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Chrome spinels from the Las Águilas mafic-ultramafic intrusion, San Luis Province, Argentina

Gabriela Ferracutti, Aberra Mogessie, and Ernesto Bjerg

With 7 figures and 3 tables

Abstract: Two groups of spinel are documented from the mafic-ultramafic rocks of Las Águilas, San Luis Province, Central Argentina. Both spinel types have chromium-aluminum rich cores. However, type I spinel cores are surrounded by chromian-aluminian rims and occur mainly in orthopyroxenites. Type II spinel cores occur mainly in dunites, and show two rims that are compositionally different: rims IIA grade from aluminian-chromite to chromian-magnetites formed by serpentinization, and rims IIB are chromian-aluminium spinel formed during the mylonitization event. Spinel rims type I and type IIA are associated with serpentinized rocks and support the role played by serpentinization processes in the modification of spinel chemistry, which also affected magmatic sulphides and platinum group minerals in the Las Águilas mafic-ultramafic rocks.

Key words: spinel chemistry, serpentinization-mylonitization processes, mafic-ultramafic rocks, tectonic tracers, PGM.

Introduction

The Las Águilas mafic-ultramafic body is located in the Eastern Sierras Pampeanas, San Luis Province, Argentina (Fig. 1). The crystalline basement of the Eastern Sierras Pampeanas comprises three main blocks (eastern, central and western), which are separated by mylonite zones (HAUZENBERGER et al. 2001, SIMS et al. 1998). The eastern and western blocks are dominated by migmatites whereas the central block, in which the Las Águilas mafic-ultramafic body occurs, is dominated by greenschist to amphibolite facies metamorphic rocks. Both tectonic and intrusive contacts between the igneous bodies and the metamorphic basement rocks were recognized in the field. Amphibolite facies metapelites are characterized by the mineral assemblage staurolite + garnet + biotite + muscovite + plagioclase + quartz + ilmenite ± fibrolite ± chlorite (570–600 °C and 5–5.7 kbar). The mafic intrusion caused a local granulite facies contact metamorphism (740 to 790 °C and 5.7 to 6.4 kbar) with a characteristic mineral assemblage consisting of garnet + cordierite + sillimanite + biotite + K-feldspar + plagioclase + quartz + rutile + ilmenite ± orthopyroxene. During cooling, mylonitization ín discrete zones retrograded most of the granulite facies rocks to amphibolite facies conditions (590 to 650 °C and 5.4 to 6.0 kbar) into the mineral assemblages garnet + biotite + sillimanite + plagioclase + muscovite + quartz + rutile ± K-feldspar (HAUZENBERGER et al. 2001).

In some areas the mafic-ultramafic bodies of San Luis show a modal stratification on a metric scale (FERRACUTTI 2005). Microscopic study of samples from surface outcrops and drill cores indicate that the Las Águilas complex consists of orthopyroxenites (orthopyroxene + plagioclase + spinel + sulphides ± platinum group minerals), websterites (orthopyroxene + clinopyroxene + plagioclase + spinel + sulphides), dunites (olivine ± orthopyroxene + sulphides + spinel ± platinum group minerals), harzburgites (orthopyroxene + olivine + sulphides + spinel ± platinum group minerals) and, mafic rocks such as norites [orthopyroxene + plagioclase ± amphibole] and gabbronorites (orthopyroxene ± clinopyroxene + plagioclase ± amphibole).

Chrome-spinel as well as disseminated and massive sulphides (pyrrhotite, pentlandite and chalcopyrite) and platinum group minerals have been documented in the mafic-ultramafic rocks (SABALÚA et al. 1981, MALVICINI & BROGIONI 1992, BJERG et al. 1996, GERVILLA et al. 1997, HAUZENBERGER 1997, HAUZENBERGER et al. 1997a, FELFERNIG 1999, MOGESSIE et al. 1998, 2000). A

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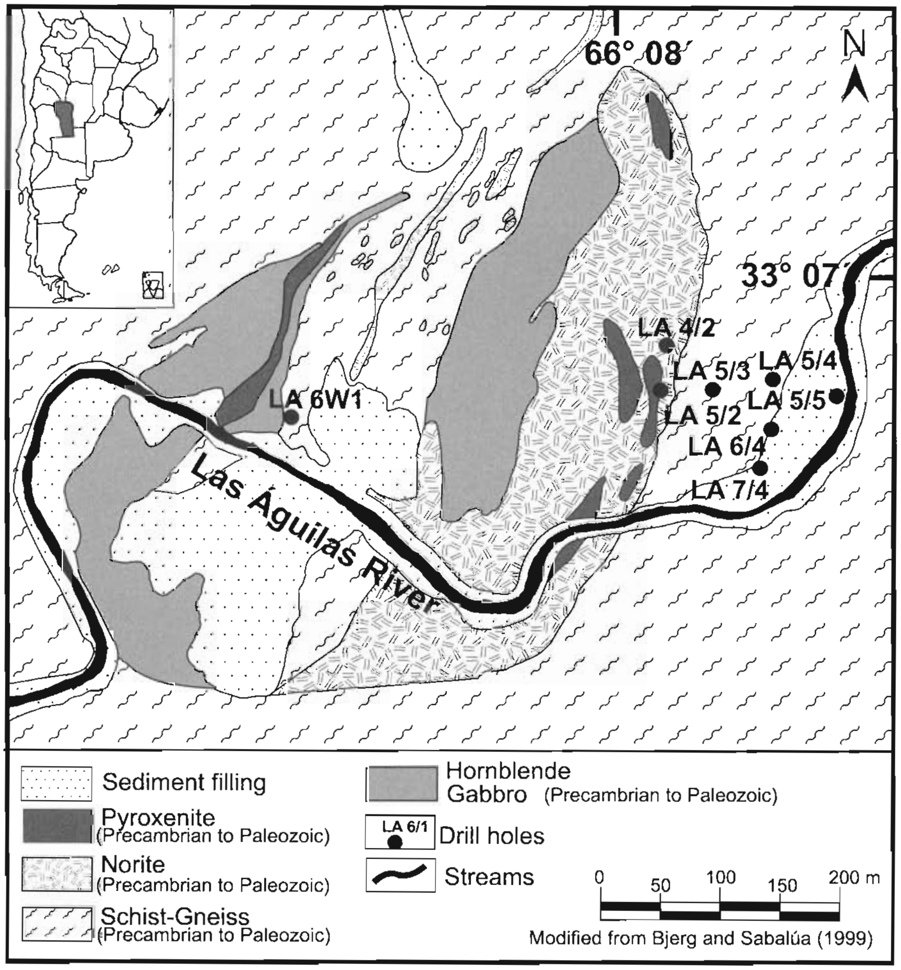

Modified from Bjerg and Sabalúa (1999)

Fig. 1. Geology and location of the Las Águilas deposit in San Luis Province; Argentina, and numbers of drill-holes, from which samples for this study were taken.

characteristic of the spinel is the presence of platinum group minerals located in the rim of zoned chrome-spinel and in serpentine veins, a feature interpreted as an indication of platinum group element remobilization processes (MOGESSIE et al. 1998, 2000).

Although in some samples primary minerals and igneous textures are present, most of the studied samples have been affected by significant serpentinization. DELPINO et al. (2005) established that the mafic-ultramafic intrusives and their gneissic-migmatitic surroundings have been overprinted by a mylonitization event with a temperature gradient from 555 °C to 764 °C and 6 to 7 kbar, occurring over a distance of approximately 7 km. According to these authors a final overprint at a temperature below 500 °C retrograded the mafic-ultramafic minerals to the assemblage serpentine + magnetite ± actinolite. This event was related to brittle fracturing and the presence of a water-rich fluid phase which also affected the ore minerals.

There are few published references mentioning the Las Águilas spinel (GERVILLA et al. 1993, HAUZENBERGER 1997 and MALVICINI & BROGIONI 1992). FELFERNIG (1999) documented brown colored spinel with homogenous chromite cores and a ferritchromite to magnetite rim. A similar zoning has been documented by MOGESSIE et al. (2000). Spinel composition allowed FERRACUTTI et al. (2004) and FERRACUTTI (2005) to classify the Las Águilas body as a layered mafic-ultramafic intrusion.

Drill core samples from Las Aguilas indicate that mafic units (norite-gabbronorites) dominate in the upper part and ultramafic units (pyroxenites-websterites and dunites-harzburgites) become more significant at depth. 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 unit (FERRACUTTI et al. 2005). The maximum concentration of these elements coincides with the mineralized units containing platinum-group minerals and spinel. The presence of spinel

Table 1. Representative electron microprobe analyses of silicates from the Las Águilas mafic-ultramafic intrusion. Cpx: clinopyroxene, Opx: orthopyroxene, Pl: plagioclase, Ol: olivine, b. d: below detection limit.

Drill hole/ Sample	7-4/147	5-5/144	7-4/146	6-4/157.8	7-4/90.1	4-2/61	5-4/98.2	6-4/157.8
Mineral	Cpx	Cpx	Opx	Opx	Pl	Pl	Ol	Ol
SiO_2	52.84	54.37	54.29	55.11	43.98	43.85	39.65	39.29
TiO_2	0.17	0.14	0.04	0.10	b. d	0.08	b. d	b. d
Al_2O_3	0.40	0.65	2.68	1.93	36.47	36.92	b. d	b. d
Cr_2O_3	0.09	0.27	0.26	0.17	b. d	b. d	b. d	b. d
Fe_2O_3	2.18	b. d	1.62	1.27	b. d	b. d	b. d	b. d
FeO	4.68	2.72	11.59	9.74	0.24	b. d	18.64	16.52
MnO	0.19	0.12	0.34	0.30	b. d	0.04	0.32	0.26
ZnO	b. d	0.09	b. d	b. d	b. d	0.13	b. d	b. d
MgO	14.72	17.33	29.50	31.19	b. d	0.26	42.94	43.89
CaO	24.56	24.07	0.29	0.27	19.45	19.53	b. d	b. d
NiO	b. d	b. d	b. d	0.01	b. d	b. d	0.17	0.15
Na_2O	0.20	0.05	0.01	b. d.	0.20	0.08	0.01	b. d
K_2O	b. d	b. d	b. d	0.01	b. d	0.03	0.01	b. d
Total	100.03	99.81	100.61	100.08	100.35	100.92	101.74	100.11
Structural formula								
O number	6	6	6	6	8	8	4	4
Si	1.93	1.98	1.92	1.94	2.03	2.01	1.00	1.00
Al	0.10	0.03	0.11	0.08	1.98	1.99		
Cr	0.01	0.01	0.01	0.01				
Fe^{3+}	0.02	0.00	0.04	0.03				
Fe^{2+}	0.11	0.08	0.34	0.29	0.01	0.00	0.39	0.38
Mg	0.92	0.94	1.55	1.64		0.02	1.61	1.62
Ca	0.91	0.94	0.01	0.01	0.96	0.96		
Na					0.02	0.01		
Total	4.00	3.98	3.98	4.00	5.00	4.99	3.00	3.00

in the paragenesis is characteristic for the mineralized zone and can be used as an exploration tool in areas where primary magmatic sulphide mineralizations have been affected by later remobilization processes and the host rocks are tectonically disturbed.

However, a detailed study dealing with the unusual chemistry of the Las Águilas spinels, which are characteristic of the mineralized zone, in relation to metamorphism was lacking. In this contribution we present the results of a detailed petrographic and geochemical study of Las Águilas spinel and discuss the processes that changed their magmatic composition, originated the observed unusual zoning and at the same time influenced the distribution of platinum group minerals.

Geological setting

The Las Águilas mafic-ultramafic rocks occur 30 km NE of San Luis city, central Argentina (Fig. 1). The outcrops trend NE–SW in an area measuring 3 km × 1 km and are part of a belt of mafic-ultramafic rocks that extends over 100 km to the NNE at the eastern margin of the Sierra Grande de San Luis, Argentina.

In this portion of the Sierra Grande de San Luis the main outcrops are metasediments and metavolcanics of Precambrian to Paleozoic age (Hauzenberger et al. 1997 b, Rapela et al. 1998, Sims et al. 1998, Von Gossen et al. 2002). The mafic-ultramafic rocks are associated with high-grade metamorphic rocks (gneisses, amphibolites and granulites) and are exposed in 10 areas extending from El Durazno in the south to San Pedro in the north. These mafic-ultramafic intrusions are built up by norites, gabbronorites, pyroxenites and peridotites with base metal sulphide mineralization (Ni–Cu–Co). According to Sims et al. (1997) who have made geological and geophysical mapping of the Sierras Pampeanas including an extensive program of SHRIMP (U–Pb and Th–Pb) and Ar–Ar geochronology, the mineralized Las Águilas mafic-ultramafic rocks are dated to be of Ordovician age.

The investigated spinel minerals were identified in samples from Las Aguilas drill cores 4-2, 5-2, 5-4, 5-5, 6-4 and 7-4 (Fig. 1). All drill cores dip to the west be-

Table 2. Representative electron microprobe analyses of spinels from the Las Águilas mafic-ultramafic body drill core samples. Inc: inclusion.

Sample	99.5-5	99.5-11	99.5-1	146.6-1	98.2_36	98.2-1	42-8	42-10	41.2-2	98-1
Spinel type	Core I (Subzone IA)	Core I (Subzone IB)	Rim IA	Core I inc Opx	Core II	Rim IIA	Core II	Rim IIB	Core II inc Opx	Core II incl Ol
SiO_2	0.15	0.13	0.21	0.17	b.d	0.35	b.d	0.01	0.32	0.30
TiO_2	0.02	0.18	0.20	0.10	0.26	0.79	0.05	0.56	0.27	0.28
Al_2O_3	46.59	39.60	27.83	42.21	28.37	9.49	30.77	10.49	29.59	27.89
Cr_2O_3	16.15	22.22	29.52	16.50	30.44	24.21	28.59	39.78	26.91	29.11
Fe_2O_3	5.12	4.81	7.98	7.93	7.30	31.99	7.07	14.87	8.49	8.53
FeO	19.36	22.07	27.72	23.92	28.23	30.90	24.25	28.65	27.82	26.67
MnO	0.25	0.22	0.37	0.26	0.25	0.25	0.20	0.57	0.22	0.26
MgO	12.88	10.56	6.07	10.15	5.44	1.94	7.38	2.42	5.80	5.94
CaO	0.01	0.01	0.04	0.06	b. d.	0.04	0.04	0.03	0.06	0.01
ZnO	1.32	0.98	0.56	0.56	b.d	b.d	0.74	0.32	1.05	1.27
Total	101.85	100.78	100.50	101.86	100.28	99.95	99.09	97.70	100.53	100.26
Structural formula based on 3 cations and 8 charges										
Si			0.01			0.01			0.01	0.01
Ti					0.01	0.02		0.02	0.01	0.01
Al	1.52	1.35	1.03	1.42	1.05	0.40	1.13	0.44	1.09	1.04
Cr	0.35	0.51	0.73	0.37	0.76	0.68	0.70	1.13	0.66	0.73
Fe^{3+}	0.11	0.10	0.19	0.17	0.18	0.86	0.17	0.40	0.20	0.20
Fe^{2+}	0.45	0.54	0.73	0.57	0.76	0.92	0.63	0.86	0.73	0.70
Mn	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01
Mg	0.53	0.46	0.28	0.43	0.26	0.10	0.34	0.13	0.27	0.28
Ca		0.00	0.00	0.00						
Zn	0.03	0.02	0.01	0.01			0.02	0.01	0.02	0.03
Total	3.00	2.99	2.99	2.99	3.02	3.00	3.00	3.00	2.99	3.00
$Fe^{2+}/(Fe^{2+} + Mg)$	0.46	0.54	0.72	0.57	0.75	0.90	0.65	0.87	0.73	0.72
$Cr/(Cr + Al)$	0.19	0.27	0.42	0.21	0.42	0.63	0.38	0.72	0.38	0.41
$Fe^{3+}/(Fe^{3+} + Cr + Al)$	0.05	0.05	0.10	0.09	0.09	0.44	0.08	0.20	0.10	0.10
Chemical formula	$(Fe_{0.46}, Mg_{0.54})(Cr_{0.18}, Al_{0.77}, Fe^{3+}_{0.05})_2 O_4$	$(Fe_{0.54}, Mg_{0.46})(Cr_{0.26}, Al_{0.69}, Fe^{3+}_{0.05})_2 O_4$	$(Fe_{0.72}, Mg_{0.28}) (Cr_{0.37}, Al_{0.53}, Fe^{3+}_{0.1})_2 O_4$	$(Fe_{0.57}, Mg_{0.43})(Cr_{0.19}, Al_{0.72}, Fe^{3+}_{0.09})_2 O_4$	$(Fe_{0.75}, Mg_{0.25})(Cr_{0.38}, Al_{0.52}, Fe^{3+}_{0.1})_2 O_4$	$(Fe_{0.90}, Mg_{0.10})(Cr_{0.36}, Al_{0.20}, Fe^{3+}_{0.44})_2 O_4$	$(Fe_{0.65}, Mg_{0.35})(Cr_{0.7}, Al_{1.13}, Fe^{3+}_{0.17})_2 O_4$	$(Fe_{0.87}, Mg_{0.13})(Cr_{0.57}, Al_{0.22}, Fe^{3+}_{0.21})_2 O_4$	$(Fe_{0.73}, Mg_{0.27})(Cr_{0.34}, Al_{0.56}, Fe^{3+}_{0.1})_2 O_4$	$(Fe_{0.71}, Mg_{0.29})(Cr_{0.37}, Al_{0.53}, Fe^{3+}_{0.1})_2 O_4$
End Members										
$MgAl_2O_4$	0.42	0.32	0.15	0.32	0.14	0.02	0.20	0.03	0.15	0.15
$FeAl_2O_4$	0.35	0.36	0.37	0.40	0.39	0.18	0.37	0.19	0.40	0.38
$MnAl_2O_4$	0.01		0.01	0.01						
$MgFe_2O_4$	0.03	0.03	0.03	0.04	0.02	0.05	0.03	0.03	0.03	0.03
$FeFe_2O_4$	0.03	0.03	0.08	0.05	0.07	0.39	0.05	0.17	0.08	0.08
$MnFe_2O_4$										
$MgCr_2O_4$	0.10	0.12	0.11	0.08	0.10	0.04	0.12	0.08	0.09	0.11
$FeCr_2O_4$	0.08	0.14	0.26	0.11	0.28	0.31	0.23	0.48	0.24	0.26
$MnCr_2O_4$								0.01		
Fe_2TiO_4			0.01		0.01	0.02		0.02	0.01	0.01
Zn-Spinel	0.03	0.02	0.01	0.01	0.00		0.02	0.01	0.02	0.03

tween 45° and 54°. Except drill core 4-2 and 5-2, which were drilled directly on the mafic-ultramafic body, all other drills cut through metamorphic rocks or recent sediments before intercepting the mafic-ultramafic rocks at different depths.

Analytical methods

A total of 71 polished thin sections of ultramafic rocks from 6 Las Águilas drill cores (drill cores 4-2, 5-2, 5-4, 5-5, 6-4 and 7-4) have been investigated by transmitted and reflected light microscopy and scanning electron microscopy (SEM).

A total of 310 spinel analyses and representative analyses of the associated silicate phases were obtained at the Institute of Mineralogy and Petrology of the University of Graz, with a JEOL 6310 SEM equipped with a LINK ISIS energy dispersive system and a MICROSPEC wavelength dispersive system. Standard analytical conditions were set to an accelerating voltage of 15 kV and 5 nA sample current. The matrix corrections were made using the ZAF procedure. The following mineral standards were used: Si, K, adularia; Al, andalusite; Fe,

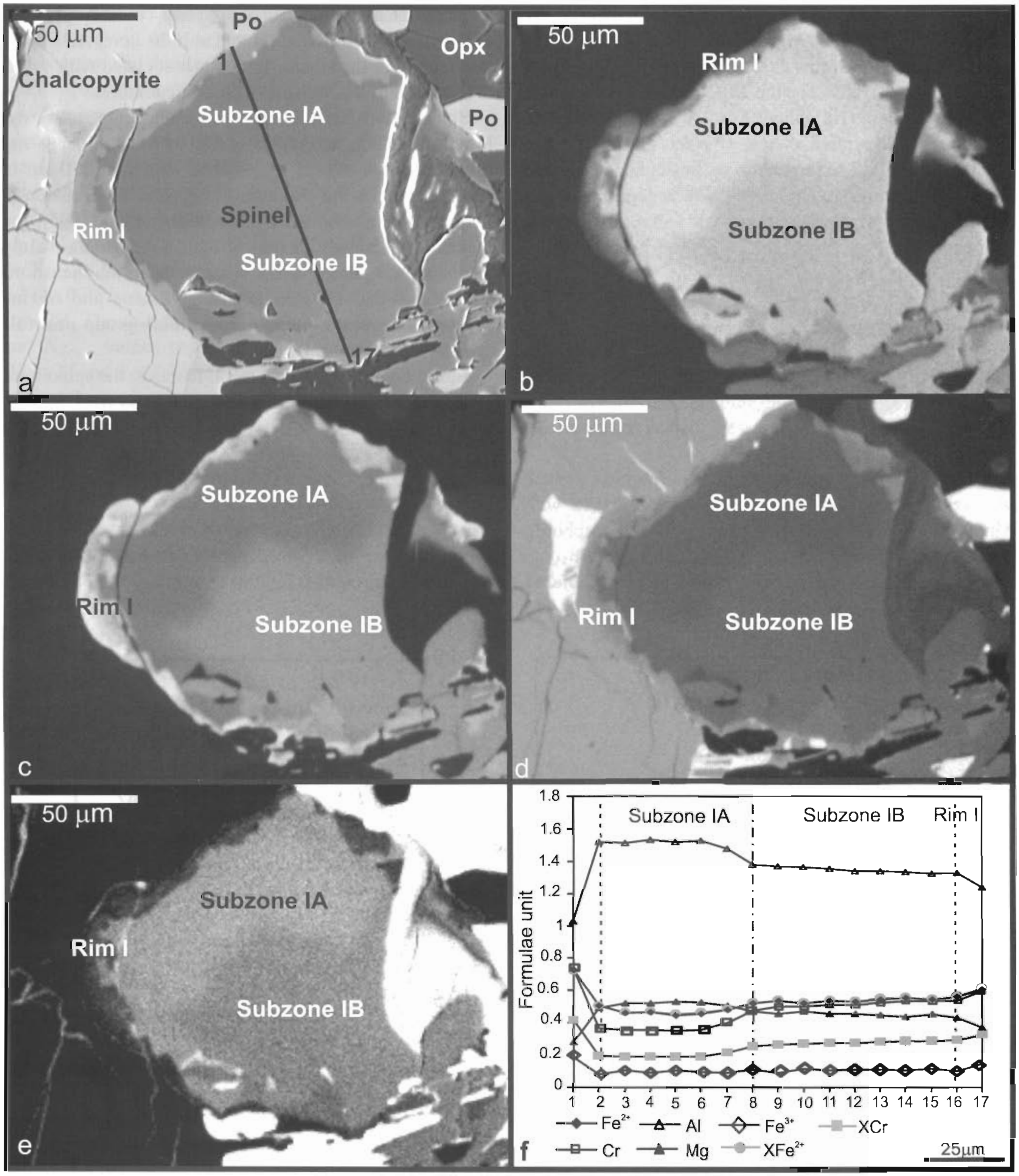

Fig. 2. Chemical zoning of spinel type I (orthopyroxenites sample number 99.5), showing core subzones and rim. **a)** Back scattered electron image. X-ray mappings: **b)** Al, **c)** Cr, **d)** Fe^{2+}, **e)** Mg., **f)** Chemical profile across spinel crystal from **a)**.

Mg, garnet or olivine; Ca, Ti, titanite; Mn, tephroite; Zn, gahnite; Cr synthetic Mg-chromite; Na, jadeite. The practical detection limits in these routine analyses vary from 0.05 to 0.1 wt% for the MICROSPEC wavelength dispersive system (Na), and 0.1 to 0.5 wt% for the LINK ISIS energy dispersive system (for the rest of the elements analyzed). The ferric iron was calculated based on the assumption of stoichiometry, which certainly imposes a limitation in interpreting small variations in ferric iron content.

Petrography and mineral chemistry

In the Las Águilas samples spinel occurs as disseminated crystals, present mainly in dunites, harzburgites and orthopyroxenites. The host rocks display different degrees of serpentinization.

The main constituents of the ultramafic rocks are olivine (Fo_{78-84} with up to 0.21 wt% NiO and 0.48 wt% MnO), orthopyroxene (En_{61-84}; Fs_{16-37}; Wo_{0-2}), subordinate interstitial clinopyroxene (En_{46-48}; Fs_{4-9}; Wo_{45-48}) and in few samples anorthite (An_{99-100}) (see Table 1). Orthopyroxene associated with spinel commonly shows clinopyroxene exsolution lamellae in its core. An important feature of the silicate minerals associated with spinel is that none of them displays coronitic textures.

Spinel grains are subhedral to anhedral, opaque to red brown in colour, and typically 440 to 1000 µm large and often fractured except for crystals less than 220 µm in size. Except for the platinum group mineral inclusion in a spinel rim mentioned by Mogessie et al. (1998), the studied minerals are devoid of inclusions. Being mainly an interstitial phase, spinel sometimes forms inclusions (maximum size 130 µm) in orthopyroxene and olivine crystals. In dunites, veins of serpentine group minerals crosscut spinel crystals.

Based on optical and chemical features, the spinels are classified into two groups: spinel type I and II.

Spinel Type I

Type I spinel is a greenish-brown chromian-spinel (Stevens 1944), with a zoned core (subzones IA and IB) sometimes surrounded by thin chromian-spinel to alumi-

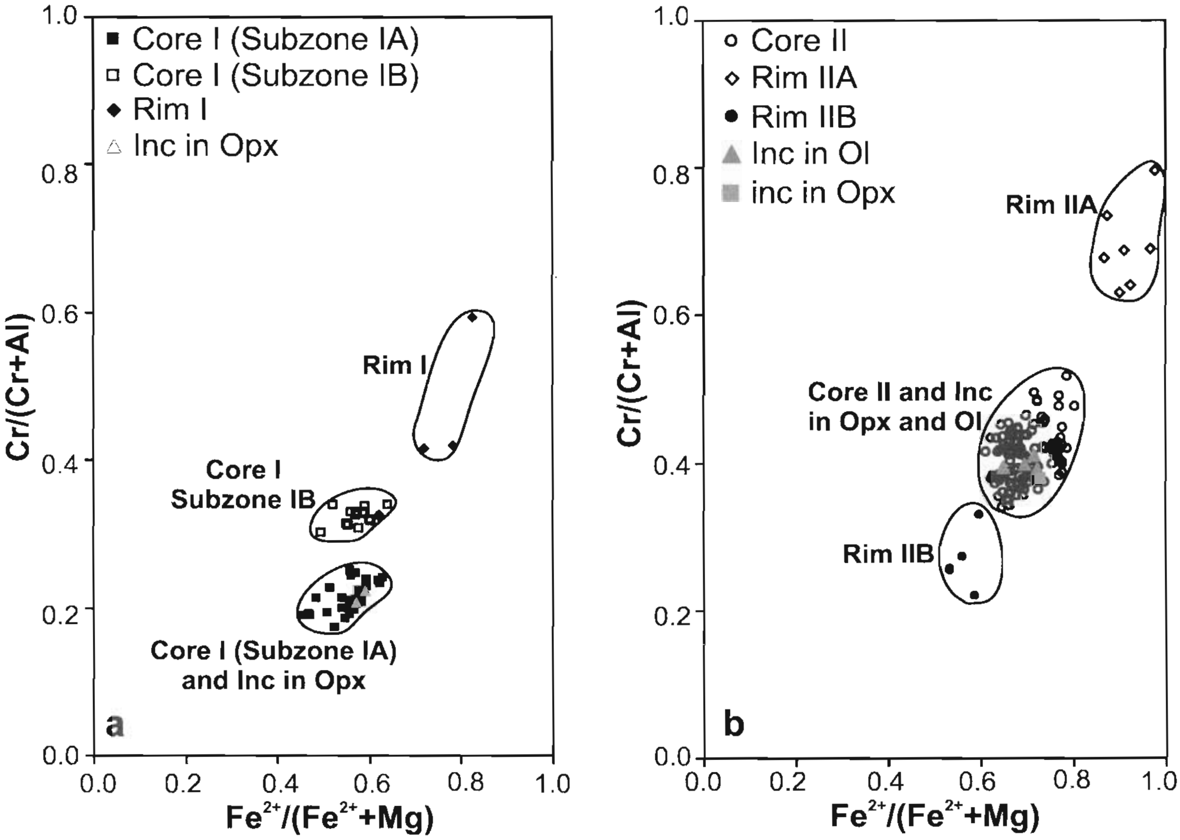

Fig. 3. Relation between $Fe^{2+}/(Fe^{2+} + Mg)$ and $Cr/(Cr + Al)$ in spinel from the La Aguilas Complex, **a)** Core type I (subzones A and B) and rim I, and **b)** Core type II and rims IIA and IIB.

nian-chromite rims (Table 2, Figs. 2 a–f and 4 a). They occur mainly in orthopyroxenites and less frequently in harzburgites and dunites.

Element mapping and chemical profiles measured across the cores of type I spinel reveals a particular non-concentric zonation (Figs. 2, 3 a and 4 a). The core subzones IA and IB are characterized by an inverse relation between Al and Cr and Mg–Fe^{2+} (Fig. 2 f).

From Fig. 3 a it is clear that although the subzones IA and IB have similar values of $Fe^{2+}/(Mg + Fe^{2+})$ $(= X_{Fe2+})$, the Cr/(Cr + Al) $(= X_{Cr})$ ratio varies from 0.17 to 0.25 in subzone IA and from 0.28 to 0.34 in subzone IB. The thin rims of type I spinels have higher X_{Cr} and X_{Fe2+} values than the central parts of the grains (Figs. 2 f and 3 a; Table 2).

Type I spinel crystals occurring as inclusions in orthopyroxene show homogeneous cores and have the same chemical composition as subzone IA spinel (Fig. 2 a–f and Table 2). Rims are absent.

A positive correlation between X_{Fe2+} vs. X_{Cr} is evident (Fig. 3 a) for spinel cores type I belonging to both disseminated and included crystals.

Spinel Type II

Type II spinel is a red brown to dark chromian-spinel that occurs mainly in dunites and harzburgites. They are characterized by the presence of homogeneous cores and two types of rims, IIA and IIB. Type II spinel cores generally have higher X_{Cr} and X_{Fe2+} values than type I spinel cores (Fig. 3 a–b). Spinel crystals included in olivine do not show any kind of rim and their composition is similar to those located interstitially between silicate grains (Fig. 3 b). The cores of both types of spinel (disseminated and included) show a clear positive correlation between X_{Fe2+} vs. X_{Cr} (Fig. 3 b).

Rims IIA, as described by Ferracutti et al. (2004) and Ferracutti (2005), are well-developed and up to 30 μm wide. Their composition covers the aluminian-chromite to chromian-magnetite interval (Fig. 4 b). Compared with the core composition, rims IIA are enriched in X_{Fe2+} and X_{Cr} (Fig. 3 b). Their Fe^{3+} contents is also significantly higher (Figs. 5 b and 4 b, Table 2).

Rims IIB are chromian-spinels (Fig. 4 b). They have the lowest values of X_{Fe2+} and X_{Cr} compared to the cores II and rims IIA (Fig. 3 b and Table 2). In these rims Al and Mg increase while Fe^{2+}, Cr and Fe^{3+} decrease (Fig. 5 c). This type of rim was recognized in spinel crystals present in few dunite samples that typically carry small (< 0.5 mm) recrystallized orthopyroxene grains located in bands indicating strong deformation.

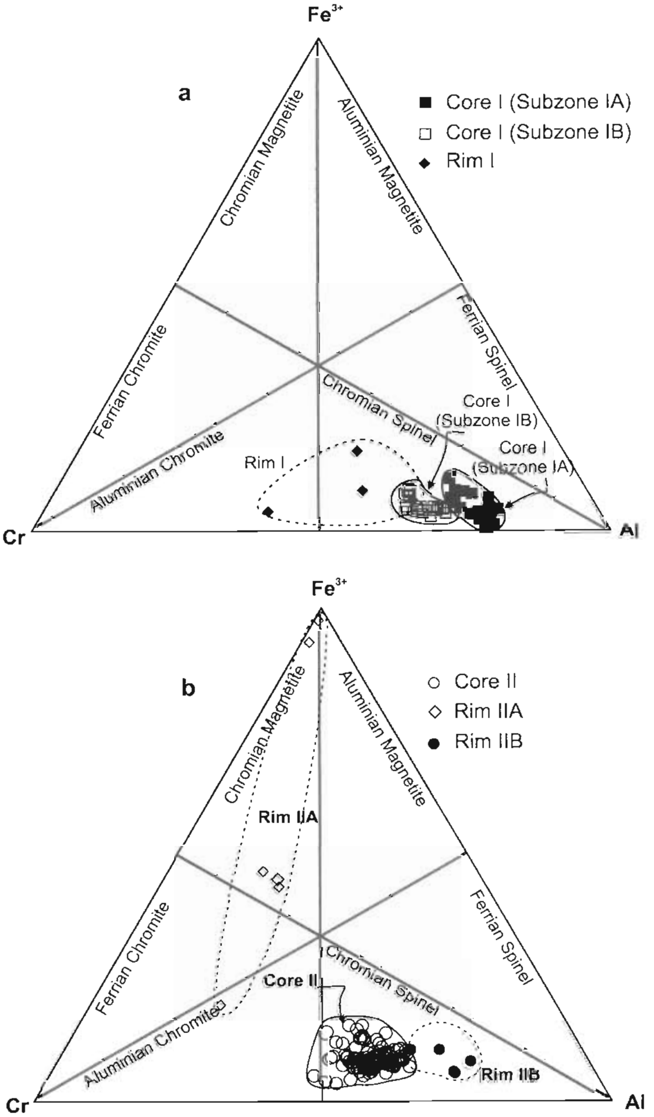

Fig. 4. Core and rim composition of spinel from the Las Aguilas complex (classification after Stevens 1944). **a)** Spinel type I and **b)** spinel type II.

Geothermometry

Temperature estimations for the Las Águilas mafic-ultramafic rocks were made considering the main mineral parageneses associated with each type of spinel. All calculations were performed using single point analyses of mineral cores. The spinel rim temperatures were not calculated due to the presence of serpentine group minerals that enclose the spinel grains and do not allow the direct contact with orthopyroxene and olivine.

Based on the orthopyroxene geothermometers (Brey & Köhler 1990 and Witt-Eickschen & Seck 1991) it was possible to estimate two ranges of temperatures for

Table 3a. Results of geothermometry. Pressure values of 7 kbar are based on HAUZENBERGER (1997), see Table 3b–c. Opx: orthopyroxene, Spl: spinel, Ol: olivine.

Mineral pair	Geothermometer	T °C Min.	T °C Max.	T °C average	N° determinations
Opx in sample with type II Spl	BREY & KÖHLER 1990	624	767	**701**	14
Opx in sample with type II Spl	WITT-EICKSCHEN & SECK 1991	637	770	**711**	15
Opx in sample with type IA Spl	BREY & KÖHLER 1990	652	782	**726**	15
Opx in sample with type IA Spl	WITT-EICKSCHEN & SECK 1991	650	826	**725**	13
Opx in sample with type IB Spl	BREY & KÖHLER 1990	608	803	**707**	8
Opx in sample with type IB Spl	WITT-EICKSCHEN & SECK 1991	652	782	**710**	8
Ol-Type II Spl	FABRIES 1979	568	732	**652**	29
Ol-Type II Spl	ROEDER et al. 1979	582	692	**570**	26
Ol-Type II Spl	SACK & GHIORSO 1991	648	787	**713**	29
Ol-Type II Spl	BALLHAUS et al. 1991	501	649	**584**	29

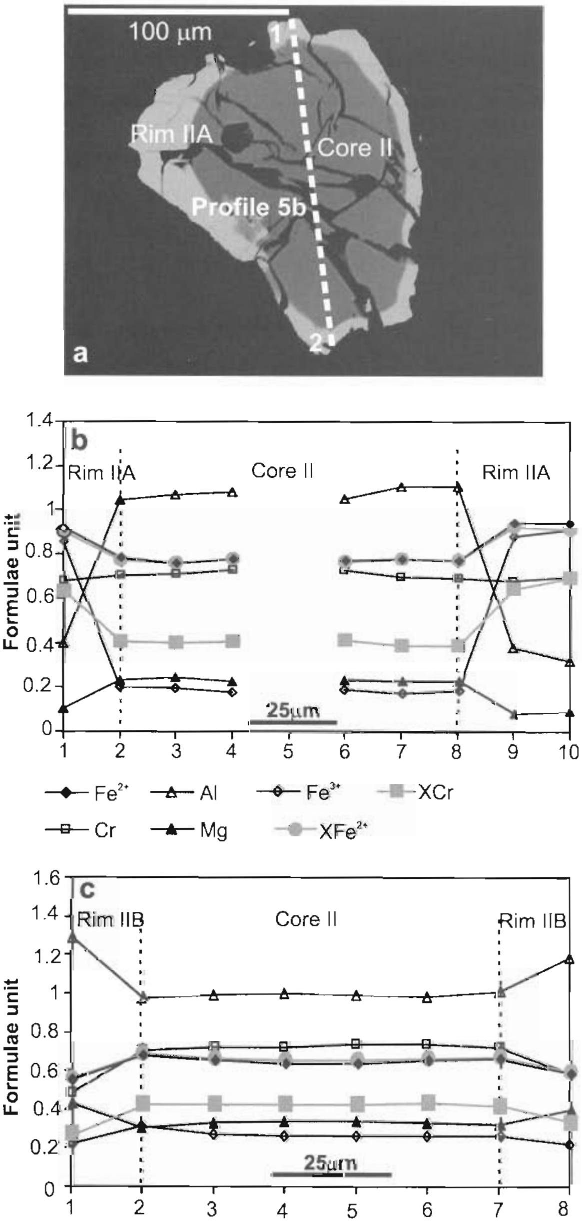

Fig. 5. a) Back scattered electron image of spinel type IIA from a dunite (sample 98.2), **b)** chemical profile of spinel type IIA from a) and, **c)** chemical profile of spinel type IIB.

each core subzone (A and B) of type I spinel. The average temperature in orthopyroxenites associated with type IA spinel is ~725 °C, and in orthopyroxenites associated with type IB spinel the calculated temperature is between 707 and 710 °C (Fig. 6b and Tables 3a–b).

Due to the fact that spinel type II is in association with both olivine and orthopyroxene, calculations were performed with the orthopyroxene (op. cit.) and the olivine-spinel geothermometers (FABRIÈS 1979, ROEDER et al. 1979, SACK & GHIORSO 1991 and BALLHAUS et al. 1991). The temperatures obtained with the orthopyroxene geothermometer are in the range 711–713 °C and with the olivine-spinel geothermometer in the range 570 to 713 °C (Fig. 6b and Tables 3a, b, c).

Discussion

Spinel zonation and chemistry

The spinel core compositions of Las Águilas are the result of a systematic compositional variation during their crystallisation from the parent magma, reflecting changes in the availability of Al and Cr (Fig. 4a–b). Such a process explains the major chemical variation of spinel cores, with a positive correlation between X_{Fe2+} and X_{Cr} (Fig. 3a–b).

As reported by DONALDSON & GROVES (1985) the compositions of chromites and spinels can be modified by metamorphism. At Las Aguilas this resulted in development of rims with distinct compositions.

Mylonitization was responsible for the formation of rims type IIB under upper amphibolite facies conditions. As pointed out in the geology section, this part of the Sierras Pampeanas consists of three metamorphic blocks (east, central and west). The Las Aguilas mafic-ultramafic intrusion is located in the central block. The three blocks are clearly separated by ductile shear zones recognised in the field to be 5 km wide, lower to middle am-

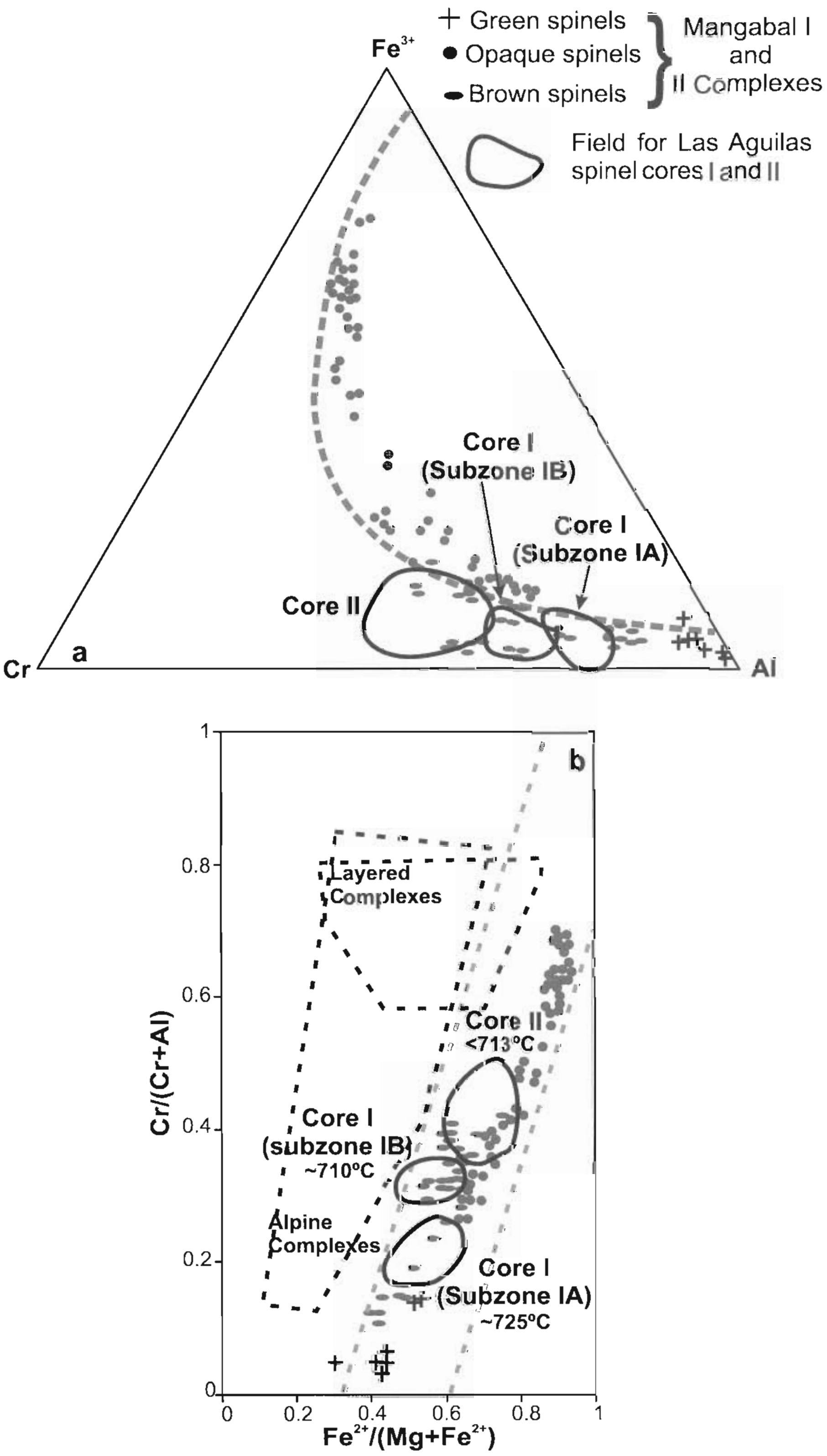

Fig. 6. Comparison of spinel core composition from the Las Aguilas complex with analyses from Mangabal I and II (Candia & Gaspar 1997). Fig. **a)** shows the diagram of trivalent ions. The dashed line indicates the solvus of high-grade metamorphic chromites according to Candia and Gaspar (1997). Fig. **b)** shows $Fe^{2+}/(Fe^{2+} + Mg)$ vs. $Cr/(Cr + Al)$ diagram for the same samples. The Cr-Al exchange is mainly due to fractionation of the magma and considering the Fe^{2+}–Mg exchange, the spinel becomes appreciably richer in Fe^{2+} as cooling proceeds, provided spinel is a minor constituent according to Irvine (1967) (explanation in the text).

Table 3 b. Orthopyroxene composition (cations per formula unit) in samples with spinel type I and II, from the Las Aguilas drill core samples, and results of geothermometric calculations according to Brey & Köhler 1991, Witt-Eickschen & Seck 1991.

Mineral	Si	Al	Cr	Ti	Ni	Fe^{2+}	Fe^{3+}	Mg	Mn	Ca	Na	T (°C) ± 26 °C Brey & Köhler (1991) at 7 kbar	T (°C) Witt-Eickschen & Seck (1991)
orthopyroxene in sample with type II spinel	1.989	0.004		0.001		0.322	0.015	1.660	0.008	0.005		652	637
	1.987	0.010	0.001	0.002		0.319	0.012	1.657	0.008	0.005	0.001	652	651
	1.931	0.091	0.006	0.003	0.001	0.333	0.035	1.568	0.011	0.021		–	770
	1.948	0.074	0.005	0.002	0.002	0.347	0.024	1.581	0.010	0.008	0.001	718	755
	1.942	0.077	0.005	0.001	0.001	0.333	0.031	1.593	0.009	0.008		718	749
	1.951	0.069	0.006	0.002		0.336	0.020	1.601	0.009	0.006		677	765
	1.932	0.080	0.005	0.003		0.324	0.045	1.592	0.009	0.010		752	734
	1.937	0.082	0.005	0.003		0.329	0.035	1.592	0.009	0.008	0.001	718	749
	1.933	0.081	0.005	0.003		0.321	0.044	1.596	0.008	0.011		767	738
	1.940	0.077	0.006	0.002		0.334	0.032	1.590	0.009	0.010		752	759
	1.961	0.054	0.004	0.001		0.315	0.019	1.626	0.010	0.009	0.001	735	726
	1.947	0.038	0.003	0.001	0.001	0.269	0.062	1.663	0.009	0.008		718	680
	1.981	0.015	0.001	0.001	0.000	0.293	0.020	1.677	0.008	0.004		624	651
	1.982	0.020	0.001	0.001	0.001	0.305	0.013	1.663	0.009	0.006		677	655
	1.973	0.021	0.001	0.001	0.001	0.284	0.031	1.676	0.008	0.005		652	651
												701	711
Mineral	Si	Al	Cr	Ti	Ni	Fe^{2+}	Fe^{3+}	Mg	Mn	Ca	Na	T (°C) ± 26 °C Brey & Köhler (1991) at 7 kbar	T (°C) Witt-Eickschen & Seck (1991)
orthopyroxene in sample with type IA spinel	1.900	0.085	0.007			0.270	0.108	1.611	0.008	0.011		773	735
	1.938	0.077				0.346	0.049	1.576	0.008	0.008		710	666
	1.959	0.051	0.002	0.001	0.001	0.290	0.029	1.655	0.010	0.005		652	680
	1.967	0.037	0.001	0.001		0.292	0.026	1.661	0.009	0.006	0.001	677	659
	1.909	0.087	0.006			0.293	0.091	1.586	0.015	0.010	0.002	758	730
	1.996	0.058	0.005			0.407	0.000	1.516	0.009	0.006		677	826
	1.923	0.094	0.000			0.339	0.062	1.560	0.012	0.009	0.002	729	671
	1.929	0.092	0.004			0.340	0.046	1.567	0.012	0.010		754	745
	1.852	0.156	0.033	0.002	0.001	0.309	0.103	1.527	0.010	0.010		752	–
	1.933	0.076	0.007	0.002		0.298	0.050	1.617	0.009	0.007	0.002	696	754
	1.967	0.021	0.001		0.002	0.289	0.047	1.659	0.009	0.002	0.003	–	650
	1.893	0.068	0.000			0.230	0.145	1.648	0.009	0.006		665	–
	1.918	0.111	0.007	0.001	0.001	0.344	0.043	1.554	0.010	0.011	0.001	767	799
	1.852	0.156	0.033	0.002	0.001	0.309	0.103	1.527	0.010	0.010		752	–
	1.938	0.080	0.005	0.003	0.000	0.288	0.034	1.635	0.009	0.010		752	747
	1.940	0.076	0.006	0.001	0.001	0.286	0.037	1.636	0.007	0.012		782	757
												726	725
Mineral	Si	Al	Cr	Ti	Ni	Fe^{2+}	Fe^{3+}	Mg	Mn	Ca	Na	T (°C) ± 26 °C Brey & Köhler (1991) at 7 kbar	T (°C) Witt-Eickschen & Seck (1991)
orthopyroxene in sample with type IB spinel	1.951	0.056	0.008	0.002		0.326		1.655	0.008	0.007		698	767
	1.953	0.051	0.003			0.301	0.042	1.631	0.008	0.008	0.001	721	692
	1.959	0.043	0.002	0.002	0.002	0.302	0.035	1.642	0.008	0.006	0.001	665	666
	1.953	0.020	0.003			0.258	0.075	1.677	0.008	0.004	0.002	608	674
	1.905	0.073	0.005	0.002		0.192	0.111	1.690	0.011	0.008	0.002	716	709
	1.963	0.044	0.000			0.308	0.029	1.649	0.000	0.006		683	652
	1.912	0.066	0.008			0.241	0.101	1.653	0.008	0.011		760	738
	1.958	0.063	0.007			0.339		1.617	0.009	0.014		803	782
												707	710

Table 3 c. Composition of olivine-spinel pairs (in wt%) from the Las Aguilas drill core samples and results of geothermometric calculations according to Sack & Ghiorso 1991, Fabries 1979, Roeder et al. 1979 and Ballhaus et al. 1991. V_2O_3 in spinel is below detection limit (b. d).

Mineral	FeO	MgO	NiO	Mineral	TiO_2	Al_2O_3	Cr_2O_3	Fe_2O_3	FeO	MgO	MnO	NiO	T(°C) Sack & Ghiorso (1991)	T(°C) Fabries (1979)	T(°C) Roeder et al. (1979)	T(°C) Ballhaus et al. (1991) at 7 kbar
Olivine	19.813	40.797	b.d	Type II spinel	0.252	29.428	29.518	7.750	27.019	6.347	0.235	b.d	745	673	572	593
	19.567	41.871	b.d		0.354	30.559	29.302	6.956	26.101	7.193	0.292	b.d	761	694	608	616
	16.796	42.762	b.d		0.071	32.326	23.596	5.840	21.763	8.167	0.317	b.d	718	678	623	612
	17.198	42.620	b.d		0.098	29.905	23.579	7.476	23.410	7.772	0.281	b.d	758	684	601	615
	19.888	42.548	b.d		0.211	34.679	25.003	7.819	26.370	7.576	0.197	b.d	730	663	590	589
	19.996	42.716	b.d		0.214	33.698	27.005	8.286	26.826	7.923	0.189	b.d	764	696	615	617
	19.527	42.024	b.d		0.288	32.457	26.563	8.105	25.112	8.129	0.285	b.d	**787**	**732**	654	**649**
	19.450	41.723	b.d		0.234	32.726	25.339	9.001	26.092	7.806	0.344	b.d	774	704	616	624
	17.326	44.339	b.d		0.179	30.447	25.252	8.878	24.577	7.233	0.318	b.d	715	655	553	591
	17.150	44.645	b.d		0.037	33.697	21.351	9.044	24.348	7.610	0.385	b.d	687	621	537	566
	17.318	43.965	b.d		0.233	30.740	24.779	9.406	25.305	7.236	0.201	b.d	715	655	553	592
	16.623	43.332	b.d		0.097	41.208	15.436	6.220	20.090	10.741	0.181	b.d	686	686	**692**	625
	16.936	42.775	b.d		0.050	32.790	21.736	7.651	23.020	8.031	0.211	b.d	719	662	592	598
	16.855	43.264	b.d		0.084	40.958	16.072	6.457	20.519	10.662	0.002	b.d	693	692	692	629
	16.929	42.628	b.d		0.165	32.593	22.327	7.420	22.892	8.168	0.219	b.d	727	674	604	609
	16.582	42.134	b.d		0.133	34.684	21.127	7.990	22.351	8.888	0.189	b.d	728	693	632	626
	18.635	42.944	0.165		0.257	28.500	30.033	6.808	28.354	5.092	0.262	0.059	653	571	–	506
	16.907	42.364	0.146		0.279	28.192	30.445	7.540	27.192	6.049	0.272	0.097	689	613	501	550
	18.766	42.823	0.143		0.203	28.954	30.725	6.244	28.534	5.092	0.218	0.045	**648**	**568**	–	**501**
	18.314	42.919	0.195		0.327	28.151	30.067	7.593	28.344	5.213	0.261	0.076	661	581	–	517
	16.154	31.480	0.140		0.270	27.886	30.931	6.849	28.261	5.218	0.230	0.052	709	630	523	549
	18.413	42.939	0.149		0.244	28.234	30.767	7.002	27.693	5.681	0.222	0.038	686	608	**499**	540
	17.024	43.881	0.057		0.210	27.287	32.543	5.958	26.593	6.072	0.270	0.025	688	618	511	552
	16.912	43.916	0.139		0.165	27.843	32.395	6.026	26.212	6.345	0.280	0.039	693	627	523	561
	16.516	43.891	0.145		0.117	40.974	17.607	8.161	23.181	9.788	0.235	0.181	670	632	598	581
	18.155	42.957	0.205		0.182	32.256	25.904	7.402	25.251	7.423	0.220	0.051	721	655	574	588
	18.000	42.583	0.118		0.192	31.340	27.335	7.348	25.439	7.201	0.230	0.097	722	658	571	589
	17.814	42.856	0.162		0.175	33.428	24.205	8.004	25.901	7.188	0.263	0.092	693	620	538	559
	18.115	42.702	0.127		0.405	24.205	33.958	7.484	26.549	5.878	0.297	0.074	745	675	549	601
													713	**652**	**582**	**584**

phibolite facies mylonite zones. A mylonite zone at upper amphibolite facies is present within the central block (Hauzenberger et al. 2001). This mylonite zone is limited to the area of mafic-ultramafic intrusions and overprints the metamorphic assemblages as well as the structural elements of the central block.

Rims type IIA and I were formed during the serpentinization process developed due to a lower-temperature final overprint. According to Delpino et al. (2005), this event produced brittle fracturing and localized retrogression on mafic-ultramafic minerals and ores by means of a water-rich fluid phase giving rise to the association serpentine + magnetite ± actinolite. Mogessie et al. (1998, 2000) recognized platinum group minerals located at the zoned spinel rims (IIA) in contact with serpentine which has formed from an altered olivine. This texture has also been interpreted as an indication of platinum group element remobilization by serpentinization processes.

Geothermometry

The range of temperatures calculated with orthopyroxene crystals from orthopyroxenites carrying type I (subzones A and B) spinel cores are higher than those corresponding to spinel-olivine pairs in dunites (type II spinel) and orthopyroxenes from harzburgites (type II spinels).

Delpino et al. (2005) documented for the mafic and adjacent basement mylonitization temperatures ranging from 668 to 764 °C, and considered the mylonitization to have developed on a pre-existing temperature gradient caused by the intrusion of mafic-ultramafic bodies. We suggest that it is during this event that type IIB spinel rims developed (Figs. 5 c and 4 b). In rocks of upper amphibolite facies (Evans & Frost 1975), spinel rim compositions are characterized by enrichment in Al and Mg and decreasing contents of Fe^{2+}, Fe^{3+} and also Cr. This is the behaviour shown by spinel rims type IIB, which

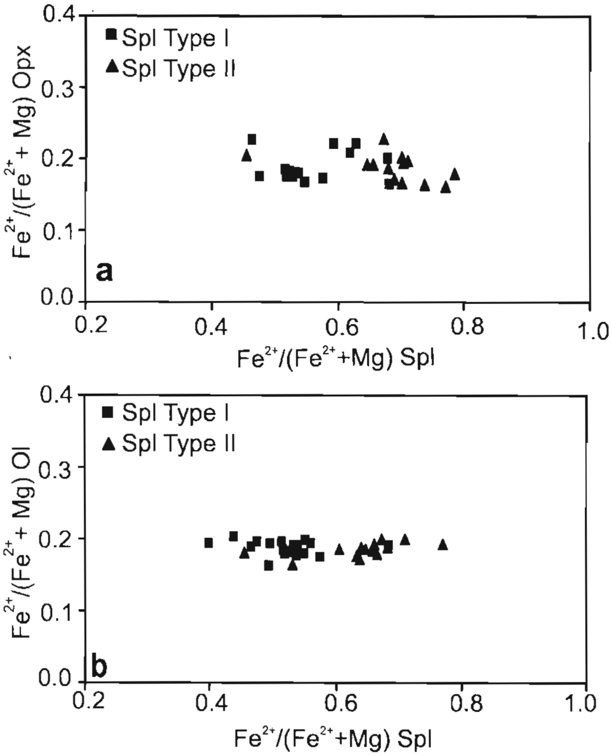

Fig. 7. Relation between $Fe^{2+}/(Fe^{2+} + Mg)$ in spinel and in orthopyroxene (**a**) and in spinel and olivine (**b**). Spinel is from intercumulate textures and from inclusions in both olivine and orthopyroxene.

occur in rocks where orthopyroxene crystallized in response to amphibolite facies conditions.

HAUZENBERGER (1997) calculated the following temperature ranges for the Las Águilas spinel-mafic mineral pairs: 610–780 °C (olivine-spinel), 800–1100 °C (orthopyroxene-olivine-spinel) and 600–1000 °C (orthopyroxene-clinopyroxene-olivine-spinel). New geothermometric determinations made by HAUZENBERGER et al. (2001) based on the olivine-spinel geothermometer of BALLHAUS et al. (1991 a) gave a temperature of 745 °C for the spinel cores and the rims yielded temperatures in the range 660–710 °C. Our geothermometric determinations (Tables 3 a–c) using the same geothermometers, gave lower temperatures than those documented by HAUZENBERGER (1997) and HAUZENBERGER et al. (2001). Our results show that each of the recognized types of spinel cores is characterized by a distinct temperature value.

Spinel composition and tectonic position

When comparing the spinel composition from Las Águilas with those from the Mangabal I and II mafic-ultramafic bodies in Brazil (CANDIA & GASPAR 1997), it is possible to establish that the Las Águilas spinels are similar to the "brown spinels" described by the above mentioned authors (Fig. 6 a–b). The chemical composition of these interstitial "brown spinels" (high Mg–Al) was interpreted as resulting from their reaction with the intercumulus liquid during the postcumulus stage. These spinels, as well as those of the Las Águilas complex, display a trend parallel to the solvus (Fig. 6 a).

It is also important to note that the spinels from Las Águilas were not affected by corona-forming reactions of the type:

forsterite + plagioclase + H_2O = clinopyroxene + amphibole + spinel (CANDIA et al. 1991)

which produce aluminous green spinel as a result of metamorphic subsolidus processes (CANDIA & GASPAR 1997). This feature and the fact that there is no Fe^{2+}-Mg exchange between the silicates (orthopyroxene and olivine) and spinels after the crystallization (Fig. 7 a–b), suggests that the spinel core compositions in Las Águilas were not affected by metamorphic processes and thus can be used to document the possible tectonic position of the Las Aguilas intrusive complex.

Spinel cores type I (subzones A and B) and type II from Las Águilas are enriched in Al and depleted in Mg (Figs. 2 f and 5 b–c). Concentration of the major element oxides in the spinel depend on: a) P–T conditions expressed by the mineral association, and b) bulk composition of the parental magma composition and its evolution. At Las Aguilas spinel Al-enrichment is in agreement with the scarcity of plagioclase in the studied host rocks (ROEDER 1994). On the other hand, Mg depletion is indicative of the spinel crystallization as a minor phase together with olivine and orthopyroxene (enstatite), giving rise to Fe^{2+}-enriched spinels.

Based on the relationship of X_{Fe2+} ratios in spinel and orthopyroxene-olivine pairs from the Bushveld Complex, IRVINE (1967) showed that when spinel is a minor constituent of the silicate host rock it becomes appreciably richer in ferrous iron as cooling proceeds while the silicate minerals (orthopyroxene or olivine) remain relatively constant in composition.

As is indicated in Fig. 7 a, b the Las Aguilas spinels, which are a minor constituent of the host rocks, show a variable X_{Fe2+} ranging from 0.40 to 0.80, whereas the silicate phases such as olivine and orthopyroxene display a constant X_{Fe2+} indicating the role played by parental magma composition and its evolution (IRVINE 1967).

Conclusions

Two groups of spinels were identified in the Las Águilas mafic-ultramafic rocks, namely type I and type II, each of them with different cores and rims. Type I spinel dominantly occur in orthopyroxene-rich rocks while type II spinels are mainly associated with dunites.

Spinel cores type I and their rims, as well as cores type II and rims type IIB are chromian-spinel, while the composition of type IIA rims cover the aluminian-chromite to chromian-magnetite field.

Type I – subzone A spinel formed at ~725 °C, type I – subzone B spinel at ~710 °C and finally, type II spinel below ~710 °C. These temperature values indicate that type I (subzone A and B) spinel occurring in orthopyroxenites crystallized earlier than type II spinel associated with dunites and harzburgites. The mafic-ultramafic rocks were reequilibrated under upper amphibolite facies metamorphic conditions (590 to 650 °C) allowing development of type IIB spinel rims.

The composition of spinel cores is inherited from the magmatic stage and reflects the composition and evolution of the magma from which they crystallized. The spread of X_{Fe2+} values of spinel is a direct consequence of its crystallization as a minor constituent of a cooling rock. The cores with the highest X_{Fe2+} crystallized at the lowest temperatures as shown by geothermometric calculations.

The fact that spinel rims type I and type IIA occur in samples with significant serpentinization supports the role played by this process in the modification of spinel chemistry. This process also affected magmatic sulphides and partially remobilized and concentrated platinum group minerals in the Las Águilas mafic-ultramafic rocks. Based on the mineral paragenesis serpentine + magnetite ± actinolite the temperature of the serpentinization processes is assumed to be below 500 °C.

Regarding the type IIB rims, it is assumed that they are a product of chemical changes associated with the metamorphic mylonitization event (555 °C to 764 °C).

The magmatic origin of spinel cores type I (subzones A and B) and II is supported by the following facts:

1) In the system Al–Cr–Fe^{3+} (Fig. 6 a) they plot along a trend which does not intercept the solvus line typical of spinel formed under high-grade metamorphic conditions.

2) No exchange of Fe^{2+} and Mg appears to have occurred between spinel cores and both olivine and orthopyroxene during the subsolidus evolution of the rocks, as indicated by their X_{Fe2+} (Fig. 7 a, b).

3) Spinels are hosted by ultramafic rocks still retaining primary magmatic features and are not the result of corona-forming reactions which would lead to the formation of aluminous green spinel.

As shown in Fig. 6 a, b there seems to be a similarity between the Las Aguilas spinels and those from the Americano and Mangabal I and II complexes from Brazil, which are considered to be small layered complexes in orogenic belts affected by metamorphism and subsolidus reaction. This confirms that the mafic-ultramafic rocks of Las Aguilas belong to a layered complex, as suggested by Mogessie et al. (2000) based on geological and geophysical evidences, and using platinum group element concentrations of these rocks related to abundances in chondrites.

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Authors' addresses:

Gabriela Ferracutti, Universidad Nacional del Sur, Departamento de Geología, San Juan 670, B8000ICN Bahía Blanca, Argentina. E-mail: gferrac@uns.edu.ar

Aberra Mogessie, Institute of Earth Sciences, Department of Mineralogy and Petrology, University of Graz, Universitaetsplatz 2, A-8010 Graz, Austria. E-mail: aberra.mogessie@uni-graz.at

Ernesto Bjerg, CONICET–Universidad Nacional del Sur, Departamento de Geología, San Juan 670, B8000ICN Bahía Blanca, Argentina. E-mail: ebjerg@uns.edu.ar

Corresponding author: Aberra Mogessie, Institute of Earth Sciences, Department of Mineralogy and Petrology, University of Graz, Universitätsplatz 2, A-8010 Graz, Austria. E-mail: aberra.mogessie@uni-graz.at