petrographic and electron microprobe analyses indicate that orthopyroxene, which makes up the bulk of the norites, is partially replaced and enclosed by light yellowish-brown ferri-tschermakitic amphibole. The olivine-rich ultramafic rocks (dunites, harzburgites, lherzolites) are partly altered to serpentine and secondary magnetite. Textural observations of dunite and pyroxenite reveal that fresh to partially serpentinised olivine, orthopyroxene and chromian spinel formed cumulates with interstitial sulphides. For these rocks, orthopyroxene-clinopyroxene geothermometry (*Lindsley* and *Anderson*, 1983) yields two different groups of temperatures, depending on whether mineral rim or core compositions are used for the calculations. The highest temperatures of ~700 °C–800 °C are found in fresh rocks using core compositions, suggesting re-equilibration to metamorphic conditions during the granulite facies metamorphism at the contact zone with the basement. Rim compositions, as well as core compositions of orthopyroxene partially replaced by amphibole along cleavages and rims give temperatures of 500 °C–650 °C (*Hauzenberger* et al., 1996), related to the late deformation and mylonitization event which affected the mafic-ultramafic rocks and the basement in the central part of the area.

Phase assemblages as well as geothermobarometeric calculations indicate granulite conditions of metamorphism with a strong regional retrograde event in the crystalline basement and re-equilibration of the mineral assemblages in the mafic-ultramafic rocks (*Hauzenberger* et al., 1996). P–T conditions of the granulite facies mineral assemblage in the crystalline basement, garnet + sillimanite + biotite + alkalifeldspar + plagioclase + quartz ± cordierite affected by the intrusion of the mafic-ultramafic body, gives values of 750 °C ± 50 °C and 5 ± 1 kbar, whereas the P–T conditions for the re-equilibrated basement mineral assemblage: garnet + muscovite + biotite + plagioclase + quartz ± staurolite ranges from 500 °C to 600 °C and 4–5 kbar. The lower temperatures are related to a late deformation and mylonitization event in the central part of the area affecting the mafic-ultramafic rocks and the high grade basement.

Geophysics

In the San Luis province a large area has been explored during this investigation using gravimeteric and magnetometeric techniques to distinguish the mineralized mafic-ultramafic intrusion from basement rocks. The gravimetry observations were performed with a La Coste-Romberg gravimeter, and the magnetometry with a proton precission magnetometer. The measurements were made on a 1.6 km interval, plotted on 1 : 20000 topographic maps. Bouger anomalies from about 15

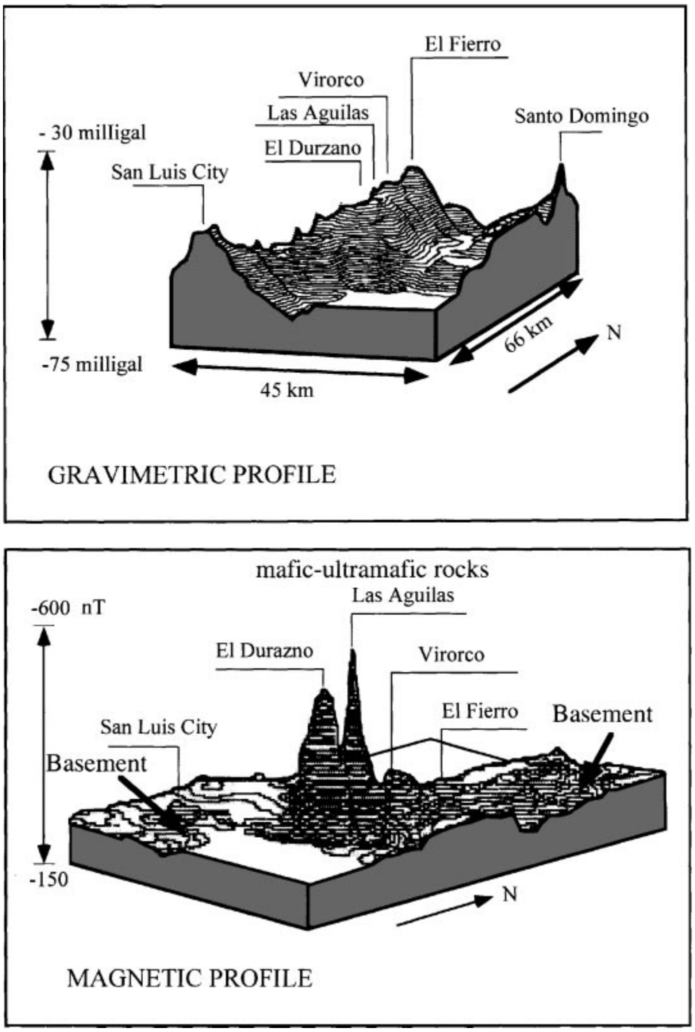


Fig. 4. **a** Gravimetric profile along the mafic-ultramafic zone (from San Luis city in the south to Santo Domingo in the north). **b** Magnetic profile along the zone of mafic/ ultramafic rocks zone (from San Luis city in the south to Santo Domingo in the north). This plot shows a strong magnetic anomaly in the areas of El Durazno, Las Aguilas, Virorco and El Fierro, all lying on the same tectonic line

to 30 milligals (Fig. 4a) define areas of mineralization. Anomalies indicate an increase of the density of the rocks underlying the basement gneisses. Samples from Las Aguilas have a density of 2.95, from Virorco 3.02 and from El Fierro 3.05 (Fig. 2). In areas with high gravimeteric anomalies, the anomalies of the earth magnetic field are of high amplitude ($\pm$ 500 nT). In this area, the magnetic profiles (Fig. 4b) rather than the absolute magnetic anomalies suggest the presence of ultramafic rocks beneath the gneiss basement. Based on the geophysical data and field observations the mafic-ultramafic body under the basement is estimated to cover an area of about 3000 km^2 (30 km E-W and 100 km N-S), *Bjerg* et al. (1997); *Kostadinoff* et al. (1998).

Geochemistry

Major and trace elements

Comprehensive analyses including major, minor, and rare earth elements have been performed on several drill core samples from the Las Aguilas mafic-ultramafic intrusion and surface mafic-ultramafic samples from Las Aguilas, Virorco, El Durazno, and El Fiero (Fig. 2).

The major and trace element compositional data are shown on MgO variation diagrams (Figs. 5a – o). The data are grouped into two. Those from drill core (closed diamond, dunites, harzburgites, lherzolites), and those from the surface (closed square, gabbroic rocks). The incompatible trace elements, such as Zr, Y, Ba Sr, Rb, La plotted versus MgO show a strong (Zr, Y, Sr) to weak (Rb, Ba, La) negative correlation for the gabbroic samples and very low values for the ultramafic drill core samples. However, the compatible trace elements, Ni and Cr show a positive correlation versus MgO for the ultramafic samples and low values with a weak positive trend for the gabbroic samples. Generally the major and trace element plots show a differentiation trend between mafic and ultramafic rocks.

Platinum – group element geochemistry

Samples (Table 1) from drill core LAS 5/3 at depths of 66.8, 80, 98.4 and 116.6 m indicate variable PGE concentrations. Sample LAS 5/3-116.6 is rich in Pt with a concentration of 17.8 ppm. These samples cover the range of relevant lithologies, i.e. norite-gabbronorite (LAS 5/3-66.8 and 98.4), lherzolite (LAS 5/3-116.6) and peridotite (LAS 5/3-80). The concentration of the PGE in these drill core samples are relatively high compared to the weakly mineralized mafic rocks on the top of the sequence (SL-samples, Table 1). One can also observe the direct correlation of the higher concentrations of Pt, Pd, Au; and in sample LAS 5/3-116.6 Os, Ir, Ru with higher concentrations of Ni and Cu.

The chondrite-normalized rare earths (REE) data in LAS 5/3 shows a bimodal distribution (Fig. 6a) with samples at 66.8 m and 98.4 (norite and gabbronorite) having a higher concentration of REE with a negative Eu anomaly; whereas those at 116.6 and 80 m (lherzolite, peridotite respectively) having low concentrations of REE and a negative Sm and Eu anomalies. Comparison with mantle normalized PGE-data (Fig. 6b), reveals that samples with negative Sm and Eu anomalies are enriched in PGE and those with only a negative Eu anomaly have lower PGE concentration (*Mogessie* et al., 1994). The samples cover a drill core section of 50 m thick unit, where a change in the rock composition, represented by the concentration of the rare earth elements, is accompanied by a variation in the PGE concentration.

The presence of spinel in the sulphide – bearing norites, dunites, harzburgites and lherzolites is characteristic for the PGE mineralized zone implying that the variation in the PGE values is dependent on mineralogy which subsequently affected the REE distribution. This observation for the mineralized section of drill core LAS 5/3 does not generally apply to the other mineralized samples from Las Aguilas. However, correlations of PGE distribution and mineralogy resulting from different processes such as partial melting, fractional crystallization of silicate

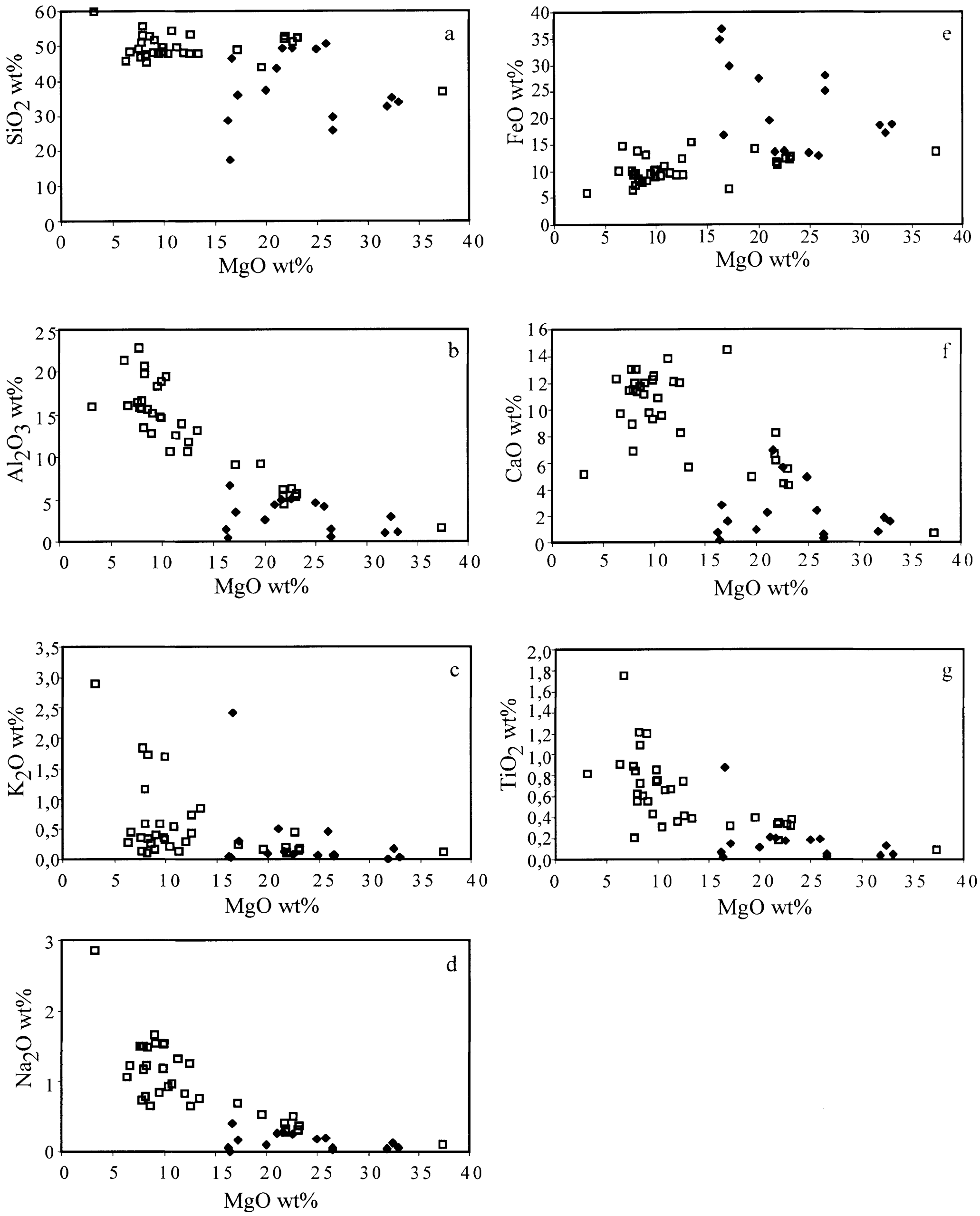


Fig. 5. Major oxide versus MgO (**a**–**g**) and trace element versus MgO (**h**–**o**) variation diagrams of ultramafic rocks (closed diamond) and mafic rocks (open squares) from San Luis province, Argentina (locations of the intrusions are indicated in Fig. 2)

magma, and hydrothermal processes have been documented for other intrusions elsewhere by several authors (*Barnes* et al., 1985; *Lee* and *Tredoux*, 1986; *Cornelius* et al., 1987).

Values of Pt+Pd/(Ir+Ru+Os) vary from 1 to 183 and ratios of Pd/Ir range from 1 to 650 (Table 1). These values lie within the range reported by *Ripley* (1990)

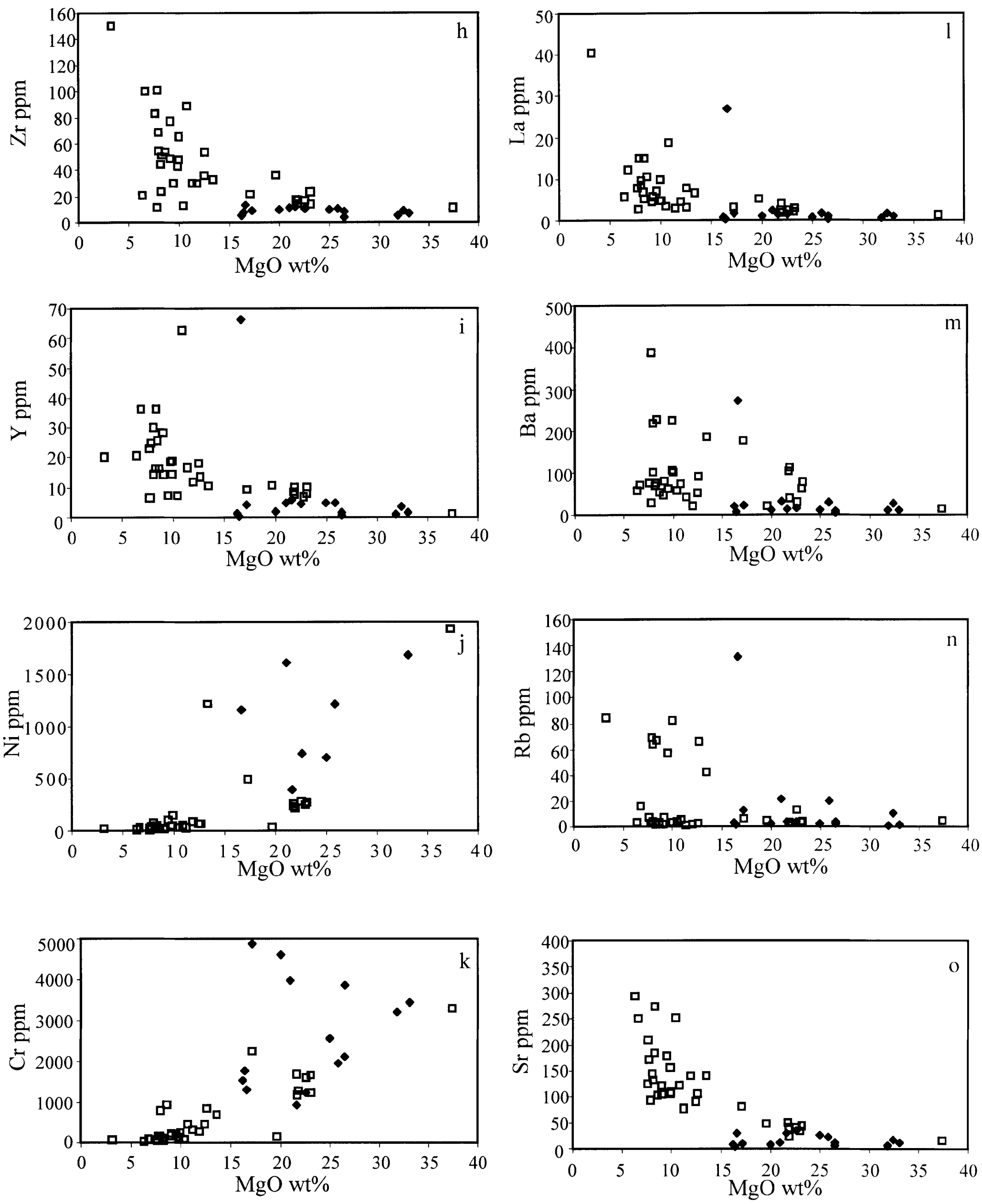
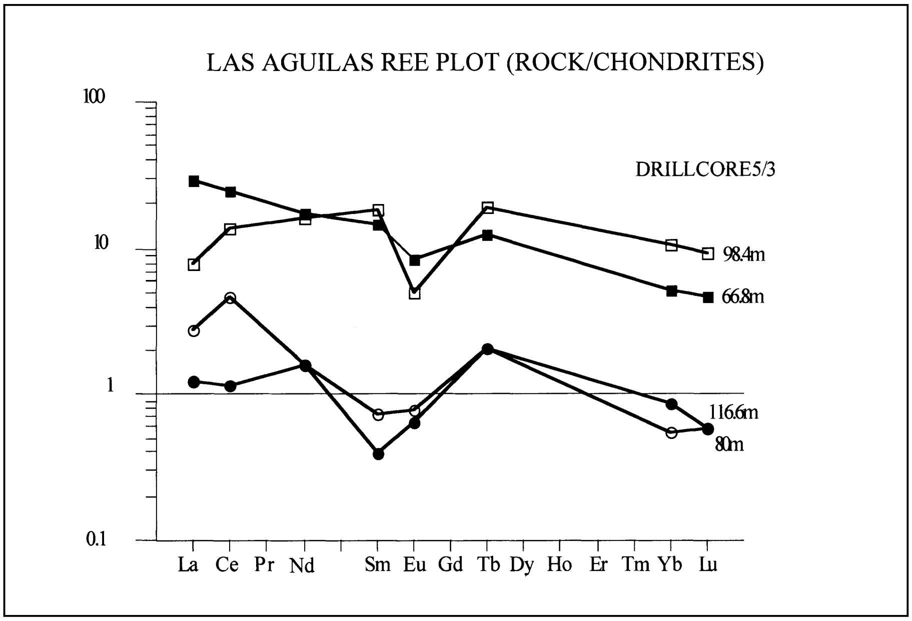


Fig. 5 (*continued*)

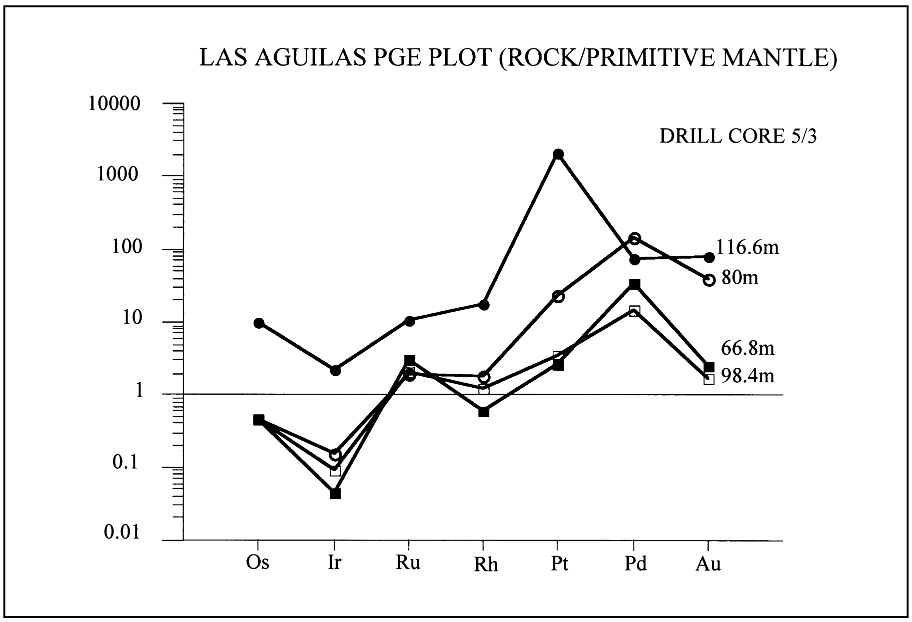
for the Babbitt PGE-enriched zone of the Duluth Complex. However, the ratio is very different compared to extremely fractionated PGE concentrations, with a Pt+Pd/(Ir+Ru+Os) ratio of >9000 for the Robie Zone mineralization in Lac des Iles, which is considered to be evidence for hydrothermal transport and deposition by some authors or to constitutional zone refining resulting from the partial melting of gabbroic cumulates (*Brügmann* et al., 1989).

Table 1. *PGE, gold (ppb), Ni and Cu (ppm) concentrations in representative samples of the Las Aguilas drill cores (LAS & LASW) and surface samples (SL), San Luis Province, Argentina*

Sample	Os	Ir	Ru	Rh	Pt	Pd	Au	Ni	Cu	Pt/Pd	Pd/Ir	Ni/Cu	Pt+Pd/ Rh+Ir+Os
LAS 5/3-80	2	1	11	3	190	650	160	5724	2018	0.29	650.00	2.84	56.00
LAS 5/3-66.8	2	1	17	1	22	150	11	2507	2508	0.15	150.00	0.99	9.05
LAS 5/3-98.4	2	1	12	2	30	67	1	2392	1120	0.45	67.00	2.14	6.47
LAS 5/3-116.6	42	10	60	29	17800	330	330	16534	47625	53.94	33.0	0.35	183.13
LASW6-328	2	1	5	1	15	23	3	141	46	0.65	23.00	3.06	5.43
LASW6-530	2	1	5	1	11	75	1	167	15	0.15	75.00	11.13	12.38
LASW6-729	2	1	5	1	5	3	1	77	39	1.67	1.00	1.97	1.14
LASW6-974	2	3	5	10	136	232	180	4842	6590	0.59	77.33	0.73	20.44
SL-96 2	1	7	1	5	6	1	252	189	30	6.00	0.14	6.30	0.54
SL-142	2	1	5	1	5	2	1	73	176	2.50	2.00	0.41	1.00
SL-177	2	1	5	1	5	2	3	18	22	0.66	2.00	0.82	1.00



a



b

Fig. 6. **a** Chondrite normalized REE plot of representative samples from the sulphide-spinel rich zone of the Las Aguilas drill core 5/3. (samples 66.8 and 98.4 are norite-gabbronorite, 116.6 is lherzolite and 80 is peridotite). **b** Mantle normalized PGE plot of representative samples from the sulphide-spinel rich zone of the Las Aguilas drill core 5/3. (samples 66.8 and 98.4 are norite-gabbronorite, 116.6 is lherzolite and 80 is peridotite)

The average PGE data of two drill cores from Las Aguilas (LAS 5/3 and LASW6, Table 2) is plotted on a chondrite normalized diagram (Fig. 7). For comparison, data from known mineralized layered mafic-ultramafic rocks are also included. The plot shows that the chondrite-normalized PGE trends of the Las Aguilas samples

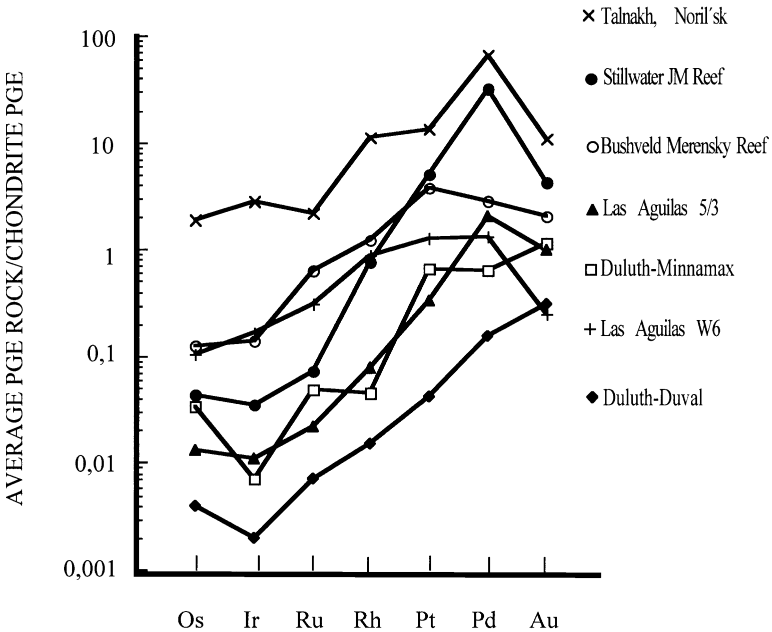


Fig. 7. Chondrite normalized PGE plot of samples from Las Aguilas mafic/ultramafic body (LA 5/3, W6) and data from Bushveld, Stillwater, Talnakh, Duluth-Duval and Duluth-Minnamax

show similar fractionation to those from other layered intrusions, such as the Stillwater, Bushveld, the Duluth and Norilsk-Talnakh. In the Pd/Ir vs. Ni/Cu plot of *Barnes* et al. (1985), the Las Aguilas samples lie in the field of layered intrusions and flood basalts (Fig. 8).

Mineral chemistry of PGM-bearing rocks

Representative electron-microprobe analyses of the silicate phases in the mafic-ultramafic rocks that host the platinum group minerals are presented in Table 3.

Orthopyroxene

The orthopyroxene is mainly enstatite with mg-values ($Mg/Mg{+}Fe^2$) ranging from 0.75 to 0.94. In a zone enriched in PGM in drill core LAS 5/3 (norites), values of Al_2O_3 range from 1.26 wt.% to 4.11 wt.% at depths of 95 m and 105 m, respectively. In addition, orthopyroxene-rich zones show an alteration sequence of Fe-Mg amphibole anthophyllite followed by brown calcic amphibole-ferri-tschermakite. The ferri-tschermakite is suggested to have formed as a result of a reaction between the new formed anthophyllite and the plagioclase matrix. This texture indicates that primary mineral assemblages of mafic-ultramafic rocks have been partially transformed to metamorphic mineral assemblages during emplacement in the continental crust.

Table 2. *Concentrations of PGE and gold (in ppb). Samples LAS 5/3 and LASW 6 are from Las Aguilas. The data for the other complexes are from the literature (*Barnes, *1985) for comparison*

	Os	Ir	Ru	Rh	Pt	Pd	Au
Chondrite	514.00	540.00	690.00	200.00	1020.00	545.00	152.00
Stillwater JM	22.00	19.00	50.00	150.00	5000.00	17300.00	640.00
PGE/Chondrite PGE	0.04	0.04	0.07	0.75	4.90	31.74	4.21
Bushveld Merensky	63.00	74.00	430.00	240.00	3740.00	1530.00	310.00
PGE/Chondrite PGE	0.12	0.14	0.62	1.20	3.67	2.81	2.04
Bushveld UG-2	–	270.00	–	540.00	3220.00	3420.00	70.00
PGE/Chondrite PGE	–	0.50	–	2.70	3.16	6.28	0.46
Duluth Minnamax	6.60	6.00	15.30	15.50	333.00	1113.00	147.00
PGE/Chondrite PGE	0.01	0.01	0.02	0.08	0.33	2.04	0.97
Duluth Duval	53.00	88.00	210.00	172.00	1300.00	710.00	38.00
PGE/Chondrite PGE	0.10	0.16	0.30	0.86	1.28	1.30	0.25
Talnakh-Norilsk	950.00	1500.00	1500.00	2240.00	13700.00	36000.00	1600.00
PGE/Chondrite PGE	1.85	2.78	2.17	11.20	13.43	66.06	10.53
Las Aguilas LAG 5/3	17.00	4.00	33.00	9.00	674.00	341.00	168.00
PGE/Chondrite PGE	0.03	0.01	0.05	0.05	0.66	0.63	1.11
Las Aguilas LASW 6	2.00	1.00	5.00	3.00	42.00	83.00	46.00
PGE/Chondrite PGE	0.00	0.00	0.01	0.02	0.04	0.15	0.30

Table 3. *Representative electron microprobe analyses of silicates from the PGE-bearing Las Aguilas mafic-ultramafic intrusion, San Luis Province Argentina*

	1	2	3	4	5	6	7	8	9	10
SiO_2	46.73	47.09	48.39	55.52	37.71	37.67	51.75	44.77	52.77	51.95
TiO_2	0.89	1.09	1.22	0.00	3.38	3.18	0.00	0.00	0.00	0.38
Al_2O_3	9.91	10.04	8.66	1.53	16.70	15.81	29.99	33.98	3.67	1.90
Cr_2O_3	0.91	1.73	0.97	0.26	1.32	0.86	0.00	0.00	0.51	0.26
FeO	6.56	5.35	7.21	12.79	6.99	13.77	0.00	0.00	13.20	3.58
MnO	0.00	0.00	0.00	0.51	0.00	0.00	0.00	0.00	0.39	0.00
MgO	19.09	17.73	17.17	25.01	19.44	13.93	0.00	0.00	28.33	16.22
CaO	11.85	12.27	12.00	0.29	0.00	0.00	13.64	18.33	0.12	24.41
K_2O	0.45	0.39	0.44	0.00	9.15	8.66	0.00	0.00	0.00	0.00
Na_2O	1.30	1.41	1.35	0.28	0.58	5.10	4.25	0.92	0.17	0.22
Total	97.69	97.09	97.41	96.19	95.27	94.39	99.63	100.21	99.06	98.92
Structural formula on the basis of number of oxygens										
	23	23	23	23	22	22	8	8	6	6
Si	6.54	6.65	6.85	7.83	5.43	5.62	2.36	2.09	1.89	1.92
Ti	0.09	0.12	0.13	0.00	0.37	0.36	0.00	0.00	0.00	0.01
Al	1.63	1.67	1.45	0.26	2.83	2.78	1.61	1.91	0.15	0.08
Cr	0.10	0.20	0.11	0.02	0.15	0.10	0.00	0.00	0.01	0.01
Fe^{+2}	0.00	0.16	0.47	1.51	0.84	1.72	0.00	0.01	0.34	0.04
Fe^{+3}	0.77	0.47	0.38	0.00	0.00	0.00	0.00	0.00	0.06	0.07
Mn	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.01	0.00
Mg	3.99	3.73	3.63	5.27	4.17	3.10	0.00	0.90	1.51	0.89
Ca	1.77	1.86	1.82	0.04	0.00	0.00	0.68	0.00	0.01	0.97
K	0.08	0.07	0.08	0.00	1.68	1.65	0.00	0.00	0.00	0.00
Na	0.35	0.38	0.37	0.08	0.16	0.15	0.37	0.08	0.01	0.02
Total	15.32	15.31	15.29	15.07	15.63	15.48	5.02	4.99	3.99	4.01

Analyses 1,2 and 3 = calcic amphibole; 4 = anthophyllite; 5 and 6 = biotite; 7 and 8 = feldspar; 9 = orthopyroxene; 10 = clinopyroxene

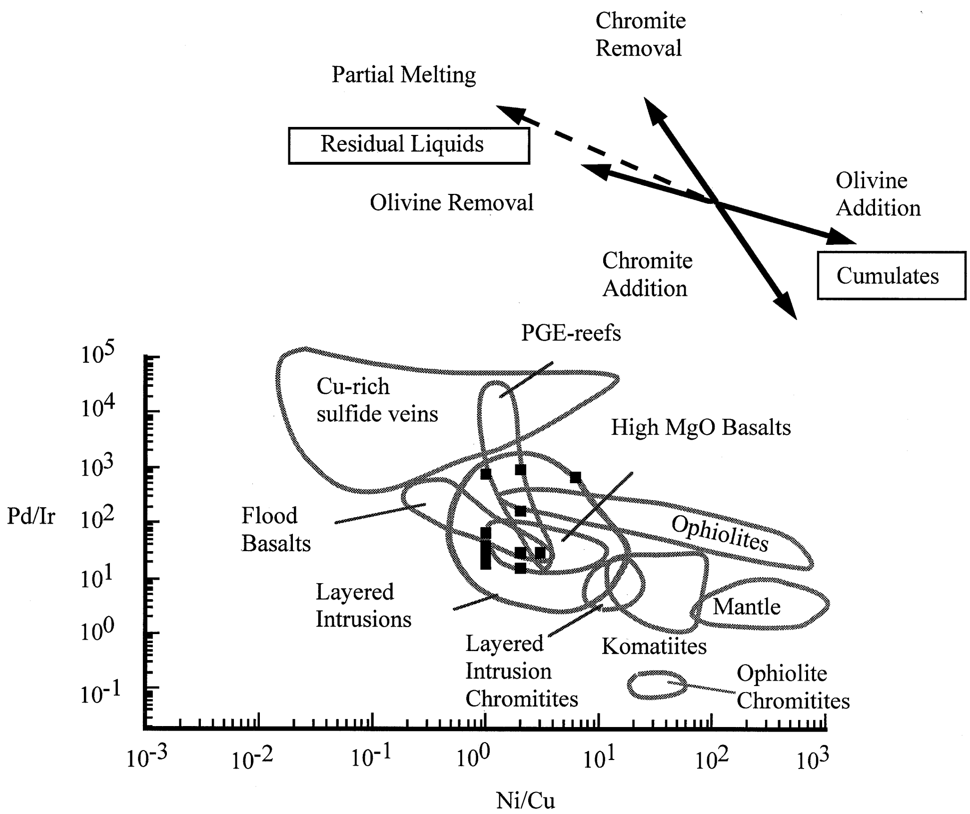


Fig. 8. Plot of Pd/Ir vs. Ni/Cu from the ultramafic intrusions of San Luis Province, Argentina. Fields are after *Barnes* et al. (1987)

Amphibole

Based on textural relations the amphiboles are classified as primary and secondary. The primary amphiboles are mainly magnesio-hornblendes with $Al_2O_3 = 10.04$ wt.%, $CaO = 12.27$ wt.%, and $MgO = 17.73$ wt.%. The secondary amphiboles are formed as a result of the alteration of orthopyroxene and clinopyroxene. These are Fe-Mg-Mn amphiboles; anthophyllites with $Al_2O_3 = 1.53$ wt.%, $CaO = 0.29$ wt.% and $MgO = 25.01$ wt.%.

Phlogopite

The mica found in the mineralized zone is Mg-rich with values ranging from 13 to 22 wt.% MgO. TiO_2 values range from 2.1 to 4.25 wt.%. The Cr_2O_3 values are also high ranging from 0.5 wt.% to 2.09 wt.%.

Plagioclase

The composition of plagioclase in the mafic rocks is variable with values ranging from $An_{61.3}$ to $An_{95.2}$. The higher An-content is observed in norites with a large modal percentage of orthopyroxene and the lower value in the gabbro norites.

Table 4. *Representative electron microprobe analyses of spinels from the Las Aguilas mafic-ultramafic body, San Luis Province Argentina*

	1	2	3	4	5
SiO_2	0	0	0	0	0
TiO_2	0.02	0	0.3	0.32	0.16
Al_2O_3	30.12	30.81	18.61	18.16	28.14
Cr_2O_3	28.19	27.99	44.85	44.56	30.96
Fe_2O_3	8.11	7.3	2.17	3.18	6.93
FeO	25.23	26.01	26.74	26.31	25.46
MnO	0.37	0.45	0.4	0.45	0.36
MgO	6.94	6.59	4.45	4.4	6.22
CaO	0	0	0.86	0	0
ZnO	0.67	0	0	1.41	1.11
K_2O	0	0	0	0	0
Na_2O	0	0	0	0	0
Total	99.83	99.15	98.38	98.8	99.34
Structural formula on the basis of 32 oxygen atoms					
Si	0	0	0	0	0
Ti	0.04	0	0.06	0.06	0.03
Al	8.85	9.09	5.9	5.76	8.41
Cr	5.55	5.54	9.54	9.47	6.21
Fe^{+3}	1.52	1.37	0.44	0.64	1.32
Fe^{+2}	5.26	5.44	6.01	5.91	5.4
Mn	0.08	0.1	0.09	0.1	0.08
Mg	2.58	2.46	1.79	1.76	2.35
Ca	0	0	0	0	0
Zn	0.12	0	0.17	0.28	0.21
K	0	0	0	0	0
Na	0	0	0	0	0
Total	24	24	24	23.98	24.01

Spinel

Representative electron-microprobe analyses (Table 4) indicate that the spinels have $X_{Mg} = Mg/(Mg+Fe^{2+})$ ranging from 0.20 to 0.48 and $X_{Cr} = Cr/(Cr+Al+Fe^{3+})$ values from 0.33 to 0.60. Although most spinel grains are homogeneous some are strongly zoned with magnetite-rich rims. The zoned spinel are characteristically found in serpentinised ultramafic cumulates. The zonation of the spinel ranges from a Cr-rich core through a ferri-chromite to a pure magnetite rim. This type of spinel alteration has been documented in metamorphosed rocks by *Evans* and *Frost* (1975) and *Mogessie* et al. (1988). Compositional variations documented in different samples of drill cores LAS 5/3 and LAS 5/2 are within the range of values for spinel reported by *Gervilla* et al. (1993) from the ultramafic units of the Las Aguilas body. In a plot X_{Cr} vs. X_{Mg} the data occupy a field to the right of spinels from ophiolites and outside the field of spinels from layered

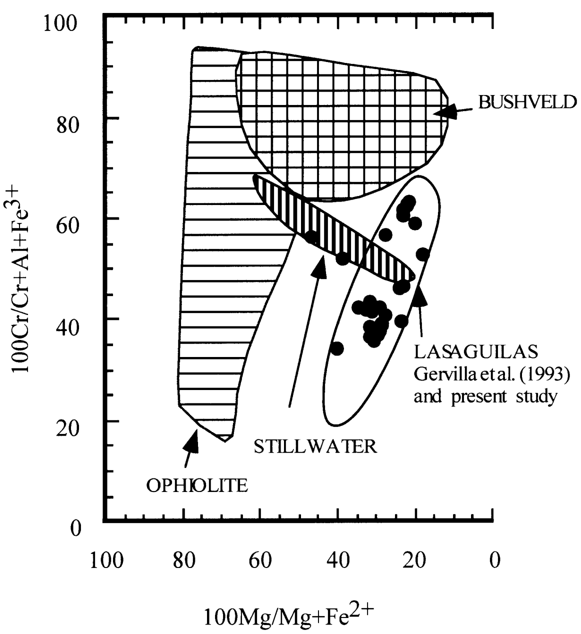


Fig. 9. Compositions of spinel from the Las Aguilas mafic-ultramafic rocks plotted on Cr/(Cr+Al+Fe^{3+}) vs. Mg/(Mg+Fe^{2+})

intrusions (Fig. 9a). The chemical data of the spinel cannot be used as indicator of the tectonic position of the mafic-ultramafic rocks of Las Aguilas. However, the high content of FeO_{total} and variable Cr-content in these Mg-rich mafic-ultramafic rocks is unusual. As reported by *Donaldson* and *Groves* (1985) the compositions of chromites can be extensively modified by metamorphism, and in the Las Aguilas chromites this might have happend during the mylonitisation process. However, this has not resulted in more homogeneous compositions of the spinels, rather formed distinct core and rim compositions as shown in Fig. 10d.

Sulphides

In the mineralized mafic-ultramafic rocks most of the samples contain abundant composite sulphides of variable texture ranging from intercumulus to vein type. The common BMS are chalcopyrite, pentlandite, and pyrrhotite. Pyrite has rarely been observed in some samples as the only sulphide phase. These sulphides can make up more than 50% modal of the rock and are found as interstitial phases in peridotites between phynocrysts of olivine and pyroxene. In the gabbroic rocks, the base metal sulphides are not abundant and occur as disseminated phases. The compositions of chalcopyrite, pyrrhotite, and pentlandite are presented in Table 5.

Arsenides

Fe-Ni-Co-S-As-bearing phases are found in the mineralized zones of the Las Aguilas drill cores. They are mainly associated with BMS and hydrous silicates such as biotite, hornblende, and serpentine. Arsenides in serpentinized olivine-rich rocks are mostly associated with Pd-Bi-Te-rich PGM. Their chemistry is variable,

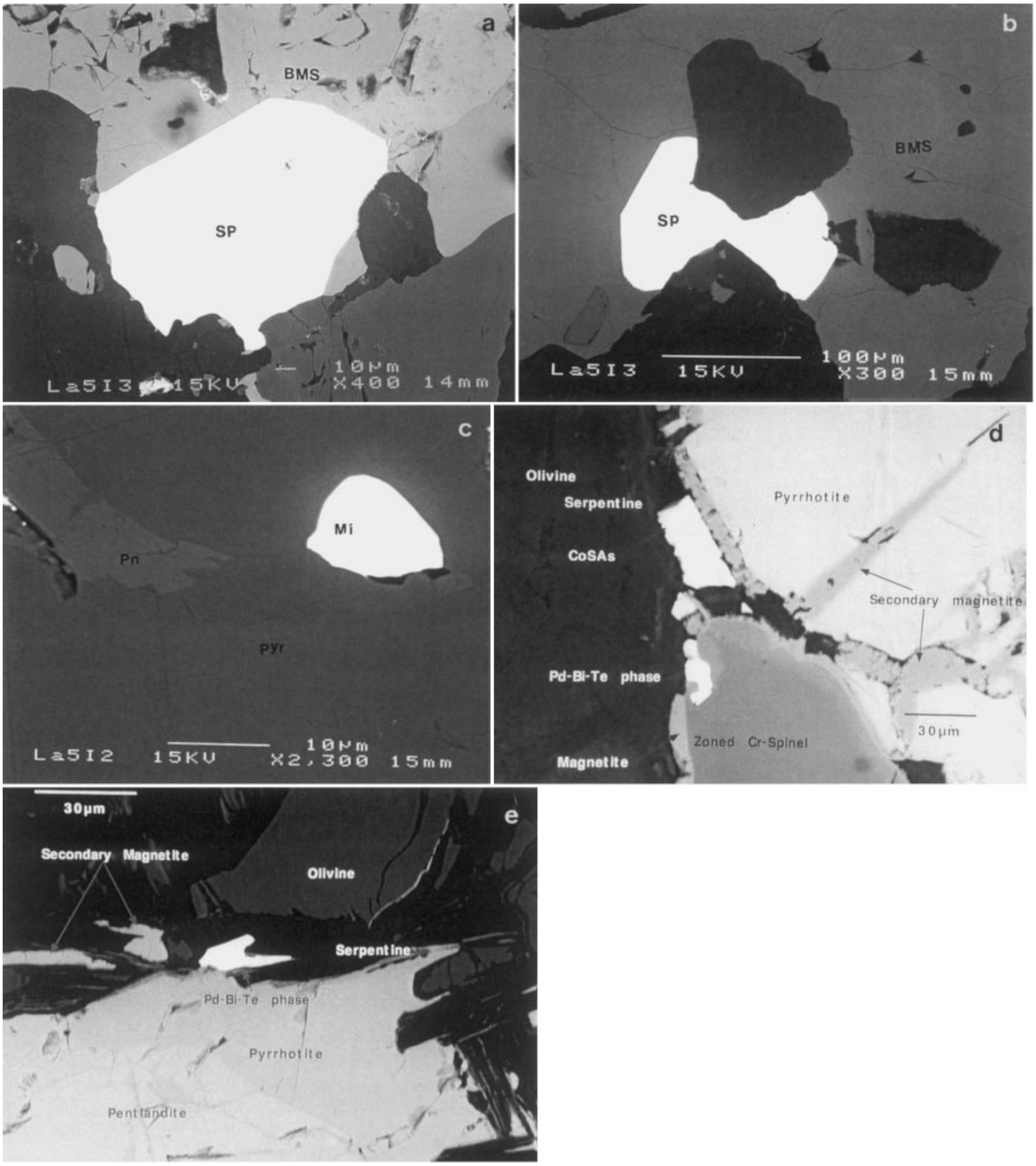


Fig. 10. **a, b** Sperrylite (SP) in a matrix of BMS (pentlandite, pyrrhotite, chalocpyrite), spinel (dark grey) and orthopyroxene (dark). **c** Pd-Bi-Te phase (michenerite, mi) in massive pyrrhotite (Pyr) and pentlandite (Pn). **d** Photomicrograph shows Pd-Bi-Te phase enclosed in a zoned Cr-spinel rim in contact with serpentine. The pyrrhotite and Cr-Spinel are altered to secondary magnetite. **e** Photomicrograph shows Pd-Bi-Te phase enclosed in a serpentinized layer

Table 5. *Representative electron microprobe analyses of sulphides and arsenides (wt.%) of the Las Aguilas mafic-ultramafic intrusion, San Luis Province Argentina*

Analysis No.	1	2	3	4	5	6
S	33.50	37.87	31.80	19.81	18.67	19.00
Fe	31.58	61.74	29.49	7.35	7.08	8.97
As	–	–	–	39.06	39.80	40.28
Co	–	0.08	2.56	24.80	20.58	12.62
Ni	–	0.26	35.90	8.66	13.26	18.82
Cu	35.17	0.05	0.22	0.30	0.55	0.30
Total	99.75	99.92	99.97	99.98	99.94	99.99
Atomic proportions						
S	48.36	51.51	45.53	33.51	31.91	32.37
Fe	26.18	48.21	24.24	7.31	6.95	8.78
As	–	–	–	28.27	29.13	29.38
Co	–	0.06	1.99	22.82	19.13	11.70
Ni	–	0.19	28.09	8.00	12.38	17.51
Cu	25.62	0.03	0.16	0.27	0.50	0.26

Analysis 1 = chalcopyrite; 2 = pyrrhotite; 3 = pentlandite; 4 = cobalt-cobalt-sulpharsenide (from sample LA5/3-98.4); and analyses 5 and 6 = cobalt sulpharsenide from sample LA5/2-90.8)

ranging from 12.62–24.80 wt.% Co, and 8.66–18.82 wt.% Ni (Table 5) and belong to the cobaltite-gersdorfite-arsenopyrite group.

Platinum-group minerals

Despite detailed field and microscopic examination of all sampled mafic-ultramafic rocks (surface and drill core samples), PGM were found only in the mafic-ultramafic rocks from the Las Aguilas drill holes. In addition to occurrences of PGM in the Las Aguilas drill cores reported by *Gervilla* et al. (1993, 1997) this paper describes a large number of PGM from the mafic-ultramafic intrusion of Las Aguilas. Most of the PGM rich zones are spinel-bearing sulphide-rich gabbronorite, pyroxenite, and dunite layers. Generally, microscopic investigations indicate that samples of drill cores above and below the spinel-sulphide – rich zone rarely contain PGM. Three types of PGM and modes of occurrences are represented:

Platinum arsenides

Sperrylite ($Pt_{33.3}As_{66.7}$) grains ranging in size from few microns to 200 μm are documented in the norite zone of the mafic-ultramafic intrusion at depths of 98.4 m in drill core LAS 5/3 and 90.8 m in drill core LAS 5/2 (Figs. 10a,b). The platinum arsenide phases are euhedral crystals occurring in sulphide- and Cr-spinel – rich

zones, mainly enclosed within pyrrhotite, pentlandite, and chalcopyrite. The coexisting silicates are Mg-rich orthopyroxene (En_{75-94}) and An-rich plagioclase ($An_{61.3-95.2}$). So far sperrylites have not been observed with hydrous silicates or enclosed in serpentinised layers of olivine-rich rocks as is the case for Pd-Bi-Te phases.

Palladium bismuthotellurides

Palladium bismuthotellurides (merenskyite-michenerite-moncheite-melonite) are found in a sulphide and spinel-rich norite zone mainly at depths of 90 to 120 m in drill cores LAS 5/2 and LAS 5/3 (Figs. 10c – e) and also in massive pyrrhotite layer. Some are euhedral grains found enclosed in sulphides with a diameter of 10 to 30 μm (Fig. 10c). The characteristic mineral assemblages for this zone are orthopyroxene + plagioclase + phlogopite + BMS (chalcopyrite + pyrrhotite + pentlandite) + spinel. Anhedral Pd-Bi-Te phases also occur in serpentinized dunite containing abundant BMS and spinel (Fig. 10d) or at the rims of altered Cr-spinel in contact with serpentine and secondary magnetite, BMS and cobalt sulphoarsenides (Fig. 10e). The secondary magnetite forms from (1) the alteration of chrome-spinel, (2) the serpentinization of olivine, and (3) the alteration of pyrrhotite. Based on the textural occurrences, we distinguish primary magmatic inclusions of Pd-Bi-Te phases in sulphides and secondary formation of Pd-Bi-Te phases in serpentinized layers.

Analyses of Pd-Te-Bi-Ni phases which occur within a massive pyrrhotite layer at a depth of 120 m in drill core LAS 5/3 give the formula $Pd_{25.3}Ni_{7.3}Te_{63.6}Bi_{3.8}$. This phase is chemically identified as merenskyite. Another Pd-phase from drill core LAS 5/2 at a depth of 105 m has a composition $Pd_{15.7}Ni_{15.7}Te_{62.5}Bi_{2.6}Fe_{3.1}$. The representative chemical data of the PGM presented in Table 6 show the variation in the composition of the palladium bismuthotellurides for different samples (at.% Pd from 15.9 to 27.7, at.% Bi 2.8–17.4 and at.% Te 46.5–61.8). The compositional variation in the Pd-phases given above is based on a substitution mechanism involving Pd and Ni, Bi and Te. This type of substitution has also been documented (with element distribution and back scattered electron images) in areas like the Duluth Complex where, a Bi-Ni-sulphide phase (parkerite) has been transformed to a Pd-Bi-Ni-Te phase with a substitution mainly involving Pd and Ni as a result of hydrothermal processes (*Mogessie* et al., 1991). This relationship may be similar to the Pt-Ni substitution for Pd, and Sb substitution for Bi in the michenerite-merenskyite phases at Sudbury reported by *Cabri* and *Laflamme* (1976).

Iridium-rhodium sulpharsenides

The iridium-rhodium phases were identified in drill cores LAS 4/2 and LAS 5/5. These phases are associated with serpentinised olivine, BMS and Ni-rich cobalt sulphoarsenides. Molybdenite (MoS_2) as well as palladium bismuthotellurides are in some cases associated with the Ir-Rh phases. They show a compositional variation from hollingworthite with 23.46 at.% Rh, 1.11 at.% Ir to irarsite with 5 at.% Rh and 43.75 at% Ir, the rest being Co, As, S, Ni.

Table 6. *Representative electron microprobe analyses (wt%) of PGM from the Las Aguilas mafic-ultramafic body, (Pd-Bi-Te phases; Anal. 1 = from drill core LAS 5/3-98.4 m; 2 = LAS 5/3-126.7 m; 3 = LAS 5/2-90.8 m; 4 = LAS 5/2-70 m; 5 = LAS 5/3-101.8 m) and 6 = sperrylite from LAS 5/3-98.4 m*

Analysis No.	1	2	3	4	5	6
S	0.46	0.00	0.48	0.84	0.00	0.00
Fe	1.37	0.58	1.90	1.72	1.20	0.01
Cu	0.00	0.00	0.00	0.00	1.48	0.00
Ni	4.57	2.85	5.86	0.57	1.13	0.03
Ru	0.00	0.00	0.00	0.00	0.00	0.00
Rh	0.00	0.00	0.00	0.00	0.00	0.00
Pd	18.87	23.31	16.58	22.84	24.12	0.00
Os	0.00	0.00	0.00	0.00	0.00	0.00
Ir	0.00	0.00	0.00	0.00	0.00	0.00
Pt	0.49	0.00	0.00	0.00	0.00	56.43
As	0.00	0.00	0.00	0.00	0.00	45.57
Bi	8.63	6.51	11.22	28.15	11.24	0.00
Te	65.61	66.64	64.01	45.98	60.49	0.00
Total	100.00	99.89	100.05	100.10	99.66	100.04
Atomic proportions						
S	1.70	0.00	1.75	3.40	0.00	0.00
Fe	2.87	1.24	3.95	3.98	2.61	0.02
Cu	0.00	0.00	0.00	0.00	2.84	0.00
Ni	9.13	5.83	11.62	1.26	2.36	0.06
Ru	0.00	0.00	0.00	0.00	0.00	0.00
Rh	0.00	0.00	0.00	0.00	0.00	0.00
Pd	20.82	26.30	18.13	27.68	27.64	0.00
Os	0.00	0.00	0.00	0.00	0.00	0.00
Ir	0.00	0.00	0.00	0.00	0.00	0.00
Pt	0.30	0.00	0.00	0.00	0.00	33.17
As	0.00	0.00	0.00	0.00	0.00	66.69
Bi	4.85	3.74	6.24	17.38	6.56	0.00
Te	60.34	62.69	58.36	46.48	57.80	0.00

Discussion

The mafic-ultramafic rocks in the San Luis province (El Durazno, Las Aguilas, Virorco, and El Fiero) carry disseminated and massive sulphide mineralization (pyrrhotite, pentlandite, chalcopyrite), accompanied by minor amounts of chromite. At the contact with the ultramafic bodies, the metamorphic country rocks show disseminated Fe-sulphides and graphite. Fe-Ni-Co-bearing sulphoarsenides are associated with the sulphides and altered silicates. PGM are identified enclosed in sulphides, at silicate-sulphide interfaces and in serpentinized layers.

It is generally accepted that certain PGM crystallized directly from the silicate magma (*Naldrett*, 1989), and the widespread association of PGE with sulphide minerals has led to the conclusion that economically significant PGE occurrences

require the segregation of sulphides into which PGE preferentially partition (*Naldrett*, 1989; *Brügmann* et al., 1989). The common encounter of certain PGM, particularly Os-Ir phases and alloys as inclusions in chromite of chromitite layers in layered intrusions (*McLaren* and *De Villiers*, 1982; *Talkington* and *Lipin*, 1986; *Merkle*, 1992) are considered to be evidence for such a segregation process. According to this model, an immiscible sulphide liquid could form when a primary silicate melt with sulphur content close to saturation, mixes with a batch of silicate liquid resulting in sulphur saturation (*Naldrett* and *von Gruenewaldt*, 1989) or the separation of immiscible sulphide liquid occurs within a convecting magma layer of a stratified chamber in response to cooling. The PGE are mainly considered to be associated with this immiscible sulphide liquid, although experimental studies on the solubility and distribution of PGE in BMS by *Makovicky* et al. (1986) do not show appreciable solubility of some PGE (Pt, Pd, Ru and Rh) in immiscible sulphide solution or chalcopyrite at magmatic temperatures of 900 °C – 500 °C.

However, several studies (*Ballhaus* and *Stumpfl*, 1986; *Boudreau*, 1988; *Mathez*, 1989; *Kinloch* and *Peyerl*, 1990; *Mogessie* et al., 1991) suggest that volatiles and fluids are indispensible for the transport and deposition of PGE in many mafic intrusions. Platinum bismuthotellurides, bismuthinides, and tellurides are considered to be remobilized at relatively low temperatures, and be transported at conditions of low-grade metamorphism (*Cabri*, 1981). A series of low – temperature Pd phases associated with silicate minerals were described from Rathbun Lake, Ontario by *Rowell* and *Edgar* (1986) and *Edgar* et al. (1989). They suggested a hydrothermal origin for the formation of the PGM, and outlined the variables controlling the PGM compositions such as pH, oxygen fugacity, and temperature of hydrothermal fluids. Further supporting evidence for significant solubility of PGE in hydrothermal solutions has been given by *Ripley* (1990) and *Mogessie* et al. (1991). These authors considered that the Pd-dominated mineralisation in the basal troctolite zone of the Duluth Complex was due to hydrothermal C-O-H-Cl – rich fluids introduced into the crystallizing magma and derived from the enclosing metasedimentary units.

For the Las Aguilas area, some authors (*Malvicini* and *Brogioni*, 1992) suggest that the primary sulphide mineralization in the mafic-ultramafic intrusion was remobilized by hydrothermal fluids related to the Ordovician metamorphism, and *Gervilla* et al. (1993) proposed that the mineralization shows characteristics indicating that it was formed by crystal fractionation of mafic melts.

Microscopic evidence reveals two distinct PGM-associations:

1. The Pd-Bi-Te and the platinum arsenide (sperrylite) phases are found enclosed in BMS (chalcopyrite, pyrrhotite or pentlandite) coexisting with orthopyroxene, plagioclase and spinel as shown in Figs. 10a,b and c. These textural occurrences indicate that the PGM are not associated with hydrous silicates or altered oxide phases such as ferrichromite, magnetite, and have formed by crystal fractionation of mafic melts.
2. Pd-Bi-Te phase such as michenerite, moncheite, and merenskyite are enclosed in serpentine layers of altered dunite and at magnetite rims of zoned chrome spinel in contact with serpentine (Figs. 10d,e).

The PGM at Las Aguilas are found in norites rich in BMS and in serpentinised dunites. The textural relationships do not suggest a primary magmatic origin for all the PGMs observed in the mineralized unit. The textural type 2 indicates that some of the PGM are not enclosed within sulfide phases and are found in serpentinized layers and at the magnetite rims of altered zoned chrome spinel. In such serpentinized zones containing Pd-Bi-Te phases, one finds arsenides of variable composition. The experimental data of *Gervilla* et al. (1994) demonstrate arsenide melts to be potential collectors of Pd. According to their experimental results mutual solubility of Ni and Pd in arsenides plays an important role at intermediate temperatures ($\sim 450\,^{\circ}C$). Moderate geologic temperatures and subsolidus processes were suggested for some occurrences of Pd-Ni arsenides (*Watkinson* and *Ohnenstetter*, 1992; *Chen* et al., 1993) whereas crystallization from late fluids (e.g. above $550\,^{\circ}C$) has been reported by *Ballhaus* and *Stumpfl* (1986); *Ohnenstetter* et al. (1992); and *Ripley* and *Chryssoulis* (1994). *Mountain* and *Wood* (1988) have indicated that elements such as Te and Bi will greatly restrict the mobility of Pt and Pd, and *Paktunc* et al. (1990) documented that the availability of Bi and Te effectively controls the extent of PGE solution in sulfide hosts, of which pentlandite is the most significant. It is therefore suggested that the PGE mineralization and the formation of Pd-Bi-Te phases is a result of local remobilization, redistribution, and recrystallization of magmatic PGE-bearing BMS due to late stage hydrothermal processes, and did not lead to dispersion of the PGE over a great distance at Las Aguilas.

The mafic-ultramafic body of Las Aguilas intruded an older amphibolite-grade crystalline basement, consisting of metapelites and metabasites in varying proportions. The thermal effect of this intrusion is indicated by the prograde granulite facies metamorphism of the crystalline basement in contact with the mafic-ultramafic rocks ($750\,^{\circ}C \pm 50\,^{\circ}C$, 5 ± 1 kbar). The metamorphic grade decreases outwards to amphibolite-greenschist facies. During this time, mafic-ultramafic rocks reequilibrated to high – grade metamorphic temperatures (700–800 °C) as deduced by the two pyroxene geothermometer of *Lindsley* and *Anderson* (1983). At a later stage, the area was deformed and strongly mylonitized. As a result, both the basement and mafic-ultramafic rocks were affected by retrograde metamorphism of upper greenschist to amphibolite facies (500–600 °C, 4–5 kbar). It is during this time that the PGE-rich sulphides were remobilized, locally transported and deposited to form the Pd-Bi-Te phases which are now observed enclosed in serpentinized layers associated with secondary magnetite and rims of zoned chrome spinels. The process of PGM formation at these temperatures is supported by the experimental results of *Makovicky* et al. (1986) who documented a sharp decrease in solubility of Pd, Pt, Ru, and Rh in pyrrhotite from 900 °C to 500 °C and for Pd to 300 °C. This causes exsolution on cooling of Pd, Ru, and Pt in the form of submicroscopic sulphide particles, and if percolating liquids bring components with high affinity for PGE such as Sb, As, Te, and Bi, etc., these elements may crystallize PGE-bearing minerals.

The mineralization of some of the PGM especially the Pd-Bi-Te phases is thus possibly related to a fluid phase during the deformation event. Field observation shows the abundance of quartz-feldspar- and tourmaline rich-pegmatite outcrops near ultramafic layers with similar strike directions. The mineralizing fluid may be

related to the pegmatite intrusions or to a fluid introduced during the mylonitization process.

Although one cannot suggest that the Las Aguilas mafic-ultramafic complex is similar to the well known layered intrusions such as the Bushveld and the Stillwater, geological and geophysical evidence suggest this complex to be a layered intrusion as also recently reported by *Sims* et al. (1997) and *Kostadinoff* et al. (1998). The mafic-ultramafic rocks of the San Luis area have been considered to belong to the same regional tectonic setting as the mafic-ultramafic rocks in Cordoba province. These are located NE of the study area, and classified as alpine type bodies (*Villar*, 1985). The PGE data of the Las Aguilas mafic-ultramafic units of the San Luis province presented in this study, do not show an alpine or ophiolite signature, this is contrary to previously proposed interpretations.

Conclusions

1. Three different compositional groups of PGM are documented in the mafic-ultramafic intrusions of Las Aguilas. These are (1) platinum arsenides ($PtAs_2$), (2) Pd-Bi-tellurides (moncheite, michenerite, merenskyite, melonite), and (3) Rh-Ir-sulphoarsenides.
2. Different textural occurrences of PGM are documented. Platinum arsenides are found mainly enclosed in BMS and in equilibrium textures with spinel and primary silicates like orthopyroxene and plagioclase. The Pd-Bi-Te phases can be classified into two textural types: (i) those enclosed in BMS as droplets, and (ii) those found in serpentinized olivine and at the magnetite rims of zoned Cr-spinel.
3. The different textures of the PGM associations at Las Aguilas are believed to be related to both primary magmatic and hydrothermal overprinting processes. The platinum arsenide (sperrylite) and the first textural type of Pd-Bi-Te phases are considered to be formed due to fractional crystallization of a sulphide-saturated mafic melt. The second textural type of Pd-Bi-Te phases and the Rh-Ir sulphoarsenides associated with hydrous phases like serpentine and secondary magnetite are considered to be formed as a result of hydrothermal processes. The remobilisation of PGE, transport and formation of PGM in the Las Aguilas mafic-ultramafic intrusion took place after the peak of granulite facies metamorphism and during the late mylonitization and deformation event (500–600 °C, 4–5 kbar) which affected both the mafic-ultramafic rocks and the crystalline basement.

Acknowledgements

This study is financially supported by the Austrian Research Council (Project Nos. FWF P09564, P10623-TEC) to AM and GH, the University of Graz Foreign Relations Office to GH, the Steiermark Government to AM and GH and the CONICET and SGCyT-UNS of Argentina to EB and JK. We would also like to thank *P. Neumayr* for reading the first draft of the manuscript and two anonymous reviewers for their constructive comments.

References

Ballhaus CG, Stumpfl EF (1986) Sulphide and platinum mineralization in the Merensky Reef: evidence from hydrous silicate and fluid inclusions. Contrib Mineral Petrol 94: 193–204

Barnes S-J (1987) Unusual nickel and copper to noble-metal ratios from the Rana layered intrusion, northern Norway. Norsk Geol Tidsskrift 67: 215–231

Barnes S-J, Naldrett AJ, Gorton MP (1985) The origin of the fractionation of platinum-group elements in terrestrial magmas. Chem Geol 53: 303–323

Bence AF, Albee AL (1968) Emperical correction factors for the electron microanalysis of silicates and oxides. J Geol 76: 382–403

Bjerg SC, Mogessie A, Bjerg E (1992) HYPER-FORM-a Hypercard program for Macintosh microcomputers to calculate mineral formulae from electron microprobe and wet chemical analysis. Comput Geosci 18 6: 717–745

Bjerg E, Delpino S, Dimieri L, Kostadinoff J, Mogessie A, Hoinkes G, Hauzenberger CA, Felfernig A (1997) Estructura y mineralizacion del area Las Aguilas – Virorco, San Luis, Argentina. VIII Cong Geol Chil Actas (II): 857–861 (Antofagasta)

Bohlen SR (1987) Pressure – temperature – time paths and a tectonic model for the evolution of granulites. J Geol 95: 617–32

Boudreau AE (1988) Investigations of the Stillwater Complex. IV. The role of volatiles in the petrogenesis of the J-M Reef, Minneapolis Adit section. Can Mineral 26: 193–208

Brogioni N (1992) El cuerpo máfico-ultramáfico de Las Aguilas, provincia de San Luis: Mineralogia de los silicatos. 1° Reun. Min. Metal. – 1° Jorn Min Petrog Metalog Rocas Ultrab Actas 379–392

Brogioni N (1994) Petrología de la faja de rocas máficas y ultramáficas de la Sierra de San Luis, Argentina. 7° Cong Geol Chil Actas 3: 967–971

Brügmann GE, Naldrett AJ, Macdonald AJ (1989) Magma mixing and constitutional zone refining in the Lac des Iles Complex, Ontario: genesis of platinum-group element mineralization. Econ Geol 84: 1557–1573

Cabri LJ (1981) Platinum group elements: mineralogy, geology, recovery. Can Inst Min Metall Spec Vol 23: 267pp

Cabri LJ, Laflamme JH (1976) The mineralogy of the platinum-group elements from copper-nickel deposits of the Sudbury area, Ontario. Econ Geol 71: 1159–1195

Caminos R, Cingolani CA, Hervé F, Linares E (1982) Geochronology of the Pre-Andean metamorphism and magmatism in the Andean Cordillera between latitudes 30° and 36° S. Earth Sci Rev 18: 333–352

Chen Y, Fleet ME, Pan Y (1993) Platinum-group minerals and gold in arsenic-rich ore at the Thompson mine. Thompson nickel belt, Manitoba, Canada. Mineral Petrol 49: 127–146

Cornelius M, Stumpfl EF, Gee D, Prochaska W (1987) Platinum group elements in mafic-ultramafic rocks of the Western Gneiss Terrain, Western Australia. Mineral Petrol 36: 247–265

Donaldson MJ, Groves DL (1985) The relevance of chromite as a petrogenetic indicator in metamorphosed komatiitic rocks and associated Ni ores. Can Mineral 23: 326

Edgar AD, Charbonneau HE, McHardy DC (1989) Pd-bismuthtelluride minerals at Rathbun Lake, Ontario: significance to post-magmatic evolution of PGE depoits. N Jahrb Mineral Monatsh 461–475

Evans BW, Frost BR (1975) Chrome spinel in progressive metamorphism – a preliminary analysis. Geochim Cosmochim Acta 39: 959–972

Gervilla F, Sabalúa JC, Carrillo R, Fenoll Hach-Ali P, Acevedo RD (1993) Mineralogy and mineral chemistry of the Las Aguilas Ni-Cu deposit, province of San Luis, Argentina.

In: *Fenoll Hach-Ali P, Torres-Ruiz J, Gervilla F* (eds) Current research in geology applied to ore deposits. Servicio de Publicaciones, Universidad de Granada, pp 461–464

Gervilla F, Makovicky M, Makovicky E, Rose-Hansen J (1994) The system Pd-Ni-As at 790 °C and 450 °C. Econ Geol 59: 1630–1639

Gervilla F, Sanchez-Anguita A, Acevedo RD, Hoch-Ali PF, Pangua A (1997) Platinum-group element sulpharsenides and Pd bismuthotellurides in the metamorphosed Ni-Cu deposit at Las Aguilas (Province of San Luis, Argentina). Mineral Mag 61: 861–877

Gordillo CE, Lancinas AN (1979) Sierras Pampeanas de Cordoba y San Luis. Acadamia Nacional de Ciencias Cordoba; Apartido de "Geologia Regional Argentina" 1: 577–650

Hauzenberger CA, Mogessie A, Hoinkes G, Felfernig A, Bjerg EA, Kostadinoff J (1996) Granulite facies metamorphism in the crystalline basement and ultramafic rocks in the Sierras Pampeanas Range, Province of San Luis, Argentina. Mitt Österr Min Ges 141: 110–111

Kinloch ED, Peyerl W (1990) Platinum-group minerals in various rock types of the Merensky Reef: genetic implications. Econ Geol 85: 537–555

Kostadinoff J, Bjerg EA, Delpino S, Dimieri L, Mogessi A, Hoinkes G, Hauzenberger CA, Felfernig A (1998) Gravimetric and magnetometric anomalies in the Sierras Pampeanas of San Luis. Asoc Geolog Arg Rev 53: 169–179

Lee CA, Tredoux M (1986) Platinum-group element abundances in the Lower and the Lower Critical Zones of the Eastern Bushveld Complex. Econ Geol 81: 1087–1095

Lindsley DH, Anderson DJ (1983) A two-pyroxene thermometer. J Geophys Res 88 [Suppl]: A887–A906 (Proc 13th Lunar Sci Conf, part 2)

McLaren CH, De Villiers JPR (1982) The platinum-group chemistry and mineralogy of the UG-2 chromitite layer of the Bushveld Complex. Econ Geol 77: 669–678

Makovicky M, Makovicky E, Rose-Hansen J (1986) Experimental studies on the solubility and distribution of platinum group elements in base-metal sulphides in platinum deposits. In: *Gallagher M, Ixer RA, Neary CR, Prichard HM* (eds) Metallurgy of basic and ultrabasic rocks. The Institution of Mining and Metallurgy, London pp 415–425

Malvicini L, Brogioni N (1992) El yacimiento hidrotermal de niquel, cobre y metales del "Grupo del Platino", Las Aguilas Este, Prov. de San Luis, Argentina. Americano de geologia economica. Acta Cordoba: 93–102

Mathez AE (1989) Interactions involving fluids in the Stillwater and Bushveld Complexes: observations from the rocks. In: *James AW, Naldrett AJ* (eds) Ore deposition associated with magmas. Rev Econ Geol 4: 21–31

Merkle RK (1992) Platinum-group minerals in the middle group of chromite layers at Marinkana, western Bushveld Complex: indications for collection mechanisms and postmagmatic modification. Can J Earth Sci 29: 209–221

Mezger K, Bohlen SR, Hanson GN (1990) Metamorphic history of the Archean Pikwitonei granulite domain and the Cross Lake Subprovince, Superior Province, Manitoba, Canada. J Petrol 31: 483–517

Mogessie A, Purtscheller F, Tessadri R (1988) Chromite and chrome spinel occurrences from metacarbonates of the Oetztal – Stubai Complex (northern Tyrol, Austria). Min Mag 52: 229–236

Mogessie A, Tessadri R, Veltman CB (1990) EMP-AMPH – a Hypercard program to determine the name of an amphibole from electronmicroprobe analysis according to the international mineralogical association scheme. Comput Geosci 16: 309–330

Mogessie A, Stumpfl EF, Weiblen PW (1991) The role of fluids in the formation of platinum group minerals, Duluth Complex, Minnesota: mineralogic, textural and chemical evidence. Econ Geol 86: 1506–1518

Mogessie A, Hoinkes G, Stumpfl EF, Bjerg EA, Kostadinoff J (1994) The petrology and mineralization of the basement and associated mafic-ultramafic rocks, San Luis province, central Argentina. Mitt Österr Min Ges 139: 347–348

Mogessie A, Hoinkes G, Stumpfl EF, Bjerg EA, Kostadinoff J (1995) Occurrence of platinum group minerals in the Las Aguilas ultramafic unit within a granulite facies basement, San Luis province, central Argentina. In: *Pašava J, Kříbek B, Žák K* (eds) Mineral deposits: from their origin to their environmental impacts. Proceedings of the Third Biennial Society of Geology Applied to Mineral Deposits (SGA) Meeting, Prague, pp 897–900

Mogessie A, Hauzenberger CA, Hoinkes G, Felfernig A, Stumpfl EF, Bjerg EA, Kostadinoff J (1996) Platinum group minerals from the Las Aguilas ultramafic unit, San Luis province, Argentina. Mitt Österr Min Ges 141: 157–159

Mountain BW, Wood SA (1988) Chemical controls of the solubility, transport and deposition of platinum and palladium in hydrothermal solutions: a thermodynamic approach. Econ Geol 83: 492–510

Naldrett AJ (1989) Magmatic sulfide deposits. Clarendon Press – Oxford University Press, New York Oxford

Naldrett AJ, Von Gruenewaldt G (1989) The association of PGEs with chromite in layered intrusions and ophiolite complexes. Econ Geol 84: 180–187

Paktunc AD, Hulbert LJ, Harris DC (1990) Partitioning of the platinum-group and other trace elements in sulfides from the Bushveld complex and Canadian occurrences of nickel-copper sulfides. Can Mineral 28: 475–488

Ramos VA (1988a) Late Proterozoic-Early Paleozoic of South America – a collisional history. Episodes 11 3: 168–174

Ramos VA (1988b) The tectonics of the Central Andes 30° to 33° S latitude. Geol Soc America, Special Paper 218: 31 1–54

Ripley EM (1990) Platinum-group element geochemistry of Cu-Ni mineralization in the basal zone of the Babbitt deposit, Duluth Complex, Minnesota. Econ Geol 85: 830–841

Ripley EM, Chryssoulis SL (1994) Ion microprobe analysis of platinum group elements in sulfide and arsenide minerals from the Babbitt Cu-Ni deposit, Duluth Complex, Minnesota. Econ Geol 80: 201–210

Rowell WF, Edgar AD (1986) Platinum-group element mineralization in a hydrothermal Cu-Ni-sulfide occurrence, Rathbun Lake, northeastern Ontario. Econ Geol 81: 1272–1277

Sabalúa JC (1986) El yacimiento de níquel-cobre-cobalto de Las Aguilas, San Luis, Argentina, Dir Gen Fab Milit 1–16 Buenos Aires (unpublished report)

Sabalúa JC, Chabert M, Santamaria G (1981) Mineralización de sulfuros de hierro, cobre y níquel en el cuerpo básico de Las Aguilas, provincia de San Luis. VIII Cong Geol Arg San Luis Actas IV: 497–507

Sims J, Skirrow RG, Stuart-Smith PG, Lyons P (1997) "Report on Geology and Metallogeny of the Sierras de San Luis y Comachingonas" 1:250 000, map sheet, Provinces of San Luis and Cordoba. Geoscientific mapping of the Sierras Pampeanas, Argentine – Australian Cooperative Project, Australian Geological Organisation (unpublished report)

Suarez AO, Prozzi C, Llambias EJ (1992) Geologia de la parte sur de la Sierra de San Luis y granitodies asociados, Argentina. Estudios Geologicos 48: 269–277

Talkington RW, Lipin BR (1986) Platinum-group minerals in chromite seems of the Stillwater Complex. Econ Geol 81: 1179–1186

Villar LM (1959) Las fajas ultrabasicas argentinas, tipos de ultramafitas y metalogenesis. IV Congr Geol Chileno 4: 610–633

Watkinson DH, Ohnenstetter D (1992) Hydrothermal origin of platinum-group mineralization in the Two Duck Lake intrusion, Coldwell Complex, northwestern Ontario. Can Mineral 30: 121–136

Wells PRA (1980) Thermal models for the magmatic accretion and subsequent metamorphism of continental crust. Earth Planet Sci Lett 46: 253–65

Authors' addresses: *A. Mogessie, Ch. A. Hauzenberger, G. Hoinkes, A. Felfernig,* Institute of Mineralogy – Crystallography and Petrology, University of Graz, Universitätsplatz 2, A-8010 Graz, Austria; *E. F. Stumpfl,* Institute of Geosciences, Mining University of Leoben, A-8700 Leoben, Austria; *E. Bjerg* and *J. Kostadinoff,* Departmento de Geologia, Universidad Nacional del Sur-CONICET, San Juan 670, 8000 Bahia Blanca, Argentina