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ZINC-RICH CHROMITE FROM PALEOPROTEROZOIC CONGLOMERATES AT TARKWA GOLD MINE, GHANA

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ABSTRACT

Zn-rich chromite is an extremely rare detrital constituent in gold-bearing meta-conglomerates of the Paleoproterozoic Tarkwaian Group of Ghana. Electron-microprobe analyses of the chromite give a mean Zn content of 13.30 wt.% ZnO, with the general formula $(Fe_{0.64}Zn_{0.36})_{\Sigma 1.00}(Cr_{1.45}Al_{0.33}Fe_{0.22})O_4$. The highest measured Zn content, 19.42 wt.% ZnO, yields the structural formula $(Zn_{0.51}Fe_{0.49})_{\Sigma 1.00}(Cr_{1.12}Al_{0.68}Fe_{0.20})_{\Sigma 2.00}O_4$, which corresponds to an (Fe,Al)-rich zincochromite. Reflectance values for this composition, measured between 400 and 700 nm in air, decrease steadily from 17.0 to 14.6% with increasing Zn content. The chemical data demontrate a large field of solid solution between chromite and zincochromite, and an extended miscibility gap in the system $(Zn,Fe)Cr_2O_4 - ZnFe_2O_4 - ZnAl_2O_4$, at least above 50 at.% $(Zn,Fe)Cr_2O_4$. The origin of the Zn-rich chromite at Tarkwa is uncertain. In the paleosource area of the Tarkwaian conglomerates, a few examples of ultramafic rocks are known, but these carry Zn-poor chromite.

Keywords: Zn-rich chromite, zincochromite, electron microprobe analyses, reflectance data, conglomerate, Paleoproterozoic, Tarkwa, Ghana.

SOMMAIRE

La chromite zincifère est un très rare composant détritique des métaconglomérats aurifères du Groupe Tarkwaien, d'âge paléoprotérozoïque, au Ghana. Les analyses à la microsonde électronique donnent, en moyenne, 13.30% en poids de ZnO dans la chromite, ce qui correspond à une formule structurale $(Fe_{0.64}Zn_{0.36})_{\Sigma 1.00}(Cr_{1.45}Al_{0.33}Fe_{0.22})O_4$. La teneur maximale en Zn, 19.42%, mène à la formule structurale $(Zn_{0.51}Fe_{0.49})_{\Sigma 1.00}(Cr_{1.12}Al_{0.68}Fe_{0.20})_{\Sigma 2.00}O_4$, ce qui correspond à une zincochromite riche en Fe et Al. La réflectance de ce matériau, mesurée entre 400 et 700 nm dans l'air, diminue de façon monotone de 17.0 à 14.6%. Les données chimiques indiquent l'existence d'une solution solide étendue entre chromite et zincochromite, et une lacune de miscibilité importante dans le système $(Zn,Fe)Cr_2O_4 - ZnFe_2O_4 - ZnAl_2O_4$, du moins pour les compositions contenant plus de 50% $(Zn,Fe)Cr_2O_4$ (base molaire). L'origine des grains de chromite zincifère demeure incertaine. Dans le socle d'où proviendrait le détritus des conglomérats tarkwaïens, il y a quelques exemples de roches ultramafiques, mais celles-ci contiennent la chromite typique, à faible teneur en Zn.

(Traduit par la Rédaction)

Mots-clés: chromite zincifère, zincochromite, données de microsonde électronique, données de réflectance, conglomérat, âge paléoprotérozoïque, Tarkwa, Ghana.

INTRODUCTION

Zinc-bearing chromite was first described by Donath (1930, 1931) from Norway. Since then, the development of the electron microprobe has resulted in discovery of additional occurrences of Zn-rich chromite the world over (*e.g.*, Thayer *et al.* 1964, Weiser 1966, 1967a, b, Schidlowski 1970, Groves *et al.* 1977, Utter 1978, Bevan & Mallinson 1980, Wagner & Velde 1985, Treloar 1987, Wylie *et al.* 1987, Béziat & Monchoux 1991, Bjerg *et al.* 1993, Challis *et al.* 1995, Liipo *et al.* 1995, Sánchez-Vizcaíno *et al.* 1995). A new mineral, zincochromite, $ZnCr_2O_4$, was proposed by Nesterov & Rumjantzeva (1987) and accepted by the Commission on New Minerals and Minerals Names (CNMMN). Oddly, re-examination of the original material of Donath from Norway by Weiser (1966, 1967a) and Moore (1977) did not confirm the high contents of zinc.

The aim of this paper is to describe a new occurrence of Zn-bearing chromite from Ghana containing the highest Zn content ever reported.

GEOLOGICAL SETTING AND MINERALOGICAL ASPECTS

The Paleoproterozoic Tarkwaian Group of Ghana contains one of the three known occurrences of early

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Precambrian quartz-pebble conglomerate currently mined for gold, the others being the Witwatersrand goldfields of South Africa and the Serra de Jacobina goldfields of Brazil. The sediments of the Tarkwaian Group consist of metaconglomerate, quartzite and minor phyllites They are products of erosion of Birimian supracrustal rocks and their coeval belt-type granitic plutons (Fig. 1), deposited under fluvial to lacustrine conditions in long, narrow intramontane grabens which, in Ghana, occur in Birimian volcanic belts *ca.* 2185–2155 Ma in age (Leube *et al.* 1990, Davis *et al.* 1994). The age of Tarkwaian sedimentation is bracketed between 2132 ± 3 Ma and *ca.* 2100 Ma (Davis *et al.* 1994, Hirdes & Nunoo 1994). The Tarkwaian rocks and the underlying Birimian basement were deformed together during the Eburnean tectonothermal event.

The gold-bearing conglomerates, which rarely contain chromite, occur in a 250-km-long NE–SW-trending unit of Tarkwaian rocks in the Banket Series of the Ashanti volcanic belt (Fig. 1). The rocks of the Banket Series consist of monomictic to oligomictic, relatively well-sorted quartz-pebble conglomerates that macroscopically show a striking similarity to many Witwatersrand reefs. Two conglomerate horizons within the Banket Series, the Main Reef and the West Reef, consistently carry economic gold values. The chromite discussed in this paper originates from heavy-mineral-enriched foreset beds in quartzite between the Upper Band and Lower Band of the Main Reef (11/33 Overlap Main Reef).

Unlike the Witwatersrand and Serra de Jacobina gold deposits, which contain major heavy-mineral constituents stable under reducing, or at least oxygen-deficient, atmospheric conditions (*e.g.*, pyrite, uraninite), the ores at Tarkwa comprise a gold – magnetite – hematite – (ilmenite) paragenesis, which is largely comparable to the "black sand paragenesis" encountered in present-day placers. Other minerals observed at Tarkwa, some of which occur only sporadically, include zircon, rutile, quartz, carbonate, sericite, chromian muscovite ("fuchsite"), chlorite, chloritoid, tourmaline, garnet, chromite, staurolite, epidote, diamond, pyrite, pyrrhotite, marcasite, chalcopyrite, and bornite (Whitelaw 1929, Junner *et al.* 1942, Sestini 1973, Kesse 1985, Hirdes *et al.* 1988, Klemd *et al.* 1993, Hirdes & Nunoo 1994). This is certainly a small number of minerals compared to more than 80 minerals in the ore-bearing horizons at Witwatersrand.

The above-listed minerals occur as allogenic minerals, authigenic minerals, and minerals present both as allogenic and authigenic constituents. Hematite is by far the most abundant opaque phase in the Tarkwaian conglomerates. Sulfides are of minimal volumetric importance. They are mainly confined to the selvages of some exogenic quartz veins or dykes, where epigenetic sulfidization of "black sand" minerals in adjacent conglomerates has led to the formation of a pyritic halo a few decimeters thick. This restricted epigenetic sulfidization bears no spatial or genetic relationship to the gold mineralization exploited at Tarkwa.

Chromite is an extremely rare constituent in the conglomerates at Tarkwa; in the specimens selected for study, only a few grains of magnetite are present which contain a core of chromite. The chromite forms idiomorphic or rounded grains up to 200 μm across in the core of larger grains of magnetite (Figs. 2a, b). The contact between the chromite core and the magnetite rim is always sharp. A rim of ferrian chromite ("ferritchromit"), which normally is very common, and was described most recently by Liipo *et al.* (1995) from Finland, is absent in all samples from Tarkwa. In some cases, a symplectitic or eutectic-like intergrowth with magnetite is present (Fig. 2b). Figure 2b also shows a core of chromite that has been broken and displaced by magnetite.

COMPOSITION OF THE CHROMITE

Analytical methods

For optical and electron-microprobe examination, six specimens containing chromite from the Main Reef of the Tarkwa gold mine were mounted in epoxy resin and polished with diamond powder on a Duerener polisher with lead laps. Measurements of reflectance were made using a Leitz Ortholux microscope equipped with a Hamamatsu photomultiplier. The standard used was SiC (Zeiss). Electron-microprobe analyses were carried out with a CAMEBAX Microbeam analyzer (Cameca Instruments). Measurement of 10 seconds duration were taken for $K\alpha$ lines at an accelerating voltage of 20 kV at 10 nA beam current. The raw data were corrected using the PAP program. Chromite (Cr, Fe), gahnite (Al, Zn), synthetic MgO (Mg), synthetic $MnTiO_3$ (Mn, Ti), and vanadinite (V) were used as standards. The proportion of FeO and Fe_2O_3 were calculated to fit the stoichiometric composition of spinel-group minerals. For the calculation of proportions of the end members, MnO and TiO_2 were added to FeO, and V_2O_3 to Fe_2O_3.

Optical properties

Under reflected light, the Zn-rich chromite is grey with a bluish tinge and isotropic, both in air and under oil immersion. The reflectance in air is between 17.0 and 14.6% in the 400–700 nm range (Table 1). There is no significant difference in reflectance among individual grains in a sample. The reflectance of the Zn-rich chromite from Tarkwa is distinctly higher than that of zinc-free chromite from the Stillwater Complex, Montana (Criddle & Stanley 1993) (Fig. 3). This is the effect of the substitution of Fe by Zn. There is, for an unknown reason, a discrepancy with the data for zincochromite of Nesterov & Rumjantzeva (1987), who proposed much lower values than those for the Zn-rich

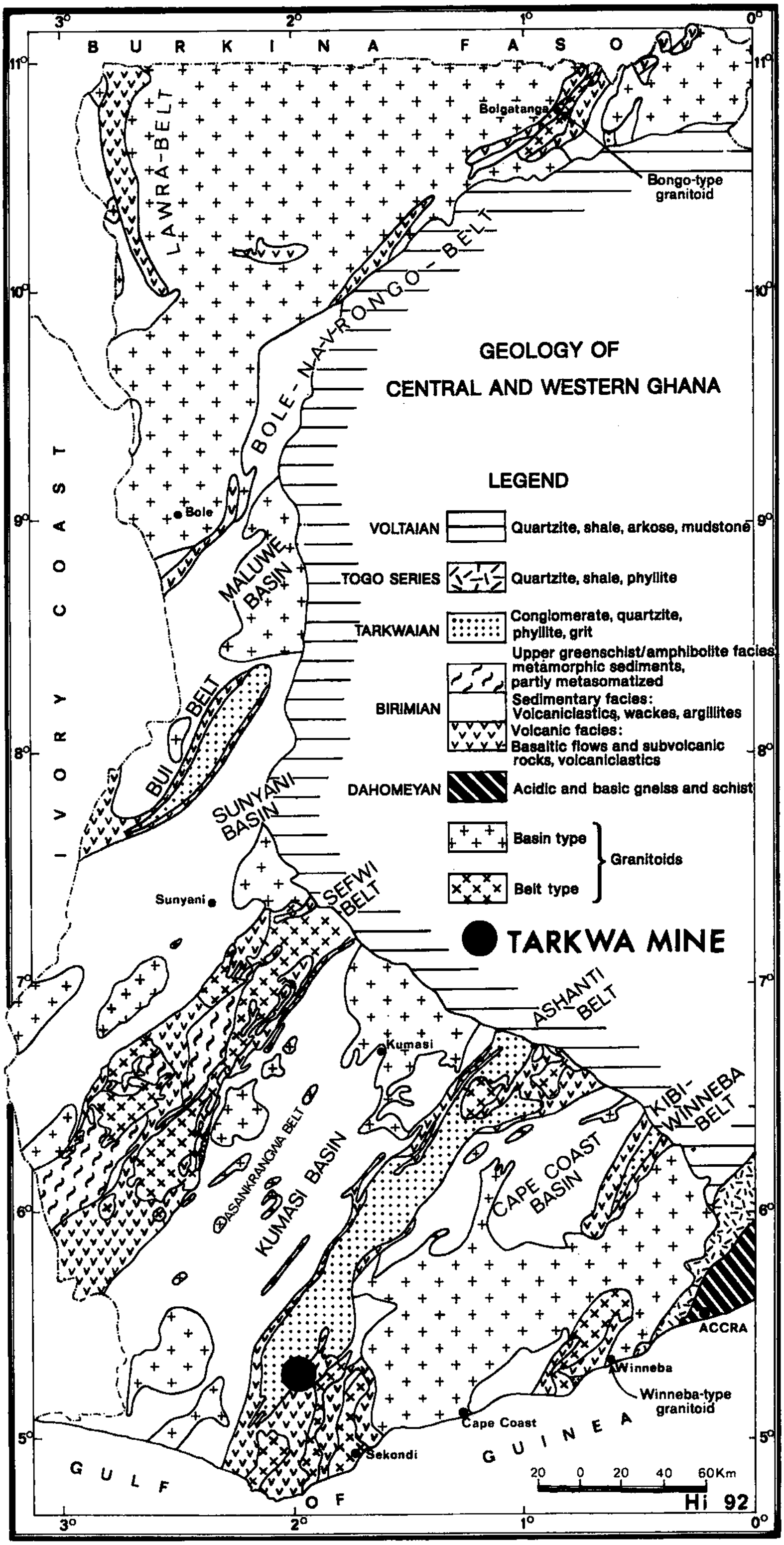

FIG. 1. Geology of central and western Ghana and position of the Tarkwa gold mine (after Hirdes & Nunoo 1994).

chromite from Tarkwa and the Zn-free chromite from the Stillwater Complex (Fig. 3).

The Tarkwa chromite is invariably surrounded by magnetite, which is grey with a brownish tint in reflected light in air and oil. The reflectance of the magnetite is typical, ranging from 21.5 to 20.1% (400–700 nm), and clearly higher than that of chromite.

Chemical composition

Electron-microprobe analyses of the chromite grains (Table 2) reveal a large compositional variation among the six samples analyzed and also within the same sample. However, single grains of chromite have a relatively homogeneous composition, as demonstrated

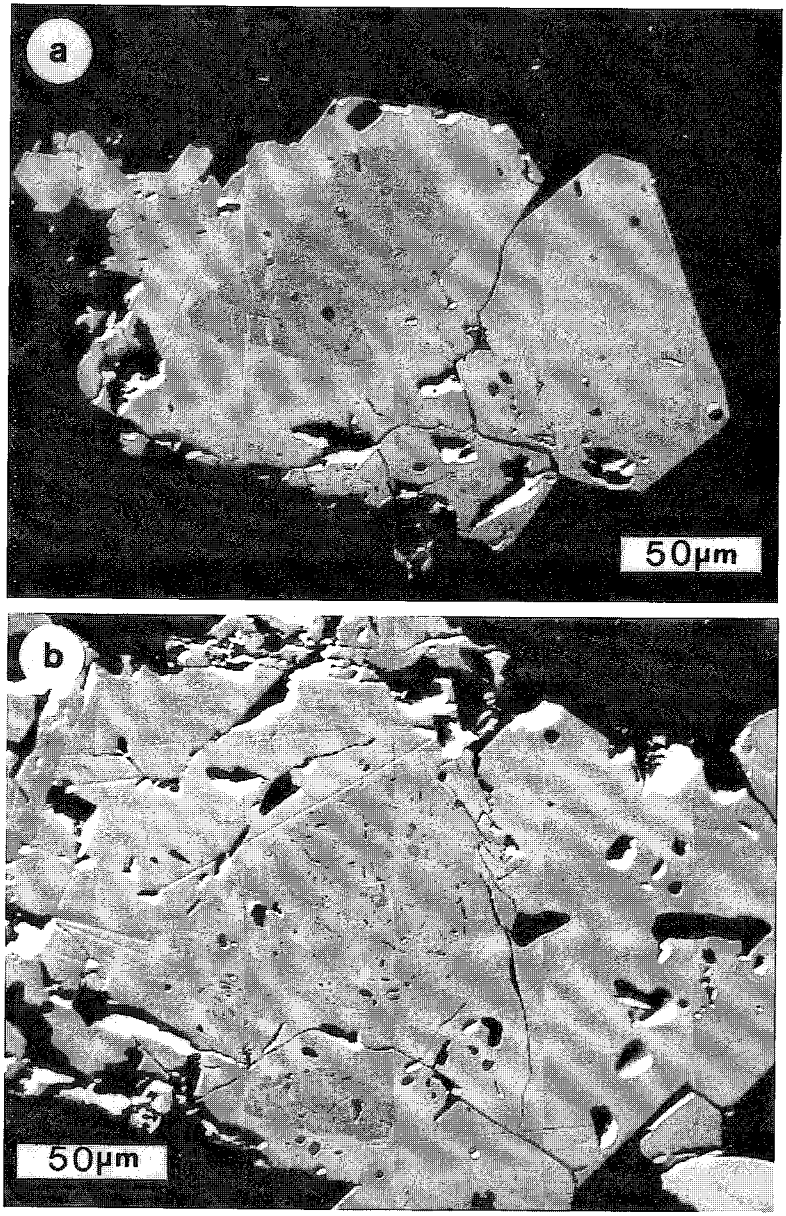

FIG. 2. Back-scattered electron images (BEI) of spinel grains in the Tarkwaian conglomerate. a. Idiomorphic chromite (dark) rimmed by magnetite. b. Chromite (dark) in a symplectite-like intergrowth with magnetite.

TABLE 1. REFLECTANCE VALUES OF (Fe,Al)-RICH ZINCOCHROMITE* FROM TARKWA, GHANA

λ nm	R% (air)	λ nm	R% (air)
400	17,00	560	15,71
420	16,84	580	15,48
440	16,72	600	15,29
460	16,47	620	15,07
480	16,28	640	14,91
500	16,18	660	14,74
520	16,06	680	14,70
540	15,83	700	14,55

* Grain number 9.

by back-scattered electron images (Figs. 2a,b), point analyses, and line scans.

The Cr content of the chromite lies between 37.17 and 60.54 wt.% Cr_2O_3, with a mean of 50.02 wt.%. There is much greater variation in Al content, between 2.70 and 16.21 wt.% Al_2O_3 (mean: 7.64 wt.%). Calculated Fe_2O_3 contents vary from 3.58 to 16.72 wt.%, with a mean of 7.77 wt.%. The highest Al content corresponds to the lowest Cr value, whereas the relationship between the Fe^{3+} and other trivalent elements is not so evident.

The calculated proportion of FeO lies between 15.73 and 24.34 wt.%, with a mean of 19.78 wt.%. All chromite grains are free of Mg, and show a nearly constant and low concentration of Mn (0.84 wt.% MnO). Vanadium and titanium were detected, at low values, only in a few grains (Table 2).

The most interesting feature of the chromite grains investigated is their unusually high Zn content. The mean concentration of Zn in the analyzed grains is 13.33 wt.% ZnO. The highest measured value is 19.42 wt.% ZnO (Table 2, grain 9) and leads to the formula $(Zn_{0.51}Fe_{0.49})_{\Sigma 1.00}(Cr_{1.12}Al_{0.68}Fe_{0.20})_{\Sigma 2.00}O_4$. As the proportion of Zn is higher than Fe in the formula, the composition corresponds to (Fe,Al)-rich zincochromite. A similar zinc content (19.09 wt.% ZnO) is reported in zoned chromite from the Sykesville district, Maryland, which occur in ultramafic rocks and metapelites (Wylie *et al.* 1987). These, however, contain much more Al (26.74 wt.% Al_2O_3) than the chromite from Tarkwa (16.21 wt.% Al_2O_3).

Chromite from the Witwatersrand, deposited in an environment comparable to the one in which the Tarkwaian conglomerates formed, contains distinctly lower concentrations of Zn (*ca.* 5.8 wt.% ZnO) (*e.g.*, Stupp 1984). To our knowledge, the highest reported value from the Witwatersrand is 10.89 wt.% ZnO for detrital grains of chromite from the South Reef, West Rand Consolidated mine (Eales & Reynolds 1983).

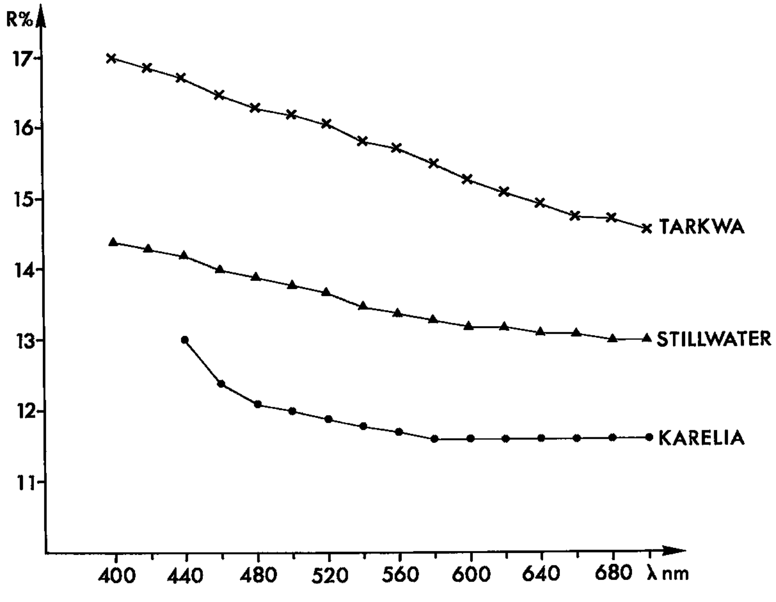

FIG. 3. Reflectance spectrum (air) of (Fe,Al)-rich zincochromite from Tarkwa, Ghana (grain 9) compared with the spectrum of Zn-free chromite from Stillwater Complex, Montana (Criddle & Stanley 1993), and of zincochromite from Karelia, Russia (Nesterov & Rumjantzeva 1987).

TABLE 2. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF Zn-RICH CHROMITE AND (Fe,Al)-RICH ZINCOCHROMITE FROM TARKWA, GHANA

grain no.*	1(2)	2(4)	3(2)	4(2)	5(5)	6(4)	7(3)	8(2)	9(2)
weight per cent									
Cr_2O_3	55,55	60,54	53,00	56,53	55,38	45,75	46,83	37,17	39,48
Al_2O_3	5,74	2,70	5,91	3,93	3,87	13,89	6,20	10,28	16,21
V_2O_3	nd	nd	nd	nd	nd	nd	nd	0,30	nd
Fe_2O_3	5,69	3,58	6,71	5,40	6,85	4,15	13,01	16,72	7,82
FeO	24,34	21,98	21,93	20,32	19,99	19,52	18,32	15,89	15,73
MgO	nd	nd	nd	nd	nd	nd	nd	nd	nd
MnO	1,05	1,41	0,96	0,69	0,77	0,80	0,81	0,48	0,60
ZnO	8,32	9,78	10,36	12,27	12,61	14,44	14,66	18,09	19,42
TiO_2	nd	nd	0,19	nd	nd	0,20	0,31	nd	nd
Total	100,69	99,99	99,06	99,14	99,47	98,75	100,14	98,93	99,26
atomic proportions									
Cr	1,598	1,781	1,554	1,674	1,636	1,300	1,368	1,082	1,116
Al	0,246	0,119	0,259	0,174	0,171	0,588	0,270	0,446	0,683
V	-	-	-	-	-	-	-	0,009	-
Fe^{3+}	0,156	0,100	0,187	0,152	0,193	0,122	0,362	0,463	0,201
Fe^{2+}	0,744	0,624	0,680	0,638	0,627	0,587	0,566	0,491	0,470
Mg	-	-	-	-	-	-	-	-	-
Mn	0,032	0,041	0,030	0,022	0,025	0,024	0,026	0,015	0,018
Zn	0,224	0,335	0,284	0,340	0,348	0,383	0,400	0,494	0,512
Ti	-	-	0,006	-	-	0,005	0,008	-	-
end-member proportions									
gahnite	12,30	5,95	12,95	8,70	8,55	29,40	13,50	22,30	34,15
franklinite	7,80	5,00	9,35	7,60	9,65	5,60	18,10	23,60	10,05
zincochromite	2,30	22,55	6,10	17,70	16,60	3,30	8,40	3,50	7,00
chromite	77,60	66,50	71,60	66,00	65,20	61,70	60,00	50,60	48,80

* The number of analyses is shown in parentheses; nd: not detected. For the calculation of the end members, V was added to Fe^{3+}, and Mn and Ti were added to Fe^{2+}.

All analyzed grains of chromite from Tarkwa are free of Mg. The data show that in Zn-rich chromite, Zn takes the place of Mg (*e.g.*, Weiser 1966, Bevan & Mallinson 1980, Wagner & Velde 1985, Pan & Fleet 1989, Béziat & Monchoux 1991, Sánchez-Vizcaíno *et al.* 1995). Owing to the inverse relationship between Fe and Zn in the Tarkwa samples, a similar substitution of Zn for Fe^{2+}, described by Challis *et al.* (1995), is also possible.

The general formula of the chromite at Tarkwa corresponds to $(Fe_{0.64}Zn_{0.36})_{\Sigma 1.00}(Cr_{1.45}Al_{0.33}\ Fe_{0.22})_{\Sigma 2.00}O_4$. The proportions of spinel end-members are as follows: 64.0 at.% $FeCr_2O_4$ (chromite), 16.5 at.% $ZnAl_2O_4$ (gahnite), 11.0 at.% $ZnFe_2O_4$ (franklinite), and 8.5 at.% $ZnCr_2O_4$ (zincochromite). In this suite, the spinel contains between 6.0 and 34.2 at.% gahnite, 5.0 and 23.6% franklinite, 2.3 and 22.6% zincochromite, and 48.8 and 77.6% chromite (Table 2). This spread illustrates a large field of solid solution between chromite and zincochromite.

Compositions of individual grains from Tarkwa are compared with those of chromite (>35 wt.% Cr_2O_3; see Wylie *et al.* 1987) selected from the literature (Fig. 4).

TABLE 3. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF MAGNETITE SURROUNDING Zn-RICH CHROMITE FROM TARKWA, GHANA

	weight per cent					
grain no.*	1 (2)	2 (1)	3 (3)	4 (2)	5 (2)	6 (2)
Fe_2O_3	69,02	68,78	68,99	68,96	68,95	67,78
Cr_2O_3	0,25	0,56	0,56	0,65	nd	1,21
V_2O_3	nd	nd	nd	nd	0,15	nd
FeO	31,14	31,29	31,21	31,32	31,06	31,09
Total	100,41	100,63	100,76	100,93	100,06	100,08

* The number of analyses is shown in parentheses; nd: not detected. Al, Mg, Mn, Ni and Ti are below the limit of detection.

The spread of values for chromite for Tarkwa is similar to that for detrital Zn-rich chromite from the Witwatersrand conglomerate, from the Pongola Group of South Africa, and from various other environments. The data also demonstrate an extended miscibility in the $(Zn,Fe)Cr_2O_4$ – $ZnFe_2O_4$ – $ZnAl_2O_4$ system, at least above 50 at.% $(Zn,Fe)Cr_2O_4$.

Electron-microprobe analyses of magnetite rimming chromite contain up to 1.2 wt.% Cr_2O_3 (Table 3, grain 6), and up to 0.15% V_2O_3 (Table 3, grain 5). All other elements are below the detection limit. Magnetite grains without a core of chromite are free of Cr. This finding suggests that the magnetite rim is a product of alteration of the chromite core.

DISCUSSION

Zinc-bearing chromite (>0.5 at.% Zn) is mostly Mg-poor and associated with sulfide mineralization in ultramafic sequences (Groves *et al.* 1977). Czamanske *et al.* (1976) explained the origin of such chromite in Alaska as a product of crystallization from a sulfide melt segregated from gabbroic magma. The same mode of formation is assumed for the Zn-bearing chromite of Western Australia (Groves *et al.* 1977, 1983).

Schidlowski (1970) and Stupp (1984) suggested a reaction between Zn-bearing circulating fluids and detrital chromite to explain the origin of zoned chromite with a Zn-rich rim and Zn-poor core in the Witwatersrand conglomerate and the Pongola Supergroup in South Africa. Frey (1988) explained zoning in the Witwatersrand chromite by a process involving diffusion of Zn from core to rim of the grains during metamorphism.

Metasomatism by Zn-rich fluids is invoked to explain the high Zn content of the zoned chromite from the Sykesville district, Maryland (Wylie *et al.* 1987), where Zn enrichment is associated with massive sulfide mineralization. Similar processes may have played a role in the formation of zoned Zn- and V-rich chromite at Outokumpu (Weiser 1966, 1967b). According to

Bjerg *et al.* (1993), the zonation and Zn-content of the chromite from the Cordillera Frontal Range, Argentina, are the product of alteration processes during serpentinization of ultramafic rocks. Associated sphalerite-bearing sulfide mineralization is considered as a possible source of the zinc in the chromite.

Unlike these examples, the grains of detrital Zn-rich chromite from Tarkwa are not zoned. Therefore, their formation in relation to circulating Zn-rich fluids in chromite-bearing conglomerates, as described by Schidlowski (1970), Stupp (1984), and Frey (1988) from South Africa, is unlikely. If chromite had crystallized from a sulfide melt at Tarkwa, as Groves *et al.* (1977, 1983) suggested for Zn-bearing chromite associated with iron–nickel sulfide ores from Western Australia, it would have required a magma enriched in Zn.

Hence, on a theoretical basis, the detrital Zn-rich chromite from Tarkwa could serve as an indicator of mineralized source-rocks, *e.g.*, ultramafic-rock-hosted sulfide bodies. However, the evidence for ultramafic source-rocks is scanty in the Birimian of Ghana. The only noteworthy occurrence of ultramafic rocks in the southernmost Ashanti belt contains chromite with an inconspicuous Zn content. A massive sulfide deposit said to contain gahnite, but no chromite, occurs in rocks of the Birimian Supergroup in Burkina Faso (Napon & Ouedraogo 1990). Minor volcanogenic massive sulfide ore consisting of disseminated sphalerite, pyrite, gersdorffite, ullmannite, and alabandite has been described by Hirdes & Leube (1989) for the Nsuta manganese mine (4 km SE of Tarkwa town), which is located in the envisaged hinterland of the paleoplacers at Tarkwa. Additional detailed mineralogical and sedimentological

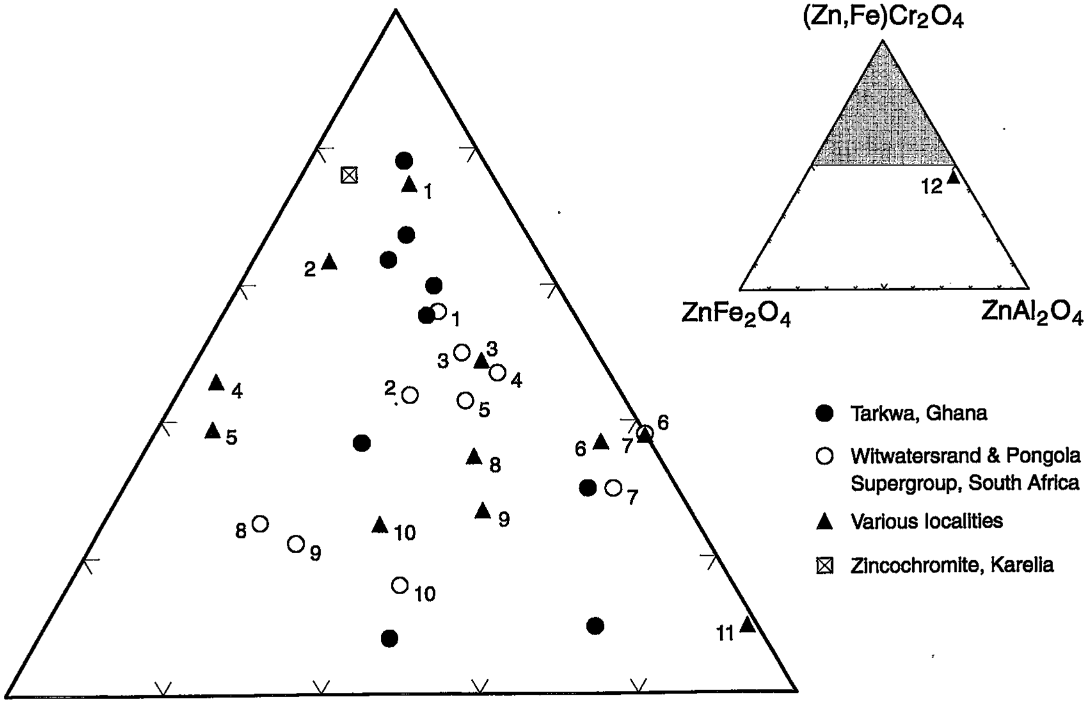

FIG. 4. Plot of the composition of samples of Zn-rich chromite from Tarkwa, Ghana (filled circles), compared with other samples taken from the literature, in terms of $(Zn,Fe)Cr_2O_4$ – $ZnFe_2O_4$ – $ZnAl_2O_4$. Open circles: Witwatersrand conglomerate and Pongola Supergroup, South Africa [1, 2, and 5: Frey (1988), 3, 6, 7, 9, and 10: Stupp (1984), 4: Eales & Reynolds (1983), 8: Utter (1978)]. Triangles: Zn-rich chromite from various environments [1: Val d'Aoste, Italy (Wagner & Velde 1985), 2: Salamanca district, Argentina (Bjerg *et al.* 1993), 3: Kambalda, Australia (Groves *et al.* 1977), 4: Outokumpu, Finland (Weiser 1966), 5: Trojan mine, Zimbabwe (Groves *et al.* 1983), 6: Mashaba mine, Zimbabwe (Bevan & Mallinson 1980), 7: northwestern Nelson, New Zealand (Challis *et al.* 1995), 8: Hemlo, Ontario (Pan & Fleet 1989), 9: Näätäniemi, Finland (Liipo *et al.* 1995), 10: Montagne Noire, France (Béziat & Monchoux 1991), 11: Outokumpu, Finland (Weiser 1967b, Treloar 1987), 12: Sykesville, Maryland (Wylie *et al.* 1987)]. Square: Zincochromite from Karelia, Russia (Nesterov & Rumjantzeva 1987).

studies of the Tarkwaian conglomerate, as well as field work in its Birimian hinterland, will be necessary to identify the source rocks of the Zn-rich chromite and the possible base-metal mineralization associated with them.

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