Compositional zoning in Zn-chromites from the Cordillera Frontal Range, Argentina

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Abstract

Serpentinised ultramafic bodies containing zoned chromite grains occur in the Cordillera Frontal Range, western Argentina. Chromites show Zn-rich Al-chromite cores (4.04 wt.% ZnO) surrounded by ferritchromite rims (1.3 wt.% ZnO) and outer Cr-magnetite rims. In intensely altered chromites which are spatially related to sulphide mineralisation, the primary chromite cores have been replaced by Zn-rich ferritchromit (7 wt.% ZnO) and they are rimmed by Cr-magnetite. In the Al-chromites the mean [Cr/(Cr + Al)] ratio is 0.53 and the [Mg/(Mg + Fe)] ratio is 0.53; they plot in the field of Alpine-type intrusions. Ferritchromit has a mean [Cr/(Cr + Al)] ratio of 0.93 and [Mg/(Mg + Fe)] ratio of 0.4. In Cr-magnetites the mean [Cr/(Cr + Al) is 0.98 and the [Mg/(Mg + Fe)] ratio is 0. Ferritchromit is always surrounded by a Cr-magnetite rim and it was formed as a reaction product owing to the irreversible dissolution of primary chromite cores. The dissolution of these cores provided the essential components for ferritchromit growth. Zn was introduced into the chromite cores and ferritchromit rims during the formation of the latter. Step-scan profiles have shown that the Zn content in the cores increases from the centre to their outer border, where they show the highest Zn values. It is suggested that Zn was introduced by the fluid phase involved in the alteration process that affected the cores and lead to the formation of the zoned chromite grains. This alteration process was also responsible for the changes in [Cr/(Cr + Al)] and [Mg/(Mg + Fe)] ratios.

KEYWORDS: chromite, zoning, ferritchromit, Cordillera Frontal Range, Argentina.

Introduction

ZN-RICH spinels, either as a primary magmatic feature, or as the result of later alteration processes, have been reported from different geological settings (Thayer *et al.*, 1964; Weiser, 1967; Groves *et al.*, 1977, 1983; Moore, 1977; Bevan and Mallinson, 1980; Wylie *et al.*, 1987; Mogessie *et al.*, 1988).

Ferrochromites from Western Australia (Groves *et al.*, 1977, 1983) inherited their high Zn content from the magmatic stage. In Outokumpu, Finland (Weiser, 1967), Helgeland area, Norway (Moore, 1977), the Mashaba chromite mine, Zimbabwe (Bevan and Mallinson, 1980) and the Sykesville district, USA (Wylie *et al.*, 1987) metasomatism has taken place and was responsible for the high Zn content of the chromites.

Chromites from two localities in the Cordillera Frontal Range, western Argentina, exhibit high Zn concentrations. The chromites occur as disseminations within serpentinised ultramafic rocks in the Salamanca district and Las Tunas area. They exhibit optical and chemical zoning, which will be described and discussed in this paper.

Location and geologic setting

Numerous serpentinized ultramafic bodies outcrop in the Cordillera Frontal Range in Mendoza province, western Argentina. They are hosted by folded NE-striking mica and amphibole schists and marbles, with mineral parageneses typical of low-grade metamorphism (Bjerg *et al.*, in press), corresponding to the Complejo Metamórfico (Cambrian, 500 ± 50 m.y.).

The ultramafic rocks, with an uncertain age (between 500 and 300 m.y.), are considered to represent part of an Alpine-type belt (Villar, 1985) and occur over a distance of 60 km, as elongated NE-striking bodies. Granodiorite and granite plutons (300 m.y., Polansky, 1972) intrude both ultramafic and metamorphic rocks which are also crosscut by dioritic dykes. The Complejo Metamórfico has also been intruded by Upper Carboniferous—Lower Permian rhyolitic and rhyodacitic rocks and is covered by Pleistocene basalt lava flows (Polansky, 1972).

The zoned Zn-rich chromites described in this paper occur within serpentinised ultramafic rocks in the Salamanca district and Las Tunas area (Fig. 1). A sulphide mineralisation (31 500 tn of proven reserves) occurs in the Salamanca district as veins (up to 3 m thick) and veinlets in a NE-SW fault zone in the western margin of an serpentinized ultramafic body. Thin veinlets and disseminations of sulphides are a common feature in the serpentinites. The ore mineral association comprises pyrrhotite, chalcopyrite and sphalerite as major constituents, as well as Co-pentlandite, mackinawite, cubanite, molybdenite and gold (Brodtkorb, 1970, 1971; Bjerg, 1984).

In the Las Tunas area there is a ultramafic–mafic sequence, composed of serpentinised ultramafic rocks, overlain by altered gabbros and basalts. Disseminated sulphides (mainly pyrrhotite, chalcopyrite and pentlandite) are present in the serpentinised ultramafic rocks. Basalts show pillow structures and are covered by low grade metasedimentary rocks. Diabase dykes cut both the serpentinised and basaltic rocks. The whole sequence has been affected by intense folding, faulting and low-grade metamorphism, which has obscured the original nature of the rocks. The ultramafic–mafic sequence has tectonic contacts with the country rock. A sheeted dyke complex has not been identified.

An ophiolitic nature of the ultramafic–mafic rocks of these two regions has been suggested by Haller and Ramos (1984). Villar and Donnari (1989) proposed that the serpentinised ultramafic rocks in the Salamanca district represent the basal section of an ophiolite complex.

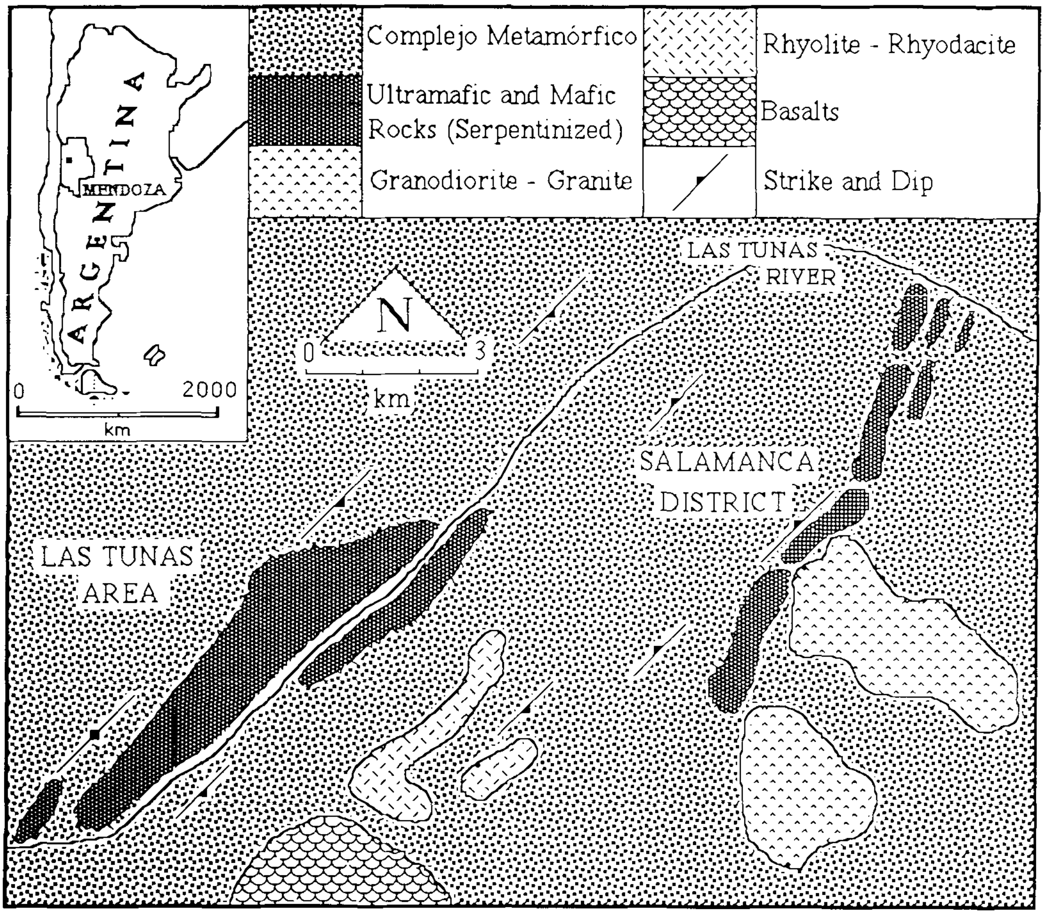

FIG. 1. Geological sketch map of the research area, indicating the location of Las Tunas area and Salamanca district.

Petrography

The serpentinites have non-pseudomorphic interpenetrating textures (Wicks and Whittaker, 1977; Wicks *et al.*, 1977), consisting of laths of gamma serpentine. XRD and microscopic studies have shown that antigorite dominates and replaces lizardite–chrysotile. The associated minerals are talc, calcite, dolomite, magnesite, amphiboles and chlorites.

The chromites are anhedrally shaped and range from 250 to 900 μm in grain size, rarely reaching 1.5 mm in diameter. The Cr-spinels are characterised by a marked zonation, defined by a core surrounded by a rim in the samples from the Salamanca district and by a core surrounded by an inner and outer rim in Las Tunas area. This zonation is defined by optical and compositional differences. Table 1 summarises relevant characteristics of the chromite grains from both localities.

Mineral chemistry

Techniques. Chromites, sulphides and silicates were studied in 20 polished and 30 thin sections. 30 chromite grains were analysed. Polishing was carried out on a Rehwald polishing machine.

For quantitative analysis, an ARL-SEMQ electron microprobe was used. Microprobe operating conditions were 20 kV and 15 nA and corrections were performed according to the Magic IV program. Calibration was achieved using the following standards: Chromite 55-G-23 AB (U.S. Geological Survey) and pure metallic Zn (ARL standard). Fe_2O_3 and FeO were discriminated using the equation of Droop (1987).

Las Tunas area spinels. Las Tunas Cores (LTC): they are aluminian chromites and can be interpreted as relict magmatic cores, owing to their [Cr/(Cr + Al)] and [Mg/(Mg + Fe)] ratios (Fig. 2*a,b*). The cores are irregularly shaped, brownish dull grey coloured and have a maximum grain size of 225 μm. They are optically homogeneous, devoid of inclusions and have a sharp contact with rim A (Fig. 3). In the large grains of LTC, the cores are chemically zoned, defined by decreasing amounts of MgO and Al_2O_3 (Table 2, analysis 5 and 6) and increases of ZnO, MnO, Fe_2O_3 and FeO (Fig. 4) The smallest relict cores that have been analysed (20 μm, Fig. 5) have optical characteristics and compositions similar to the large cores. Only the ZnO content is higher in these small cores (4.04 wt.%, Table 2, analysis 10). Occasionally, the disseminated spinels have a core, the optical and chemical characteristics of which are the same as those of rim A. This means that the primary LTC have been totally replaced by ferritchromit.

Rims A: they show a higher reflectivity than the core and are grey in colour with a slight brownish tint; they are slightly anisotropic and usually not more than 60 μm wide (Fig. 3). Microprobe analyses (Table 2) revealed a Cr_2O_3 content of 35.60 wt.% and FeO (total iron) of 52.69 wt.%. Rims A are classified as ferritchromit. From their inner to their outer margin they show decrease in Al_2O_3, MgO and Cr_2O_3 content and increase in

TABLE 1: Summary of characteristics of chromite grains from Las Tunas area and Salamanca district. The oxides (in wt.%) are the mean values of 10 analyses.

	Las Tunas area			Salamanca district	
	LTC	Rim A	Rim B	SC	Rim B
Mineral	Al-chromite	Ferritchromit	Cr-magnetite	Ferritchromit	Cr-magnetite
Colour	Brownish dull gray	Grey with brownish tint	Gray	Brownish gray	Gray
Shape	Anhedral with embayments	Anhedral	Anhedral	Anhedral	Anhedral
Silicate inclusions	No	Small, in the contact with rim B	Big in contact with hosting silicates	Small, only in contact with rim B	Big (also some sulphide inclusions)
Cr_2O_3	40.43	33.55	1.64	59.87	0.47
MgO	9.73	0.54	0.00	2.71	0.00
Fe_2O_3	4.24	33.61	67.13	7.88	69.06
FeO	18.44	27.77	31.06	23.08	31.11
Al_2O_3	24.30	1.30	0.05	0.96	0.00
ZnO	0.87	1.24	0.00	4.99	0.14

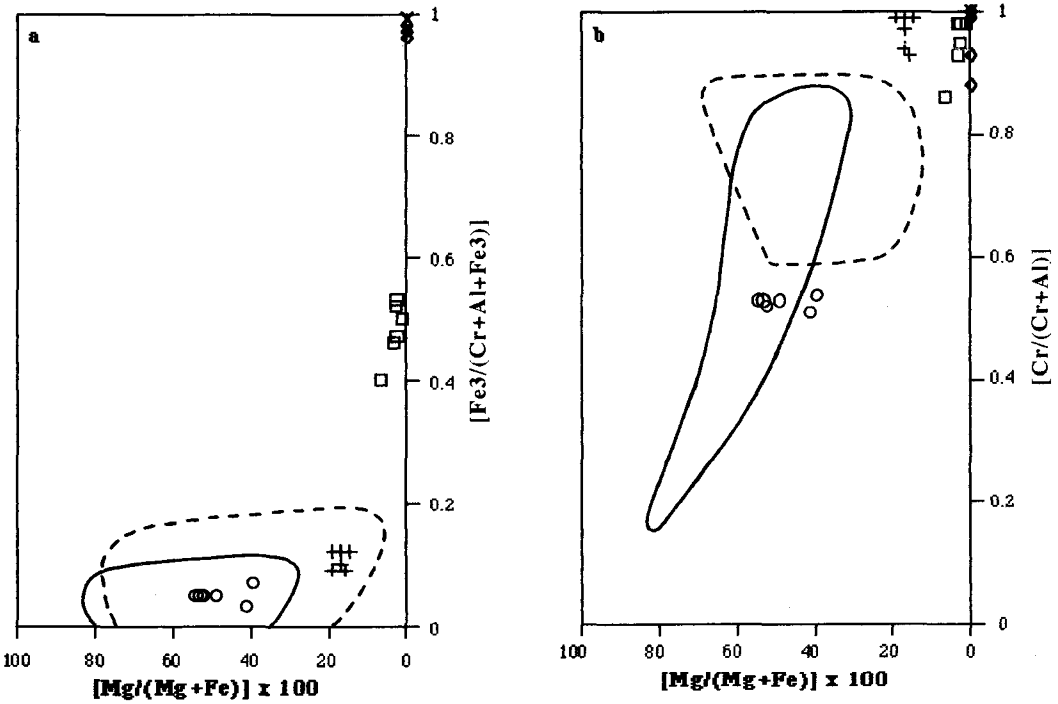

FIG. 2(*a*) and (*b*). Chromite alteration trends in chromite grains from Salamanca district (S) and Las Tunas area (LT). Fields of Alpine-type intrusions (solid line) and layered intrusions (dashed line) are also shown. Symbols: ○ LTC (LT), □ Rim A (LT), ◇ Rim B (LT), + SC (S), × Rim B (S).

FeO (total iron) and MnO. The ZnO content remains constant (Fig. 4 and Table 2, analysis 7 and 8). These rims contain small secondary silicate inclusions, restricted to a 8 μm wide zone, at the contact with rim B.

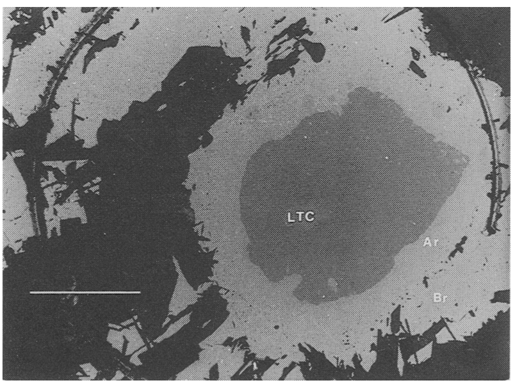

FIG. 3. Chromite grain from Las Tunas area included in serpentine matrix, with well developed zonation: (LTC) the core, (Ar) the A rim and (Br) the B rim; silicate inclusions restricted to the contact between the latter two. Scale bar represents 125 μm.

Rims B: in all samples studied these rims are characterised by a grey colour, higher reflectance than rim A, and by their optical and compositional homogeneity. Their width ranges from 20 to 40 μm. Anhedral and subhedral silicate inclusions are present (Fig. 3), the smallest in the contact with rim A and the largest ones (25 μm) towards their outer edge. They show both interstitial and replacement textures at their contact with the host silicates. These rims represent chromian magnetites; their maximum Cr_2O_3 reaches 2.34 wt.% (Table 2, analysis 9).

Salamanca district spinels. Salamanca Cores (SC): their chemical composition is similar to that of rim A from Las Tunas area and they are therefore classified as ferritchromit. Their grain size ranges from 50 to 200 μm, they are irregularly shaped and of brownish grey colour. Inclusions of serpentine minerals (Fig. 6) occur only close to the contact with rim B. They are Cr-rich, depleted in Al and Mg and have a ZnO content ranging from 4 to 7 wt.% (Table 1, analysis 1 an2). Occasionally, the outermost edge, at the contact with rim B, shows a slight increase in its Al_2O_3 content (2.85–1.19 wt.%, Fig. 7 and Table 2, analysis 3).

Rims B: these rims are compositionally identi-

TABLE 2: Microprobe analyses from Salamanca district (SC - core: 1, 2 and 3; rim B: 4) and Las Tunas area (LTC - core: 5 and 6; rim A: 7 and 8; rim B: 9; Small LTC: 10); n.a. : not analysed.

A.Nr.	1	2	3	4	5	6	7	8	9	10
Cr_2O_3	61.28	57.00	58.54	0.71	40.96	39.58	35.60	34.35	2.34	39.19
TiO2	0.30	0.54	0.24	0.05	0.00	0.00	0.19	0.26	0.04	0.00
MgO	2.70	2.64	2.50	0.00	11.19	7.47	1.13	0.19	0.00	7.61
Fe_2O_3	7.21	8.67	6.84	69.00	3.98	5.63	28.59	34.03	66.81	2.84
FeO	23.21	22.41	23.68	31.24	17.64	20.36	26.97	27.56	31.19	19.50
$Al2O_3$	0.04	2.28	2.85	0.00	24.86	22.60	3.85	0.40	0.02	25.05
MnO	0.61	0.27	0.76	0.03	1.01	1.36	2.55	3.22	0.08	0.93
ZnO	4.69	7.00	4.85	0.23	0.19	2.52	1.38	1.32	0.00	4.04
$V2O_3$	n.a.	1.49	n.a.	n.a.	0.24	0.24	0.08	0.05	0.05	0.23
TOTAL	100.04	102.30	100.26	101.26	100.07	99.76	100.34	101.38	100.53	99.39

Structural Formula (32 O)

Al	0.01	0.77	0.97	0.00	7.22	6.83	1.33	0.14	0.01	7.52
Fe $^{3+}$	1.59	1.61	1.49	15.81	0.74	1.08	6.31	7.63	15.40	0.54
Fe $^{2+}$	5.71	5.42	5.75	7.95	3.64	4.37	6.61	6.87	7.99	4.15
Mg	1.18	1.14	1.08	0.00	4.11	2.86	0.49	0.08	0.00	2.89
Ti	0.07	0.12	0.05	0.01	0.00	0.00	0.04	0.06	0.01	0.00
Mn	0.15	0.06	0.18	0.01	0.21	0.30	0.63	0.81	0.02	0.20
Cr	14.25	13.03	13.43	0.17	7.99	8.03	8.25	8.09	0.56	7.89
Zn	1.02	1.49	1.04	0.05	0.03	0.48	0.30	0.29	0.00	0.76
V	--	0.34	--	--	0.05	0.05	0.01	0.01	0.01	0.05
mg	17.13	17.37	15.81	0.00	53.03	39.55	6.90	1.15	0.00	41.05

cal to rims B from the Las Tunas area. They are grey in colour, have a higher reflectance than the core and are classified as chromian magnetites (Table 2, analysis 4). Their maximum ZnO con-

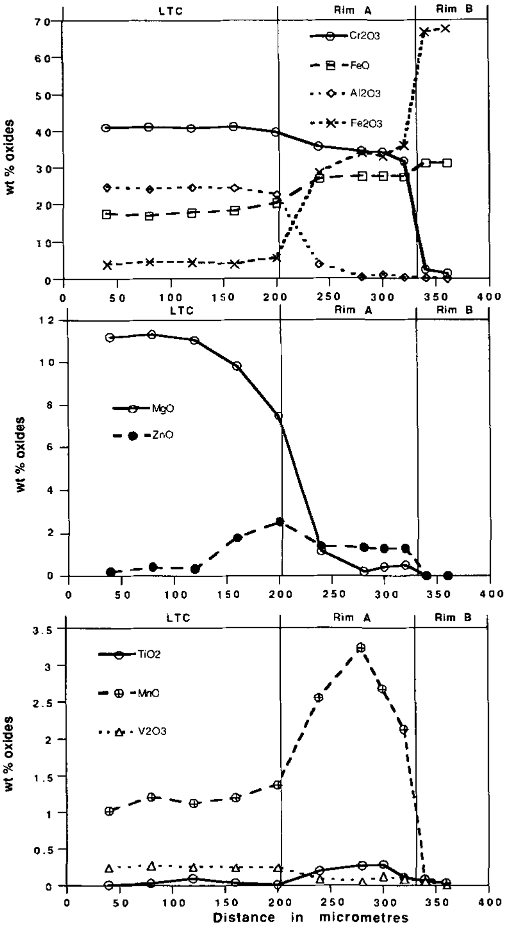

FIG. 4. Compositional variations from the centre of the core to rim B in one chromite grain from Las Tunas area.

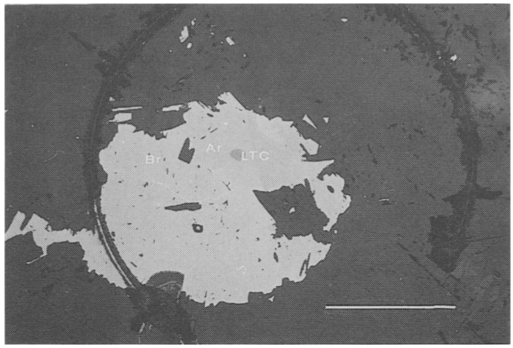

FIG. 5. Anhedral chromite grain from Las Tunas area, in a silicate matrix, which shows a small (LTC) core surrounded by a wide A rim (Ar) which outwards is succeeded by a B rim (Br). Scale bar represents 160 μm.

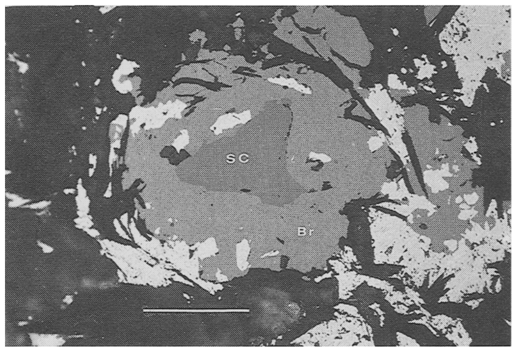

FIG. 6. Anhedral ferritchromite grain from Salamanca district associated with serpentine minerals and sulfides, where it is possible to distinguish the core (Sc), which in its lower left corner show a narrow darker zone (with higher Al_2O_3 content) and in its upper left corner a very small silicate inclusion in contact with the outer B rim; the B rim (Br) shows sulfide and silicate inclusions. Scale bar represents 60 μm.

tent is 0.23 wt.%, whereas the other oxides with the exception of FeO (total iron), have values close to zero (Table 2, analysis 4 and Fig. 7). Rims B range in width from 150 to 200 μm (Fig. 6), bearing anhedral and subhedral silicate inclusions (serpentine minerals) and anhedral sulphide inclusions (chalcopyrite). These rims show replacement textures at their contact with the host silicates, sometimes filling spaces between amphibole pseudomorphs. Sulphides, where present, partially replace these rims.

Significance of chrome-spinel zoning

The Al-chromite LTC plot into a restricted area in the field of Alpine type chromites (Fig. 2*a,b*), with rims A (ferritchromit), rims B (Cr-magnetite) and the SC following a regular path toward the magnetic corner (Fig. 2*a* and Fig. 8) and the ferrochromite corner (Fig. 2*b*). This is in accordance with an alteration trend (Bliss and MacLean, 1975).

Step scan profiles were made on 15 spinel grains from the Las Tunas area serpentinites. They all show a similar optical and chemical zonation. In the step scan profile shown in Fig. 4, it can be seen that the chemical composition of the LTC shows slight variations only, mainly restricted to its external border and that major chemical changes occur within rim A. The following compositional trends defining the zonation are considered significant; (*a*) Zno increases from the centre and reaches its maximum value at the edge of the core; (*b*) in rim A, the Zno content is lower compared with the core and decreases towards the contact with rim B, where all the oxides with the exception of FeO, Fe_2O_3 and Cr_2O_3 decrease to levels close to zero. In the small LTC (26 μm, Fig. 5), the main constituents show the same general trend as in the big LTC (250 μm, Fig. 3), the main difference being their higher ZnO contents (maximum 4.04 wt.%). In their rims A and B the main constituents and ZnO reach the same values and show a similar trend as in the A and B rims related to the bigger LTC.

In some grains the primary LTC has been

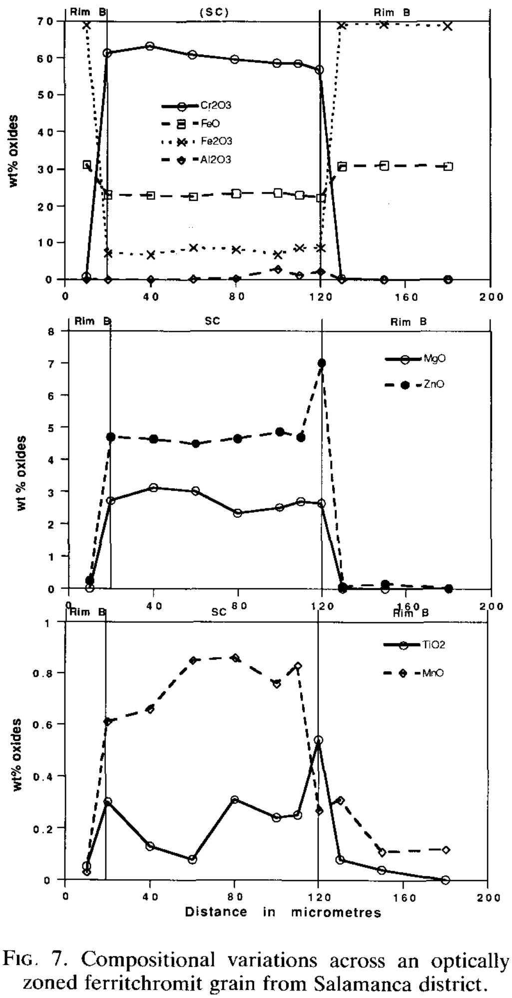

FIG. 7. Compositional variations across an optically zoned ferritchromit grain from Salamanca district.

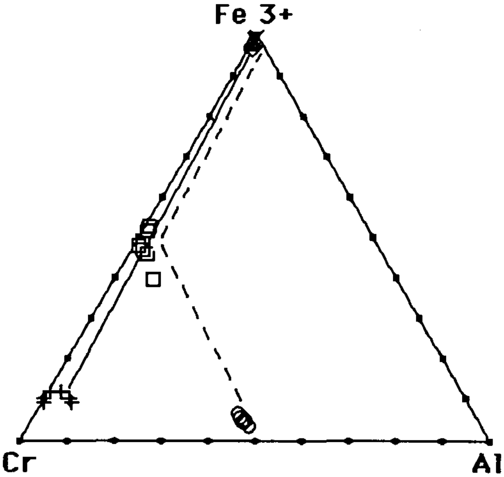

FIG. 8. Compositional variation and alteration trend of spinels from Las Tunas area (dashed line) and Salamanca district (solid line). Symbols as in Fig. 7*a*,*b*.

completely altered and is now replaced by a phase compositionally identical with rim A and surrounded by rim B. In these grains the main constituents show the same trend as in the rims A and B surrounding the Al-chromite LTC.

Step scan profiles were made on 8 spinel grains from the Salamanca district serpentinites. In one of these profiles (Fig. 7), it can be seen that the SC has high values of Cr_2O_3. ZnO shows a smooth gradient and attains its highest value (7 wt.%) at one edge, in the contact with rim B. The absence of primary cores in the Salamanca district, is interpreted as the result of a more intense alteration process.

Discussion

According to Evans and Frost (1975), metamorphic zoned chromites are characterised by a core rich in Cr and Fe^{2+} and Al-, Mg-rich rims. This certainly does not apply to the spinels from Salamanca district and Las Tunas area. The LTC Al-chromites still retain primary magmatic features, as demonstrated by their [Cr/(Cr + Al)] and [Mg/(Mg + Fe)] ratios. However, the optical and chemical zonation of the Zn-chromites from the Cordillera Frontal Range are interpreted as the result of alteration processes and this is supported by the following facts:

1. In ultramafic rocks, chromite grains are commonly euhedral and if a new phase is added, the original interface will remain unchanged (Bliss and McLean, 1975). The Al-chromites LTC show

textural evidence of having been partially replaced by ferritchromit, i.e. anhedral shapes and embayments, which indicates that alteration advanced from all directions, inward towards the centre of the grains.

2. The anhedral LTC are always surrounded by a chemically and optically well defined ferritchromit A rim, with inclusions of serpentine minerals restricted to its contact with rim B. This suggests that ferritchromit formed as a polycrystalline aggregate which allowed communication between the growing ferritchromit and the dissolving cores. Similar observations have been reported from the Sykesville district by Wylie *et al.*, 1987.

3. The changes in the main constituents of LTC, SC, rims A and B, suggest compositional gradients, with MgO, Al_2O_3, FeO (total iron) and Cr_2O_3, moving outwards. Part of the Cr_2O_3 was incorporated in the B rims (1 wt.% Cr_2O_3), which makes them different from the anhedral, ragged magnetites disseminated in the main mass of serpentine which do not contain Cr_2O_3. Part of the Al_2O_3 and the Cr_2O_3 was incorporated into the serpentine minerals (antigorite) which contain up to 2.39 wt.% Al_2O_3 ad 0.55 wt.% Cr_2O_3.

4. As serpentinisation was the major post-magmatic event in the area, the alteration process and the fluids involved, are attributed to the serpentinisation process, probably in connection with regional metamorphism, which have affected all ultramafic rocks in the study area.

The Zn content of this Al-chromites is not a primary magmatic feature. Zn was introduced into the chromites during the alteration process. This is supported by the following evidence:

1. In the central part of the LTC, the highest ZnO value measured is 0.41 wt.%, an amount that increases toward the contact with rim A (2.52 wt.%). This smooth gradient in ZnO content is considered as evidence for addition of Zn from an external source. It is very unlikely that despite the alteration process, the LTC could still retain a primary magmatic gradient.

2. The smallest relict LTC analysed also prove the addition of Zn to the system during this alteration process; they show the highest ZnO content measured in Al-chromite grains.

3. Those spinels which were most intensely affected by the alteration process have cores composed of ferritchromit, as in the Salamanca district, where the SC have the composition of the A rims and the highest ZnO values measured (7 wt.%).

4. The high Zn content of the SC indicates that in the Salamanca district there was more Zn available; this is probably linked to the presence of a sulphide mineralisation that includes sphalerite which originated within the ultramafic rocks. It was affected by post-emplacement regional metamorphism, remobilised and redeposited in veins (mainly located in fault zones) and as disseminations, in the serpentinised ultramafic bodies.

5. Whole-rock analysis of serpentinites from the Salamanca district devoid of sulphides reveal 160 ppm Zn. Those serpentinites with disseminated sulphides (mainly pentlandite, pyrrhotite and chalcopyrite and minor sphalerite) have 500 ppm Zn. These Zn contents are higher when compared with the average Zn content (50 ppm) in the serpentinites from Las Tunas area where, so far, sphalerite has not been recognised among the disseminated sulphides (pyrrhotite, pentlandite and chalcopyrite).

Conclusions

The optical and chemical zonation of the Zn-chromites from the Cordillera Frontal Range, Argentina, is interpreted as the result of alteration processes. This is supported by textural and compositional evidence. The fluids involved in the alteration process were related to the serpentinisation process, which affected the ultramafic rocks in this area.

The high Zn content of the chromites was not inherited from the magmatic stage. This is demonstrated by the gradient in ZnO content in the chromites, which attain their highest ZnO content at their outer edge.

The alteration process was responsible for both ferritchromit formation and Zn addition to the chromites. Whole-rock analysis have shown that there is a strong relationship between the ZnO content in the serpentinised ultramafic rocks, the ZnO content in chromites and ferritchromit and the degree of alteration of chromite. The presence of a spatially associated sulphide mineralisation which comprises sphalerite, indicates that this mineral was the most probable source of Zn.

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