American Mineralogist, Volume 72, pages 413–422, 1987

Compositional zoning in unusual Zn-rich chromite from the Sykesville district of Maryland and its bearing on the origin of "ferritchromit"

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ABSTRACT

Chromite from the Morgan Run melange, Maryland Piedmont, exhibits anomalously high ZnO concentrations of over 19 wt% ZnO. The chromite is complexly zoned, optically and chemically, and occurs as an accessory phase in a laminated quartz-magnetite rock, and in ultramafite, adjacent blackwall zones, and the surrounding metapelite.

From core to edge, four zones can be identified in some of the chromite grains: a central transparent zone that is a solid solution along the gahnite-chromite join, a two-phase "ferritchromit" zone, a narrow anisotropic zone, and an outer magnetite zone. The occurrence of "ferritchromit," *without an outer magnetite zone,* surrounding a gahnite-chromite core hosted by metapelite, demonstrates that "ferritchromit" is *not* a reaction zone that forms between chromite and magnetite. Rather, "ferritchromit" most likely forms as a precipitate that is in local equilibrium with a solution that is deriving nutrient from an irreversibly dissolving chromite core.

Geologic evidence suggests that Zn was introduced into this system early in a multistage hydrothermal event that extended from sea-floor hydrothermal alteration to regional metamorphism. The Zn (and Cu in the associated chalcopyrite) was most likely leached from basalts that probably underlay the host strata during the time of sea-floor hydrothermal activity.

INTRODUCTION

During the latter half of the nineteenth century, Cu and Fe were mined from the Sykesville district, Carroll County, Maryland. Although never mined for Co, the ore is known to contain Co thiospinels, and the district is the type locality for carrollite (Faber, 1852). Renewed interest in the district in 1980 resulted in the drilling of several exploratory holes by the Noranda Mining Company, which later gave the drill cores to the Maryland Geological Survey. It was during the examination of these cores that the spinels with which this paper is concerned were discovered.

Chromite rich in Zn is considered unusual enough to be reported in the literature whenever it is found. Examples of the most notable occurrences are given in Table 1. Until this report, the highest ZnO content of spinels considered to be chromite (greater than 35 wt% Cr_2O_3) was reported by Weiser (1967) from Outokumpu, Finland (analysis C, Table 1), as 12 wt% ZnO. A ZnO content in excess of 0.5 wt% is considered significant (Groves et al., 1983). In this paper we report chromite with ZnO in excess of 19 wt%, which, to our knowledge, is the highest value ever reported. The chromite occurs in altered ultramafic rocks, in adjacent metapelite and banded quartz–iron oxide rock, and in the metasomatic zones separating them. It exhibits complex chemical and optical zoning, which we shall describe and discuss in this paper.

LOCATION AND GENERAL GEOLOGY

The Sykesville district is located in the western piedmont of Maryland within the Morgan Run Formation (Fig. 1). The Morgan Run is a melange consisting of a pile of discontinuous slices and blocks of metagraywacke, pelitic schist, metaquartzite, ultramafic rocks, and amphibolites. The Morgan Run Formation and the olistostromal Sykesville Formation make up the Liberty Complex (Muller et al., 1985). Within the district, the rocks strike approximately N30°E and dip steeply to the east. Locally, the rocks have been metamorphosed to the upper-greenschist facies although lower-amphibolite facies may have been attained in some parts of the district (Candela et al., unpub. ms.).

The ores of the Sykesville district are composed primarily of chalcopyrite, magnetite, and quartz with lesser amounts of cobaltiferous pyrite, a cobalt thiospinel (carrollite or more commonly siegenite), sphalerite, bornite, and hematite. The sulfides are found within and adjacent to a finely laminated quartz-magnetite host, which is located at the contact between altered ultramafic rocks (ser-

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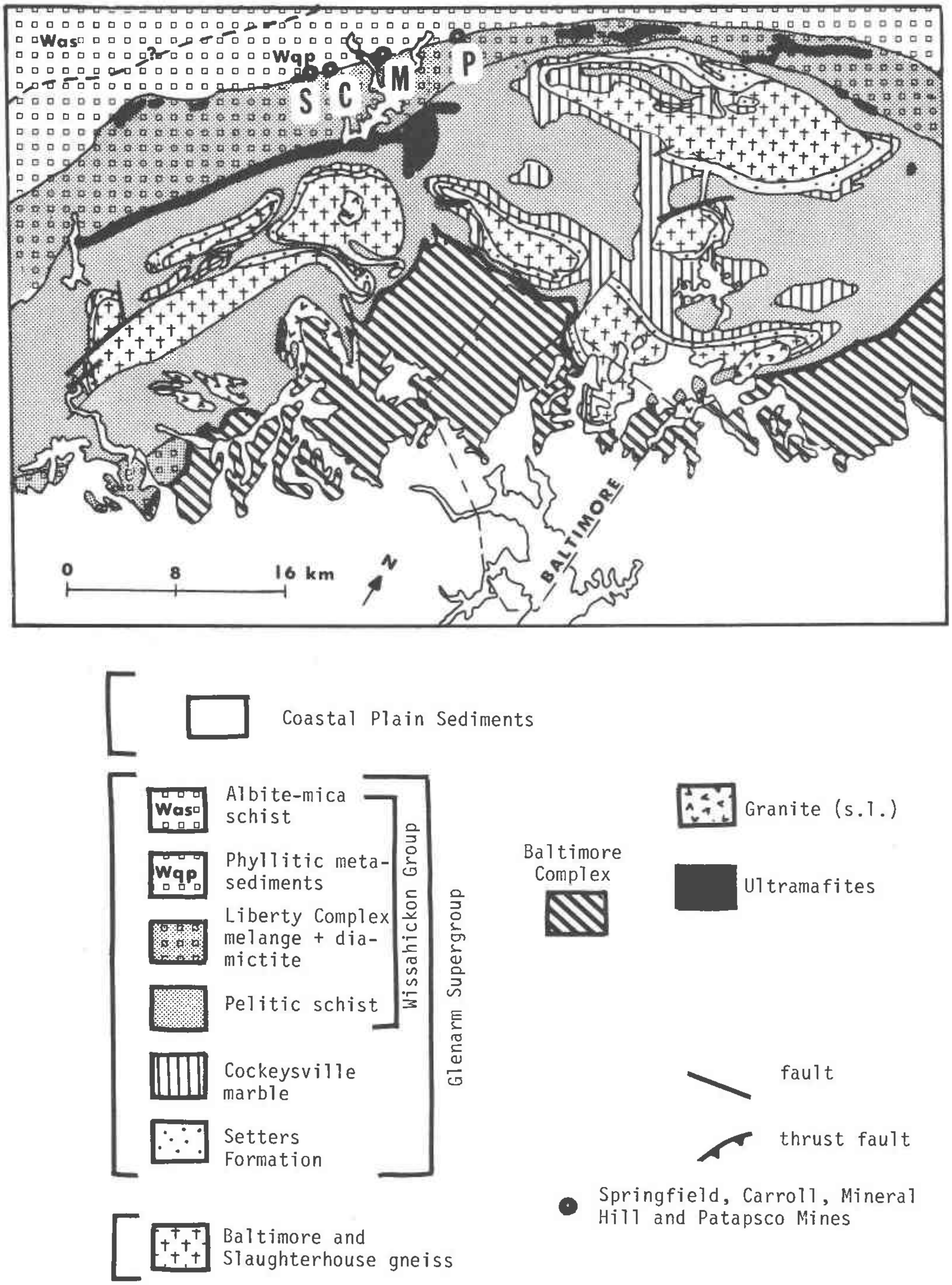

Fig. 1. Geologic map of part of the Maryland Piedmont showing the location of the major mines in the Sykesville district (after Muller and Chapin, 1984).

pentinite) and the other units of the Morgan Run Formation. On the basis of textural, mineralogical, and chemical arguments, the quartz-magnetite rock is considered to have been formed as a chemically precipitated sediment (Candela et al., unpub. ms.). Also developed at this contact are metasomatic, nearly monomineralic, zones of epidote, chlorite, actinolite, and talc. The original boundary between the ultramafite and the pelitic country rock is the chlorite-actinolite boundary (Broadhurst et al., 1983). The zoned chromites described in this report have been found in the serpentinite, in the actinolite zone of the ultramafite, in the quartz-magnetite rock, in the chlorite zone of the metapelite, and in the pelitic schist adjacent to the ore zone.

TABLE 1. Chromites with anomalously high Zn contents

	1	2	3	4	5	6	7	8	9	10
TiO_2	0.18				0.60	0.35	0.48	0.05	0.90	0.05
Al_2O_3	13.8	7.4	19.8	0.35	11.34	7.0	0.42	8.72	2.98	26.74
Cr_2O_3	49.30	54.0	38.8	41.48	34.43	52.2	71.70	53.12	56.95	35.21
Fe_2O_3	1.80	3.0	50.49		22.66			5.49	23.29	2.25
FeO	21.60	17.1			22.83	27.6	15.10	23.76		16.66
MnO	8.02	2.0	<4		0.79	0.3	3.40	1.65	3.48	1.26
MgO	0.70	4.3	<2	4.68	6.43	9.9	7.10	1.91	0.15	0.80
ZnO	4.27	5.28	12.0	2.62	0.28	0.6	1.70	5.62	8.74	19.09

Note: Columns are (1) Bevan and Mallinson (1980), Zimbabwe; (2) Thayer et al. (1964), Finland; (3) Weiser (1967), Finland; (4) Donath (1931), Norway; (5) Moore (1977), Norway; (6) Pearre and Heyl (1960), Pennsylvania; (7) El Gorsey (1976), iron meteorite; (8) Groves et al. (1977), Australia; (9) Wagner and Velde (1985), Italy; (10) this study, Maryland.

ANALYTICAL METHOD

Samples were collected from two 2-in. (2.54 cm) drill cores, from outcrops, and from mine dumps. The rocks were studied by standard petrographic techniques using both transmitted and reflected light. Reflectance was measured with a Leitz MPV system using a SiC standard. Individual mineral grains were analyzed by an ARL electron-microprobe located in the Mineral Sciences Division of the U.S. National Museum (Smithsonian Institution), and the data were reduced by the methods of Bence and Albee (1968). Magnetite (Fe) (USNM 114887), cobalt metal (Co), chromite (Al, Cr, Mg) (USNM 117075), ilmenite (Ti) (USNM 96189), gahnite (Zn) (USNM 145883), manganite (Mn), and Ni-Fe alloy (Ni) were used as standards (Jarosewich et al., 1980). In the microprobe analyses, Fe_2O_3 and FeO have been calculated from total FeO by assuming that (1) there are four oxygens in the spinel formula and (2) the sum of the divalent cations equals one.

OPTICAL PROPERTIES OF ZONED CHROMITE

Four zones that exhibit distinct optical characteristics are found in the Sykesville chromite (Table 2). However, all four zones are not equally well developed in all samples. In particular, the two outermost zones are not present in chromite found in the metapelite host and the two innermost zones have not been found in chromite hosted by the quartz-magnetite unit. These relationships will be discussed later. Furthermore, all the zones are not homogeneous, and in some specimens, the zones may be more complex than in others. Nonetheless, generalizations about the zones can be made.

The cores of the chromite grains, referred to as zone A, are irregularly shaped, low-reflectance, isotropic regions whose boundaries with the surrounding zone B are sharply defined (Fig. 2). In most samples, zone A is a homogeneous phase with uniform reflectance, gray color, and yellow-orange internal reflections (Table 2). In some samples the outer edge is marked by a rim of lower reflectance, and the interior may exhibit a mottled appearance (Fig. 2c). The polishing hardness of zone A is greater than that of zone B. In thin section, zone A is transparent. This zone contains several types of inclusions that are smaller than 1 μm; the most abundant are spindle-shaped and anisotropic.

Zone B has a slight bluish color and higher reflectance than zone A. Viewed at low magnification, it appears to be homogeneous, but with oil immersion and higher magnification, two phases are clearly evident (Fig. 2c).

TABLE 2. Optical properties of zoned chromite

			Reflectance				
Zone		Color	λ	%	Anisotropy	Polishing hardness	Internal reflections
A		Gray	438	13.6	isotropic	zone A > zone B	orange; abundant to scarce
			481	13.2			
			546	12.8			
			591	12.6			
			646	12.4			
B	B_1	Bluish gray	$R \simeq$ 13–14%		isotropic	zone B_1 > zone B_2	red orange; increasing in abundance from the boundary with zone A outward
	B_2	Bluish gray	$R \simeq$ 19–20%		isotropic		absent
C		Bluish gray	438	19.3	strongly anisotropic	zone C ≈ zone B_2	absent
			481	18.7			
			546	18.5			
			591	18.9			
			646	18.1			
D		Pink	438	20.4–21.6	isotropic to weakly anisotropic	zone D ≥ zone C	absent
			481	20.0–21.4			
			546	20.1–21.8			
			591	20.2–22.3			
			646	19.3–22.3			

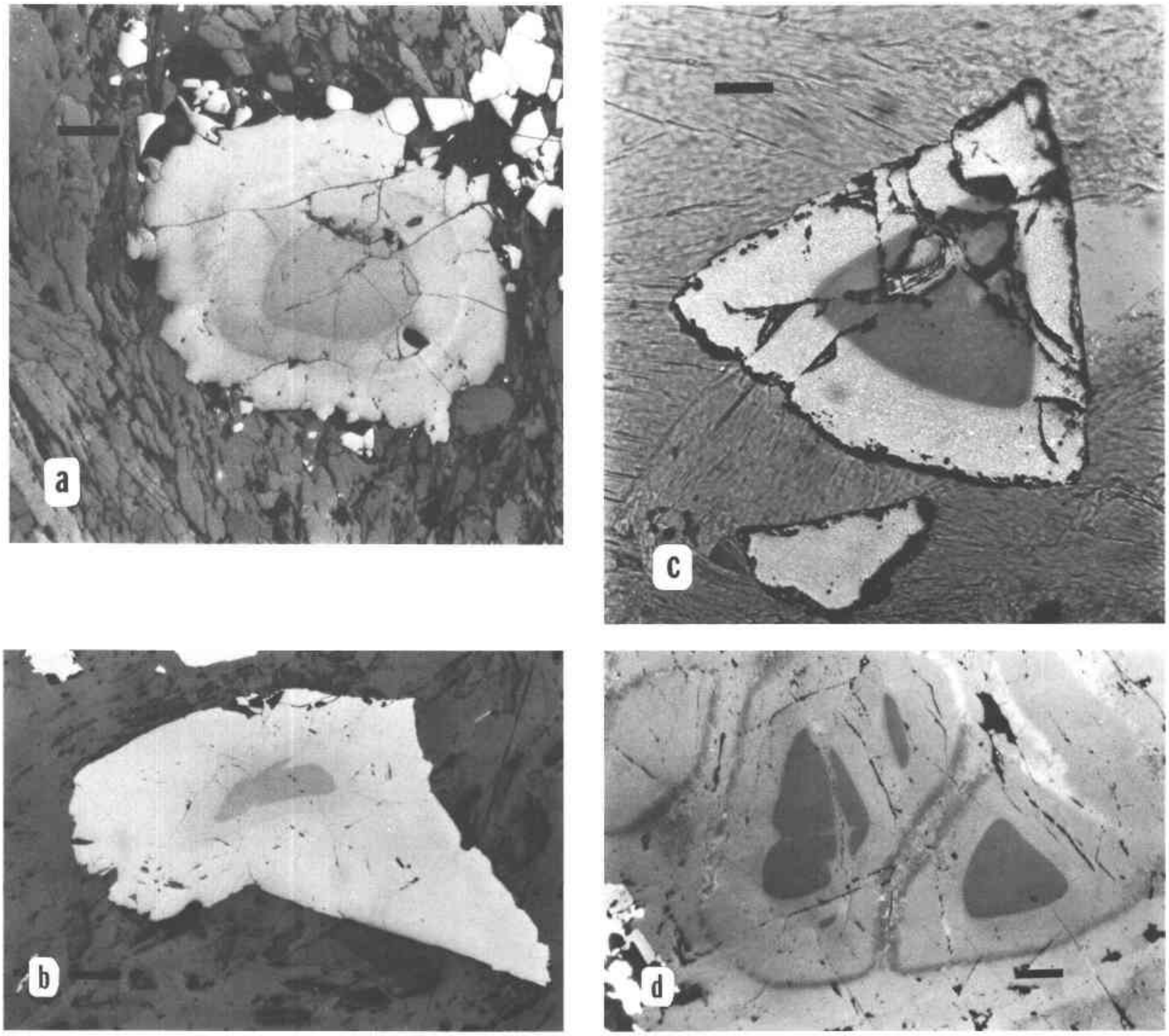

Fig. 2. Photomicrograph of zoned chromites. (a) Chromite from the actinolite zone of the ultramafite (partially crossed nicols, reflected light). Four zones are evident. Bar = 0.2 mm. (b) Chromite from the chlorite zone of the metapelite (uncrossed nicols, reflected light). The two outermost zones, C and D, cannot be distinguished because the photomicrograph was not taken under crossed nicols. Bar = 0.2 mm. (c) Photomicrograph of zoned chromite from a metapelite host. The outermost two zones (C and D) are absent. Zone B "ferritchromit" is composed of two phases. Uncrossed nicols, reflected light. Bar = 0.2 mm. (d) Zoned chromite from a serpentinite host. Partially crossed nicols, reflected light. Bar = 0.1 mm.

Generally, a low-reflectance host surrounds irregularly shaped, higher-reflectance blebs. In some chromite grains, the blebs are elongated and confined to three crystallographic directions {111}, giving the mineral a "Widmanstätten pattern." In most samples, the abundance of the higher-reflectance phase increases from the boundary with zone A outward, and a concomitant increase in the abundance of internal reflections in the lower-reflectance phase occurs. In the chromites from the metapelite host, the guest-host relationship is reversed abruptly at the outer edges of zone B where the higher-reflectance phase becomes the host. Whatever the host, the guest blebs are less than 1 μm in size. The largest blebs are found close to the boundary with zone A in the chromites from the metapelite. In many of the samples, the blebs are so small that they are barely visible. Because of their small size and intimate association, no reflectances could be measured from either phase. However, the low-reflectance phase has a slightly higher reflectance than zone A, and the higher-reflectance phase has about the same reflectance as zone D. From these qualitative observations, the estimates given in Table 2 were obtained. The lower-reflectance phase has the greater hardness. In some samples, spindle-shaped anisotropic inclusions were observed to be in optical continuity with similar inclusions found in zone A.

TABLE 3. Microprobe analyses of zone A in Sykesville chromites

Host rock:	Metapelite		Chlorite*		Actinolite		Serpentinite	
Analysis no.:	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
TiO_2	0.01	0.03	0.02	0.08	1.24	0.98	0.05	0.03
Al_2O_3	26.58	26.74	22.46	22.66	22.44	22.36	23.67	23.09
Cr_2O_3	35.61	35.21	37.47	37.38	38.47	38.12	39.45	38.88
Fe_2O_3	0.08	1.57	1.30	2.13	0.76	1.60	1.81	2.65
FeO	18.76	17.49	21.98	19.92	24.06	20.30	19.31	18.61
MnO	1.07	1.26	1.26	1.27	2.09	1.66	1.55	1.39
MgO	0.96	0.80	1.30	0.84	1.44	0.99	4.48	3.89
ZnO	16.47	19.09	10.72	14.84	7.84	13.95	9.20	11.10
Total	99.54	102.20	96.52	99.12	98.27	99.80	99.53	99.91
			Cation proportions, total oxygens = 4					
Ti	0.000	0.001	0.000	0.002	0.032	0.025	0.001	0.001
Al	1.052	1.041	0.927	0.924	0.901	0.899	0.920	0.909
Cr	0.945	0.920	1.038	1.022	1.037	1.029	1.032	1.027
Fe^{2+}	0.514	0.460	0.618	0.540	0.670	0.550	0.473	0.493
Fe^{3+}	0.002	0.037	0.033	0.052	0.019	0.039	0.046	0.063
Mn	0.030	0.035	0.037	0.037	0.060	0.048	0.041	0.039
Mg	0.048	0.039	0.068	0.044	0.073	0.050	0.218	0.194
Zn	0.408	0.466	0.277	0.379	0.197	0.352	0.268	0.274
Total	3.000	3.000	3.000	2.999	2.990	2.992	3.000	3.000

* Some of the chemical analyses of the spinels from the chlorite host give low totals. We think this is due to sample preparation. We have included them because they are useful in showing general compositional trends.

Zone C is a narrow (maximum width, 0.05 mm), highly irregular zone found between zones B and D (Fig. 2d). Its most characteristic feature is its distinct anisotropy. Bireflectance is not visible either in air or oil. Reflectances given in Table 2 are approximate because the highly irregular nature of the zone means that there is a high likelihood that some of zone B or C was included in the measurement. Bireflectance is too small to be measured. Zone C has the bluish color of zone B and a reflectance that is very similar to the average reflectance of the two phases of B. In fact, zone C cannot be distinguished from zone B in plane light even though the boundary between them is sharp. Zone C grades into zone D.

The reflectance of the outermost zone D varies from about 20% near the boundary with zone C to 22% near the grain edges. Compared to zone B, the color is distinctly pink. The zone is generally isotropic although weakly anisotropic samples are not uncommon.

COMPOSITIONAL RELATIONS

Chemical analyses of each of the four zones from five grains are given in Tables 3–6. The grains are identified according to their host-rock type. No analyses of zones A and B are given from the quartz-magnetite host or of zones C and D from the metapelite host. These zones were absent from these specimens.

TABLE 4. Microprobe analysis of zone B in Sykesville chromites

Host rock.:	Metapelite		Chlorite*		Actinolite		Serpentinite	
Analysis no.:	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)
TiO_2	0.14	0.14	0.18	0.17	0.13	0.25	0.34	0.69
Al_2O_3	10.87	5.05	6.11	2.78	7.09	1.07	5.83	0.78
Cr_2O_3	32.76	33.43	36.32	33.86	34.25	32.71	36.60	34.96
Fe_2O_3	21.04	25.97	20.61	25.57	22.47	30.51	22.94	29.63
FeO	25.43	25.95	27.39	26.95	25.02	26.27	25.99	27.80
MnO	1.85	2.04	1.89	1.83	2.30	2.49	2.11	2.36
MgO	0.28	0.21	0.28	0.21	0.30	0.16	1.53	0.92
ZnO	9.05	6.58	5.04	3.98	7.33	4.28	4.76	2.37
Total	101.43	99.38	97.82	95.13	98.89	97.91	100.10	99.51
			Cation proportions, total oxygens = 4					
Ti	0.004	0.004	0.006	0.006	0.004	0.008	0.010	0.022
Al	0.496	0.248	0.295	0.266	0.341	0.056	0.275	0.039
Cr	1.003	1.102	1.177	0.608	1.104	1.143	1.156	1.181
Fe^{2+}	0.495	0.713	0.767	0.789	0.681	0.756	0.698	0.781
Fe^{3+}	0.664	0.643	0.520	0.699	0.551	0.790	0.555	0.750
Mn	0.061	0.072	0.066	0.068	0.080	0.093	0.071	0.085
Mg	0.016	0.013	0.017	0.014	0.018	0.011	0.091	0.059
Zn	0.259	0.202	0.153	0.129	0.221	0.140	0.140	0.085
Total	2.999	2.998	3.001	2.998	2.998	2.997	2.997	2.992

* Some of the chemical analyses of the spinels from the chlorite host give low totals. We think this is due to sample preparation. We have included them because they are useful in showing general compositional trends.

TABLE 5. Microprobe analysis of zone C in Sykesville chromites

Host rock: Analysis no.:	Quartz–Fe oxide (17)	Chlorite* (18)	Actinolite (10)	Serpentinite (20)
TiO_2	0.47	0.17	0.18	0.64
Al_2O_3	1.25	1.28	0.28	0.00
Cr_2O_3	32.75	28.47	23.96	23.63
Fe_2O_3	29.76	33.39	42.09	42.65
FeO	31.44	26.80	27.82	28.64
MnO	1.11	1.83	1.89	1.57
MgO	0.23	0.14	0.13	0.73
ZnO	0.88	3.74	3.03	1.72
Total	97.88	95.84	99.38	99.58
	Cation proportions, total oxygens = 4			
Ti	0.016	0.006	0.007	0.022
Al	0.065	0.069	0.015	—
Cr	1.133	1.034	0.859	0.857
Fe^{2+}	0.916	0.792	0.815	0.831
Fe^{3+}	0.781	0.889	1.111	1.115
Mn	0.041	0.071	0.079	0.061
Mg	0.015	0.010	0.009	0.050
Zn	0.028	0.127	0.103	0.058
Total	2.995	2.998	2.998	2.994

* Some of the chemical analyses of the spinels from the chlorite host give low totals. We think this is due to sample preparation. We have included them because they are useful in showing general compositional trends.

TABLE 6. Microprobe analysis of zone D in Sykesville chromites

Host rock: Analysis no.:	Quartz–Fe oxide (21)	Chlorite (22)	Actinolite (23)	Serpentinite (24)
TiO_2	0.06	0.04	0.03	0.11
Al_2O_3	0.00	0.00	0.00	0.00
Cr_2O_3	1.45	0.86	2.28	4.32
Fe_2O_3	65.51	66.33	65.68	63.75
FeO	31.07	30.28	31.16	31.07
MnO	0.08	0.06	0.09	0.09
MgO	0.07	0.05	0.07	0.18
ZnO	0.00	0.00	0.00	0.00
Total	98.24	98.16	99.30	99.52
	Cation proportions, total oxygens = 4			
Ti	0.003	0.001	0.001	0.005
Al	0.000	0.000	0.000	0.000
Cr	0.062	0.037	0.096	0.178
Fe^{2+}	0.991	0.993	0.999	0.982
Fe^{3+}	1.935	1.961	1.897	1.815
Mn	0.003	0.002	0.004	0.004
Mg	0.006	0.005	0.005	0.014
Zn	0.000	0.000	0.000	0.000
Total	3.000	2.999	3.002	2.998

The most unusual feature of the chemistry of the chromites is the extremely high ZnO content found in the cores of all analyzed specimens. A maximum of 19.09 wt% ZnO was found in a chromite in the metapelite host in the narrow band of lowest reflectance in zone A at the boundary with zone B. The cores of the chromite can be described as a solid solution between gahnite ($ZnAl_2O_4$) and chromite ($FeCr_2O_4$). In the chromite from the metapelite host, the proportion of the two endmembers is approximately 1:1.

Figure 3 shows the cation proportions as a function of position across a zoned chromite from the actinolite host. Although the absolute values of the cation proportions vary among specimens, the relative changes are the same in all specimens (with the exception of Ti). Therefore, this sample will serve to illustrate the chemical changes across zones.

From the center of the core outward to zone B, the relative proportions of the trivalent cations do not change significantly. On the other hand, the proportions of the divalent cations show significant variations. Generally, Zn increases from the grain center, reaching a maximum at the contact with zone B. The increase in Zn correlates with decreases in Mn, Mg, and Fe^{2+}.

Zone B is a two-phase field. However, the compositions given in Table 4 are composites of the two phases. The segregation of the two phases was on too small a scale to enable us to obtain analyses from either one independently. Chromite exhibiting exsolution is rare. It has been reported from the Giant Nickel mine in British Columbia (Muir and Naldrett, 1973), from the Fiskenaesset Complex in Greenland (Ghisler, 1976; Steele et al., 1977), from small ultramafic bodies from Red Lodge, Montana (Loferski and Lipin, 1983), and from the Stillwater Complex, Montana (Loferski and Lipin, 1983). Most of the compositions from zone B of the Sykesville chromite plot within the two-phase region proposed by Loferski and Lipin (1983) (Fig. 4). An Al-rich phase and an Al-poor, Fe-rich phase are consistent with the optical data on reflectance and internal reflections given in Table 2. Seven analyses plot near but outside the two-phase region. This is to be expected given that variations in temperature, pressure, and divalent cation chemistry must affect the shape and size of the miscibility gap.

The conditions that result in the development of optically visible exsolution are not known. As Loferski and Lipin (1983) have pointed out, metamorphism is not always a necessary condition. They speculated that the miscibility gap may be largest when the MgO content is small. Therefore, chromites with low MgO will be the ones to show exsolution. This conclusion is consistent with the compositions of zone B of the Sykesville chromite for which MgO is less than 1.5 wt%. The two phases are coarsest in chromite from the metapelite host, which has an MgO content of less than 0.3 wt%. The high ZnO content may also contribute to the development of exsolution although it has not been reported in any other zoned high-Zn chromites.

The term "ferritchromit" was first used by Spangenberg (1943) to describe highly reflecting borders found around isolated chromite grains in serpentinite. The composition of zone B is consistent with many reported analyses of "ferritchromit" (Haggerty, 1976) and will hereafter be referred to as "ferritchromit." Typically, "ferritchromit" is enriched in Fe and sometimes in Ni, Co, Ti, Mn, and Zn and depleted in Al and Mg with respect to the core that it surrounds. "Ferritchromit" has been reported to be both enriched and impoverished in Cr. The "ferritchromit zones" on the Sykesville chromites are enriched in Cr, Mn, Fe, and in most cases Ti (Fig. 3 is the exception for Ti) and depleted in Al, Mg, and Zn. The

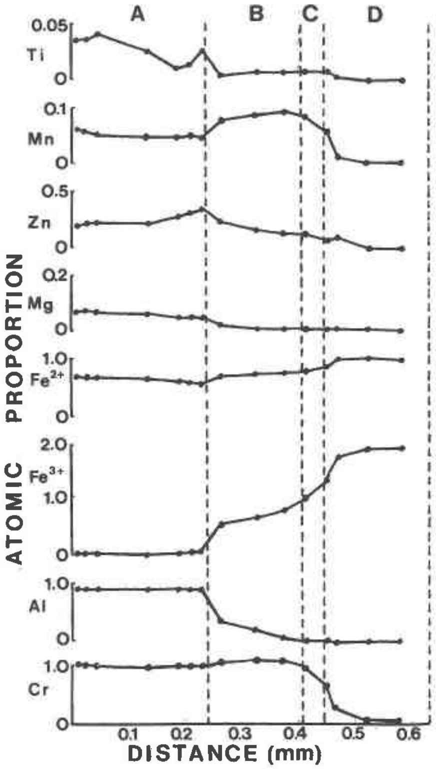

Fig. 3. Cation proportions as a function of position across a zoned chromite shown in Fig. 2(a) from an actinolite host.

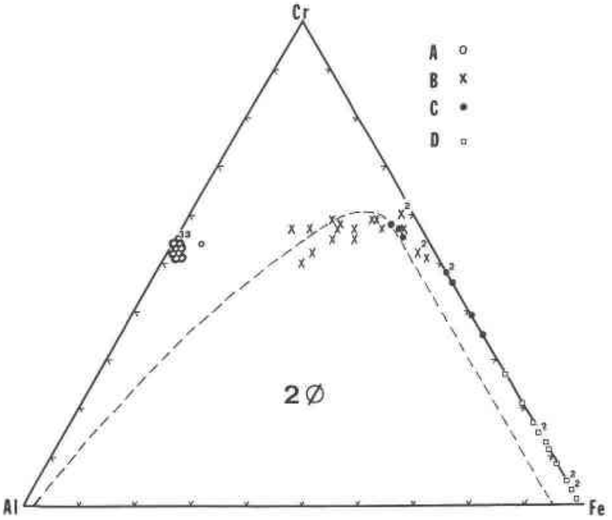

Fig. 4. Compositional plot of trivalent cations from zoned chromites from Sykesville. The approximate position of the solvus delineating the two-phase (2ϕ) field is from Loferski and Lipin (1983). Superscripts indicate the number of analyses in excess of one per data point.

Mn content is somewhat high in the "ferritchromit," ranging from a low of 1.9 wt% to a high of 2.5 wt%, although it does not approach the 14.4 wt% given for a Mn-rich chromite from northern Greece (Paraskevopoulos and Economou, 1981).

The compositions obtained for the anisotropic zone C show that it is intermediate between "ferritchromit" and the magnetite of zone D. The distinct anisotropy of zone C suggests that the phase does not have the isometric spinel structure.

Although the chemical variations among the zones illustrated in Figure 3 are similar for all the Sykesville chromites that we have studied, the compositions of the cores and the "ferritchromit" vary with distance from the serpentinite body. Figure 5 gives the range in weight percent for all oxides analyzed from each of the host rocks indicated. The host rocks in the metasomatic zone are identified by their dominant mineral phase and are listed in order from the serpentinite outward to the metapelite country rock. The chemical variations shown in Figure 5 coincide with the chemical changes in the host rocks because the same hydrothermal activity formed both the ore deposits and the metasomatic zones. The relative amounts of the various oxides are controlled by their chemical potentials at each point in the system, by physical parameters such as permeability (which may affect the flow of fluids), and by the minerals along the path that the fluids have followed before coming in contact with the spinels. Whatever the details of the factors governing the final chemistry of the chromites, it appears from the data given in Figure 5 that the chemistry was established after the chromites were incorporated into their hosts.

Discussion

The story of the origin of the complex pattern of zoning and the unusual chemistry of the Sykesville chromites must begin with the crystallization or recrystallization of the chromites during the formation of the mantle protolith, although their chemistry has been altered by geologic processes subsequent to their crystallization. Candela et al. (unpub. ms.) have described the evidence for a detrital emplacement of the serpentinite on the sea floor and the sedimentary accumulations of chromite in the overlying chemically precipitated quartz-magnetite rock and detrital pelitic sediments.

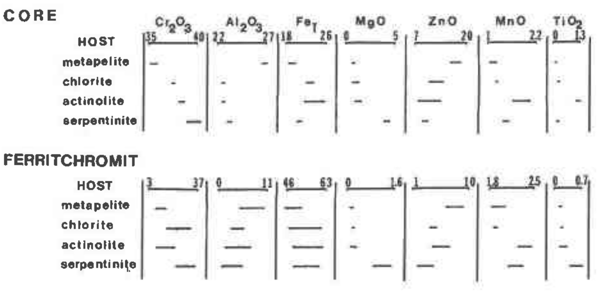

Fig. 5. Variations in composition (in weight percent) relative to kind of host rock for all oxides analyzed from the "ferritchromit" (zone B) and the core (zone A) of the chromite from Sykesville.

It seems unlikely that the high ZnO content of the Sykesville chromite is a primary magmatic or mantle feature. Zn-rich chromite has been reported from the Plan d'Albard minettes by Wagner and Velde (1985) and from an iron meteorite by El Gorsey (1976). If these chromites are orthomagmatic, as appears likely, they originated from magmas much different from those that gave rise to the chromite at Sykesville. Groves et al. (1977, 1983) have concluded that high-Zn ferrochromite from Western Australia crystallized directly from an Archean peridotite magma and from a coexisting sulfide-oxide magma. However, the highest ZnO contents in their study area (3–6 wt% ZnO) are reported from accessory chromites in the sulfide ore and from highly altered talc and carbonate-bearing serpentinite where the possibility of modification of the original chromite chemistry by metasomatism cannot be ruled out. Furthermore, none of these localities have chromite with ZnO contents close to those of the Sykesville district. At other localities noted for their high-Zn chromite, notably Outokumpu, Finland (Weiser, 1967), Helgeland area, Norway (Moore, 1977), and the Mashaba chromite mine, Zimbabwe (Bevan and Mallinson, 1980), metasomatism is clearly indicated. At Outokumpu, the geologic setting is similar to that of Sykesville. It is here that the ZnO contents are the highest previously reported (up to 12 wt%). Hydrothermal activity is known to have taken place at Sykesville, and sphalerite is ubiquitous in the sulfide ore deposits found there (Candela et al., unpub. ms.). We therefore think that metasomatism by Zn-rich hydrothermal solutions modified the original chromite compositions.

The evidence suggests that the Zn metasomatism took place after the chromites were emplaced in their hosts. Chromite is found in all units present, and there is a clear relationship between the mineralogy of the host and the concentrations of ZnO in the chromite cores (Fig. 5). Furthermore, all chromite cores show a smooth gradient in ZnO content with the highest values found at the core-"ferritchromit" boundary (Fig. 3). It is unlikely that the ZnO content could have been altered postdepositionally to reflect host-rock mineralogy while still retaining a predepositionally established gradient.

The Zn metasomatism either predated or coincided with the earliest stages of serpentinization of the ultramafite. An inverse correlation exists between MgO and ZnO in the spinel cores (Fig. 3), and these cores are anomalously low in total MgO (in all cases less than 4.2 wt% and in most cases less than 2 wt%). This indicates that as ZnO was added to the chromite, MgO was removed.

The origin of "ferritchromit" has been the subject of controversy for many years. For example, in some places the evidence suggests that it is an overgrowth on a chromite core formed when Cr and Fe and other cations were liberated from silicates in the parent ultramafite and concentrated in an aqueous fluid during serpentinization (Ulmer, 1974). In others, "ferritchromit" appears to be formed during regional metamorphism as a reaction product between the chromite core and a magnetite rim that was added when Fe was liberated from silicates during serpentinization (Bliss and McLean, 1975). At other locations the evidence suggests that diffusion of Mg and Al out of the spinel to form adjacent chlorite leaves behind a "ferritchromit" residue (Beeson and Jackson, 1969). At Sykesville, as the following discussion will show, the evidence suggests that diffusion of Fe^{3+} outward from the core, irreversible dissolution of some of the core, and precipitation of the "ferritchromit" all play a role.

Hoffman and Walker (1978) showed that in the ultramafic bodies of East Dover, Vermont, the degree of recrystallization (and serpentinization) and the thickness of "ferritchromit" rims correlate inversely with the Fe^{3+} content of the core chromites. They concluded that under the conditions of "ferritchromit formation," Fe^{3+} was more mobile than Cr and Al. As the chromite cores dissolved, the Fe^{3+} was forced out, later to accumulate in the "ferritchromit." Some Cr^{3+} was also forced out although its mobility was far less than that of Fe^{2+} or Fe^{3+}. Some oxidation of Fe^{2+} derived from the dissolution of the core also may have contributed to Fe^{3+} in the "ferritchromit." The cores of the Sykesville chromite are very low in Fe^{3+} compared to chromite in other serpentinites in the Appalachian Piedmont. The highest $Fe^{3+}/(Fe^{3+} + Cr^{3+} + Al)$ ratios found are only 0.025 and most are less than 0.015. Although this could reflect the primary chemistry of the chromite, the migration of Fe^{3+} outward is an equally plausible explanation.

Evidence that the formation of the "ferritchromit" was preceded by or coincided with an irreversible dissolution of the core comes in part from textural relations. The cores are anhedral and highly irregular in form. The core-"ferritchromit" boundary is sharp, both chemically and optically. In addition, the chemical gradients in the "ferritchromit" are not those expected to result from diffusion of species such as Cr^{3+}, Al^{3+}, or Ti^{4+} in or out of the spinel core. These observations argue against diffusion in the solid state as being a dominant factor in the formation of the "ferritchromit." Furthermore, Cr and Mn attain their highest concentrations in the "ferritchromit." If diffusion were the active process driven by differences in the chemical potentials of the oxides in the core and outermost rim, these high concentrations could only form if there were discontinuities in the activities of Cr_2O_3 and MnO such that higher concentrations corresponded to lower activities. On the basis of the assumption that the solubilities of the Cr^{3+} and Fe^{3+} phase components of the spinel were probably low in the fluid involved in the dissolution of the core, the most reasonable explanation for the formation of the "ferritchromit" is that it formed as a polycrystalline aggregate, which allowed communication between the growing "ferritchromit" and the dissolving cores. The "ferritchromit" was most likely in local equilibrium with the fluid that was driving the irreversible dissolution of the core. Once communication ceased, the source of Zn, Cr, and Al was cut off. Further growth was dominated by Fe and decreasing amounts of Cr probably liberated during full-scale serpentinization.

The idea that dissolution of the core provides the essential nutrient for the growth of the "ferritchromit" is supported by the development of a "ferritchromit" zone around the cores of chromites found in the metapelite. These same chromites lack the outer magnetite-rich zones (C and D) because the liberation of Fe from the host-rock minerals did not take place in the metapelite protolith as it did during the hydration of the ultramafite. Therefore, the "ferritchromit" in the metapelite could not have formed as a reaction product, and there is no nearby source of Cr other than the core.

The formation of the anisotropic zone C could have been a discrete event separate from the formation of the outermost magnetite-rich zone D. However, its boundaries with both the "ferritchromit" and zone D are irregular, indicating that it either formed as part of some continuous depositional process that began with "ferritchromit" and ended with magnetite, or as a reaction between the two during later metamorphic events. The latter explanation seems unlikely since no reaction rim formed between the "ferritchromit" and the core even though their chemistries are quite different. If zone C did form as part of a continuous process, as the evidence seems to indicate, it may have originally crystallized as an isotropic spinel and inverted to some lower-symmetry form as temperature decreased. That this anisotropic phase has not been reported in "ferritchromit" literature seems somewhat surprising. We have also found it around "ferritchromit" from the State Line district on the Maryland-Pennsylvania line. Perhaps it has been overlooked elsewhere. However, it may be rare, and its formation may be somehow related to the metamorphic history of the Maryland Piedmont and therefore confined to this region.

CONCLUSIONS

The high Zn content of the Sykesville chromite is probably related to the Cu-Co-Zn-Fe mineralization in the district. The hydrothermal fluids responsible for the mineralization probably leached Zn and Cu from basalts that underlay the host strata during the time of hydrothermal activity. The Cu, preferentially in the univalent state under hypogene conditions (Candela and Holland, 1984), was deposited as chalcopyrite (which is present in the ultramafite), whereas Zn was incorporated into the spinels. The transition from conditions conducive to Zn metasomatism to conditions that yielded the low-Zn outer zones of the spinel may be indicative of a transition from infiltrative sea-floor hydrothermal alteration to serpentinization by infiltrating regional metamorphic fluids.

Groves et al. (1983) have suggested that Zn-rich chromites can be used as a prospecting tool for Cu-Ni mineralization associated with dunites and komatiites. Spry and Scott (1986) pointed out that gahnite is found associated with many of the sulfide deposits in the Appalachians and the Scandinavian Caledonides. At Sykesville the occurrence of both gahnite (Shannon, 1923) and Zn-rich chromites supports the conclusion that Zn-rich spinels are indicators of Cu-Zn-Ni-(Co) sulfide mineralization.

ACKNOWLEDGMENTS

We are grateful to Eugene Jarosewich for his assistance with the microprobe analyses and to the Maryland Geological Survey for providing the drill cores for study.

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MANUSCRIPT RECEIVED SEPTEMBER 3, 1986
MANUSCRIPT ACCEPTED DECEMBER 1, 1986