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ZONED Zn-RICH CHROMITE FROM THE NÄÄTÄNIEMI SERPENTINITE MASSIF, KUHMO GREENSTONE BELT, FINLAND

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Abstract

Chromite from the Archean Näätäniemi serpentinite massif, Kuhmo greenstone belt, Finland, exhibits high concentrations of Zn, up to 4.4 wt% ZnO. The chromite is zoned, optically and chemically; the best-preserved chromite cores can be divided into two groups on the basis of their composition. Type-I chromite is interpreted as a relict core, with Cr/(Cr + Al) values from 0.58 to 0.76 and Mg/(Mg + Fe^{2+}) values from 0.53 to 0.60; the core of type-II chromite has been altered to "ferritchromit"; Mg/(Mg + Fe^{2+}) values range from 0 to 0.37. In the core of type-I and -II chromite, Zn shows no correlation with the other divalent cations (Mg, Mn and Fe^{2+}). On the basis of their Zn content, type-I and type-II chromite resemble those examples reported from metamorphosed volcanic-type iron–nickel sulfide ores from Western Australia, though the suite of type-I chromite from the Näätäniemi serpentinite massif displays higher Mg (12.1 wt% MgO) and Al (20.9 wt% Al_2O_3) contents.

Keywords: chromite, zoning, serpentinite, Archean, Kuhmo greenstone belt, Finland.

Sommaire

La chromite du massif de serpentinite de Näätäniemi, d'âge archéen, de la ceinture de roches vertes de Kuhmo, en Finlande, contient jusqu'à 4.4% (en poids) de ZnO. La chromite est zonée, optiquement aussi bien que chimiquement. Certains des coeurs les mieux préservés ont une composition interprétée comme relique magmatique (type I), avec des rapports Cr/(Cr + Al) entre 0.58 et 0.76, et Mg/(Mg + Fe^{2+}) entre 0.53 et 0.60. D'autres (dits de type II) ont une composition transformée, correspondant maintenant à la "ferritchromit", et le rapport Mg/(Mg + Fe^{2+}) va de 0 à 0.37. Dans le coeur des deux types de chromite, la teneur en Zn ne montre aucune corrélation avec celle des autres cations bivalents (Mg, Mn et Fe^{2+}). Les teneurs en Zn des types I et II rappelle la chromite des minerais à Fe–Ni métamorphisés et d'origine volcanique en Australie occidentale, quoique la chromite de type I de Näätäniemi possède une teneur plus élevée en Mg (12.1% de MgO par poids) et en Al (20.9% Al_2O_3).

(Traduit par la Rédaction)

Mots-clés: chromite, zonation, serpentinite, archéen, ceinture de roches vertes, Kuhmo, Finlande.

Introduction

Chromite rich in Zn is considered unusual enough to be reported in the literature whenever it is found. Zn-rich spinel has been reported from different geological settings (Thayer *et al.* 1964, Weiser 1967, Groves *et al.* 1977, 1983, Moore 1977, Bevan & Mallinson 1980, Wylie *et al.* 1987, Bjerg *et al.* 1993, Halkoaho 1994), and a Zn content in excess of 0.5 wt% ZnO is considered significant (Groves *et al.* 1983). In most cases, high Zn content in chromite is caused by metasomatism; only in the example described from sequences of ultramafic flows in Western Australia (Groves *et al.* 1977, 1983) is the Zn considered to be inherited from the magmatic stage.

This paper discusses accessory chromite from the Näätäniemi serpentinite massif, in the Kuhmo greenstone belt of Archean age, in eastern Finland. The chromite occurs as optically and chemically zoned cumulate grains in Archean serpentinites and exhibit high concentrations of Zn.

Location and Geological Setting

The Kuhmo belt in eastern Finland (Taipale *et al.* 1980, Piirainen 1988) is a typical Archean greenstone belt surrounded by granitoid rocks. It forms a narrow composite north-trending belt approximately 20 km wide and 200 km long. The belt, which is one of the most intensively investigated Archean belts in the Fennoscandian shield (Taipale *et al.* 1980, Taipale 1983, Piquet 1982, Piirainen 1988, Luukkonen 1992), can be divided into three parts, namely the southern (Tipasjärvi), middle (between Kuhmo and Suomus-

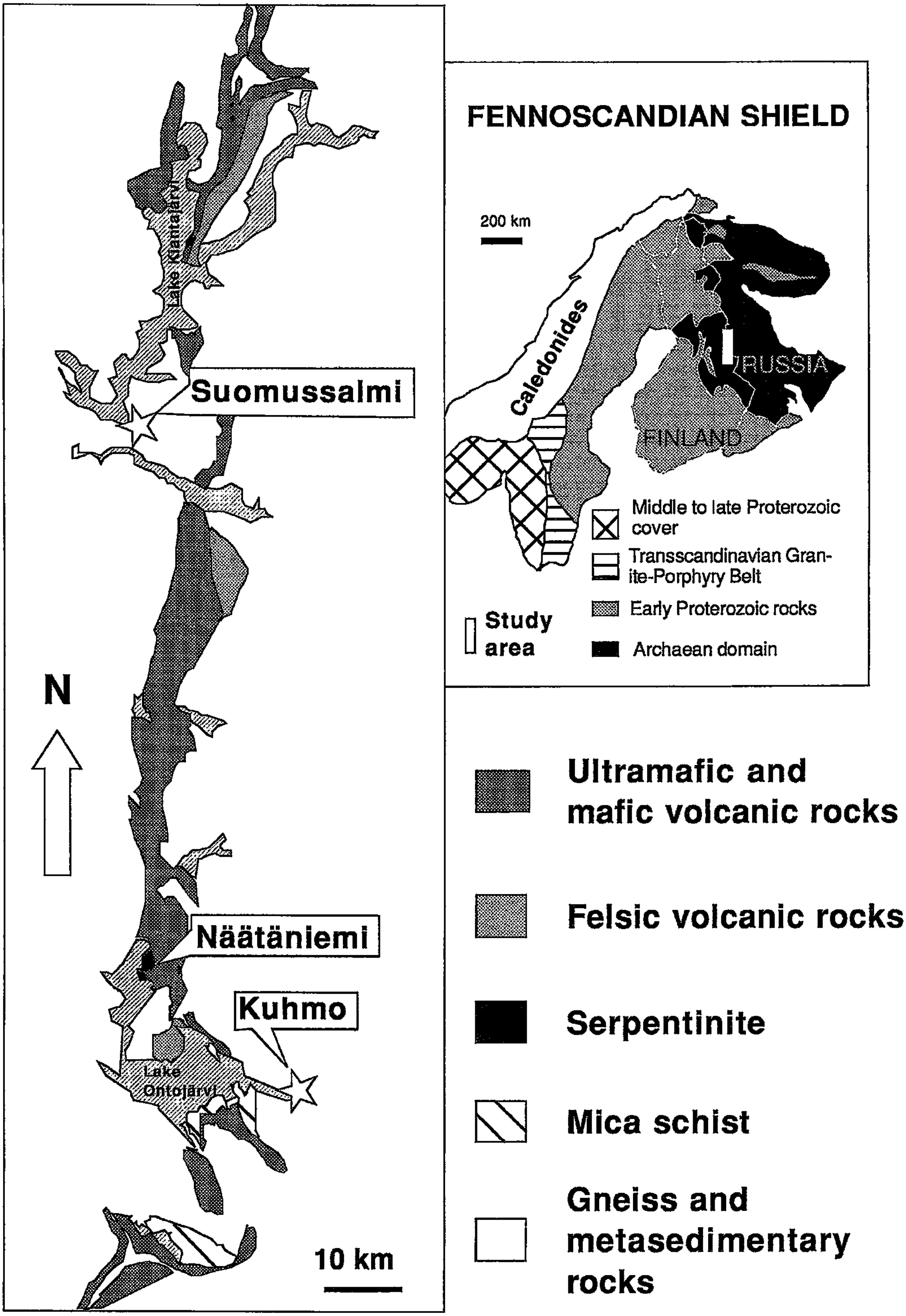

FIG. 1. Geological sketch map of the Kuhmo greenstone belt, showing the locations of Näätäniemi serpentinite massif. Modified after Hanski (1984).

salmi), and northern (Suomussalmi) areas (Fig. 1). It has been dated at between 2.99 (Vaasjoki & Sakko 1991) and 2.75 Ga (Vaasjoki *et al.* 1989) and is composed principally of volcanic rocks and subordinate volcano-sedimentary and sedimentary rocks, which have been divided into three lithological units. Each unit is characterized by its own volcanic series: 1) andesite (Luoma group), 2) serpentinite – tholeiite – komatiite – basaltic komatiite (Kellojärvi Group), and 3) rhyolite – rhyodacite – Fe-rich tholeiite – komatiite – basaltic komatiite (Ontojärvi Group) (Taipale *et al.* 1980). The Kellojärvi group is cross-cut by a dyke of Fe-rich tholeiite dated at 2.79 Ga (Luukkonen 1988).

The ultramafic rocks have a multistage history, affected by at least three phases of deformation and two phases of intrusion of granitic magma, and are composed predominantly of serpentinite, having been deformed and metamorphosed under conditions of the greenschist or lower amphibolite facies (Piquet 1982, Taipale 1983, Blais & Auvray 1990, Tuisku & Sivonen 1984).

The serpentinites in the Archean Kuhmo greenstone belt have been considered to be metamorphosed cumulates of the komatiitic series (Blais *et al.* 1978), but on the basis of the high values of the $(La/Sm)_N$ and $(Sm/Yb)_N$ ratios and high TiO_2 contents, the Näätäniemi serpentinites differ from typical ultramafic rocks of komatiitic origin (Hanski 1982, 1984). An ophiolitic nature of this serpentinite massif has been suggested by Piirainen (1991).

Petrography

The samples used in this investigation were selected from those of the Research Project on Archean Areas (Piirainen 1991), and from outcrops of the Näätäniemi serpentinite massif. The Näätäniemi massif is located in the middle sub-belt and consists of Archean serpentinites cross-cut by an early Proterozoic differentiated dyke dated at 2.2 Ga (Hanski 1984).

The serpentinite is dunitic in composition; the primary minerals other than chromite have disappeared completely. Olivine (Fo_{96}) and clinopyroxene of metamorphic origin occur as relict grains in rare samples. The dominant minerals of the serpentinite, antigorite and lizardite, formed at the expense of olivine. Accessory minerals include magnetite and geikielite (Liipo *et al.* 1994).

Chromite is ubiquitous as an accessory cumulus phase in all the samples analyzed. Most of the chromite occurs in the form of disseminated euhedral to subhedral grains 20 to 400 μm in diameter. These are zoned, with a homogeneous core surrounded by an inner and an outer rim (Fig. 2). This zonation is defined by optical and compositional differences.

Chemical Composition of the Chromite

Electron-microprobe analyses were performed on compositionally zoned grains of chromite from the Näätäniemi serpentinite massif. A representative sampling of the 232 analyses is presented in Table 1. The chromite has been extensively analyzed to cover the full range of variations from aluminous chromite through "ferritchromit" to chromian magnetite. Table 1 summarizes relevant characteristics of the chromite grains.

The mineral analyses were performed with a wavelength-dispersion JEOL JCXA 733 electron microprobe equipped with LINK AN10 automation at the Institute of Electron Optics, University of Oulu. The acceleration voltage was 15 kV, the sample current, 15 nA, and the spot size, 2 μm. The following standards were used: synthetic rutile for Ti, synthetic corundum for Al, hematite for Fe, periclase for Mg, and pure metallic standards for the remaining elements. The practical limit of detection in these routine analyses varies from 0.01 to 0.05 wt%. Results were corrected with an on-line ZAF program. Ferrous and ferric iron were distributed on the basis of stoichiometry by the method of Carmichael (1967).

Compositional variations in the core

The core of each preserved grain is irregularly shaped and grey in reflected light. It is optically homogeneous, free of inclusions and has a sharp contact with a lighter grey rim, whereas in those grains that are more intensely altered, the grey core has disappeared; such grains can be classified as chromian magnetite or magnetite.

In terms of composition, the best-preserved cores may be divided into two groups. Type-I chromite has a X_{Mg} [$Mg/(Mg + Fe^{2+})$] value greater than 0.4 and a X_{Cr} [$Cr/(Cr + Al)$] value between 0.58 and 0.76. In type-II chromite, the core has undergone more profound alteration, and is depleted in Mg and Al, and enriched in Mn, Fe^{2+} and Fe^{3+} (X_{Mg} from 0 to 0.37) compared to type-I chromite. It can be classified as "ferritchromit" (Table 2). From an exploration viewpoint, the most significant compositional oddity about the core zone is its consistently high Zn content, from 2.18 to 3.74 wt% in type-I chromite and from 1.47 to 4.36 wt% in type-II chromite.

Compositional variations in spinel have generally been represented on bivariate plots of X_{Mg} *versus* X_{Cr} or X_{Fe} [$Fe^{3+}/(Cr + Al + Fe^{3+})$] (Irvine 1965, 1967, Dick & Bullen 1984). On such diagrams, chromite from komatiites and stratiform intrusions cannot be discriminated, though chromite from komatiites plots in a different field from chromite in ophiolitic complexes. Type-I chromite plots in the overlapping field of ophiolites and stratiform intrusions, and differs from chromite of komatiitic origin, whereas type-II chromite

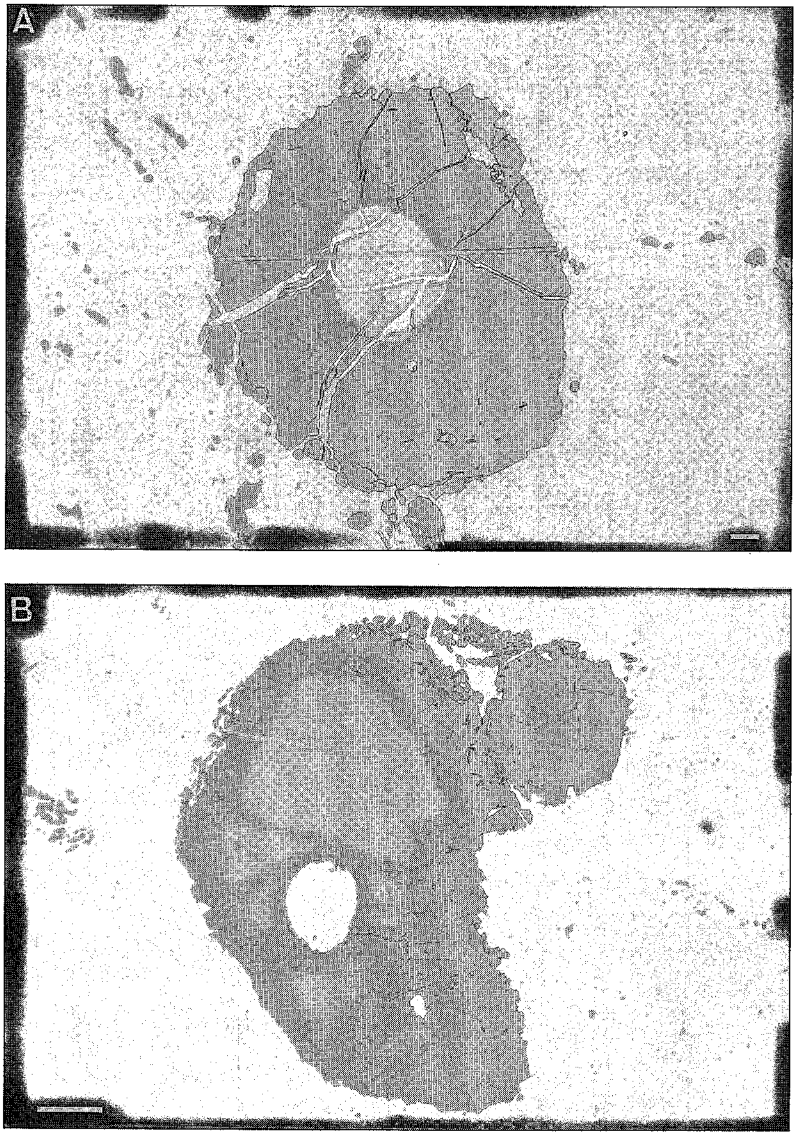

FIG. 2. Back-scattered electron images of the zoned grains of chromite from the Näätäniemi serpentinite massif. A) type-I chromite, and B) type-II chromite. Lines show the locations of the step-scan profiles. Scale bar 10 μm in A and 100 μm in B.

plots mostly outside those fields (Fig. 3).

Intragrain compositional variations

Euhedral to subhedral crystals of chromite are characterized by an inner rim, which propagates along fractures, reflected in optical and compositional differences. The inner rim shows a higher reflectivity than the core and is light grey in reflected light. Compositionally, it is classified as "ferritchromit". Compared with the core, the inner rim is enriched in Fe^{3+}, Fe^{2+}, Mn, and Ti, and depleted in Mg, Cr, Al and Zn. The outer rim has a higher reflectivity than the inner rim and consists of chromian magnetite. The outer rim is enriched in Fe^{3+} and Fe^{2+}. Both inner and outer rims contain small inclusions of secondary silicate.

Step-scan profiles from type-I chromite (Fig. 4) and type-II chromite (Fig. 5) reveal that the chemical composition of the core zones shows only slight variations, mainly restricted to its external border; important chemical changes occur within the inner rim. Zn

TABLE 1. SUMMARY OF CHARACTERISTICS OF CHROMITE GRAINS FROM THE NÄÄTÄNIEMI SERPENTINITE MASSIF, KUHMO GREENSTONE BELT, FINLAND

		Chromite Type I	Chromite Type II	Inner rim	Outer rim
Mineral		chromite	chromite	magnetite	magnetite
Colour		Dark grey	Dark grey	Grey	Light grey
Shape		Anhedral	Anhedral	Anhedral	Anhedral
Inclusions		No	No	Small, rarely	Commonly
TiO_2	Wt%	0.35	0.69	0.56	0.27
Al_2O_3		20.04	13.05	0.38	0.08
Cr_2O_3		48.63	44.34	29.38	9.83
Fe_2O_3		1.87	7.62	37.30	57.62
FeO		14.55	27.72	25.21	28.12
MnO		0.79	2.14	1.55	0.48
MgO		11.89	1.94	2.59	1.43
ZnO		2.80	1.85	0.98	0.13

The compositions reported are mean values of ten analyses. The proportions of Fe^{2+} and Fe^{3+} are allotted according to stoichiometry.

reaches its maximum value at the edge of the core and decreases toward the contact with outer rim, where the level of all the cations with the exception of Fe^{2+}, Fe^{3+} and Cr approach zero.

The Zn content of the cores shows only slight variations, and the difference between the maximum content in the edge of the core and the average values in the core is small, below 1 wt%. In the cores of type-I and type-II chromite, Zn shows no correlation with the other divalent cations (Mg, Mn and Fe^{2+}). Decrease of Mg correlates with increase in Mn and Fe^{2+}.

TABLE 2. REPRESENTATIVE RESULTS OF ELECTRON–MICROPROBE ANALYSES OF CHROMITE FROM THE NÄÄTÄNIEMI SERPENTINITE MASSIF, KUHMO GREENSTONE BELT, FINLAND

	1	2	3	4	5	6	7	8	9	10
Sample	9A	9A	10			2.3	756.2	756.2		
Chromite	type I	type I	type I	rim A	rim B	type II	type II	type II	rim A	rim B
wt %										
TiO_2	0.56	0.51	0.30	0.42	0.09	0.72	2.63	1.15	1.02	0.07
Al_2O_3	20.98	20.39	19.90	0.43	0.01	13.63	10.42	10.06	0.81	0.01
Cr_2O_3	46.15	46.15	47.95	40.60	5.34	43.22	42.35	48.69	38.75	5.65
Fe_2O_3	2.39	3.04	2.10	28.20	63.13	8.69	9.12	6.70	26.89	62.47
FeO	14.72	14.24	14.02	22.58	27.35	27.25	26.90	25.41	27.17	30.76
MnO	0.89	0.80	0.74	1.47	0.28	2.51	2.37	2.30	2.84	0.09
MgO	11.32	11.59	12.10	4.48	2.02	2.02	1.82	2.66	0.57	0.05
NiO	0.24	0.10	0.13	0.44	1.13	0.15	0.17	0.12	0.44	0.56
ZnO	3.48	3.29	2.63	1.08	0.11	2.28	4.36	3.30	2.11	0.00
Total	100.73	100.11	99.86	99.69	99.45	100.47	100.15	100.39	100.60	99.67
Number of ions calculated on 32 (O) basis										
Ti	0.1050	0.0962	0.0560	0.0918	0.0206	0.1483	0.5542	0.2418	0.2297	0.0165
Al	6.1622	6.0246	5.8763	0.1466	0.0025	4.4176	3.4433	3.3004	0.2827	0.0047
Cr	9.0961	9.1458	9.5010	9.3867	1.2854	9.3954	9.3856	10.714	9.1292	1.3772
Fe^{3+}	0.4477	0.5732	0.3962	6.2067	14.469	1.7984	1.9242	1.4032	6.0289	14.484
Fe^{2+}	3.0676	2.9853	2.9373	5.5216	6.9663	6.2661	6.3047	5.9138	6.7712	7.9272
Mn	0.1871	0.1705	0.1571	0.3638	0.0722	0.5855	0.5634	0.5415	0.7163	0.0238
Mg	4.2076	4.3296	4.5206	1.9543	0.9169	0.8266	0.7616	1.1056	0.2554	0.0230
Ni	0.0488	0.0198	0.0251	0.1028	0.2757	0.0324	0.0373	0.0270	0.1054	0.1394
Zn	0.6403	0.6080	0.4872	0.2331	0.0251	0.4637	0.9029	0.6771	0.4647	0.0000
X_{Mg}	0.5783	0.5919	0.6061	0.2641	0.1163	0.1165	0.1078	0.1575	0.0363	0.0029
X_{Cr}	0.5961	0.6029	0.6179	0.2614	0.1163	0.6802	0.7316	0.7645	0.9700	0.9966
X_{Fe}	0.0285	0.0364	0.0251	0.9846	0.9981	0.1152	0.1304	0.0910	0.3905	0.9120

$X_{Mg} = Mg/(Mg + Fe^{2+})$, $X_{Cr} = Cr/(Cr + Al)$, $X_{Fe} = Fe^{3+}/(Fe^{3+} + Cr + Al)$. The proportions of Fe^{2+} and Fe^{3+} are allotted according to stoichiometry. Rim A: inner rim; rim B: outer rim.

Discussion

Chromite from serpentinites can exhibit a wide range in composition, which reflects differences in metamorphic conditions (Evans & Frost 1975). The composition of type-I chromite plots in the overlapping fields of stratiform and ophiolitic chromites, with inner rims ("ferritchromit"), outer rims (chromian magnetite) and type-II chromite following a regular path toward the magnetite and ferroan chromite corner (Fig. 3). This is in accordance with an alteration trend established by many (Bliss & MacLean 1975, Evans & Frost 1975, Hoffman & Walker 1978, Kimball 1990). Hoffman & Walker (1978) observed that the thickness and composition of the chromian magnetite and magnetite rims are correlated inversely with Fe^{3+} content of the core chromite and positively with the extent of serpentinization of the ultramafic rocks. In type-I chromite, Fe^{3+} content ranges from 0.13 to 0.73, and in type-II chromite, it ranges from 0.28 to 3.68, though the thickness and composition of the rims A and B in type-I and -II chromites are similar (Figs. 2, 4 and 5).

On the bases of reasonably high X_{Mg} and X_{Cr} and low Fe^{3+} values, type-I chromite may be interpreted as a relict magmatic core, only slightly modified by metamorphism. In comparison with magmatic spinel in komatiites reported earlier from the Kuhmo greenstone belt, Finland, which have been suggested to be closest to a possible primary composition (Blais & Auvray 1990), and with other occurrences from serpentinized Archean ultramafic cumulates (Arndt 1977, Arndt *et al.* 1977, Nisbet *et al.* 1977, Groves *et al.* 1977, 1983, Donaldson & Bromley 1981), type-I chromite from the Näätäniemi serpentinite massif has higher Mg (12.1 wt% MgO) and Al (20.9 wt% Al_2O_3) contents, resembling those from ophiolitic cumulates. However, on the basis of their Zn content, type-I and type-II chromites resemble those reported from metamorphosed volcanic-type iron–nickel sulfide ores from western Australia (Groves *et al.* 1977, 1983, Donaldson & Bromley 1981).

Zinc content of chromite

The chromite in the Näätäniemi serpentinite massif contains anomalously high Zn contents. Similar high Zn contents occur in "ferrochromit" associated with nickel deposits in Western Australia (Groves *et al.* 1977, 1983, Donaldson & Bromley 1981), where the high Zn content is interpreted as primary magmatic feature.

Step-scan profiles made on the chromite grains from the Näätäniemi serpentinite massif show that the Zn content of the core is constant and decreases in inner and outer rims. Constant Zn content of the core may be a result of contamination by S-rich sedimentary rocks, recrystallization during metamorphism or inheritance

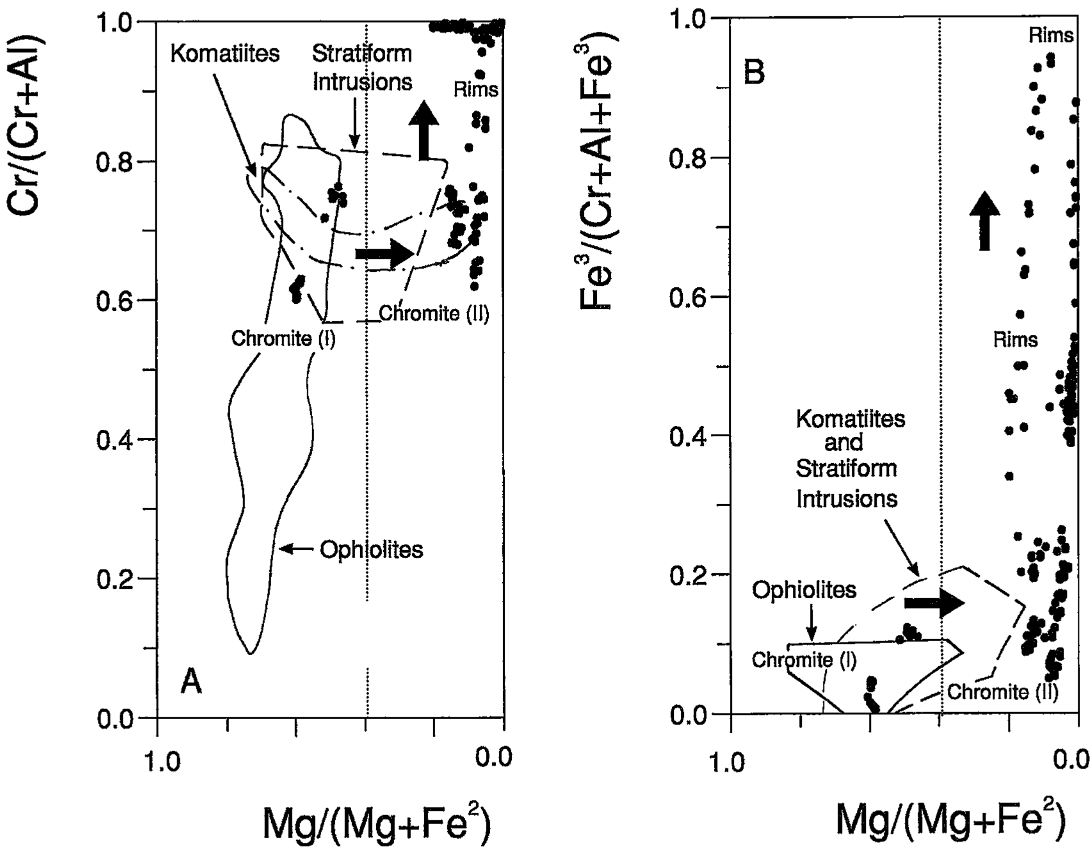

FIG. 3. Composition of chromite plotted on projections of the spinel prism of Stevens (1944). The fields for the various types of complexes shown in A (X_{Cr} *versus* X_{Mg}) and B (X_{Fe} *versus* X_{Mg}) are based on Irvine (1967), Bird & Clark (1976), Dick & Bullen (1984) and Zhou & Kerrich (1992). Arrows indicate behavior expected as a result of alteration involving a decrease in Mg first and Al afterward.

from the magmatic stage, as noted by Groves *et al.* (1977, 1983). The following facts support a magmatic origin of the high Zn content of the chromite, although crustal contamination of magma is an equally possible explanation, as pointed out by Irvine (1965) and Groves *et al.* (1977).

1) In many cases, an increase in the level of Zn correlates with a decrease in Mg content (Wylie *et al.* 1987, Bjerg *et al.* 1993), whereas the cores of type-I chromite show no correlation between concentration of Zn and of other divalent cations. Type-I chromite also has a moderate to high content of Mg and Al, together with a high Zn content.

2) Grains of type-II chromite were affected more intensely by the serpentinization process, having a core composed of "ferritchromit". The Zn content of the type-II chromite reaches up to 4.36 wt%, which is not significantly higher than that in type-I chromite. This suggests that there is no enrichment of Zn during the alteration process.

3) At other localities noted for their Zn-enrichment in chromite, metasomatism is clearly indicated and related to Zn-bearing mineralization (Wylie *et al.* 1987) or ores (Thayer *et al.* 1964, Weiser 1967), whereas at Näätäniemi, no significant sources for Zn are known to occur. This could be an indication of the possible existence of mineralization in the area, however.

CONCLUSIONS

The optical and chemical zonation of the zincian chromite from the Archean Näätäniemi serpentinite massif is interpreted to result from intense metamorphism and several phases of serpentinization. Despite the serpentinization, the core of type-I chromite has retained a primary magmatic signature, as demonstrated by its X_{Cr} and X_{Mg} values. The high Zn content of the chromite is inherited from the magmatic stage, which is demonstrated by the gradient

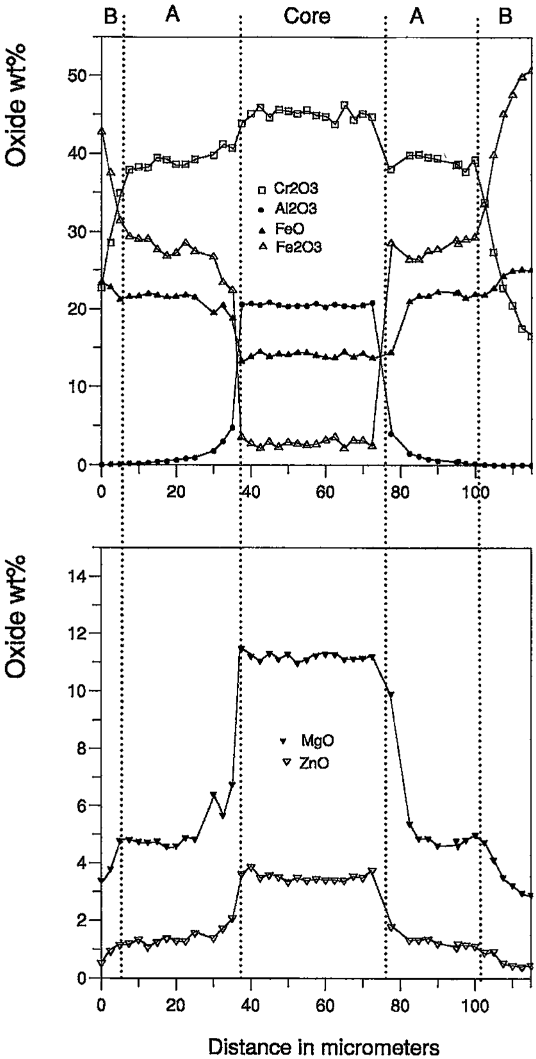

FIG. 4. Compositional variations from outer rim to outer rim in one grain of type-I chromite from the Näätäniemi serpentinite massif. A: inner rim, and B: outer rim.

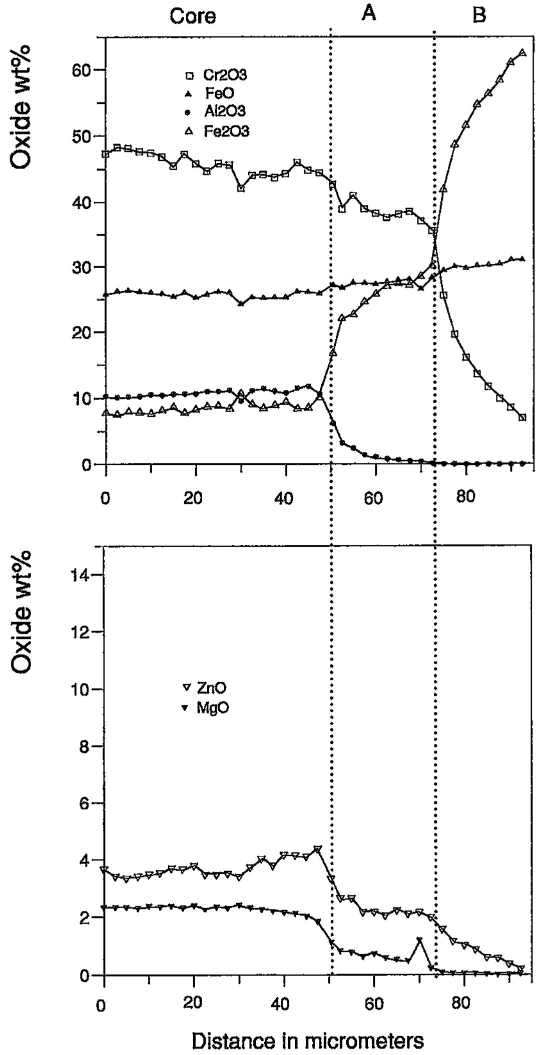

FIG. 5. Compositional variations from the center of the core to outer rim in one grain of type-II chromite from the Näätäniemi serpentinite massif. A: inner rim, and B: outer rim.

in Zn content in the chromite, with a uniformly high Zn content in the core, and a decrease toward the outer rim.

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