

ALTERED CHROME ORES FROM THE COOLAC
SERPENTINE BELT, NEW SOUTH WALES,
AUSTRALIA

H. G. GOLDING AND P. BAYLISS,¹ *School of Applied
Geology, The University of New South Wales.*

ABSTRACT

Altered chrome ores from the Coolac Serpentine Belt, New South Wales, include chloritic and nonchloritic assemblages. In the chloritic ores the primary chromite is usually an aluminum-rich variety which is partly replaced by secondary chromite, or by a chemically equivalent oxide mixture; and by chlorite. Chemical analyses of chromite concentrates and electron probe scans across chromite variants show the secondary chromites to contain more chromium, more total iron, more ferric but less ferrous iron, less aluminum and less magnesium than the primary chromites. Much of the chlorite developed from serpentine and pyroxene; when aluminum, released from chromite during oxidation, became available. Some chlorite which originated in other ways, however, occurs in the same ores.

In the nonchloritic assemblages, primary chromium-rich chromite contains magnetite within fissures and is associated with serpentine-containing accessory awaruite. Diffusion at some chromite-magnetite contacts however resulted in a mineral resembling the secondary chromite of the chloritic assemblages.

The non-chloritic assemblages developed during serpentinization in conditions of low oxygen activity, and tended to persist during subsequent conditions of increased oxygen activity which induced the oxidation of aluminum-rich chromite. In conditions of high oxygen activity chromium-rich chromite also oxidized and associated serpentine was chloritized. The involvement of rodingitic assemblages in these reactions ranged from negligible to intense.

INTRODUCTION

Numerous features of the podiform (or alpine-type) chromite segregations, as presented by Thayer (1946, 1956, 1960, 1964), suggest their potential value as petrogenetic indicators for the enclosing rocks which are frequently deformed and metasomatized. A prerequisite to studies of chromite segregations, from this point of view, is the recognition of the nature and extent of deformation and metasomatism within the segregations themselves. An evaluation of these features for the chromite deposits of the Coolac Serpentine Belt, New South Wales, Australia, was made by Golding (1966). The deposits are of podiform type and evolved through accumulative, deformational and metasomatic stages, each of which left an imprint on the ores. It was suggested that disrupted chromite segregations were stranded during mobilization of the abyssal mafic magmas in which they accumulated; and captured by underlying harzburgitic mush. Upward replacement of these disrupted segregations as autoliths entrained within the mush, in the manner proposed by Thayer (1964), presumably followed. The ensuing metasomatic

¹ Present address: Department of Geology, University of Calgary, Calgary, Alberta.

stage was marked by serpentinization, chloritization and rodingitization of the surrounding rocks and of the gangue silicates within the ores, and by the alteration of the chromite.

This paper emphasizes the metasomatic stage in the development of the Collac ores. The extent of the alteration is outlined, the nature of the metasomatic products is indicated, the derivation of some products is traced and aspects of the metasomatism are discussed. Insofar as the reconstruction of premetasomatized mineral assemblages is indicated the study bears on earlier stages in the evolution of the ores

THE COOLAC SERPENTINE BELT

The Coolac Serpentine Belt is a steeply inclined, meridionally trending, alpine-type, ultramafic sheet, 56 km long and up to 2 km thick. It pene-

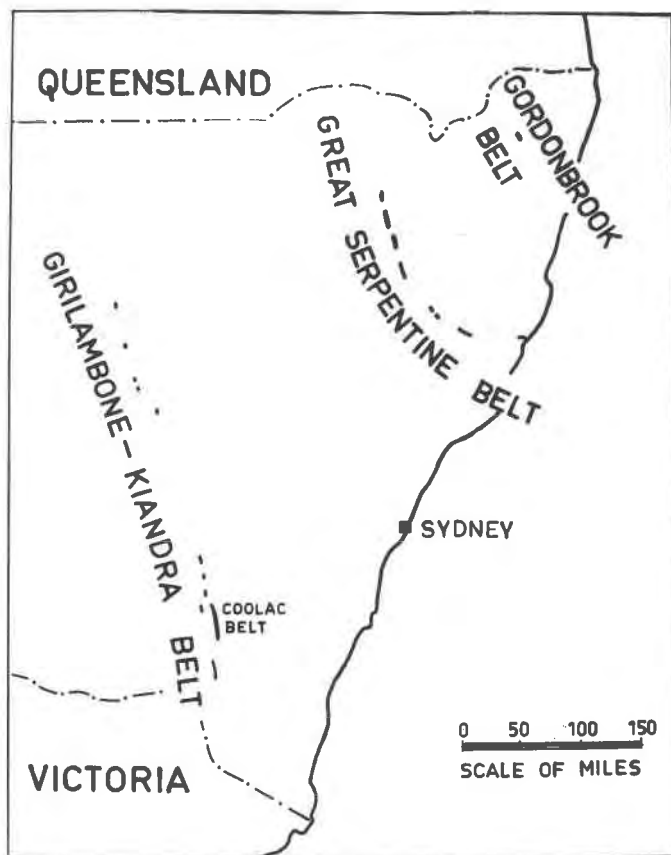


FIG. 1. Sketch-map of Eastern New South Wales, Australia, showing the distribution of the ultramafic belts.

trates eugeosynclinal metasediments and metavolcanics on the west and abuts a granite mass at a major fault contact on the east. The age of all these rocks is lower Palaeozoic and probably post-Ordovician. The Coolac Belt lies within a more extensive zone of scattered ultramafic bodies, which trends south-south east from Girilambone in the centre of New South Wales to the vicinity of Kiandra in the south-east of the State (Rayner, 1961) over a distance exceeding 500 km. The location of the Coolac Belt within the Girilambone-Kiandra Belt and the geographic relation of both to the better known Great Serpentine Belt (Benson, 1913) and to the Gordonbrook Belt (Raggatt, 1925) of New South Wales are indicated in Figure 1.

The Coolac Belt consists predominantly of massive, partly serpentinized harzburgite associated with subordinate dunitic serpentinite, wehrlite and uralite-gabbro. A zone of sheared serpentinite flanks the west of the Coolac Belt. Numerous small, dyke-like rodingitic segregations occur within the harzburgite and serpentinite. The rodingites include variable assemblages of chlorite, grossular and hydrogrossular, vesuvianite and relict clinopyroxene, and are regarded as metasomatized clinopyroxenite and gabbro. The chromite deposits occur within harzburgite or serpentinite. Much serpentinite wall-rock is awaruite-bearing (Golding, 1963). Many chromite deposits are penetrated by dykes and veins of rodingite which is similar to that in the country rock. The accessory chromite grains in the harzburgite and serpentinite include altered, opaque, corroded anhedral enclosing residual cores of translucent brown or yellow primary chromite; and some of these grains are surrounded by colourless chlorite. These accessory chromite-chlorite assemblages appear to be similar to some of those in the chromite deposits which are considered hereunder.

METHODS

Some 200 thin sections, 100 polished blocks and 12 polished thin sections of chrome ore obtained from 40 deposits distributed along 50 km of the Belt, have been examined. The cell edges of 60 chromites were determined from the high-angle reflections on X-ray diffraction powder photographs taken with a 114.6 mm Debye-Scherrer camera using either cobalt or chromium radiation. The accuracy for primary chromite is $\pm 0.005 \text{ \AA}$ and for secondary chromite is $\pm 0.01 \text{ \AA}$.

The relative concentration of the major metal constituents in the associated variants of chromite (4 specimens) and in the associated chromite and magnetite (1 specimen) have been compared using an electron probe micro-analyser. With the exception of the microanalyses for aluminium and magnesium in specimen 1b, which were inadvertently

made on the uncoated specimen surface, superposed straight-line paths for the scans for the different metals have been obtained within 3 microns. The electron probe traces have been evaluated semiquantitatively by reference to approximate absolute values for metal concentrations in the primary chromite. The reference values were obtained from chemical analyses of chromite concentrates, or from the cell edge of the primary chromite using a linear relation between the cell edge and the $\text{Cr}_2\text{O}_3:\text{Al}_2\text{O}_3$ weight percent ratio for the Coolac chromites (Golding, 1966).

Refractive indices of gangue minerals were measured to ± 0.005 and optical determinations have been confirmed by X-ray methods for olivine, garnet, vesuvianite, pyroxenes, serpentine and chlorite. An X-ray diffractometer was used with oriented chlorite slides to measure from 002 to 006 in order to calculate the 001 spacing. Chlorite samples for spectrographic analysis have been purified by heavy liquid separation and magnetic removal of chromite particles. The electron probe provided additional data for serpentine and chlorite.

CHROMITE

The $\text{Cr}_2\text{O}_3:\text{Al}_2\text{O}_3$ weight percent ratio of the primary chromite varies from 34:34 in some deposits to 62:6 in others and the cell edge varies sympathetically from 8.213 Å to 8.317 Å. There is a bimodal frequency distribution of the deposits, with respect to this ratio, with major and secondary maxima at about 57 and 37 weight percent of Cr_2O_3 . The chromite textural units include infrequent euhedral and nodular grains of single crystal character, frequent grain aggregates of various kinds, and cataclastic segments of grains and aggregates. The ratio of altered to primary chromite in specimens varies from traces in most of the chromium-rich chromite to 5 volume percent or more in aluminium-rich chromite, but chromite of both compositional types in the marginal portions of some deposits is extensively altered.

In thin section, primary chromite is translucent and the color ranges from yellow to red with increasing Cr_2O_3 and increasing slice thickness. The associated opaque material is either altered chromite or secondary magnetite, but oblique fissures in primary chromite appear dark or opaque as a result of refraction. In reflected light, altered chromite varies from relatively dense, smooth-polishing secondary chromite to pitted, poorly- and nonpolishing material. The reflectance of secondary chromite is variable but usually distinctly higher than for associated primary chromite. The material between the cavities in much pitted, altered chromite is notably heterogeneous with respect to color, reflectance and internal reflections. Replacement ore-textures which result from chromite

alteration include: (1) Crystallographically oriented replacement lamellae, either in parallel or in the form of rosettes (Fig. 2); (2) Rim replacements of isolated chromite units (Fig. 3); (3) Isolated domains (Fig. 4) and fissure-selvages (Fig. 3) of pitted material; and (4) Zonal sequences of primary chromite, dense to porous secondary chromite, and pitted nonpolishing material (Fig. 5), which suggest that a front of the dense material advanced ahead of the pitted material during replacement which proceeded inward from fissures.

More complex zonal textures in some ores result from the interference

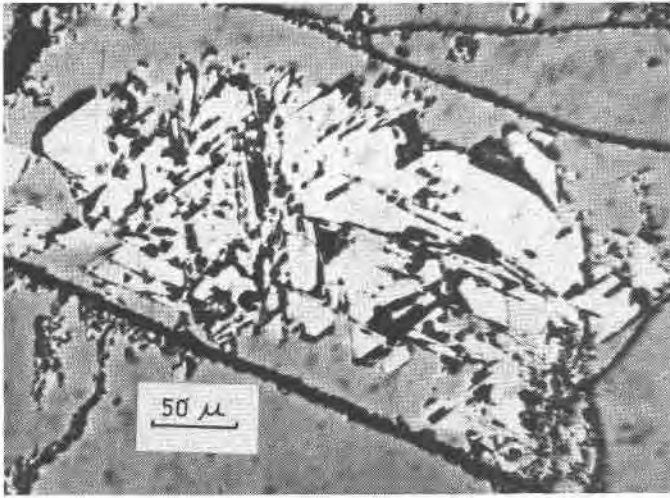


FIG. 2. Rosette lamellae of iron- and chromium-enriched secondary chromite (white) within primary chromite (grey). Oriented pits (black) separate the lamellae. Specimen 2. Reflected light; air.

of replacement fronts originating at different fissures; and possibly from superimposed alteration episodes. In other ores the altered chromite includes finely pitted domains from which threads of secondary chromite radiate into primary chromite. In yet other ores delicate intergrowths of primary and secondary chromite are associated with oriented cavities in some domains but with an unknown translucent phase in adjacent domains.

Broad peripheral embayments of unaltered chromite units are ascribed to magmatic solution in the abyssal stage. A finely denticulate peripheral zone is superposed over similar broad embayments in some altered chromite. The denticulate zone involves primary and secondary chromite gangue silicates, unidentified phases and cavities.

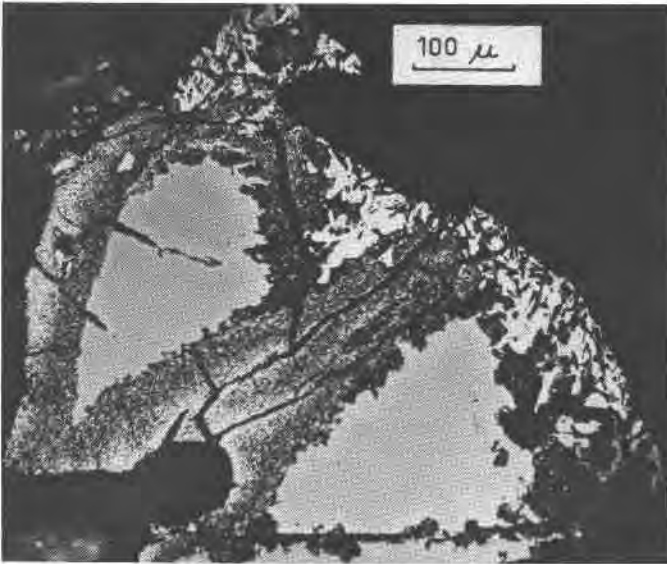


FIG. 3. Blebs of iron- and chromium-enriched secondary chromite (white) and pitted alteration products of chromite (mottled) replacing primary chromite (grey), peripherally and along fissures. The surrounding material (black) is chlorite. Specimen 1b. Reflected light; oil.

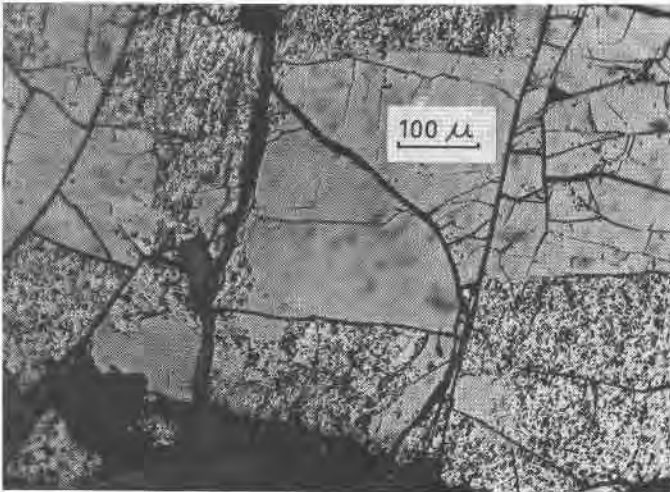


FIG. 4. Domains of pitted, altered chromite within primary chromite at the junction of chromite with a major chlorite veinlet (dark grey, lower left). Specimen 4. Reflected light; air.

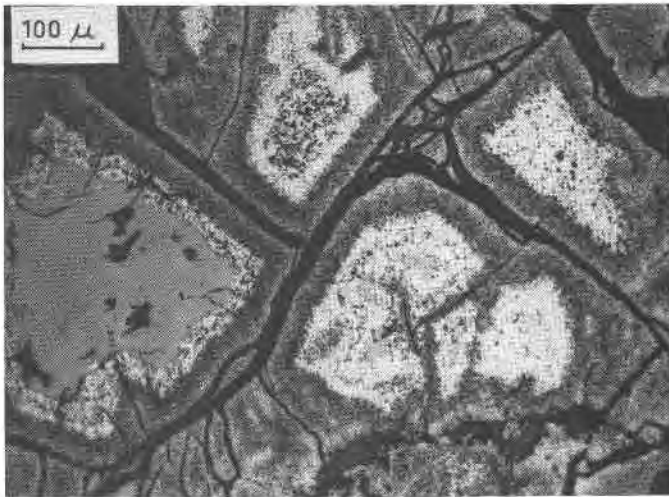


FIG. 5. Fissure-controlled, zonal replacement of primary chromite by alteration products. The smaller cells between fissures are completely replaced by dark non-polishing material (mottled grey) but the larger cells contain residual cores of primary chromite (smooth, grey) surrounded by zones of porous secondary chromite (white) and dark material. Chlorite (black) occupies the fissures.

Specimen 5.

Reflected light; oil.

TABLE 1. CHEMICAL ANALYSES OF CHROMITE CONCENTRATES FROM
QUILTER'S NORTH DEPOSIT, COOLAC SERPENTINE BELT

Specimen	1-a	1-b
Cr ₂ O ₃	34.1	44.8
Al ₂ O ₃	31.8	20.2
Fe ₂ O ₃	6.3	15.4
V ₂ O ₃	<0.1	<0.1
FeO	7.7	6.6
MgO	16.5	11.5
MnO	0.2	0.2
CaO	0.1	<0.1
NiO	nil	nil
TiO ₂	<0.1	<0.1
SiO ₂	0.7	0.2
Loss	nil	0.6
Totals	97.6	99.8

1a: Chromite containing 5 volume percent of altered chromite. From massive, centrally disposed ore.

1b: Chromite containing 40 volume percent of altered chromite. From sheared marginal spotted ore.

TABLE 2. ALTERATION, COMPOSITION AND CELL SIZES OF CHROMITE FROM SELECTED COOLAC CHROME ORES^a

Specimen	Altered ^b chromite	Chromite composition ^c					Cell Size Å	
		Cr ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	Primary chromite ±0.005	Secondary chromite ±0.01
1a ^d	5	35.8	32.8	6.6	8.1	16.6	8.219	
1b ^d	40	45.5	20.4	15.7	6.7	11.6	8.221	8.29
2	0 ^f	39	29				8.227	8.31
3	5	52.8	14.3	5.8	13.5	13.5	8.270 ^j	
							8.282	
4	2 ^g	56.8	14.8	0.1	16.9	11.4	8.287	
5	0 ^h	57	12				8.299	8.40
6	2 ⁱ	58.1	11.5	5.3	11.0	14.0	8.296	8.34
7 ^e	trace	58.5	11.7	5.3	10.9	13.5	8.305	

^a Specimens 1 to 7 are from different deposits respectively located at 8, 1.5, 40, 5, 18, 7 and 35 km from the northern extremity of the Coolac Belt. The wall rocks in general are of serpentinized harzburgite and clinochrysotile-lizardite serpentinite ± rodingite, but for specimen 2 are antigorite serpentinite.

^b Volume percent of total chromite, estimated visually.

^c Except for specimen 1b compositions approximate to those for primary chromite. Analyses (1a, 1b, 6 and 7) have been recalculated to total 100 after omitting minor constituents, correcting for impurities and (specimens 3 and 4) allocating total Fe to FeO and Fe₂O₃ (Bateman, 1945). Oxide values for specimens 2 and 5 are derived from cell sizes; accuracy ± 3.

^d Specimens 1a and 1b are respectively slightly altered chromite from massive, centrally disposed ore and strongly altered chromite from spotted, sheared, marginal ore, from the same deposit. The gangue in both is pale grey chlorite with traces of clinopyroxene.

^e Contains 4 volume percent of magnetite in fissures. Serpentine gangue.

^f Up to 70 flanking bluish-green chlorite selvages which abut lizardite.

^g Up to 25 flanking a vein of pink chrome chlorite enclosing suspected zoisite.

^h But 90 in marginal, spotted ore containing a bluish-green chlorite matrix mixed with lizardite in places.

ⁱ But 15 in associated chromite replaced by chrome chlorite and zoned chrome garnets.

^j This variation is ascribed to incipient alteration of chromite.

Chemical analyses of chromite concentrates (specimen 1a) from massive centrally disposed ore and (specimen 1b) from strongly altered marginal ore from a single deposit are compared in Table 1. Data on the amount of alteration, approximate compositions and cell parameters of these and other selected specimens are summarized in Table 2.

Bulk compositions (specimens 1a and 1b, Tables 1 and 2) and electron probe scans across chromite variants (Figs. 5 to 8) reveal enrich-

ments of chromium and iron and depletions of aluminium and magnesium in the altered chromites as compared with the associated primary chromites. In the following semiquantitative statement of these compositional differences evaluated from the electron probe analyses, percentages are by weight of total sample as exemplified for chromium.

Chromium in specimen 1b (Fig. 7) increases from about 25 percent in the unaltered chromite to about 29 percent in the altered variants, or by 4 percent. Similar increases by 3 or 4 percent are registered for the secondary materials in all specimens. The increases are sharp and consistent.

Iron increases by 12 percent in some porous, high-reflecting material (Fig. 5); but varies widely within a single rosette (enriched by 6 to 12 percent, Fig. 6) and within a single pitted domain (average enrichment by 5 percent, Fig. 8). In specimen 1b (Fig. 7) the pitted selvage (F, H) and the dense secondary chromite (B) are enriched by 5 and 10 percents respectively.

Aluminum is sharply and consistently depleted by 4 percent in both dense and pitted materials (3 specimens) and by 6 and 9 percent in the associated dense and pitted variants respectively of specimen 1b (Fig. 7).

Magnesium decreases gradationally by 3 percent in a porous, high-reflecting variant (Fig. 5), less than 2 percent in dense and pitted variants of two specimens, but shows no appreciable variation in specimen 1b.

Other constituents: A test for sulphur in porous, high-reflecting material (Fig. 5) was negative but a little silicon (lacking in the primary chromite) is present.

Primary magnetite was not recognized in the Coolac ores but secondary magnetite, rarely exceeding 2 volume percent of the ore minerals, frequently occurs in contact with unaltered chromium-rich chromite. The magnetite either occupies fissures some of which also contain serpentine, or it forms accretionary rims to isolated cataclastic chromite units. Altered chromite and magnetite seem to be mutually exclusive, but some magnetite is separated from primary chromite by narrow selvages of material having an intermediate reflectance which resembles secondary chromite. The magnetite is usually dense and in places contains exsolved haematite lamellae.

An electron probe scan across a magnetite-chromite contact (specimen 7) revealed more than 5 times as much iron in the magnetite. The latter contains only about 1 percent of chromium. A test for nickel revealed about 1 percent in the magnetite but none in the chromite. Traces of manganese were registered for both. The iron content of this magnetite is more than $2\frac{1}{2}$ times greater than that in the rosette-lamellae (Fig. 2) which is the best crystallized secondary chromite encountered.

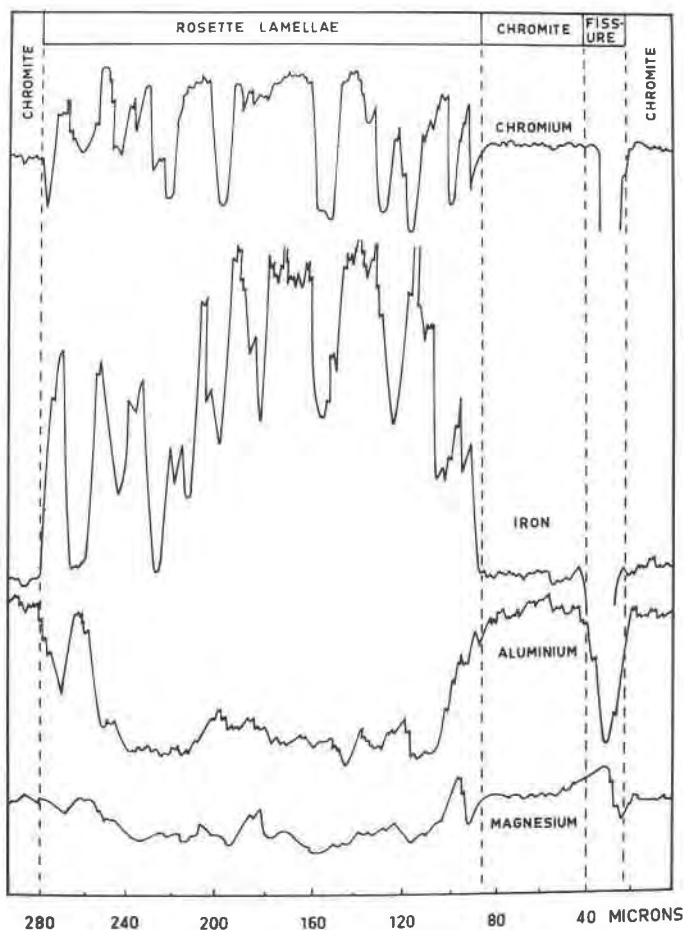
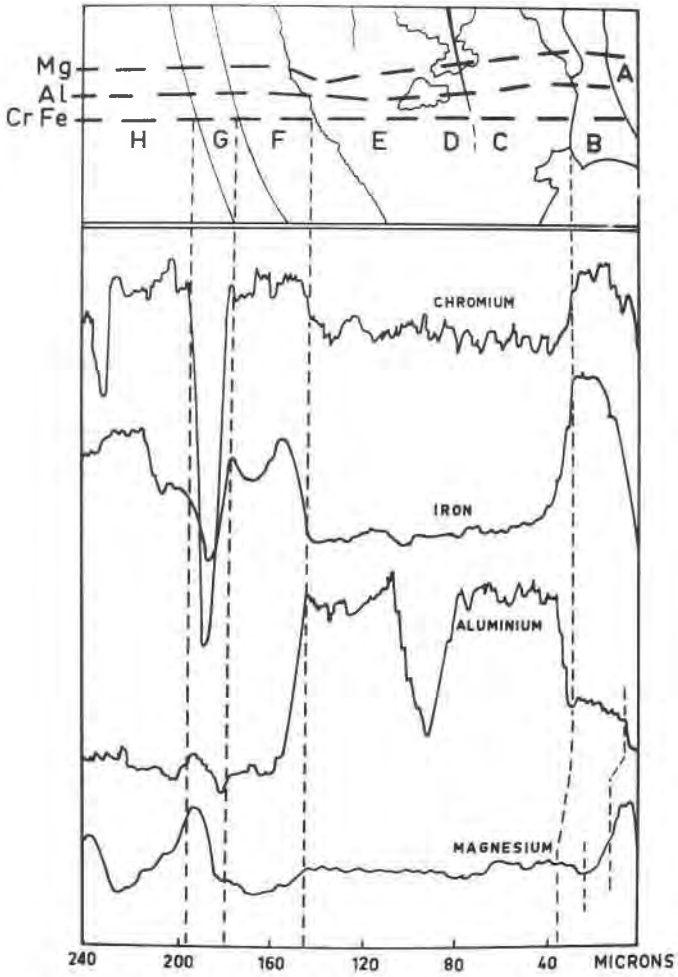
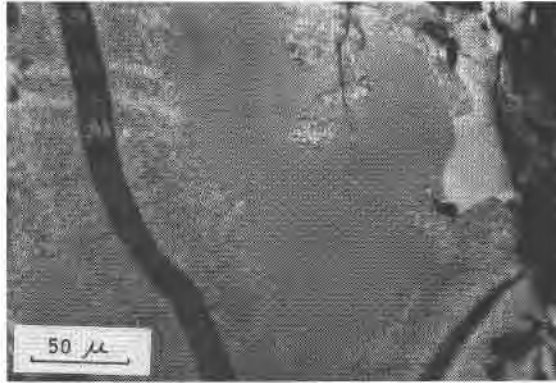


FIG. 6. Electron probe scans for chromium, iron, aluminum and magnesium across primary chromite (designated chromite) and rosette lamellae of secondary chromite in a portion of specimen 2. The rosette lamellae form a unit similar to that illustrated in Figure 2.

THE GANGUE MINERALS

The chromium-rich chromite is usually associated with serpentine with or without relict olivine. The aluminum-rich chromite is associated with clinopyroxene and chlorite with or without subordinate serpentine and olivine. In relict undeformed portions of ore, the gangue occupies cuspid interspaces (Jackson, 1961) between primary chromite units. It may represent trapped intercumulus liquid, but the primary silicates are usually altered. Such gangue is referred to hereunder as intimate to distinguish it from that occurring as veinlets or occupying breccia spaces.



The relative movement of ore masses and silicate mush during re-emplacment may have resulted in the fortuitous juxtaposition of serpentine with ore containing aluminium-rich chromite (Fig. 9).

Characteristic general features of the Coolac ores are firstly the predominance of chlorites and serpentine minerals as gangue and secondly convergent metasomatism of various pre-existing silicates to chlorite-rich assemblages.

The chlorite in hand specimens is bluish-green, grey, pink or lavender. In thin sections it is colorless, variably crystallized, usually optically positive and polarizes in first order or anomalous brown colors. Some chlorite shows a relict serpentine mesh-texture in which the mesh collars (Francis, 1956) or both collars and cores, polarize in anomalous blue colors. The basal spacings of chlorites from 19 specimens range from 14.19 Å to 14.34 Å. The aluminum content (x) was calculated from the formula $d(001) = 14.55 - 0.29x$ (Brindley, 1961). The ferrous iron content (y) was calculated firstly from the basal spacing intensities (Brown, 1955) and secondly from the (060) spacing, using the formula $d(060) = 9.19 + 0.03y$ (Brindley, 1961). The results obtained are compatible with the spectrographic data for three samples (Table 3). A plot of all the chlorite formulas shows a rather even distribution about $(\text{Mg}_{4.8}\text{Fe}_{0.2}\text{Al})(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$. The compositions range across the lower part of the clinochlore field of Hey (1954) and overlap into the fields of sheridanite and penninite.

The serpentine in hand specimens is green, brown or yellow. Most is a mixture of lizardite and clinochrysotile, and reveals mesh-texture in thin section. Impurities in these mixed serpentines include iron oxides, complexes of the iddingsite type which may involve ferro-brucite and stevensite; and traces of awaruite, heazlewoodite, other sulphides and native copper. Some serpentine identified from diffractograms as pure lizardite reveals a relict disrupted mesh texture in thin section, and electron probe



FIG. 7. Electron probe scans for chromium, iron, aluminium and magnesium across a portion of specimen 1b. The paths scanned are indicated by thick broken lines in the diagram above the traces.

- A : Chlorite.
- B : Dense secondary chromite.
- C, E: Primary chromite.
- D : Median fissure associated with pitted material.
- F, H: Pitted alteration products.
- G : Fissure containing chlorite.

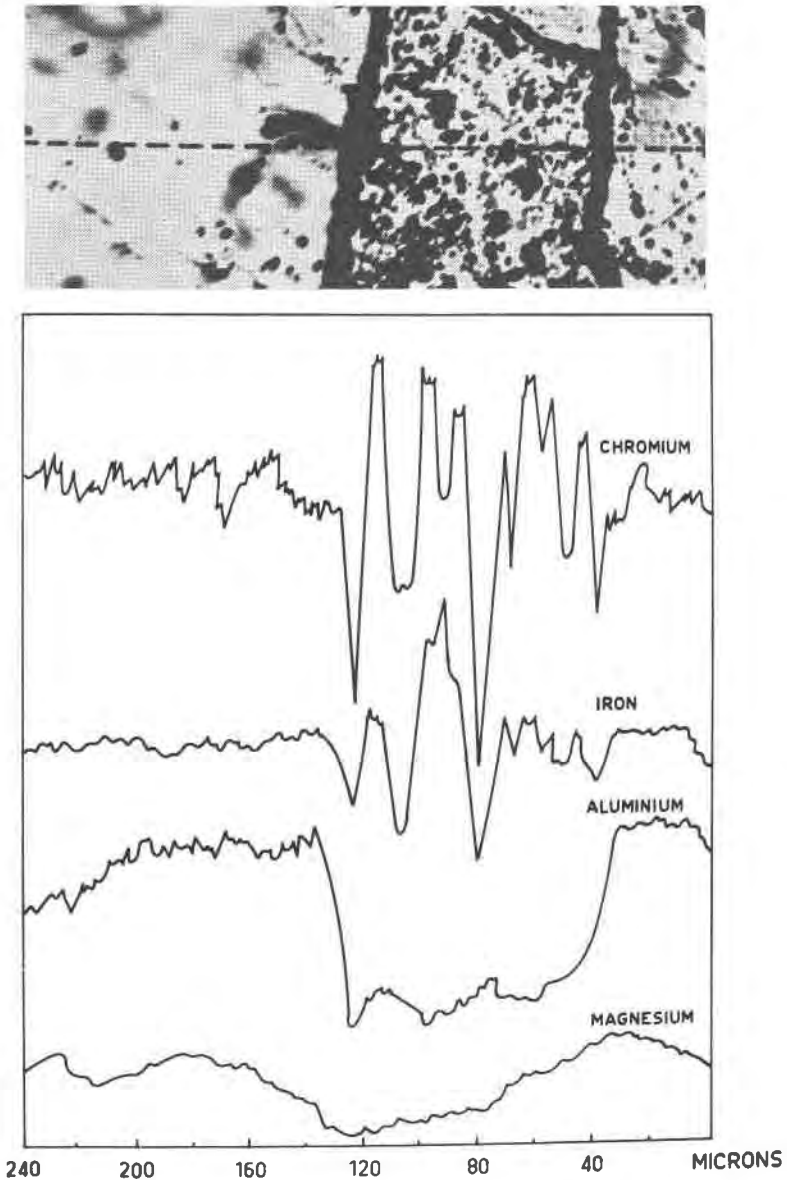


FIG. 8. Electron probe scans for chromium, iron, aluminium and magnesium across a cataclastic segment of coarsely pitted altered chromite in specimen 3. The segment is separated from primary chromite or incipiently altered chromite by fissures.

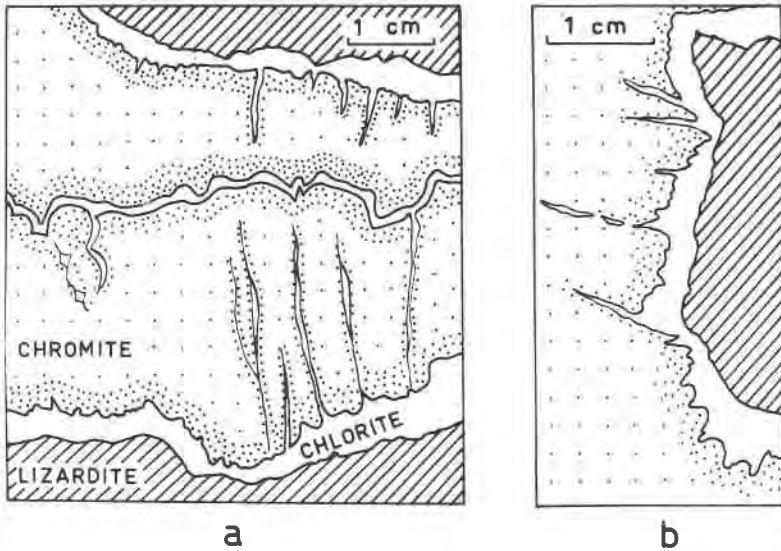


FIG. 9. Sketches of hand specimens of chrome ore.

- a: Chlorite in the narrow vertical fissures derived partly from clinopyroxene. Chlorite in the wide upper and lower selvages between chromite and lizardite, and chlorite in the lateral median veinlet, derived from serpentine.
- b: Chlorite separating lizardite and chromite, and replacing both. Altered chromite observed microscopically increases toward chlorite, as indicated by the intensity of the shading. Specimen 2.

TABLE 3. THE COLOR, BASAL SPACING AND HEAVY METAL CONTENT OF CHLORITES IN 3 COOLAC CHROME ORES

Specimen	4	3	8
Color of powder	Pale grey	Lavender	Pink
$d(001)$ Å	14.25	14.27	14.34
Wt. %			
Cr	1.02	1.85	1.80
Fe	1.2	0.2	0.2
Ni	0.14	0.17	0.15
Mn	0.027	0.004	0.006
Equiv. wt. %			
Cr ₂ O ₃	1.49	2.76	2.63
FeO	1.54	0.26	0.26

scans indicate the presence within it of iron- and aluminium-enriched domains. Of 45 X-rayed gangue specimens containing chlorite, serpentine or both, 22 registered chlorite only, 14 serpentine only and 9 contained members of both groups.

Other gangue minerals include grossular ($n=1.735$), hydrogrossular ($n=1.700$ to 1.715), chrome grossular and uvarovite ($n=1.820$ to 1.830), vesuvianite, diopsidic pyroxene ($\beta=1.690$), scarce colorless amphibole, olivine, rare bronzite, and rare suspected zoisite. Intimate diopside and amphibole alter to fibrous relics which merge into chlorite containing micron-wide garnets and rare yellow tablets of suspected anatase. The garnets and vesuvianites of rodingite veins are 20 to 100 microns wide.

ALTERED CHROMITE—CHLORITE RELATIONSHIPS

Partly chloritized intimate clinopyroxene and amphibole make contact with sensibly unaltered chromite in some ores, but are extensively or completely chloritized against altered chromite in others. Unmodified, colorless rodingitic assemblages penetrate unaltered chromite in some ores. Narrow (50 micron) selvages of green chrome grossular separate colorless grossular from incipiently altered chromite in others. Veins of megascopically pink chrome chlorite associated with rodingitic garnet, vesuvianite or suspected zoisite penetrate strongly altered chromite; and some large chrome garnets in similar assemblages have chromite cores. Chlorite derived from serpentine or olivine is always closely associated with altered chromite.

Other textural criteria for a genetic relation between altered chromite and chlorite include: (1) A progressive increase in the amount of altered chromite toward chlorite rims and veinlets (Fig. 3), veins (Fig. 4), and selvages (Fig. 9); (2) Zonal sequences of primary chromite, altered chromite, chlorite and serpentine (Fig. 9); (3) The replacement of primary chromite jointly by altered chromite and chlorite, and the simultaneous replacement of serpentine by chlorite (Fig. 9). The replacement of primary chromite jointly by altered chromite, chlorite, chrome garnet and other translucent phases (specimen 6); and (4) Relict serpentine mesh-texture in chlorite associated with altered chromite (specimens 2 and 5).

Electron probe scans across chlorite and lizardite selvages (Fig. 9) reveal additional zonation. Chromium is lacking in the chlorite except over a width of 150 microns immediately flanking the altered chromite. Aluminum increases progressively over the whole chlorite selvaige toward the altered chromite. The iron- and aluminum-enriched domains in the lizardite increase in size and frequency toward the chlorite.

DISCUSSION AND CONCLUSIONS

The chemical composition of the opaque alteration products. The bulk chemical analyses of specimens 1a and 1b (Table 1) show an iron enrichment in the altered products, which corresponds to a pronounced enrichment in ferric iron partly at the expense of ferrous iron. The combined data from these bulk analyses and from the electron probe analyses indicate that the secondary products contain more chromium and more total iron, more ferric iron although less ferrous iron, but less aluminum and magnesium than the primary parental chromites. Weight gains in the chromium and iron exceed weight losses in the aluminum and magnesium by a factor of 2 and roughly represent antithetic gains and losses in the number of heavy and light atoms. The most pronounced enrichment at a given point is that for iron but the most consistent within domains of altered chromite is that for chromium, while the most pronounced and consistent depletion is that for aluminum. The smooth-polishing, denser secondary chromites exhibit greater heavy metal gains than the pitted materials. Minor reversals in the direction of migration of atoms such as the local diffusion of chromium from chromite into abutting garnet are strongly overcompensated by the dominant trends. Differences between the concentrations of iron, chromium and aluminum in the altered as compared with the primary chromites tend to be sharply defined whereas those for magnesium are gradational. The uneven distribution of iron in the altered products suggests variable diffusion and segregation.

The opaque products are therefore regarded as iron- and chromium-enriched secondary chromites or secondary products. Somewhat similar chemical changes were recorded for altered chromites in Egypt (Amin, 1948) and in North Carolina (Miller, 1953) but the gains in Cr_2O_3 were less marked, some gains in FeO accompanied pronounced gains in Fe_2O_3 and losses in MgO and Al_2O_3 were both pronounced.

In contrast with these secondary products in the chloritic Coolac ores, which are intimately related both spatially and genetically to the primary, parental chromites; the magnetite in specimen 7, and presumably that in other non-chloritic ores, is a magnetite *sensu stricto* which has no such proximate genetic relation to the abutting primary chromite. Products with a reflectance intermediate between those for primary chromite and magnetite also develop at some magnetite-chromite contacts in the Coolac ores. Their composition is unknown but possibly approximates to that of the secondary chromites in the chloritic ores. The chromite-magnetite-serpentine association has been recorded elsewhere by Stockwell (1944), Maxwell (1949), Horninger (1941) and Gafenauer

(1956) and the intermediate products or "grey magnetite" by Horninger (1941), Ramdohr (1960) and Vaasjoki and Heikkinen (1961).

The mineralogy of the opaque alteration products. Only spinel lines were detected on X-ray powder photographs of the opaque alteration products. Cell size values for these products vary widely but are consistently greater than those for the respective primary, parental chromites. The X-ray photographs however are of poor quality because of heterogeneity and/or poor crystallinity. The best crystallized alteration product is the rosette material (Fig. 2) for which a cell edge of 8.31 Å in conjunction with the compositional data characterize it as a chromite of variable composition. Such chromite probably contains trivalent ions (mainly Fe³⁺ and Cr³⁺) in excess of the 1:2 divalent to trivalent cation ratio believed to be attained in primary chromites (Thayer, 1956).

A strongly magnetic fraction of specimen 1b yielded a cell size value of 8.29 Å, indicative of chromite, but the material responsible for the lines on the X-ray photograph may have been restricted to the better crystallized variant (B, Fig. 7), a material itself heterogeneous as revealed by its variable reflectance. For the pitted materials, cell-size values of 8.34 Å (specimen 6) and 8.40 Å (specimen 5) are respectively compatible with the presence of maghemite and magnetite, although not exclusively indicative of these minerals (Rait, 1946). Furthermore since the powder patterns may represent only a fraction of otherwise effectively amorphous materials, and because electron probe data shows similar materials (specimens 1b and 3) to contain substantial amounts of chromium, aluminum and magnesium as well as iron, their mineralogy remains obscure. Pending a more detailed study these poorly crystallized products are regarded as probable mixtures of chrome- and iron-rich spinels perhaps with hematite or eskolaite. Alteration products of chromite possibly to be included in the same broad category have been designated as mixtures of chrome spinels and magnetite (den Tex, 1955), chrome spinels and maghemite (Deer, Howie and Zussman, 1962), iron-rich chromite or magnetite with martite (Baker, 1956, 1962), the chromian equivalent of martite (Mukherjee, 1966), and as colloidal alteration products of chromite (Heisleitner, 1952). Solid solutions of sesquioxides have also been suggested for similar products (Rait, 1946, 1950).

Some alteration mechanisms. The predominant alteration of the Coolac ores apparently involves the oxidation of primary chromite and the concomitant chloritization of associated serpentine, olivine and pyroxene. This oxidation was presumably initiated at lattice defects within micro-fissures above some threshold value of oxygen activity, which was

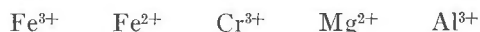
controlled by the physical and chemical nature of the vapors penetrating the ore, and the physical and chemical constitution of the chromite. The oxidation of three ferrous ions introduces an excess of three positive charges which might be neutralized by the expulsion of one aluminum ion, and similarly the oxidation of two ferrous ions might be neutralized by the expulsion of one magnesium ion.

Factors influencing the selective expulsion of cations from the chromite during oxidation probably included the preference of particular cations for specific lattice sites in the spinel structure, and the cation sizes. Data from Wells (1962, p. 489) and Evans (1964, p. 173) suggests that the sequences: Cr^{3+} Al^{3+} Fe^{2+} Mg^{2+} Fe^{3+} represents decreasing cation stability in tetrahedral coordination from right to left and decreasing cation stability in octahedral coordination from left to right, in the spinel structure. The two end-members of this series might therefore be expected to be the most stable during the alteration of chromite. Of the remaining cations it might be concluded from its central position in the series that Fe^{2+} is the least stable. A tendency toward the expulsion of Fe^{2+} , however, would presumably be nullified by oxidation and the resulting Fe^{3+} would enter a tetrahedral site and displace aluminum or magnesium.

The ionic radii of the predominant cations in chromite are $\text{Al}^{3+}=0.51 \text{ \AA}$, $\text{Cr}^{3+}=0.63 \text{ \AA}$ and $\text{Fe}^{3+}=0.64 \text{ \AA}$ for the trivalent ions and $\text{Mg}^{2+}=0.63 \text{ \AA}$ and 0.66 \AA , and $\text{Fe}^{2+}=0.70 \text{ \AA}$ and 0.74 \AA for the divalent ions in tetrahedral and octahedral coordination respectively (after Ahrens, 1952, cited in Vermass and Schmidt, 1959).

Preferential mobility of the aluminum over the magnesium ions might thus be expected as a result of the smaller size, and the location of the former in large octahedral holes as compared with the larger magnesium ions occupying smaller tetrahedral holes.

These considerations suggest that the sequence:



is one of increasing mobility of cations (increasing tendency for total expulsion from the chromite system) from left to right, under the predominating conditions which operated during the alteration of the Coolac ores. This sequence differs from that proposed by Jeljazkova-Panajotova (1964), for the increasing mobility of elements in chromite elsewhere, in the reversed positions of the chromium and magnesium ions.

The suggested expulsion of light metal cations to balance the excess charge caused by oxidation of iron originally present in chromite, however, only partly accounts for the observed metal gains and losses. Once initiated, however, other factors would influence continued ionic migra-

tion. Factors visualized include cavity formation, the introduction of ferric and ferrous iron from outside the system, and the oxidation of the introduced ferrous iron. Cavity formation and enlargement may have resulted from local lattice contraction incident to oxidation, from the diffusion of Fe^{3+} and Cr^{3+} into the cavity walls from which the expulsion of Al^{3+} and Mg^{2+} continued, from the diffusion and coalescence of lattice vacancies, from the bulk removal of material in solution, suspension or vapor, and from the dehydration of transient hydrous complexes. The converse tendency toward closure of cavities, however, also existed as a result of the entry of iron, the expanding cell size of the iron- and chromium-enriched spinels, the sealing of cavities by dispersed oxide systems, and the growth and incursion of chlorite and other silicates into the cavities. Fluctuations in redox and other conditions from point to point and with time during alteration influenced the heterogeneity and variability of the products.

The metasomatic stage in the evolution of the ores. Two principal assemblages characterize the metasomatic stage in the development of the Coolac chrome ores: the chloritic assemblage which includes oxidized chromite, and the nonchloritic (serpentine) assemblage which includes substantially unaltered chromite associated with magnetite. The former is more complex and variable than the latter. These two assemblages correspond broadly with those associated with the subtractive mode of chromite alteration and with the accretionary magnetite modification of chromite respectively (Thayer, 1956), and possibly with the "verde-antique"—antigorite—chrome-chlorite and "buckskin weathering" serpentine assemblages respectively (Thayer, 1966).

The chloritic assemblage typically includes partly oxidized aluminium-rich primary chromite, while the primary chromite associated with magnetite is chromium-rich. This relation might be expected from the parageneses prior to serpentinization. Thus the chromium-rich chromite was usually associated with predominant olivine (probably containing 8 to 10 weight percent of FeO), which became extensively serpentinized, apparently in conditions of relatively weak oxygen activity favorable to the mobilization and limited oxidation of iron to magnetite and to the formation of awaruite. The aluminum-rich chromite however was associated with predominant (presumably iron-poor) diopside and either subordinate olivine or no olivine, an assemblage which became only slightly serpentinized.

Subsequently in conditions of increased oxygen activity the less stable aluminum-rich chromite oxidized readily and the released aluminum transformed diopside, serpentine and residual olivine to chlorite. Minor

contributions to the chloritic assemblages apparently resulted from the independent transformation of (presumably somewhat aluminous) diopside and amphibole to chlorite and garnet. Major contributions resulted from the injection and rodingitization of gabbroic or clinopyroxenitic veins. When injection and/or rodingitization coincided with chromite oxidation the complexity of the products increased.

The chromium content of the intimate clinopyroxenes is unknown and minor contribution of chromium to chromiferous silicates from this source cannot be excluded. Most chrome chlorite in the ores, however, has a mixed rodingitic paragenesis; or occurs as monomineralic veinlets in ores which also contain separate veinlets of chrome grossular and less commonly of vesuvianite. The local diffusion of chromium into normal rodingitic grossular, and the absence of colored silicates in the rodingites of the country rocks thus point to chromite as the chromium source in the chromiferous silicates most of which have rodingitic affinities. The genesis of the rodingites in general is beyond the scope of this discussion but it is evident that the involvement of rodingitic vein material in the alteration of the Coolac ores ranged from negligible to intense.

Experimental data (Bowen and Tuttle, 1949; Yoder, 1952; Nelson and Roy, 1958; and Gillery, 1959) are compatible with temperatures of chlorite formation above those for chrysotile. Lipman (1964) suggested a temperature range of 520° to 680°C for the reaction between aluminous chromite and magnesium silicates to form chlorite, under plutonic conditions, as exemplified by accessory assemblages in peridotite of the Klamath Mountains. The transformation of a metastable aluminian serpentine to chlorite however is possible at lower temperatures. Observations on the Coolac ores indicate that much of the chlorite post-dates serpentization. Some of this chlorite, moreover, appears to have developed via an aluminian serpentine.

The metasomatic stage in the development of the Coolac chrome ores presumably commenced, during the initial cooling of the peridotite mass, with minor formation of chlorite from intimate clinopyroxene, and with the injection and concurrent rodingitization of gabbroic and clinopyroxenitic dykes. Rodingitization probably continued during the ensuing serpentization, when magnetite was deposited within chromium-rich chromite. Except for minor diffusion at chromite-magnetite contacts such assemblages tended to persist. During post-serpentine hydrothermal episodes, or accompanying fluctuations in temperature or gas pressure in a protracted period of serpentization; aluminum-rich chromite was oxidized and associated silicates chloritized. While chromium-rich chromite was more stable than aluminum-rich chromite in given oxidizing conditions, and for a given MgO:FeO ratio of the chro-

mite, such chromite also oxidized above some threshold value for oxygen activity and promoted chloritization of associated serpentine. In such conditions any earlier-formed magnetite may have lost its identity in the final products of metasomatism. That some of the secondary ore-mineral assemblages are supergene modifications of altered hypogene assemblages seems unlikely in view of the general absence of other indications of aggressive weathering in the Coolac Belt.

ACKNOWLEDGMENTS

The authors are indebted to The Broken Hill Proprietary Company, Australia and to the Mines Department of New South Wales for the chemical analyses of chromite concentrates; to Mr. G. T. See of the University of New South Wales for the spectrographic determination of the heavy metals in three specimens of chlorite; and to Mr. Van Peer of the Atomic Energy Commission, Lucas Heights, New South Wales for operating the electron probe microanalyzer.

REFERENCES

- AMIN, M. S. (1948) Origin and alteration of chromites from Egypt. *Econ. Geol.* **43**, 133–153.
- BAKER, G. (1956) Basement complex rocks in the Cycloops Ranges—Sentani Lake region of Dutch New Guinea. *Nova Guinea* **7**, 13–39.
- (1962) *Detrital Heavy Minerals in Natural Accumulates with Special Reference to Australian Occurrences*. Monograph Ser. I, Australasian Inst. Mining. Met. Melbourne.
- BATEMAN, J. D. (1945) Composition of the Bird River chromite, Manitoba. *Amer. Mineral.* **30**, 596–600.
- BENSON, W. N. (1913) The geology and petrology of the great serpentine belt of New South Wales. *Proc. Linn. Soc. N.S.W.* **38**, 490–517.
- BOWEN, N. L. AND O. F. TUTTLE (1949) The system $MgO-SiO_2-H_2O$. *Geol. Soc. Amer. Bull.* **60**, 439–460.
- BRINDLEY, G. W. (1961) Kaolin, serpentine and kindred minerals. In G. Brown, ed., *The X-ray Identification and Crystal Structures of Clay Minerals*, Mineral. Soc. London, p. 51–131.
- BROWN, G. (1955) Intensities of 001 reflections of mica and chlorite-type structures. *Mineral. Mag.* **30**, 657–665.
- DEER, W. A., R. A. HOWIE AND J. ZUSSMAN (1962) *Rock Forming Minerals, V. 5*. Longmans, London.
- EVANS, R. C. (1964) *An Introduction to Crystal Chemistry*. 2nd Ed., Cambridge Univ. Press, Cambridge.
- FRANCIS, G. H. (1956) The serpentine mass in Glen Urquhart, Invernesshire, Scotland. *Amer. J. Sci.* **254**, 201–226.
- GOLDING, G. H. (1963) The occurrence of terrestrial nickel-iron in serpentinite near Coolac, New South Wales. *Aust. J. Sci.* **26**, 152–3.
- (1966) *The Constitution and Genesis of the Chrome Ores in the Coolac Serpentine Belt, N.S.W. Australia*. Ph.D. Thesis, University of New South Wales.
- GRAFENAUER, S. (1956) Mineralogical-chemical characteristics and secondary alteration of Macedonian chromites. *Rudarsko-Met. Zbornik*, **2**, 227–251. [Yugoslavian with German abstract].
- GILLERY, G. H. (1959) X-ray study of synthetic Mg-Al serpentines and chlorites. *Amer. Mineral.* **44**, 143–152.

- HEISLEITNER, G. (1952) *Serpentin und Cromerz-Geologie der Balkanhalbinsel und eines Teiles von Kleinasien*. Geol. Bundesanst., Vienna.
- HEY, M. H. (1954) A new review of the chlorites. *Mineral. Mag.* **30**, 277–292.
- HORNINGER, G. (1941) Beobachtungen am Erzinhalt von Gesteinen und an chromerz aus Tampadel in Schlesien. *Mineral. Petrog. Mitt.* **52**, 315–345.
- JACKSON, E. D. (1961) Primary textures and mineral associations in the ultramafic zone of the Stillwater Complex, Montana. *U. S. Geol. Survey. Prof. Pap.* **358**.
- JELJAZKOVA-PANAJOTOVA, M. (1964) Remarks on the metamorphism of the chrome spinels. *God. Sofskiya Univ., Biol.—Geol.—Georg., Fak. 2—Geol.*, **57**, 43–74. [Russian with German summary].
- LIPMAN, P. W. (1964) Structure and origin of an ultramafic pluton in the Klamath Mountains, California. *Amer. J. Sci.* **264**, 199–222.
- MAXWELL, J. C. (1949) Some occurrences of chromite in New Caledonia. *Econ. Geol.* **44**, 525–544.
- MILLER, R. (1953) The Webster-Addie ultramafic ring, Jackson County, North Carolina and the secondary alteration of its chromite. *Amer. Mineral.* **38**, 1134–1147.
- MUKHERJEE, S. (1966) Indian chromites. *Econ. Geol.* **61**, 964–6.
- NELSON, B. W. AND R. ROY (1958) Synthesis of chlorites and their structural and chemical composition. *Amer. Mineral.* **43**, 707–725.
- RAGGATT, H. G. (1925) Chromium, cobalt, nickel. *Geol. Surv. N. S. W. Dep Mines Bull.* **13**.
- RAIT, J. R. (1946) An X-ray investigation into the constitution of chrome ores. *Iron Steel Inst. London, Spec. Rept.* **32**, 175–209.
- (1950) *Basic Refractories*. Iliffe, London.
- RAMDOHR, P. (1960) *Die Erzminerale und ihre Verwachsungen*. Akademie-Verlag, Berlin.
- RAYNER, E. O. (1961) *The mineralogy and genesis of the iron-rich copper ores of the Cobar Province, New South Wales*. Ph.D. Thesis, University of New South Wales.
- STOCKWELL, C. H. (1944) Chromite deposits of the Eastern Townships, Quebec. *Trans. Can. Inst. Mining Met.* **47**, 71–86.
- TEX, E. DEN (1955) Secondary alteration of chromite. *Amer. Mineral.* **40**, 353–355.
- THAYER, T. P. (1946) Preliminary chemical correlation of chromite with the containing rocks. *Econ. Geol.* **41**, 202–217.
- (1956) Mineralogy and geology of chromium. In M. J. Udy, ed., *Chromium, vol. I, Chemistry of Chromium and Its Compounds*, Amer. Chem. Soc. Monograph **132**, 14–52.
- (1960) Some critical differences between alpine-type and stratiform peridotite-gabbro complexes. *Intern. Geol. Congr., 21st., Copenhagen, part 13*, 247–259.
- (1964) Principle features and origin of podiform chromite deposits, and some observations on the Guleman-Soridag District, Turkey. *Econ. Geol.* **59**, 1497–1524.
- (1966) Serpentinization considered as a constant volume metasomatic process. *Amer. Mineral.* **51**, 685–710.
- VAASJOKI, O. AND A. HEIKKINEN (1961) On the chromites of the Kemi Deposits, North-western Finland. *Comm. Geol. Finlande Bull.* **194**, 1–26.
- VERMAAS, F. H. S. AND E. R. SCHMIDT (1959) The influence of ionic radii of cations and covalent forces on the unit cell dimensions of spinels. *Beitr. Mineral. Petrogr.* **6**, 219–232.
- WELLS, A. F. (1962) *Structural Inorganic Chemistry*. Oxford University Press, London.
- YODER, H. S. (1952) The MgO-Al₂O₃-SiO₂-H₂O system and related metamorphic facies. *Amer. J. Sci. Bowen Volume*, 569–627.