# ZINCOCHROMITE FROM THE GUANIAMO RIVER DIAMONDIFEROUS PLACERS, VENEZUELA: EVIDENCE OF ITS METASOMATIC ORIGIN

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## Abstract

Zincochromite associated with chromite and magnesiochromite was found in heavy-mineral concentrates from the Quebrada Grande placer deposit in the Guaniamo River diamondiferous district, Venezuela. It occurs in subhedral to anhedral grains from 0.1 to 0.7 mm in size. Reflectance measurements show an increase of reflectance values with FeFe<sub>2</sub>O<sub>4</sub> content in spinel solid solution. The Vickers microhardness (load 100 g) is 1367(84) kg/mm<sup>2</sup>. Zincochromite containing 60 mol.% ZnCr<sub>2</sub>O<sub>4</sub> has a unit cell with a value of a equal to 8.271(3) Å. As revealed by EPMA, zincochromite grains are markedly zoned, with the rim and microfissures enriched in Zn. Furthermore, the chromite crystals partly replaced by zincochromite indicate high-temperature metasomatic processes involving a Zn- and Mn-bearing fluid phase. All chromian spinel compositions observed underwent, more or less intensely, this replacement. The chemical formula of the zincochromite richest in Zn from Guaniamo can be written:  $(Zn_{6.499}Fe^{2+}_{0.613}Mn^{2+}_{0.511}Mg_{0.434}Ni_{0.022})_{\Sigma 8.079}(Cr_{9.639}Al_{4.742}Fe^{3+}_{1.262}Ti_{0.213}V^{3+}_{0.040})_{\Sigma 15.921}O_{32}. A large extent of Mn-for-Fe^{2+}_{0.613}Nn^{2+}$ substitution has been observed. In some grains, the number of Mn atoms per formula unit exceeds  $Fe^{2+}$ . Statistically, taking into account the Fe<sup>3+</sup> concentration, zincochromite was formed at higher oxygen fugacities than its chromite and magnesiochromite precursors. EPMA traverses of zoned zincochromite and Zn-bearing magnesiochromite crystals indicate the substitution mechanisms  $3Zn \rightarrow 2(Fe^{2+} + Mn) + Mg$  and  $4Zn \rightarrow (Fe^{2+} + Mn) + 3Mg$ , besides the  $Zn \rightarrow (Fe^{2+} + Mn)$  and  $Zn \rightarrow Mg$  replacements. Chromite and magnesiochromite contain low, but consistent Zn concentrations, which demonstrate an early Zn enrichment of the magmatic system. Their chemical compositions are compatible with chromian spinels occurring in diamondiferous kimberlites and lamproites. Considering the presence of Zn-bearing chromites in several kimberlite-bearing areas on a worldwide scale, the occurrence of zincochromite at Guaniamo points to its use as a mineral indicator of kimberlites.

Keywords: zincochromite, chromite, magnesiochromite, metasomatic processes, high-temperature Zn- and Mn-bearing fluid, heavy concentrates, kimberlites, lamproites, Guaniamo, Quebrada Grande placer, Venezuela.

## SOMMAIRE

La zincochromite associée à la chromite et la magnésiochromite a été observée dans des concentrés lourds provenant du placer de Quebrada Grande, situé dans le district diamantifère de Guaniamo au Venezuela. Elle se présente en cristaux subautomorphes à xénomorphes de 0.1–0.7 mm. Des mesures de pouvoir réflecteur montrent que celui-ci augmente avec la teneur en FeFe<sub>2</sub>O<sub>4</sub> en solution solide du spinelle. La microdureté Vickers (poids de 100 g) est de 1367(84) kg/mm<sup>2</sup>. La zincochromite contenant 60% (base molaire) de ZnCr<sub>2</sub>O<sub>4</sub> possède une maille avec *a* égal à 8.271(3) Å. Les analyses à la microsonde électronique révèlent que les cristaux de zincochromite sont remarquablement zonés, avec la bordure et les microfissures enrichies en Zn. Par ailleurs, les cristaux de chromite partiellement remplacés par la zincochromite font entrevoir des processus métasomatiques de haute température impliquant une phase fluide transportant Zn et Mn. Tous les grains observés ont subi, plus ou moins intensément, ce remplacement. La composition chimique de la zincochromite la plus riche en Zn s'écrit: (Zn<sub>6.499</sub>Fe<sup>2+</sup><sub>0.613</sub>Mn<sup>2+</sup><sub>0.511</sub>Mg<sub>0.434</sub>Ni<sub>0.022</sub>)<sub>28.079</sub> (Cr<sub>9.639</sub>Al<sub>4.742</sub>Fe<sup>3+</sup><sub>1.262</sub>Ti<sub>0.213</sub>V<sup>3+</sup><sub>0.040</sub>)<sub>215.921</sub>O<sub>32</sub>. Une substitution importante de Fe<sup>2+</sup> par Mn est observée. Certains cristaux présentent un nombre d'atomes de Mn par unité formulaire supérieur à Fe<sup>2+</sup>. Statistiquement, considérant la teneur en Fe<sup>3+</sup>, la zincochromite paraît s'être formée à une fugacité d'oxygène plus élevée que ses précurseurs, à savoir, la chromite et la magnésiochromite. Les traversées à la microsonde électronique des cristaux zonés de zincochromite et de magnésiochromite et de magnésiochromite et la magnésiochromite.

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zincifère montrent qu'outre les remplacements  $Zn \rightarrow (Fe^{2+} + Mn)$  et  $Zn \rightarrow Mg$ , les mécanismes de substitution suivants se présentent :  $3Zn \rightarrow 2(Fe^{2+} + Mn) + Mg$  et  $4Zn \rightarrow (Fe^{2+} + Mn) + 3Mg$ . La chromite et la magnésiochromite contiennent de faibles concentrations de Zn qui attestent d'un enrichissement précoce en Zn du système magmatique. Les compositions chimiques de ces spinelles sont compatibles avec les spinelles chromifères des kimberlites et lamproïtes diamantifères. En tenant compte de l'apparition des spinelles chromifères et zincifères dans plusieurs districts à kimberlites dans le monde, la zincochromite apparaît comme un minéral indicateur prometteur de ce type d'environnement.

*Mots-clés:* zincochromite, chromite, magnésiochromite, processus métasomatiques, fluide de haute température à Zn et Mn, concentrés lourds, kimberlites, lamproïtes, Guaniamo, placer de Quebrada Grande, Venezuela.

#### INTRODUCTION

In Venezuela, Zn-bearing spinels and the rare mineral zincochromite have been found in the Guaniamo River area, at the Quebrada Grande placer deposit located within the Guayana Shield Province. They occur in heavy concentrates from Pliocene – Quaternary alluvial deposits up to twenty meters thick, deposited on the granitic bedrock. The Quebrada Grande placer is diamondiferous, and has been exploited for several years.

In the heavy concentrates studied, zincochromite is associated with pyroxene, Mg-bearing ilmenite (2.6 to 3.5 wt.% MgO), Zn-bearing chromite, magnesiochromite, chromite, cassiterite, columbite–tantalite, topaz, monazite, rutile, zircon, pyroxene and native gold (Parfenoff 1979). This association reflects a mafic, kimberlitic or lamproitic source supplying zincochromite, chromian spinel, ilmenite and pyroxene on one hand, and a paragenesis typical of the granitic bedrock on the other.

The aim of this study is to provide analytical data on various grains of chromian spinel occurring in heavy concentrates and derived from mafic sources in order to: 1) determine their compositional variation, 2) study their subsequent chemical modifications, namely the behavior of Zn during the late-magmatic processes, 3) investigate the origin of the zincochromite by providing data on its composition, relationship with associated chromian spinel, with a view to estimate its conditions of formation. Furthermore, the application of Zn-bearing spinels for the exploration of diamondbearing kimberlite and lamprophyre is assessed.

## THE LOCAL GEOLOGICAL CONTEXT

The Guaniamo River area has been intensely prospected for kimberlites over the last thirty years. The diamondiferous deposits of the Venezuelan Guyana Shield were briefly described by Cassedanne (1979). According to Rodriguez *et al.* (1999), the Guaniamo River drains an important kimberlite-bearing district discovered in 1983, and comprising at least ten diamondiferous kimberlite sills. Sobolev *et al.* (1998) carried out a detailed mineralogical study of diamond crystals and noted that they are related to an eclogitic environment composed of silica-undersaturated corundum eclogites on the one hand and silica-rich, coesite eclogites, on the other. The latter probably originated from a subducted oceanic slab. An exhaustive study of diamond crystals was conducted by Kaminsky *et al.* (2000, 2006). They concluded that in large part, the diamondiferous placers were derived from the Guaniamo kimberlite sills; however, a substantial proportion of diamond related to an eclogitic source was recognized. Two separate diamond populations were observed, indicating their own primary sources.

## REVIEW OF THE LITERATURE ON ZN-RICH SPINELS

Spinel solid-solutions belonging to the gahnitehercynite series are well known and have been extensively studied (Saalfeld 1964, Stoddard 1979, Tulloch 1981, Batchelor & Kinnaird 1984, Sabatier 1986, Sandhaus & Craig 1986). In many cases, the occurrence of Zn-rich aluminous spinels is related to sulfide mineralization. This is, for example, the case of Cu-Pb-Zn-Ag deposits in Namaqualand, South Africa (Spry 1987), the Zn-Pb-Cu sulfide deposit at Mamandur, southern India (Chattopadhyay 1999), and the Broken Hill deposit in Australia (Spry et al. 2003). Considering these occurrences, Spry & Scott (1986) and Heimann et al. (2005) suggested the use of zincian spinel as a guide to sulfide ores. In contrast, solid solutions between MgAl<sub>2</sub>O<sub>4</sub> and ZnAl<sub>2</sub>O<sub>4</sub> are much less abundant in nature (Schmetzer & Bank 1985).

Zinc concentrations in chromian spinel are rather exceptional, restricted to metasomatic parageneses only locally related to sulfide mineralization. Zinc-bearing chromite was first reported from Norway by Donath (1931), and this occurrence was restudied by Seeliger & Mücke (1969) and Moore (1977). Thayer et al. (1964) described chromite containing 5.8 wt.% ZnO from the Outokumpu deposit in Finland. Zoned grains of chromite from the same deposit occurring in a contact zone between quartzite and serpentinite located at the hanging wall of the orebody were examined by Weiser (1967), who found up to 12.0 wt.% ZnO. He observed a concomitant increase in Zn and Al, implying the presence of a  $ZnAl_2O_4$  – FeCr<sub>2</sub>O<sub>4</sub> solid solution. Bevan & Mallinson (1980) reported zoned chromite containing up to 4.3 wt.% ZnO from the Mashaba chromite mine in Zimbabwe. Treloar et al. (1981) described chromian spinel containing up to 26.93 wt.% ZnO from the cordierite-amphibole-bearing rocks occurring in the vicinity of the Outokumpu deposit. The rim of chromite crystals is enriched in Zn with respect to the core. Significant concentrations of Zn, up to 5.6 wt.% ZnO, were found in chromian spinel related to Ni-Cu sulfide mineralizations in Western Australia (Groves et al. 1983). Wagner & Velde (1985) reported the occurrence of a Zn-bearing chromian spinel (up to 8.74 wt.% ZnO) in a peralkaline arfvedsonite-bearing minette at Plan d'Albard, France. Von Knorring et al. (1986) observed Zn-bearing chromite (up to 13.98 wt.% ZnO) included in uvarovite crystals from the Cr-bearing skarn mineralization associated with the Outokumpu copper deposit. Zoned zinc-rich chromian spinel (up to 19.09 wt.% ZnO) was discovered in a metapelite zone at the contact of Cu-Co-Zn mineralization associated with mafic-ultramafic rocks (Wylie et al. 1987). Lépine et al. (1988) and Béziat & Monchoux (1991) reported zincochromite from hydrothermally altered metabasic rocks associated with the Salsigne gold deposit, France. Magnetite with relics of Zn-bearing chromian spinel was observed at the Busovaca copper deposit, Bosnia and Herzegovina (Jurkovic & Jakšić 1994). Weiser & Hirdes (1997) conducted a detailed study of zincochromite with a maximum of 19.42 wt.% ZnO from the Tarkwa gold mine conglomerates in Ghana. Barnes (2000) reported a Zn enrichment in chromite in komatiites and concluded that it resulted from low-temperature alteration processes. Strongly zoned grains of chromian spinel with a Zn-rich core (up to 7 wt.% ZnO) and a Cr-rich magnetite rim occur in Yellowknife and Wawa lamprophyres in Canada (Armstrong & Barnett 2003). Gahlan & Arai (2007) described Co, Zn (up to 7.5 wt.% ZnO) and Mn-rich chromian spinel occurring in the mantle section of the Proterozoic Bou-Azzer ophiolite, Morocco.

In all these cases, except for the Zn-rich spinel from the Tarkwa (Weiser & Hirdes 1997), Outokumpu (Treloar *et al.* 1981) and Salsigne (Lépine *et al.* 1988, Béziat & Monchoux 1991) deposits, the chemical composition of spinel is characterized by the ratio [Zn/ $\Sigma M^{2+}$ ]<sub>at.</sub> < 0.5. We are thus dealing with in most cases a solid solution in which the ZnCr<sub>2</sub>O<sub>4</sub> component does not predominate. Consequently, such material must be classified as Zn-bearing chromite.

A spinel of composition ZnCr<sub>2</sub>O<sub>4</sub> discovered at the Velikaya Guba uranium deposit located in the Zaonezskiy Peninsula on the northern shore of Lake Onega, South Karelia, Russia, was defined as a new mineral named zincochromite by Nesterov & Rumyantseva (1987). It occurs in association with chromiferous aegirine, Cr-, V-bearing micas, chromdravite, dolomite and quartz. According to information from the New South Wales Mines Department in Sydney, zincochromite also occurs at Dolo Hills, Young County, N.S.W., Australia.

## METHODS OF INVESTIGATION

Electron-microprobe analyses (EPMA) were carried out using a CAMECA SX-50 instrument (BRGM- CNRS microprobe laboratory, C. Gilles, analyst) with analytical conditions as follows: 20 kV acceleration voltage, 20 nA sample current,  $K\alpha$  analytical lines for all the elements, standards: NaAlSi<sub>3</sub>O<sub>8</sub> (for Si and Al), TiO<sub>2</sub> (for Ti), Cr<sub>2</sub>O<sub>3</sub> (for Cr), MgAl<sub>2</sub>O<sub>4</sub> (for Mg), Fe<sub>2</sub>O<sub>3</sub> (for Fe), MnTiO<sub>3</sub> (for Mn), ZnO (for Zn), NiO (for Ni), and V metal (for V). The analytical results were corrected using the PAP correction program (Pouchou & Pichoir 1984). Detection limits, calculated using the method of Ancey *et al.* (1978), vary from 0.01 to 0.03 wt.%.

A scanning electron microscope (SEM) equipped with a Si(Li) detector was used for the investigation of compositional zoning of the zincochromite grains. The reflectivity of zincochromite was measured under the following operating conditions: plane-polarized light, normal incidence, monochromator, photomultiplier with the S<sub>20</sub> cathode, standard SiC, objective  $16 \times$ , half-field prism illuminator.

The procedure used for the calculation of the structural formula of the spinel is based on the number of atoms per formula unit obtained from EPMA results. Minor concentrations of Ni, V and Si were omitted, and the total  $[Fe^{2+} + Mn]_{at}$  was taken into account instead of individual Mn and  $Fe^{2+}$  values. The calculation steps were: (1)  $Fe^{3+}$  and  $Ti^{4+}$  are combined with the corresponding amount of Fe<sup>2+</sup> atoms in order to form  $FeFe_2O_4$  and  $FeTiO_3$ , respectively; (2) the  $ZnCr_2O_4$ component is obtained, and if Zn cannot be entirely accommodated, the ZnAl<sub>2</sub>O<sub>4</sub> component is calculated; (3) the  $Fe^{2+}$  and Cr remaining after these two steps are used to form FeCr<sub>2</sub>O<sub>4</sub>; if there is still an excess of  $Fe^{2+}$ , it is expressed as  $FeAl_2O_4$ ; (4) in the case of Cr remaining after the third step, the MgCr<sub>2</sub>O<sub>4</sub> component is calculated; (5) any remaining amounts of Mg and Al are used to form MgAl<sub>2</sub>O<sub>4</sub>. In general, a small residue of Mg atoms remains, which can be accounted for by Si and V, which were disregarded during the calculation procedure.

Assuming Ti<sup>4+</sup> introduction into the structure in the form of the Fe<sub>2</sub>TiO<sub>4</sub> component, the calculation of end members leads systematically to an important final excess of trivalent ions. For this reason, the calculation was done assuming the introduction of Ti<sup>4+</sup> as FeTiO<sub>3</sub>. This hypothesis yields consistent results, leaving only a very low Mg excess, as indicated above. It should be noted that an extensive solid-solution of FeTiO<sub>3</sub> in magnetite at high temperature was suggested by several authors (Chevallier *et al.* 1955, Nicholls 1955, Haggerty 1976).

#### THE GRAINS OF CHROMIAN SPINEL

The grains of chromian spinel range in size from about 0.1 to 0.7 mm. Two types of chromian spinel were observed in the samples studied: 1) Chromian spinel nearly devoid of Zn or showing Zn concentrations lower than 2 wt.%. In polished section, some of



FIG. 1. Back-scattered electron (BSE) image of a subhedral crystal of chromite extensively replaced metasomatically by zincochromite. The line of the EPMA traverse is indicated. The numbers refer to analytical points in Figure 5.

the subhedral grains exhibit a cracked and polygonized surface, indicating a volume variation due to chemical changes subsequent to the crystallization of the spinel (Fig. 1); others are homogeneous in reflected light. The EPMA results reveal that the chemical composition of these spinels corresponds to magnesiochromite and chromite (Table 1). 2) Smooth subhedral to anhedral grains of a Zn-rich chromian spinel (in general, ZnO > 12 wt.%). Some crystals are optically homogeneous, and can be classified as zincochromite (Nesterov & Rumyantseva 1987). Others show a well-developed zoning, only evident by EPMA. In some cases, the SEM examination reveals a metasomatic replacement leading to the formation of Zn-rich chromian spinel and zincochromite (Fig. 1), which is described further below. According to EPMA results, these grains can be classified as zincochromite, Zn-bearing chromite or Zn-bearing magnesiochromite (Fig. 2).

#### CHROMITE

The EPMA results reveal chemical compositions clustered around two distinct areas on the  $(Fe^{2+}+Mn)$  –

Zn – Mg plot (population E, Fig. 2), which differ in their  $[(Fe^{2+} + Mn)/Mg]_{at.}$  value. Chromite shows very high  $Cr_2O_3$  concentrations, reaching up to 62 wt.%, the  $Y_{Cr}$  values varying from 0.62 to 0.86 (Table 1, anal. 1 to 9).

Compositions 1 to 4 (Table 1) correspond to chromite enriched in Zn and Mn, and associated with zincochromite (Fig. 1). It is characterized by the average  $Y_{Cr}$ value of 0.63 and a [Cr/Al]at, value varying from 1.65 to 1.80. In comparison with the chromite compositions described below, its Fe<sup>3+</sup> content is close to zero. This indicates its formation at low fugacities of oxygen. Although the occupancy of octahedral sites is rather constant, an important variability exists with regards to the tetrahedral positions, causing a split between two clusters of the assemblage E on the  $(Fe^{2+} + Mn) -$ Zn – Mg diagram (Fig. 2). This is essentially due to a strong variation in the MgO content (Table 1, anal. 1,2 and 3,4, respectively). Note that this variation occurs within a single crystal of chromite (Fig. 1). These two compositions differ also in the MnO content, the Mg-poor chromite being enriched in manganese (Table 1). The Zn concentrations are generally higher than 1 wt.% ZnO. Besides FeCr<sub>2</sub>O<sub>4</sub>, the FeAl<sub>2</sub>O<sub>4</sub> component

appears among the calculated end-members, whereas  $MgCr_2O_4$  is systematically absent (Table 1).

The EPMA of three different grains of chromian spinel (Table 1, anal. 5 to 9) correspond to chromite (population E, Fig. 2). The compositions close to 80 at.% (Fe<sup>2+</sup> + Mn) (Table 1, anal. 5 to 8) are characterized by an average [Cr/Al]<sub>at.</sub> value equal to 5.1, whereas that approaching 70 at.% (Fe<sup>2+</sup> + Mn) (Table 1, anal. 9) exhibits a [Cr/Al]<sub>at.</sub> value of 8.4. This denotes a variability in chemical composition involving octahedral sites, including Fe<sup>3+</sup>. Taking into account its concen-

tration, the chromite grains with the highest (Fe<sup>2+</sup> + Mn) values appear to be formed at higher fugacities of oxygen (Table 1). Among minor elements, low but consistent concentrations of Ti were observed, as well as very low contents of Ni and V, which are near the EPMA detection limit. Tetrahedral positions are predominantly occupied by Fe<sup>2+</sup>. However, significant concentrations of Mn were noted, which correspond to 2.7–6.1 % of the occupancy of the tetrahedral sites. The Mn content decreases in concomitant manner with Fe<sup>2+</sup> (Table 1, anal. 9). Zinc was invariably detected; the

TABLE 1. SELECTED COMPOSITIONS OF CHROMITE AND MAGNESIOCHROMITE, GUANIAMO, VENEZUELA

		E										F			
	1	2	3	4	5	6	7	8	9	10	11	12			
$\frac{\text{SiO}_2 \text{ wt\%}}{\text{TiO}_2}$ $\frac{\text{Cr}_2\text{O}_3}{\text{V}_2\text{O}_3}$	0.06 0.10 48.93 0.10	0.02 0.22 49.40 0.13	0.03 0.12 46.95 0.12	0.03 0.11 46.49 0.06	0.06 0.24 57.05 0.05	0.05 0.21 57.90 0.05	0.07 0.24 57.73 0.05	0.07 0.32 54.98 0.00	0.11 0.11 62.53 0.00	0.10 0.18 60.31 0.11	0.09 0.24 59.23 0.00	0.01 0.23 57.76 0.02			
Al <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> * FeO MnO ZnO NiO	18.59 0.59 22.49 2.80 1.20 0.07	18.46 22.62 2.18 0.82 0.07	18.61 0.80 24.82 4.45 1.81 0.01	18.86 24.78 3.68 1.50 0.08	7.23 3.40 25.04 1.96 0.98 0.09	6.92 3.33 25.42 1.98 0.34 0.06	7.14 3.29 25.27 2.04 0.19 0.11	9.09 3.93 25.63 1.48 0.52 0.08	4.97 2.76 21.66 0.93 0.15 0.00	9.02 4.49 13.62 0.12 0.09 0.20	10.83 3.27 13.17 0.21 0.08 0.21	10.08 5.86 11.71 0.11 0.03 0.14			
MgO Total	5.75	6.05	2.76	2.91	3.33	3.62	3.65	3.85	6.62	13.01	13.16	14.18			
Si <i>apfu</i> ** Ti Cr V Al Fe <sup>3</sup> * Fe <sup>2</sup> * Mn Zn Ni Mg	0.015 0.019 10.099 0.020 5.720 0.116 4.909 0.619 0.231 0.014 2.238	0.004 0.042 10.240 0.028 5.706 - 4.960 0.483 0.158 0.015 2.363	0.007 0.024 9.914 0.026 5.858 0.161 5.544 1.007 0.357 0.002 1.099	0.009 0.021 9.971 0.012 6.028 - 5.620 0.845 0.301 0.017 1.174	0.017 0.051 12.763 0.012 2.409 0.725 5.926 0.469 0.204 0.204 1.404	0.014 0.044 12.879 0.011 2.293 0.706 5.980 0.471 0.071 0.013 1.517	0.019 0.051 12.833 0.011 2.366 0.697 5.942 0.486 0.040 0.025 1.530	0.018 0.067 12.086 - 2.979 0.822 5.960 0.348 0.107 0.018 1.594	0.030 0.023 13.726 - 1.627 0.576 5.029 0.218 0.031 - 2.740	0.026 0.034 12.290 0.019 2.741 0.870 2.935 0.027 0.017 0.042 4.998	0.022 0.046 11.992 3.269 0.648 2.899 0.045 0.015 0.043 5.021	0.002 0.045 11.745 0.002 3.056 1.134 2.519 0.024 0.007 0.030 5.436			
Y Y Y Y	0.634 0.359 0.007	0.642 0.358 -	0.622 0.368 0.010	0.623 0.377 -	0.803 0.151 0.046	0.811 0.144 0.045	0.807 0.149 0.044	0.761 0.187 0.052	0.862 0.102 0.036	0.773 0.172 0.055	0.754 0.205 0.041	0.737 0.192 0.071			
$X_{(Fe2*+Mn)} \\ X_{Zn} \\ X_{Mg}$	0.691 0.029 0.280	0.683 0.020 0.297	0.818 0.045 0.137	0.814 0.038 0.148	0.799 0.025 0.176	0.802 0.009 0.189	0.804 0.005 0.191	0.788 0.013 0.199	0.654 0.004 0.342	0.371 0.002 0.627	0.369 0.002 0.629	0.318 0.001 0.681			
FeFe <sub>2</sub> O <sub>4</sub> FeTiO <sub>3</sub> ZnCr <sub>2</sub> O <sub>4</sub> (Fe,Mn)Ce	0.73 0.16 2.89 r <sub>2</sub> O <sub>4</sub>	0.35 1.99	1.01 0.20 4.47	0.18 3.79	4.54 0.43 2.55	4.43 0.37 0.89	4.36 0.43 0.50	5.14 0.56 1.34	3.61 0.19 0.39	5.48 0.29 0.21	4.07 0.39 0.19	7.11 0.38 0.09			
MgCr <sub>2</sub> O <sub>4</sub> ZnAl <sub>2</sub> O <sub>4</sub> (Fe,Mn)Al	- - 2O4	- -	-	-	2.46	3.94	4.36	1.33	23.76	46.13	42.77	49.36 -			
MgAl <sub>2</sub> O <sub>4</sub>	7.93 27.91	5.52 29.72	23.13 13.57	22.18 14.80	15.09	- 14.39	- 14.82	18.64	- 10.19	16.83	20.26	- 18.83			

<sup>\*</sup> calculated for 24 cations and 64 positive charges. \*\* Calculated on the basis of 32 atoms of oxygen and normalized to 24 cations. \*\*\* Defined as  $Cr(ZM^{3*}, Al/ZM^{3*}, Fe^{2*}/ZM^{3*}, (Fe^{2*} + Mn)/\SigmaM^{2*}, Zn/ZM^{2*}, Mg/ZM^{2*}, ZM^{2*} = Fe^{2*} + Mn + Zn + Mg. The letters E and F refer to the plot shown as Figure 2. The data were acquired with an electron microprobe.$ 



FIG. 2. Plot of chemical compositions of chromian spinels from the Guaniamo River in terms of the  $M^{2+}$  cations. Results of EPMA traverses of four zoned crystals, A, B, C, D, are plotted (see Table 5 for analytical results). Populations E and F correspond to the Zn-poor chromite (E) and magnesiochromite (F) whose compositions are given in Table 1. Point G corresponds to the theoretical composition on which the zoned zincochromite crystals A to C converge (see text for explanations).

highest concentrations are close to 1 wt.% ZnO (Table 1, anal. 5 to 9). The calculation of end-members shows the predominance of  $FeCr_2O_4$  and a consistent presence of  $MgCr_2O_4$  (Table 1). The systematic absence of  $FeAl_2O_4$  is noteworthy.

#### MAGNESIOCHROMITE

Subhedral crystals having the composition of magnesiochromite are rather rare among the samples we studied. Our EPMA results are given in Table 1 (anal. 10 to 12). They reveal the maximum occupancy of tetrahedral sites by Mg equal to 67.8%. Magnesiochromite compositions plot on the  $(Fe^{2+} + Mn) - Zn$ - Mg diagram between 60 and 70 at.% Mg (Fig. 2, assemblage F). Its average  $Y_{Cr}$  value is 0.75, and the [Cr/Al]<sub>at.</sub> ratio is 4.0. The Ti and V concentrations are comparable to those observed for chromite. The average occupancy of octahedral positions by Fe<sup>3+</sup> is about 6%. Besides Mg and Fe<sup>2+</sup>, which are predominant at the tetrahedral sites, the presence of Mn, Zn and Ni is notable. Magnesiochromite is poor in Zn with respect to chromite, its concentration being invariably lower than 0.1 wt.% ZnO (Table 1). Furthermore, the Mn content is significantly lower than in chromite, but the Ni concentration is distinctly greater (Table 1).

#### ZINCOCHROMITE

This mineral forms subhedral crystals with predominant {111} and {011} or anhedral grains from 0.1 to 0.7 mm in size. It does not differ in its habit and size from chromite and magnesiochromite. Under the binocular microscope, the grains of zincochromite are dark green in case of crystals devoid of  $Fe^{3+}$  or reddish brown for grains with significant  $Fe^{3+}$  content. The luster is vitreous, and zincochromite is translucent in thin sections.

In reflected light, zincochromite is dark grey, showing rare green or reddish brown internal reflections, becoming quite visible in oil immersion. It is isotropic. The reflectivity was measured on two grains whose chemical composition differs in Fe<sub>2</sub>O<sub>3</sub> concentration. There is a notable increase of reflectance with the FeFe<sub>2</sub>O<sub>4</sub> content in solid solution (Table 2, Fig. 3). Thus, the Fe<sup>3+</sup>-free zincochromite, whose chemical formula can be written as  $(Zn_{0.601}Mg_{0.293}Fe^{2+}_{0.084}Mn_{0.034})_{\Sigma1.012}$  (Cr<sub>1.366</sub>Al<sub>0.611</sub>V<sub>0.005</sub>Ti<sub>0.004</sub>S<sub>0.002</sub>)<sub>\Sigma1.988</sub>O<sub>4</sub>, has a reflectance very close to that reported by Wylie *et al.* (1987) for Zn-rich chromite, being only slightly higher than the reflectance of chromite enriched in Fe<sup>3+</sup>, with a chemical formula  $(Zn_{0.571}Mg_{0.199}Fe^{2+}_{0.190}Mn_{0.048})_{\Sigma1.008}$ 

 $(Cr_{1.668}Al_{0.225}Fe^{3+}_{0.088}Ti_{0.008}V_{0.002})_{\Sigma 1.991}O_4$ , shows a significantly higher reflectance (Table 2, Fig. 3), which is, however, still lower than that of zincochromite from the Tarkwa deposit in Ghana, studied by Weiser & Hirdes (1997) (Fig. 3). The latter is characterized by a higher FeFe<sub>2</sub>O<sub>4</sub> content. As pointed out by these authors, there is a discrepancy between these data and the values published by Nesterov & Rumyantseva (1987) for nearly pure zincochromite, which are stated to be close to the reflectance of chromite (Fig. 3).

The Vickers microhardness (VHN) was measured on several grains using a load of 100 g. Ten indentations yielded the average value of 1367(84) kg/mm<sup>2</sup>, the measurements ranging from 1226 to 1427 kg/mm<sup>2</sup>. These values are much higher than the average VHN =  $620 \text{ kg/mm}^2$  (load 10–20 g) reported by Nesterov & Rumyantseva (1987).

TABLE 2. REFLECTANCE OF ZINCOCHROMITE FROM GUANIAMO IN AIR

λnm	R	(%)	λnm	R (%)				
	1	2		1	2			
420 440 460	15.3 14.2 13.8	17.5 16.3 15.6	560 580 600	12.6 12.5 12.4	14.3 14.1 14.0			
480 500 520 540	13.5 13.2 12.9 12.6	15.4 15.1 14.8 14.4	640 660 680 700	12.3 12.1 12.1 12.0 12.0	13.6 13.6 13.5 13.4			

The X-ray powder pattern (Table 3) was obtained from zincochromite devoid of Fe<sup>3+</sup> whose composition and reflectance are indicated above (Table 2, grain 1, 0.6 mm in size). The cell parameter a, refined by least squares, is 8.271(3) Å (V 565.9 Å<sup>3</sup>; Z = 8). The calculated density for the above given formula is 4.808  $g/cm^3$ .

Selected results of EPMA of zincochromite are given in Table 4. The analyses were carried out on about twenty different grains. The chromium concentration is highly variable,  $Y_{Cr}$  ranging from 0.61 to 0.84. This variation is independent of the Zn content. Similarly, a large range of Al concentrations is observed,  $Y_{Al}$  values varying from 0.11 to 0.37. Consequently, the [Cr/Al]at. varies from 1.65 to 7.40 (Table 4). With regards to the Fe<sup>3+</sup> content, it also exhibits an important variation, but the occupancy of octahedral positions by Fe<sup>3+</sup> does not exceed 8%. Unlike the zincochromite from Karelia (Nesterov & Rumyantseva 1987), the spinel examined is characterized by low concentrations of SiO<sub>2</sub> and V<sub>2</sub>O<sub>3</sub>,

TABLE 3. X-RAY POWDER PATTERN OF ZINCOCHROMITE FROM GUANIAMO

I	d(meas)	d(calc)	h	k	1	I	d(meas)	d(calc)	h	k	1
5 9 10 1 7 6 8	4.770 2.928 2.492 2.385 2.068 1.689 1.593	4.775 2.924 2.494 2.388 2.068 1.688 1.592	1 2 3 2 4 5	1 2 1 2 0 2	1 0 1 2 0 2	9 3 4 2 1 3 5 2	1.462 1.308 1.2615 1.2467 1.1939 1.1059 1.0764 1.0334	1.462 1.308 1.2614 1.2469 1.1939 1.1053 1.0768 1.0339	4 6 5 6 4 6 7 8	4 2 3 2 4 3 0	0 3 2 4 2 1 0

Ni-filtered CuKa radiation, camera 240 mm in circumference; the intensities were estimated visually. The values of d are expressed in Å.



FIG. 3. Reflectances of zincochromite in air. Symbols: mgt: magnetite, chr: chromite (Picot & Johan 1982); 1, 2: zincochromite, Guaniamo, Venezuela (Table 1, this paper); 3: zincochromite, Tarkwa, Ghana (Weiser & Hirdes 1997); 4: zincochromite, Sykesville, U.S.A. (Wylie et al. 1987); 5: Velikaya Guba, Russia (Nesterov & Rumyantseva 1987).

generally below the detection limits of our electron microprobe. The  $TiO_2$  concentration, although generally low, approaches 1 wt.% in some cases (Table 4).

As seen in Table 4, the  $X_{Zn}$  values range from 0.51 to 0.81. The zincochromite from Guaniamo is characterized by extensive substitution of Mn for Fe<sup>2+</sup>. The Mn content varies strongly from one grain to another. Consequently, the [Fe<sup>2+</sup>/Mn]<sub>at</sub> value ranges from 0.56 to 3.87, indicating that in some cases, the number of Mn atoms per formula unit exceeds Fe<sup>2+</sup>. The EPMA results show that the occupancy of tetrahedral sites by Mn commonly exceeds 10%, and can attain 13% (Table 4, anal. 3). The important variation in the  $X_{Mg}$  values reveals that substitutions at tetrahedral sites are much more complex than the simple (Fe<sup>2+</sup> + Mn)-for-Zn replacement. The calculation of end members allows us to conclude that for certain compositions, the Cr

concentration is not high enough to completely saturate Zn in the form of  $ZnCr_2O_4$ , thus accounting for the  $ZnAl_2O_4$  component.

The compositions of zincochromite can be divided into three distinct groups: (i)  $(Fe^{2+} + Mn)$  is present exclusively as  $(Fe,Mn)Al_2O_4$ , (ii)  $(Fe^{2+} + Mn)$  forms  $(Fe,Mn)Cr_2O_4$  and  $(Fe,Mn)Al_2O_4$  end-members, or (iii)  $(Fe,Mn)Al_2O_4$  is absent and  $(Fe^{2+} + Mn)$  forms exclusively  $(Fe,Mn)Cr_2O_4$  associated with MgCr\_2O\_4 (Table 4). This reflects extensive chemical variations in the occupancy of octahedral and tetrahedral positions of the structure of zincochromite.

The EPMA traverses were performed on several subhedral crystals of Zn-bearing chromian spinel. The results of four of them (A to D) are plotted on the  $(Fe^{2+} + Mn) - Zn - Mg$  diagram (Fig. 2), and selected compositions are given in Table 5. Three crystals exam-

TABLE 4. SELECTED COMPOSITIONS OF ZINCOCHROMITE, GUANIAMO, VENEZUELA

	1	2	3	4	5	6	7	8	9	10	11
SiO, wt%	0.09	0.21	0.02	0.00	0.16	0.09	0.06	0.03	0.05	0.11	0.11
TiO	0.99	0.95	0.02	0.65	0.08	0.02	0.11	0.28	0.26	0.88	0.09
Cr <sub>2</sub> Ô <sub>2</sub>	42.69	42.70	52.61	56.16	44.12	43.52	50.64	58.49	46.72	51.51	56.90
V,0,	0.18	0.13	0.06	0.00	0.07	0.00	0.22	0.06	0.13	0.08	0.09
Al,Õ,	14.09	14.19	10.43	6.79	16.99	17.70	15.19	5.30	13.92	9.58	7.40
Fe <sub>3</sub> O <sub>3</sub> *	5.87	5.52	1.08	2.30	1.78	2.19	0.41	3.47	4.43	4.54	4.43
FeÔ	2.57	2.18	2.56	1.33	9.11	9.13	2.56	6.08	8.45	5.23	3.65
MnO	2.11	3.44	4.25	2.36	2.75	2.93	1.18	1.55	4.07	3.32	2.91
ZnO	30.82	29.99	28.53	26.31	24.12	23.92	23.84	21.47	20.17	20.04	19.85
NiO	0.10	0.10	0.00	0.00	0.05	0.00	0.00	0.04	0.02	0.06	0.10
MgO	1.02	0.88	0.40	3.37	0.38	0.53	5.76	3.70	2.15	4.35	5.69
Total	100.53	100.29	99.96	99.27	99.61	100.03	99.97	100.47	100.37	99.70 <sup>-</sup>	101.22
Si apfu**	0.025	0.060	0.006	-	0.046	0.026	0.015	0.009	0.014	0.032	0.031
Ti	0.213	0.203	0.004	0.144	0.016	0.004	0.023	0.060	0.054	0.186	0.018
Cr	9.639	9.655	12.147	12.965	9.864	9.649	10.935	13.342	10.354	11.530	12.554
V	0.040	0.024	0.014	-	0.013	-	0.039	0.011	0.023	0.016	0.017
AI	4.742	4.782	3.589	2.337	5.660	5.849	4.890	1.802	4.597	3.196	2.434
Fe³⁺	1.262	1.188	0.237	0.506	0.380	0.462	0.085	0.753	0.935	0.967	0.930
Fe <sup>2+</sup>	0.613	0.522	0.625	0.324	2.155	2.142	0.584	1.468	1.981	1.239	0.851
Mn	0.511	0.834	1.051	0.583	0.658	0.696	0.273	0.379	0.965	0.796	0.687
Zn	6.499	6.325	6.152	5.672	5.037	4.952	4.808	4.573	4.174	4.190	4.090
Ni	0.022	0.024	-	-	0.011	-	-	0.010	0.003	0.013	0.022
Mg	0.434	0.374	0.174	1.468	0.160	0.220	2.346	1.591	0.898	1.835	2.365
Y <sub>Cr</sub> ***	0.616	0.618	0.760	0.820	0.620	0.605	0.688	0.839	0.652	0.735	0.789
Y <sub>AI</sub>	0.303	0.306	0.225	0.148	0.356	0.366	0.307	0.113	0.289	0.204	0.153
Y <sub>Fe3+</sub>	0.081	0.076	0.015	0.032	0.024	0.029	0.005	0.048	0.059	0.061	0.058
X (Fe2+ + Mn)	0.139	0.168	0.209	0.113	0.351	0.355	0.107	0.230	0.367	0.252	0.192
$X_{Zn}$	0.807	0.785	0.769	0.705	0.629	0.618	0.600	0.571	0.521	0.520	0.512
X <sub>Mg</sub>	0.054	0.046	0.022	0.182	0.020	0.027	0.293	0.199	0.112	0.228	0.296
FeFe <sub>2</sub> O <sub>4</sub>	7.92	7.47	1.48	3.16	2.39	2.89	0.53	4.71	5.86	6.06	5.83
FeTiO <sub>3</sub>	1.78	1.70	0.03	1.20	0.13	0.03	0.19	0.50	0.45	1.56	0.15
ZnCr <sub>2</sub> O <sub>4</sub>	60.52	60.74	76.02	70.90	61.94	60.44	60.33	57.25	52.31	52.57	51.31
(Fe,Mn)Cr <sub>2</sub> C	Ĵ₄ -	-	-	6.38	-	-	8.27	17.65	12.57	17.13	13.24
MgCr <sub>2</sub> O <sub>4</sub>	-	-	-	3.76	-	-	-	8.61	-	2.63	14.20
∠nAl <sub>2</sub> O <sub>4</sub>	21.08	18.83	0.98	-	1.32	1.60	-	-	-	-	-
(⊢e,Mn)Al₂C	0 <sub>4</sub> 3.52	7.03	19.44	-	32.74	32.61	1.66	-	17.81	-	-
MgAl <sub>2</sub> O <sub>4</sub>	5.17	4.22	2.04	14.60	1.48	2.43	29.02	11.28	11.00	20.05	15.27

\* Calculated for 24 cations and 64 positive charges. \*\* Calculated on the basis of 32 atoms of oxygen and normalized to 24 cations. \*\*\* See Table 1 for definition. The compositional data were acquired with an electron microprobe. ined (A to C) can be classified as zincochromite, and the fourth one (D) is Zn-rich magnesiochromite (Fig. 2). Despite the fact that most of zincochromite crystals are optically homogeneous, our EPMA results reveal that they are markedly zoned. In general, their rims are enriched in Zn and impoverished in Mg with respect to the cores. Moreover, an enrichment in Zn occurs along the microfissures (Fig. 4). An interesting association of zincochromite and chromite within a single crystal is illustrated in Figure 1. It shows a pervasive replacement of chromite (Table 1, anal. 1 to 4; Fig. 2 population E) by zincochromite (Table 5, anal. 1 to 4; Fig. 2, population A). Relics of chromite remain in several islets cemented and enveloped by veinlets of zincochromite, which also forms a thin rim on the original chromite crystal (Fig. 1).

TABLE 5. SELECTED COMPOSITIONS OF ZONED CRYSTALS OF ZINCOCHROMITE AND Zn-RICH CHROMIAN SPINEL, GUANIAMO, VENEZUELA

	А				В				С				D			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SiO <sub>2</sub> wt% TiO <sub>2</sub>	0.06 0.10	0.03 0.17	0.00 0.12	0.24 1.23	0.08 0.29	0.18 0.22	0.04 0.37	0.10 0.29	0.01 0.30	0.01 0.30	0.01 0.31	0.02 0.30	0.00 0.11	0.03 0.12	0.01 0.13	0.00 0.12
$Cr_2O_3$ $V_2O_3$	43.58 0.06	45.58 0.11	41.34 0.07	47.43 0.20	44.87 0.18	45.51 0.16	45.99 0.16	45.88 0.21	53.90 0.11	52.65 0.13	53.47 0.10	52.72 0.13	53.96 0.06	54.98 0.10	54.47 0.10	54.98 0.07
Al <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> *	18.83	15.76	18.21 2.88	13.32	14.53 4.62	13.98 4.91	13.78 5.15	13.70 5.07	11.39 3.19	11.12 2.94	10.76	9.92 2.51	12.28 3.94	12.10 3.18	11.61 2.46	11.87 3.18
FeO MnO ZnO	2.81	10.88 3.62 21.45	3.62	3.66	4.27 21.44	5.19 3.79 25.61	8.69 4.68 18.78	7.48 4.33 21.11	4.92 5.01	3.02 6.38	4.19	3.15 4.61	3.98 3.11	4.57 3.11	3.92 3.45	4.22 3.22
NiO MgO	0.01	0.00	0.05	0.02	0.04	0.05	0.07	0.00	0.05	0.01	0.07	0.06	0.16	0.08	0.10	0.09
Total	101.47	100.10	98.45 1	100.80	99.50 1	00.93 1	100.03	100.18 1	100.80	99.44 1	100.08	99.76	99.88	100.22	99.43 <sup>-</sup>	100.47
Si apfu **	0.017	0.008	-	0.068	0.023	0.049	0.011	0.027	0.003	0.004	0.004	0.006	-	0.009	0.002	-
Cr V	9.456	10.186	9.256 0.015	10.619	10.026	0.040	0.078	10.214	0.082	0.084	0.005	0.005	11.328	0.023	0.020	0.023 11.589 0.015
Al Fe³⁺	6.090 0.391	5.249 0.480	6.078 0.615	4.444	4.839 0.983	4.646	4.556	4.547	3.651 0.652	3.654 0.617	3.544 0.530	3.358 0.542	3.842 0.788	3.779 0.635	3.723 0.503	3.728 0.637
Fe²⁺ Mn	2.431 0.654	2.571 0.867	2.679 0.869	2.904 0.877	1.720 1.022	1.223 0.906	2.038 1.113	1.761 1.034	1.119 1.154	0.704 1.506	0.979 1.041	0.757 1.121	0.883 0.699	1.014 0.698	0.892 0.796	0.942 0.726
Zn Ni	4.619 0.001	4.477	4.269 0.011	4.173 0.005	4.474 0.008	5.333 0.010	3.890 0.016	4.390	3.089 0.011	3.634 0.003	4.035 0.015	5.054 0.014	2.380 0.034	2.345 0.016	3.045 0.022	2.660 0.019
Mg	0.306	0.100	0.180	0.151	0.802	0.558	0.971	0.843	2.648	2.176	1.952	1.079	4.011	3.937	3.253	3.660
Y*** Y	0.593 0.382	0.640 0.330	0.580 0.381	0.685 0.286	0.633 0.305	0.641 0.293	0.644 0.287	0.645 0.287	0.729 0.230	0.731 0.230	0.744 0.223	0.754 0.212	0.710 0.241	0.723 0.237	0.735 0.234	0.726 0.234
Υ <sub>Fe3+</sub> X <sub>(Fe2++Mn)</sub>	0.025 0.385	0.030 0.429	0.039 0.444	0.029 0.466	0.062 0.342	0.066 0.265	0.069 0.393	0.068 0.348	0.041 0.284	0.039 0.276	0.033 0.252	0.034 0.234	0.049 0.198	0.040 0.214	0.031 0.211	0.040 0.209
X <sub>Zn</sub> X <sub>Mg</sub>	0.577 0.038	0.559 0.012	0.534 0.022	0.515 0.019	0.558 0.100	0.665 0.070	0.486 0.121	0.547 0.105	0.386 0.330	0.453 0.271	0.504 0.244	0.631 0.135	0.299 0.503	0.293 0.493	0.382 0.407	0.333 0.458
FeFe <sub>2</sub> O <sub>4</sub>	2.45	3.01	3.85 0.22	2.85	6.17 0.51	6.56 0.39	6.82 0.65	6.76 0.51	4.08	3.86 0.53	3.32 0.54	3.40 0.54	4.94 0.18	3.98 0.19	3.16	3.99 0.19
ZnCr <sub>2</sub> O <sub>4</sub> (Fe,Mn)Cr <sub>2</sub>	57.86 ,O₄	56.09	53.44	52.61	56.17	63.83	48.78	55.16	38.68	45.53	50.53	63.32	29.88	29.37	38.17	33.33
MgCr <sub>2</sub> O <sub>4</sub>	1.37 -	7.72 -	4.49	14.33	6.77 -	-	15.18 -	9.00 -	23.60 10.26	23.01 4.17	21.16 2.26	11.70 -	14.65 26.57	17.17 25.61	17.68 17.58	16.62 22.66
∠nAl₂O₄ (Fe,Mn)Al₂	04 24 56	-	-	-	-	3.26	-	-	-	-	-	-	-	-	-	-
$MgAl_2O_4$	34.56 3.58	0.98	35.74 2.25	0.81	20.73 9.65	6.31	12.04	9.98	- 22.86	- 22.89	- 22.19	7.62 13.42	- 23.78	- 23.67	23.19	23.20

\* Calculated for 24 cations and 64 positive charges. \*\* Calculated on the basis of 32 atoms of oxygen and normalized to 24 cations. \*\*\* See Table 1 for definition. The letters A, B, C, D refer to the plot shown as Figure 2. The compositional data were acquired with an electron microprobe. The EPMA traverse (Fig. 5) shows sharp compositional differences between the two types of spinel. As mentioned above, the rim is strongly enriched in Zn (up to 26 wt.% ZnO). The manganese distribution does not exhibit any important variations between chromite and zincochromite (Fig. 5). Statistically, an increase of Fe<sup>3+</sup> concentration is observed in zincochromite, but remains nearly constant on the grain scale. The  $Y_{Cr}$  of zincochromite lies between 0.58 and 0.69 (Table 5). The zincochromite A is characterized by very low Mg, which ranges from 1.2 to 3.8% at tetrahedral sites. Thus, taking into account a rather constant concentration of Mg, the major variation within the tetrahedral sites consists in a Zn-for-(Fe<sup>2+</sup> + Mn) substitution (Fig. 2).

The crystal of type B contains several minute inclusions of incompletely replaced chromite with  $X_{7n}$  equal to 0.37 (Fig. 2). The make-up of the octahedral site is remarkably constant, except for chromite inclusions, for which the Cr content slightly increases ( $Y_{Cr} = 0.66$ ) compared to zincochromite (Table 5). The EPMA traverse reveals a concomitant variation of Mg and Mn throughout the crystal, with an average [Mg/Mn]<sub>at</sub> value of 0.77 ( $\sigma = 0.11$ ). According to Figure 2, the Zn increase implies a decrease not only in (Fe<sup>2+</sup> + Mn) as for grain A, but also in Mg. The  $X_{Zn}$  value varies from 0.49 to 0.67. The calculated correlation in the plot of zincochromite B compositions (Fig. 2) intercepts the  $(Fe^{2+} + Mn) - Zn$  axis at  $[(Fe^{2+} + Mn)_{0.135}Zn_{0.865}]$ , and the  $(Fe^{2+} + Mn) - Mg$  axis at  $[(Fe^{2+} + Mn)_{0.710}Mg_{0.290}]$ . This leads to the substitution scheme  $Zn \rightarrow 0.665 (Fe^{2+})$ + Mn) + 0.335Mg or, more simply,  $Zn \rightarrow 0.666(Fe^{2+} +$ 



FIG. 4. Results of EPMA traverse of zincochromite (grain C, Fig. 2, Table 5). Rims are enriched in Zn. Furthermore, a Zn enrichment appears along microfissures. The average spacing of analytical points is 39 μm. Symbols: ♦ with heavy line: ZnO, ▲ with dashed line: MgO, × with solid line: FeO (calculated), ● with dashed line: MnO, ■ with solid line: Al<sub>2</sub>O<sub>3</sub>, \* with solid line: Cr<sub>2</sub>O<sub>3</sub>, ■ with dashed line: Fe<sub>2</sub>O<sub>3</sub> (calculated).

Mn) + 0.333Mg, which corresponds to the substitution  $3Zn \rightarrow 2(Fe^{2+} + Mn) + Mg.$ 

The EPMA results show that the grains of type C (Fig. 2) are characterized by a rim enriched in Zn and a progressive decrease of Zn content toward the core (Fig. 4). The composition of octahedral sites remains nearly constant (Table 5), with the mean value of  $Y_{Cr}$ (standard deviation shown in parentheses) 0.74(0.01),  $Y_{A1}0.22(0.01)$  and  $Y_{Fe3+}0.04(0.01)$ . The MnO content rises smoothly from the rim (3.6 wt.%) to the core (6.4 wt.%) of the crystal. The magnesium concentration is inversely correlated with the Zn content. The  $X_{Zn}$  values range from 0.39 to 0.63. The calculated correlation line intercepts the axes in the plot on Figure 2 at  $[(Fe^{2+} +$  $Mn_{0.178}Zn_{0.822}$  and [(Fe<sup>2+</sup> + Mn)<sub>0.380</sub>Mg<sub>0.620</sub>], respectively. This yields  $\text{Zn} \rightarrow 0.246(\text{Fe}^{2+} + \text{Mn}) + 0.754\text{Mg}$ , which is close to  $Zn \rightarrow 0.25(Fe^{2+} + Mn) + 0.75Mg$ . As a result, the substitution can be expressed as  $4Zn \rightarrow$  $(Fe^{2+} + Mn) + 3Mg.$ 

The Zn-rich magnesiochromite (grain D, Fig. 2, Table 5) exhibits, like zincochromite grains (A to C), a Zn-enriched rim of zincochromite with 19.58 wt.% ZnO (Fig. 2). The core shows Zn concentrations close to 12 wt.% ZnO. Disregarding the extremely Zn-rich value,  $X_{Zn}$  varies from 0.29 to 0.38 (Table 5, Fig. 2). As to Mn, its concentration remains nearly constant, with a mean of 3.22 (0.16) wt.% MnO, except for the rim, where it increases up to 4.31 wt.%. The occupancy of octahedral sites is remarkably constant, with an average [Cr/Al]<sub>at</sub>. value of 3.06. As can be seen in Figure 2, the composition of tetrahedral sites remains at a nearly constant value of (Fe<sup>2+</sup> + Mn), on average 20.76 (0.70) at.%. Thus, the zoning of this crystal can be interpreted in terms of a simple Zn → Mg substitution.

#### DISCUSSION

To our knowledge, the zincochromite from the Guaniamo River area is the second richest specimen in Zn observed in nature after that described as a new mineral from Karelia, Russia, which is very close to the ZnCr<sub>2</sub>O<sub>4</sub> end-member (Nesterov & Rumyantseva 1987). The SEM and EPMA investigations reveal that the Guaniamo River zincochromite originated by the metasomatic replacement of chromite and magnesiochromite by a Zn- and Mn-bearing high-temperature fluid. All compositions of primary chromite and magnesiochromite underwent a partial or total transformation by this metasomatic fluid, leading to Zn-rich chromian spinel or zincochromite. This explains a large chemical variability among Zn-rich chromian spinels (Fig. 2), which is due to a large variation in chemical composition of their precursors. It seems, however, that statistically, the crystals of chromite were more commonly replaced than crystals of magnesiochromite.

We stress that there is no evidence of primary zincochromite or even Zn-rich chromian spinel. All of these compositions are of metasomatic origin. As is



FIG. 5. Results of EPMA traverse of the chromite crystal shown in Figure 1 (grain A, Fig. 2, Table 5). The average spacing of analytical points is 31 μm. Symbols: ♦ with heavy line: ZnO, ▲ with solid line: MgO, ♦ with light line: FeO (calculated), ● with solid line: MnO, ● with dashed line: Al<sub>2</sub>O<sub>3</sub>, ■ with solid line: Cr<sub>2</sub>O<sub>3</sub>, ■ with dashed line: Fe<sub>2</sub>O<sub>3</sub> (calculated).

obvious from textural relationships, the metasomatic process took place after the crystallization of the chromian spinel, during the late magmatic stages. Low but consistent Zn contents in chromite and magnesiochromite, approaching 1 wt.% ZnO (Table 1), indicate an enrichment of the magmatic system in Zn since its early stages.

Note that the correlation lines calculated for the plot of zoned crystals (A to C) on Figure 2 converge to a point whose composition (in at.%) is close to:  $[Zn_{80}(Fe^{2+} + Mn)_{18}Mg_2]$  which, recalculated on the basis of eight atoms, gives the following composition of the tetrahedral sites for the theoretical zincochromite richest in Zn:  $[Zn_{6.400}(Fe^{2+} + Mn)_{1.440}Mg_{0.160}]_{\Sigma 8}$  (Fig. 2, point G). We believe that this composition reflects the proportions of  $M^{2+}$  elements in equilibrium with the fluid phase. This is corroborated by the compositions of zincochromite richest in Zn (Table 4, anal. 1 to 3), which plot near this theoretical point. Furthermore, the maximum Zn concentration for the zincochromite examined corresponds to  $X_{Zn}$  of 0.81 (Table 4, anal. 1), which thus confirms our hypothesis.

Taking into account an important decrease in  $[Fe^{2+}/Mn]_{at}$  in zincochromite with respect to chromite and magnesiochromite (Tables 1, 4 and 5), the transport of Mn *via* the fluid phase becomes a likely explanation.

However, the Mn distribution within zincochromite crystals does not show a well-pronounced zoning, which would imply different rates of diffusion for Zn and Mn (Bevan & Mallinson 1980). It is interesting to recall that the site-preference energy for <sup>IV</sup>Mn<sup>2+</sup> is as high as for <sup>IV</sup>Zn<sup>2+</sup> (Navrotsky & Kleppa 1967). This explains the different behavior of Mn<sup>2+</sup> with respect to Fe<sup>2+</sup> and Mg<sup>2+.</sup> The concentration of vanadium is higher in zincochromite than in the chromian spinels devoid in Zn (Tables 1, 4). This indicates a possible presence of V in the fluid. The role of metasomatic processes involving a fluid phase and being responsible for the formation of Zn-rich chromian spinels is mentioned by Weiser (1967), Schidlowski (1970), Bevan & Mallinson (1980), Wylie *et al.* (1987) and Frey (1988).

Recently, the occurrence of Zn-rich chromian spinel was reported from several diamondiferous areas around the world. The use of this mineral as an indicator of kimberlites has been suggested by Armstrong & Barnett (2003). These authors stressed the fact that chromite with elevated Zn (up to 7 wt.% ZnO), low Mg and Al, moderate to high Cr and moderate to low total Fe has been documented as inclusions in diamond from Sierra Leone and Brazil. Furthermore, zinc-rich chromite was found at the Nsork area of Rio Muni, Equatorial Guinea, and is considered as the principal mineral indicator of

the metakimberlites at Mitzic (Gabon). Menzies *et al.* (2003) stated that any potential change in Zn concentration of chromite is of interest in kimberlite prospection owing to the empirically observed relationship with temperature. Considering these various observations, the Guaniamo River occurrence of zincochromite reinforces its use as a mineral indicator of kimberlite.

The moderate occupancy of octahedral sites by Al and the low Mg content distinguish the suite studied from chromian spinel occurring in ophiolitic complexes (Augé 1982, Dick & Bullen 1984, Johan 1986, Thalhammer 1996), Alaskan-type intrusions (Nixon *et al.* 1990, Slansky *et al.* 1991, Malitch 1996, Johan *et al.* 2000, Johan 2002, 2006) and stratiform intrusions (Irvine 1967, Prendergast 1987, Hatton & Von Gruenewaldt 1987). On the other hand, there are similarities with chromian spinel observed in kimberlites (Boyd & Nixon 1975, Mitchell & Clarke 1976, Mitchell 1978, Gurney *et al.* 1993, O'Brien & Tyni 1999, Barnes & Roeder 2001, Armstrong & Barnett 2003, Menzies *et al.* 2003, Sobolev & Logvinova 2005, McKinnon-Matthews 2005, Roeder & Schulze 2008).

Although the complexly zoned grains of chromian spinel showing the "magnesio-ulvöspinel - magnetite trend typical of kimberlite (Mitchell & Clarke 1976, Mitchell 1978, O'Brien & Tyni 1999, Daniels 2003, Roeder & Schulze 2008) were not observed in the heavy mineral concentrates studied, there are some indications that the Guaniamo River suite of chromian spinel can be attributed a kimberlitic or lamprophyric origin. First of all, high Cr<sub>2</sub>O<sub>3</sub> contents (Table 1) are characteristic of chromian spinel included in diamond (Gurney et al. 1993, Kaminsky et al. 2000). Taking into account the South Australian diamond exploration database (McKinnon-Matthews 2005), the suite of Guaniamo chromite and magnesiochromite (Table 1) falls within the Argyle lamproite field on the Cr<sub>2</sub>O<sub>3</sub> – MgO diagram. Furthermore, chromite from Guaniamo shows low MgO and elevated MnO contents (Table 1). Similar compositions were reported by Armstrong & Barnett (2003) from the Yellowknife and Wawa lamprophyres. As has been already mentioned, these compositions of chromian spinel, like those from Guaniamo, are enriched in Zn. It must be stressed that Sobolev & Logvinova (2005) studied heavy mineral concentrates from kimberlite and lamproite of the Udachnaya pipe in Yakutia, and concluded that accessory chromian spinel displays a wide range of Mg# (50-80) and Cr# (20-90) in contrast with the chromian spinel included in diamond crystals, which show a relatively narrow range of Cr# (75-90), but a wide range in Mg# (50-80). The chemical composition of chromian spinel grains from Guaniamo is compatible with these compositional limits, which are, however, so large that their discriminatory value is rather low. Finally, we stress the fact that the large compositional variability of chromian spinel occurring in heavy mineral concentrates at Guaniamo reflects a complex history of the source rocks, including their transformation by high-temperature metasomatic processes involving a fluid phase.

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