THE MINERALOGY OF THE CHROME SPINELS OF THE BIRD RIVER SILL, MANITOBA

A Thesis Presented to the Geology Department
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requirements for the Degree of
Master of Science

by

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ABSTRACT

Hematite exsolves from specimens of the Bird River chromite on heating. Exsolution begins in iron-rich areas, such as the rims of crystals and marginal to fractures where deuteric alteration of the chromite has occurred. With prolonged heating, exsolution extends throughout the crystals; optimum heating conditions in air are 1000°C at one atmosphere for seventy two hours. X-ray fluorescence analyses and cell edge determinations were made on nonmagnetic and ferromagnetic fractions of the concentrates. Two spinel phases were recognised in X-ray diffraction powder photographs of the four chromite specimens having the most pronounced rims. These two phases represent the altered, iron-rich rim and the central area of the crystals. Cell edge variation with composition is discussed. 'Stratigraphic' variation of the parameters was investigated; in the chromite mineral itself, $\mathrm{Cr}_2\mathrm{O}_3$ and total iron increase towards the top of the sill, Al₂O₃ remains constant across the section and MgO appears to decrease slightly towards the top of the sill; cell edges increase generally with increasing 'stratigraphic' order. Magnetism may depend on the proportion of ferrous to ferric iron in the chromite molecule. The evidence suggests that hematite will exsolve from any chromite which has a Cr:Fe ratio of about 1.2:1 or less.

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CHAPTER I - INTRODUCTION

i. General Statement

Chromite was discovered in the Bird River Sill in 1942 by G. M. Brownell (1942) and J. D. Bateman (1943). Some metallurgical work during the war years proved the deposit to be then uneconomic. In the present study, specimens were collected from ten successive horizons over a total 'stratigraphic' distance of seventy-eight feet. The chromite is concentrated in the upper part of the peridotite which forms the lower portion of the sill.

In 1943, Brownell discovered that the Bird River chromite developed an exsolution pattern after being heated above 700°C. This thesis describes an investigation of this phenomenon. Heating experiments were carried out on ten specimens. Polished section studies showed the development of hematite lamellae in each one. Mineralogical and chemical techniques were employed to clarify this exsolution and its relation to the composition and cell edges of these chromian spinels.

ii. Short Note on Spinel Mineralogy

Deer, Howie and Zussman (1962, Vol. 5, pp 56-68)
have given a complete account of spinel mineralogy. Their
chapter contains considerable data concerning the structure,
composition and cell edge of spinels. The following is a

brief resume of spinel mineralogy with special reference to the chromium-bearing members of the group.

The spinel group is divided by Deer, Howie and Zussman (1962, Vol. 5.) into three series : the spinel series, the magnetite series and the chromite series. The Bird River spinels are best classed in the latter group, although on the basis of cell edge determinations, some overlap occurs with the spinel series. The mineral studied is actually a chromian spinel but it is simpler to refer to it as chromite throughout the thesis. The composition of the Bird River chromites is complex with small variations from one horizon to another. Al203 is high, averaging 15-20% while the Cr:Fe ratio averages 1.1:1. Deer, Howie and Zussman (1962, Vol. 5.) describe the chromite series as varying between the two ideal end members magnesiochromite (MgCr $_2$ O $_4$) and chromite (Fe"Cr $_2$ O $_4$). A more general expression of the formula may be given as (Mg,Fe") Cr204. However, Fe" and Al" can substitute for Cr" so the formula is best written thus; R $^{"}$ $0 \cdot R$ $^{"'}$ $_2O_3$, where R $^{"}$ includes Fe" and Mg" and R" includes Fe", Al" and Cr ".

The structure of the spinel mineral allows for 32 oxygen ions and 24 cations in the unit cell. Of the latter 8 are in positions with 4-fold tetrahedral co-ordination (the 'A' positions) and 16 are in positions with 6-fold octahedral co-ordination (the 'B' positions). Barth and

Posnjak (1932) recognised both normal and inverse structural types as follows.

Normal 8 R" in A, 16 R" in B

Inverse 8 R" in A, 8 R" ≠ 8 R" in B.

(Deer, Howie and Zussman 1962, Vol. 5).

Chromite is of the normal structural type.

Exsolution within naturally occurring chromites was noted by Ramdohr (1931) and Wijkerslooth (1943).

G. M. Brownell (1942) described exsolution occurring in natural specimens of Bird River chromite. Rigby, Lovell & Green (1946) refer to the exsolution of an R203 phase while investigating the action of reducing gases on chromite.

iii. Scope of Thesis

Although the main part of the thesis is mineralogical a brief description of the sill and its relation to the enclosing rocks is given. Ten specimens were collected from ten sharply defined horizons, varying from half an inch to six inches in thickness. In conjunction with heating experiments on each specimen, polished sections were examined, X-ray fluorescence analyses carried out and cell edges were determined in the hope of relating both the exsolution of hematite and the 'stratigraphic' position of the specimens to some chemical or crystallographic characteristics. The average Cr:Fe ratio for the Bird River chromites is l.l:l.

Concentrates of each chromite were made and six of the ten

were found to have a ferromagnetic fraction. X-ray fluorescence analyses were carried out on the chromitites as well as on both fractions of mineral concentrates. The exsolved mineral was identified as hematite by X-ray diffraction powder photographs. Doubled lines show that naturally occurring chromites can exist as two spinel phases with slightly different cell edges, both of which fall within the aluminate-chromite range given by Thayer (1956). The presence of the two phases does not imply magnetism in the mineral concentrate. Total iron in all the mineral concentrates was proportioned between FeO and Fe2O3 in the manner described in Appendix IV and the iron contents are discussed in relation to magnetism and the size of the unit cell.

iv. Acknowledgements

The writer is indebted to Dr. G. M. Brownell for suggesting this problem and for his advice and support. Dr. R. B. Ferguson has made valuable criticism and suggestions concerning the X-ray diffraction studies and the chemical calculations. The writer would like to thank Mr. K. Ramlal for analysing the samples on the X-ray Fluorescence Spectrometer in the Geology Department at the University of Manitoba. Mr. R. Pyrhitko of the Geology Department of the University of Manitoba kindly took the photographs using the Zeiss Ultraphot.

CHAPTER II

THE GENERAL GEOLOGY OF THE BIRD RIVER SILL

i. General Statement

The Bird River Sill occurs in south-eastern Manitoba, north-east of Lac du Bonnet (Fig. 1). An all weather road from Lac du Bonnet to the Gordon Lake Nickel Mines (Ontario) parallels Bird River close to the sill. Fig. 2 shows a general geological map of the area and the location of the samples that were collected.

The topegraphy of the area is typical of the Precambrian Shield in Manitoba. The Sill parallels Bird River which is the main drainage system of the area. The chromite bearing horizon is usually defined as a low ridge, the surrounding areas being drift filled and covered by swamp and muskeg. The chromitite bands form shallow grooves along the peridotite outcrop due to their lesser resistance to glacial abrasion.

The earliest geological work in this area was done by Moore in 1912. Numerous reports and papers have followed:

Cooke (1921); Wright (1924); Brownell (1942); Bateman (1943, 1945); Osborne (1949); Springer (1949, 1950); and Davies (1952, 1955, 1958). Some drilling was done in 1944 by Petra Chromite Limited, and it proved a large deposit of chromite.

Downes and Morgan (1951) of the Department of Mines

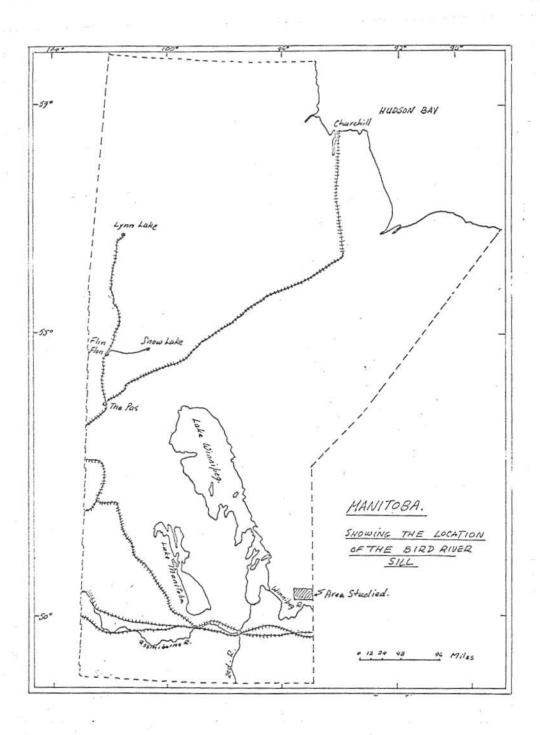
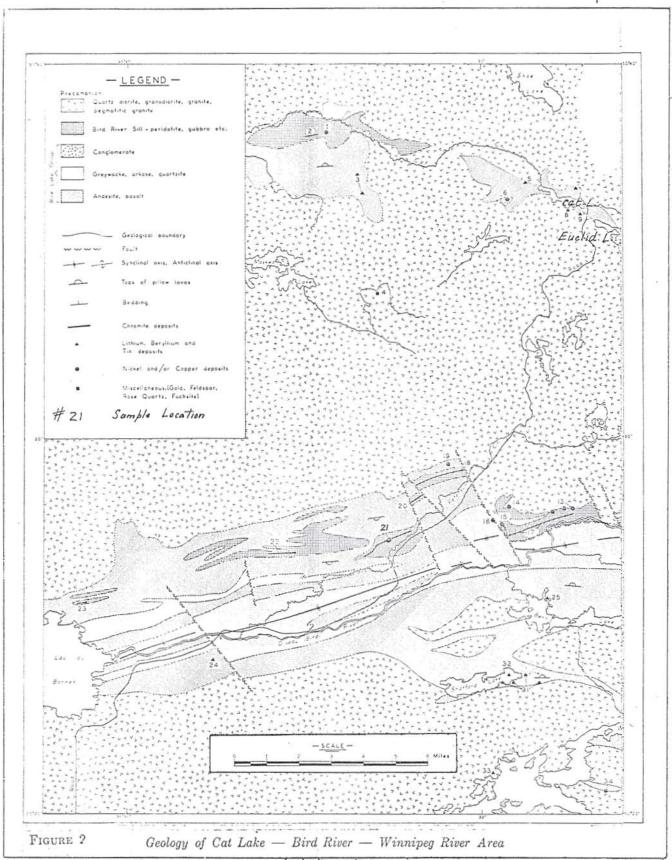


FIGURE 1. Locality Map (After Davies et al., 1962)



(After Davies et al., 1962.)

and Technical Surveys, Ottawa made a study on the ultilisation of low grade domestic chromite. They concluded that considerable beneficiation of the ore would be necessary to bring it to an economically acceptable grade.

Table I shows the stratigraphic column and age relationships between the rocks, as given by Davies (1955). The consolidated rocks of the area are Precambrian in age and are partly covered by Pleistocene glacial deposits. The Bird River sill intrudes rocks of the Rice Lake Group, which are considered to be the oldest rocks of the area. The Rice Lake Group consists of volcanic and sedimentary rocks occurring in a belt, three to four miles wide, along Bird River.

ii. The Geological Environment of the Sill

a. The Rice Lake Group

This group of rocks forms an elongated, steeply dipping belt parallel to Bird River. To the north of the river the lavas are principally andesitic in composition, fine-to medium-grained, and fresh looking in hand specimen. They are dark green to grey in colour. Original structures such as pillows and flow lines are preserved. South of Bird River the volcanic rocks are more altered than those to the north. However, they have been correlated on the basis of composition and stratigraphic position (Davies, 1955).

TABLE I TABLE OF FORMATIONS (After Davies, 1955)

RECEN	T AND PLEIST	CENE GLA	GLACIAL CLAY AND SAND								
	U N	CONFORMIT	Y								
A	INTRUSIVE	Trap, diabase Pegmatite dykes and sills Granite, granodiorite, Quartz diorite.									
R											
С		-Intrusive Contac									
Н	ROCKS	Hornblende Gabbro, Peridotite, pyroxenite, hornblendite.									
E		- Intrusive Conta									
A	RICE LAKE	Silicified Rock Arkose Greywacke, tuff	, quartz								
N	GROUP	mica schist Andesite, basal	t and derived schists								

The greywacke, tuff and quartz mica schists, considered to be the oldest members of the sedimentary unit of the Rice Lake Group, outcrop along Bird River. The contact between the sedimentary and volcanic rocks is obscured on the north side of the river.

The arkose, though considered to be stratigraphically above the greywacke, tuff and quartz mica schists, is partly interbedded with the greywacke. Similarly beds of greywacke are interbedded with the main arkose. A division between coarse-grained arkose and a medium-to fine-grained type may be made. The coarse-grained arkose is characterised by large clear quartz 'eyes'.

Interbedded silicified rocks in the sediments and volcanics are considered by Davies (1955) to be a silicification of their host rocks. He bases his arguments on textural similarities between the silicified and unsilicified portions in the same rock unit.

b. Intrusive Rocks:

The Bird River Sill ranges in thickness up to six thousand feet, averaging three thousand feet. It is divided into two parts, a lower consisting mainly of peridotite and an upper which contains the chromitite horizons. Conformably above the peridotite are the gabbroic rocks comprising the upper portion of the sill. The most common gabbroic phase

is a medium-to coarse-grained rock composed almost equally of labradorite and green hornblende, with magnetite, sphene, epidote and biotite as accessory minerals. The degree of secondary alteration is less pronounced than in the peridotite. The contact between the peridotite and the gabbro is marked by a narrow drift-filled depression. Only rarely may this contact be seen (Davies, 1955). The sill as a whole is intrusive into rocks of the Rice Lake Group and, in the area studied, into the lower volcanic series of the Group.

Intrusive granitic rocks outcrop north and south of the belt of Rice Lake rocks. They are grey to pink in colour, and either equigranular, porphyritic or gneissic in texture. These differences do not reflect compositional variations. Davies (1955) has suggested that there is no significant difference between the ages of the various granites intruding the Rice, Group.

Pegmatite dykes, sills and irregular masses cutting the sediments and volcanics vary considerably in size.

A microcline-bearing pegmatite may be recognised as distinct from albite-rich varieties. No correlation has been made between the pegmatites and their possible parent granites.

The granite north of Bird River contains irregular areas of andesitic and gabbroic rocks whose correlation

with other basic rocks in the area is uncertain. Northwest striking diabase dykes, composed principally of equal amounts of andesine and amphibole also cut the granitic rocks.

c. Structural Setting

Top determinations from pillowed lavas in the area indicate a synclinal axis closely parallelling Bird River, the south limb of which appears to be overturned since the sediments there dip southwards between 75° and 80°.

The rocks of the Rice Lake Group and the Bird River sill have been correlated with similar rocks of the Cat Lake - Euclid Lake area (Davies, 1955). This is the basis for the suggestion, that, taken together, these rocks form the limbs of a southeasterly plunging anticline. An anticlinal axis passing through Star Lake is shown by Davies in the 'Geology and Mineral Resources of Manitoba' (Davies et al., 1962).

Considerable transverse faulting north of Bird River has cut the Rice Lake Group and the Bird River sill into several blocks offset from each other. A major longitudinal fault at the west end of Bird Lake brings the sediments of the Rice Lake Group into contact with the intrusive rocks of the sill.

d. Mineral Deposits of the Area

The mineral deposits of the Cat Lake - Bird River

area may be divided into three groups.

- i. The chromitite horizons of the Bird River sill.
- ii. The lithium and beryllium deposits.
- iii. The base metal deposits.

The chromitite bands occur, as noted earlier, at the top of the peridotite zone in the Bird River sill.

The main zone is 8 to 10 feet wide and is composed of six bands \(\frac{1}{2} - 6 \) inches thick. Below the main zone are several other bands from \(\frac{1}{2} \) to 4 inches thick, from four of which specimens were collected for study. The lowest band studied is seventy feet below the main zone. In lateral extent these bands are highly persistent, although offset by the faulting. Large tonnages have been estimated for the sill, but mining would be complicated by the offset faulting and the poor grade of the ore. A 'stratigraphic' section of the ten horizons studied is given in Fig. 3.

Pegmatite dykes occurring round the edges of the granitic intrusions contain several interesting mineral deposits. The most significant of these are the lithium pegmatites near Bernic Lake about four miles south-west of Bird Lake. These nearly horizontal pegmatites have a complex mineralogy of lithium-bearing minerals such as spodumene, amblygonite, petalite and lepidolite.

Considerable interest has been shown in a large body of pollucite in a pegmatite at Bernic Lake estimated to

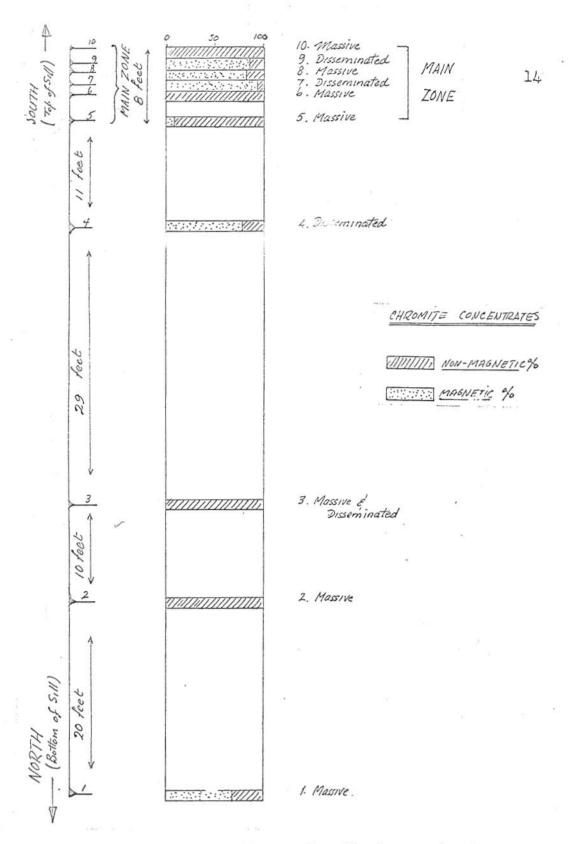


FIGURE 3. The Bird River Chromitite Horizons showing a 'Stratigraphic' Section and Description of the Chromitites with percentage of Magnetic and Non-magnetic fractions of the Concentrates.

contain 300,000 tons averaging 20-30% cesium (Davies et al., 1962). In the intermediate zones of these pegmatites, small amounts of beryl are concentrated; however, the mineral is more common in pegmatites of low lithium content, often with small amounts of tantalite-columbite, topaz, uraninite and monazite. The largest deposit of beryl occurs at Greer Lake. Age determinations on uraninite from the Huron beryl deposit gave an age of 2,600 million years which is regarded as the minimum age for the Superior province of the Precambrian shield (Davies, 1955).

Base metal deposits occur at the edges of the gabbro and peridotite. To the west of Bird Lake sulphides occur in fractured peridotite and granite. The sulphide lenses are composed of massive and disseminated pyrrhotite, pentlandite, chalcopyrite, cubanite, pyrite and magnetite.

Gold, feldspar, rose quartz and fuchsite (chrome bearing, green mica) have been discovered in the area. Some feldspar of ceramic quality was quarried at Greer Lake between 1933 and 1939.

A more detailed account of the economic mineral deposits in this area is given by Davies et al. (1962).

CHAPTER III

POLISHED SECTION OBSERVATIONS ON NATURAL AND HEATED CHROMITITES

i. Naturally Occurring Chromitites

On the basis of variation in hand specimens they were grouped into three classes as follows (see Fig. 3 for location of numbered specimens):

- a. Densely packed crystal aggregates, fine-grained, 'massive'. Specimens 1 and 8.
- b. Less densely packed crystals, coarser-grained, 'massive'. Specimens 2, 3, 5, 6, and 10.
- c. Crystals disseminated around oval masses of serpentinised olivine. Specimens 4, 7 and 9.

The groundmass, or gangue material, between the chromite crystals is composed of secondary minerals derived from olivine and pyroxene. Serpentine is by far the most common mineral with penninite and tremolite associated with it (A. Juhas, personal communication). The gangue minerals range in colour from white, through pale greyish blue, to pale apple green.

All the specimens, both massive and disseminated, are compact as opposed to friable. On fresh surfaces the chromite crystals impart a metallic lustre to the rock. Fine stringers of gangue minerals, mainly serpentine with

some calcite cut through the massive specimens.

The specimens that appear in the hand specimen to be 'massive' are seen in polished section to be an aggregate of chromite crystals evenly distributed throughout the rock. The three specimens referred to as being 'disseminated' specimens 4, 7 and 9 are of interest as the chromite crystals are interstitial to large round or oval masses of serpentinised olivine. A thin section of this type of chromitite from the Bird River deposit was loaned to the writer by Mr. A. Juhas. It may be seen from this section (Plate I) that the chromite generally occurs outside large serpentinised olivines where the gangue appears to be altered pyroxene. This suggests that the olivine crystals and the chromite crystals settled together with later crystallization of the pyroxene from interstitial liquid. In places a chromite crystal may be seen within a large altered olivine crystal suggesting that some of the crystallization of these two minerals was contemporaneous.

With a low power objective the chromite is seen as rounded octahedral crystals. Numerous crystals from all horizons show central cores of gangue. Although usually round these inclusions may also be square, rectangular or L-shaped, as noticed in specimen 1. Specimen 8 has single chromite crystals each with several rounded inclusions of gangue suggesting that they are inclusions rather than

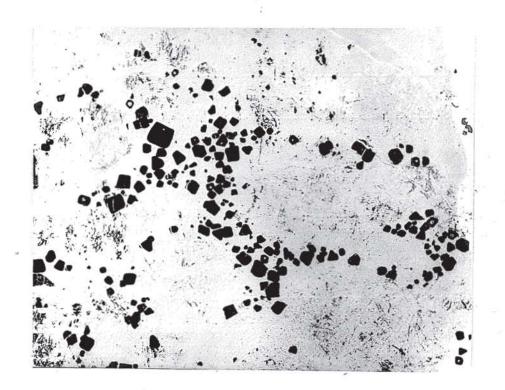


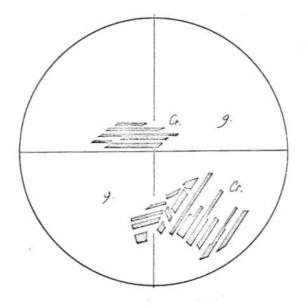
PLATE I

THIN SECTION OF DISSEMINATED CHROMITE (x 4)

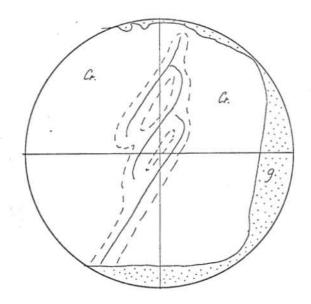
centres about which crystallisation began. Many crystals do, however, have a large round central inclusion.

Fractured crystals are not common but a few may be noticed in each specimen. Fractures are filled with gangue but are rarely wide. Stresses imposed on these rocks must have been considerable as they have been folded from their original horizontal position into the nearly vertical attitude which they now occupy. The small number of broken grains may be explained by the comparative ease with which the gangue minerals could have adjusted to the deformation without affecting the more tough and compact chromite octahedra.

Most of the naturally occurring chromites from
Bird River which have been examined during the preparation
of this thesis show rims around the crystals of a slightly
lighter grey colour under reflected light. These rims are
presumably of a different composition from the central cores
of the crystals. Further examination of polished sections
showed that this phase which exists as rims, is also present
along the edges of broken grains and marginal to fractures
within a crystal (Fig. 4B). This feature does not show
clearly on a photograph so it is represented by a sketch.
The lighter material does not occur at the edges of the
inclusions within the crystals. The idea that this
phenomenon is due to zoning of the chromite crystals is



A. Skeletal Crystals of Chromite. Specimen 4 (x 450).



B. Alteration along Fractures in Natural Chromite. Specimen 4 (x 450).

FIGURE 4. Diagrams Showing Textures in Natural Chromite from Bird River.

therefore untenable, since the minor phase occurs at the edges of broken crystals as well as at a rim around the euhedral crystals. A more satisfactory explanation would attribute the rims to deuteric alteration of the chromite at an early stage after crystallization. Similar features are noted by Smith and MacGregor (1963) in their recent paper on the use of chrome spinels in petrographic studies of ultramafic intrusions.

In specimen 4 (Fig. 4A) a few chromite crystals were found whose growth seems to parallel some crystal—lographic direction of another mineral competing with it during crystallisation. This specimen is of the disseminated type and shows chromite interstitial to large, rounded, serpentinised olivine crystals. The pattern of the chromite 'skeleton' suggests a possible orientation parallel to pyroxene cleavage directions, pyroxene being the principal interstitial mineral to the rounded serpentinised olivine crystals.

Of the ten specimens collected, numbers 2, 6, 8 and 10 show very tiny rods and plates of a mineral exsolving from the chromite. Magnification required to see this feature is of the order of 850 times. These tiny inclusions, suggested by Brownell (1942) to be either hematite or magnetite, are aligned crystallographically and may be described as an 'incipient Widmanstätten

pattern'. These rods and plates are most commonly seen at the centres of the chromite crystals but not in the rims. The other specimens do not show any evidence of exsolution either in the rims or in the central parts of the crystals.

ii. Development of Exsolution on Heating

In a study made in the Economic Geology Laboratory at the University of Manitoba, Brownell (1942) found that on heating specimens of the Bird River chromitite in excess of 700°C, an exsolution pattern developed. Brownell concluded that one trivalent element was in excess of the ideal molecular formula and since this was most likely to be iron, he surmised that the solute phase was hematite.

The ten specimens collected from different horizons for this thesis were cut into rectangular blocks for the heating experiments and were held at 1000°C for 72 hours, at one atmosphere in air. It was not possible to heat previously polished sections and then repolish the same surface for study since alteration occurred at the surface and the sections had to be reground. To avoid any discrepancies due to surface effects, heated specimens were cut in half and the cross section polished to observe crystals at the centre of the block. All specimens on cooling showed exsolution. Other than the work by Brownell (1942) the only reference to exsolution in heated chromites is that of Rigby, Lovell & Green (1946) who mention the exsolution of

an R203 phase on heating.

Of prime importance in this study was the identification of the solute mineral. Specimen 1 showed the best exsolution in a coarse Widmanstätten pattern. A chromite concentrate of this specimen was prepared (Appendix I) and was found to have a non-magnetic and a ferromagnetic fraction in the amounts 31.0% and 69.0% respectively. Separate heating of the concentrated fractions and subsequent examination in a polished section grain mount (Appendix III) showed a heavier exsolution pattern in the ferromagnetic fraction. X-ray diffraction powder photographs were taken of these two heated concentrates, and hematite was positively identified together with chromite. Confirmation of the identification was obtained indirectly by comparing the streak of the natural and heated chromitites being ground for polished section work. In each case the heated chromitite had a cherry-red streak indicating the presence of hematite. Hence hematite was proved to exsolve from this chromite when heated for 72 hours at 1000°C at one atmosphere in air.

Hematite exsolved from specimens 2, 6, 8 and 10 which showed exsolution as tiny rods and plates before heating as well as from those specimens which showed no previous exolution under the highest magnification available. The ten specimens developed three kinds of exsolution

patterns. The most common type illustrated by specimens 4, 5, 7 and 8 show hematite exsolving at the rims in a dense Widmanstätten pattern which is only clearly resolved under high magnification (Plate II B). A few blades and patchy areas may be seen at the centres of some crystals (Plate II C). It seems that, since the rims are prominent in specimens 4, 5, 7 and 8, exsolution first develops in the rims, and that the two are related. At present it will be sufficient to suggest that the rim phase is more iron-rich and hence exsolution is more likely to occur in these areas.

Specimens 1, 2 and 6 show the best developed Widmanstätten patterns. Specimen 1 has a very coarse Widmanstätten pattern (Plate II D) composed of thick stubby blades of hematite which are discontinuous, giving a graphic appearance to the texture. Specimen 2 on the other hand shows an extremely delicate and finely developed pattern with long, thin, straight blades intersecting without thickening in the classic manner.

The remaining specimens (3, 9 and 10) developed an irregular pattern with an indistinct resemblance to a Widmanstätten pattern. Irregular patches of hematite rather than plates or blades are seen.

No relationship between the three groups of chromitites and the type of exsolution was recognised.



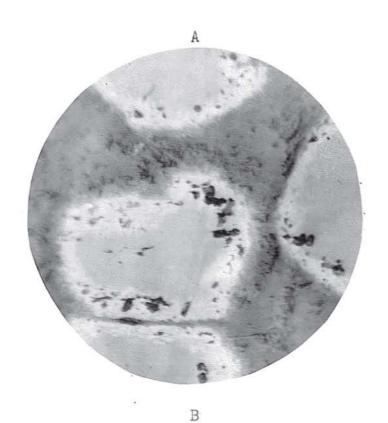


PLATE II

DEVELOPMENT OF EXSOLUTION

- A. Crystal of Chromite showing no exsolution. (x 184)
- B. Exsolution in the rim of the crystal only. (x 312)

For the most part exsolution is most pronounced at the rims and at the edges of inclusions within the crystals. The rims and areas along the fractures may be iron-rich and therefore are likely places for the exsolution of hematite to begin. The inclusions within the crystals may tend to act as centres from which exsolution may begin.

Because of the strong Widmanstätten pattern developed in specimen 1 it was decided to use this specimen for a more detailed heating experiment. Twelve small blocks were cut from the specimen and placed in a furnace at 1000°C at one atmosphere in air. One was removed after each 12 hour period, so that the longest heating period was 144 hours. The specimens were each polished after cooling and studied with a metallographic microscope. Specimen 1 of the natural unheated chromite showed no evidence of exsolution under the highest available magnification. Rims are common in the octahedral crystals. Inclusions are rare and fractures show alteration along them. After 12 hours the chromite showed exsolution in the rims, which under high power resolved into a fine grouping of hematite blades parallel to the (111) planes. All the crystal sections showed the blades to be parallel to the euhedral sides of the crystals. Each succeeding polished section (i.e. those heated for longer periods) showed stronger development of hematite blades at the rims with extensions into the

centres of the crystals. Simultaneously tiny rods and plates appeared in the central areas of the crystals. After 36 hours they became thicker and more stubby and by 84 hours the pattern was completed throughout the crystals. A series of photographs are presented illustrating this development (Plate II A, B, C and D).

CHAPTER IV

X-RAY FLUORESCENCE ANALYSES

i. Analytical Methods

Concentrates of the chromites were prepared for analysis (Appendix I). The amount of serpentine adhering and included in grains of chromite was a minimum and estimated at less than 2%. The effects of these impurities are considered negligible to the interpretation of the general trends.

The analyses were done on the A.R.L. Vacuum X-ray Quantometer in the Geology Department of the University of Manitoba. Preparation methods of the pellets for analysis are given in Appendix II. The beads which were made with the chromite concentrates appeared to be completely fused, though if some grains were not fused the analysis result would be affected only in a minor way.

To calibrate the X-ray Fluorescence Unit three standards were prepared by Bristol, Coats and Wicks (1963). Instrument precision is $\angle 0.2\%$ while the accuracy may be given generally as 0.4% of the amount of the element present (K. Ramlal - personal communication). The analytical error is unlikely to exceed 0.5% of the amount of the element present and is therefore negligible when

the general trends of the analyses are considered.

The totals of the concentrate analysis do not always total 100% because of small amounts of volatiles and undetermined elements (Ni, Mn etc.) and the effect of the analytical error. These results therefore are not truly comparable yet the effect of each of the above three factors is so small as to be of negligible importance and do not affect any one value more than any other.

ii. Total Rock Analyses

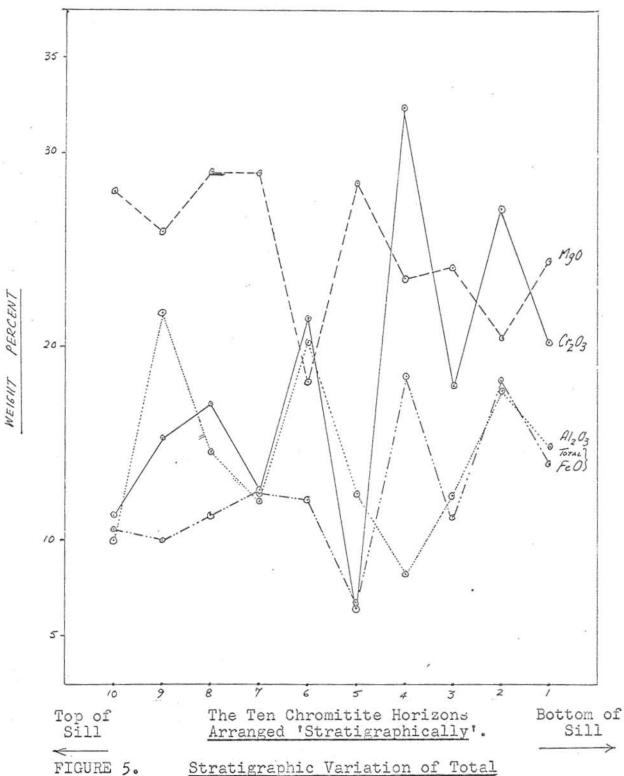
Table II shows the analyses of the chromitites. Volatile constituents account for most of the deficiency from 100% of the analysis with lesser amounts of minor elements such as Ni and Mn. These were not determined. Total iron is given as FeO. Fig. 5 shows the analyses plotted 'stratigraphically'. As can be expected MgO is the most abundant constituent as it occurs in the serpentine as well as in the spinel. SiO₂ is exclusively in the serpentine. Al₂O₃ and FeO are almost equal in seven of the ten analyses. Of the others, two have more Al₂O₃ than FeO, while the third exception (Specimen 4) has low Al₂O₃ (8.2%) and high FeO (18.6%) but is distinguished by having the highest Cr₂O₃ content (32.7%) of all ten specimens.

CaO varies considerably, being due to the calcite stringers cutting through the rocks rather than an

TABLE II X-RAY FLUORESCENCE ANALYSES OF THE BIRD RIVER CHROMITITES

TOTAL ROCK ANALYSES

Specimen Number	Cr ₂ O ₃	Total Fe as FeO	Al ₂ O ₃	MgO	SiO ₂	CaO	TiO ₂	K ₂ 0	Total- less Volatiles
TR 1	20.4	14.0	14.8	25.0	13.8	0.40	0.20	-	88.6
TR 2	27.3	18.4	17.8	20.5	11.0	0.50	0.28	0.02	95.8
TR 3	18.5	11.1	14.5	24.2	21.0	3.60	0.15	0.03	93.1
TR 4	32.7	18,6	8.2	23.5	14.8	0.60	0.24	-	98.6
TR 5	6.5	6.7	9.8	28.5	29.2	6.00	0.04	0.10	86.8
TR 6	21.6	12.1	17.9	18.2	12.4	7.50	0.28	-	90.0
TR 7	12.5	12.3	12.0	29.0	23.0	1.40	0.16	-	90.4
TR 8	17.0	11.3	14.5	29.0	17.0	0.40	0.24	-	89.4
TR 9	15.2	10.0	21.8	26.5	15.8	1.60	0.09	0.05	91.0
TR 10	11.2	10.5	9.9	28.1	24.4	3.70	0.60	0.03	88.4



Stratigraphic Variation of Total Rock Analyses

intrinsic feature of the composition. TiO_2 is of the order of 0.1 to 0.2% with the exception of specimen 10 (0.6%). K_2O occurs in five of the ten specimens in amounts from 0.02% to 0.1%. The anomalous values for TR 5 and its low total cannot be explained.

iii. Analyses of the Concentrates

Concentrates of the chromite were prepared for analysis (Appendix I), and six of the ten were found to have a ferromagnetic fraction. This magnetic fraction was termed 'ferromagnetic' since it was separated with a hand magnet. The two fractions were analysed separately. (Table III) The amount of ferromagnetic chromite in each sample is shown in Fig. 3 on page 14. This section will be confined to a discussion of the composition of the concentrates and its relation to the substitutions which can take place in the crystal structure of the Spinel Group. A comparison between the non-magnetic and ferromagnetic fractions will be made. Figure 6 represents the 'stratigraphic' variation in composition of the concentrates. An explanation of this figure is necessary. The variation in composition is plotted for the four major elements of the chromite: $\mathrm{Cr}_2\mathrm{O}_3$, total iron as FeO, Al₂O₃ and MgO. The non-magnetic fraction is plotted as a solid line joining circles and the ferromagnetic fraction as a broken line joining squares. For convenience

TABLE III X-RAY FLUORESCENCE ANALYSES
OF THE

BIRD RIVER CHROMITES

A. ANALYSES OF THE NON-MAGNETIC CONCENTRATES

Specime Number	n Cr ₂ 03	Total Fe as FeO	^{Al} 2 ^O 3	MgO	SiO ₂	CaO	TiO ₂	К ₂ О	Total- less Volatiles
C 1	41.5	32.4	13.0	8.5	1.5	0.20	0.58	-	97.7
C 2	42.5	31.0	15.8	8.7	0.8	Tr.	0.58	-	99.7
C 3	42.6	31.2	14.1	8.7	1.5	1.2	0.46	-	99.8
C 4	44.5	32.0	14.0	9.2	Tr.	Tr.	0.70	-	100.1
C 5	43.0	31.7	15.4	7.5	0.1	Tr.	0.57	-	98.3
c 6	42.0	29.3	15.0	7.6	1.6	2.3	0.56	-	98.4
C 7	43.5	34.6	13.7	6.7	Tr.	Tr.	0.94	-	99.4
C 8	43.5	33.1	13.6	8.0	0.1	Tr.	0.84		99.1
0 9	44.1	36.1	13.6	5.5	Tr.		1.00	-	100.3
C 10	37.3	27.0	22.8	10.0	0.7	1.0	0.37		99.1

B. ANALYSES OF THE FERROMAGNETIC CONCENTRATES

	Spe	cimer	1	Total Fe as							Total- less
M 4 42.0 36.5 11.8 6.9 0.8 0.04 0.70 - 98.7 M 5 41.5 32.3 13.8 8.5 1.0 Tr. 0.60 0.15 97.8 M 7 41.2 38.0 11.6 6.6 0.6 Tr. 0.88 0.10 99.0 M 8 41.4 32.5 13.0 9.7 1.4 Tr. 0.80 0.02 98.8					A1203	MgO	SiO ₂	CaO	TiO2	K ₂ 0	Volatiles
M 5 41.5 32.3 13.8 8.5 1.0 Tr. 0.60 0.15 97.8 M 7 41.2 38.0 11.6 6.6 0.6 Tr. 0.88 0.10 99.0 M 8 41.4 32.5 13.0 9.7 1.4 Tr. 0.80 0.02 98.8	M	1	40.0	33.5	11.6	8.3	1.5	0.05	0.61	0.02	95.6
M 7 41.2 38.0 11.6 6.6 0.6 Tr. 0.88 0.10 99.0 M 8 41.4 32.5 13.0 9.7 1.4 Tr. 0.80 0.02 98.8	M	4	42.0	36.5	11.8	6.9	0.8	0.04	0.70	-	98.7
M 8 41.4 32.5 13.0 9.7 1.4 Tr. 0.80 0.02 98.8	M	5	41.5	32.3	13.8	8.5	1.0	Tr.	0.60	0.15	97.8
Will Company the Company of the Comp	\mathbb{M}	7	41.2	38.0	11.6	6.6	0.6	Tr.	0.88	0.10	99.0
M 9 42.4 36.1 11.8 7.5 0.5 Tr. 0.84 0.15 99.3	\mathbb{M}	8	41.4	32.5	13.0	9.7	1.4	Tr.	0,80	0.02	98.8
	\mathbb{M}	9	42.4	36.1	11.8	7.5	0.5	Tr.	0.84	0.15	99.3

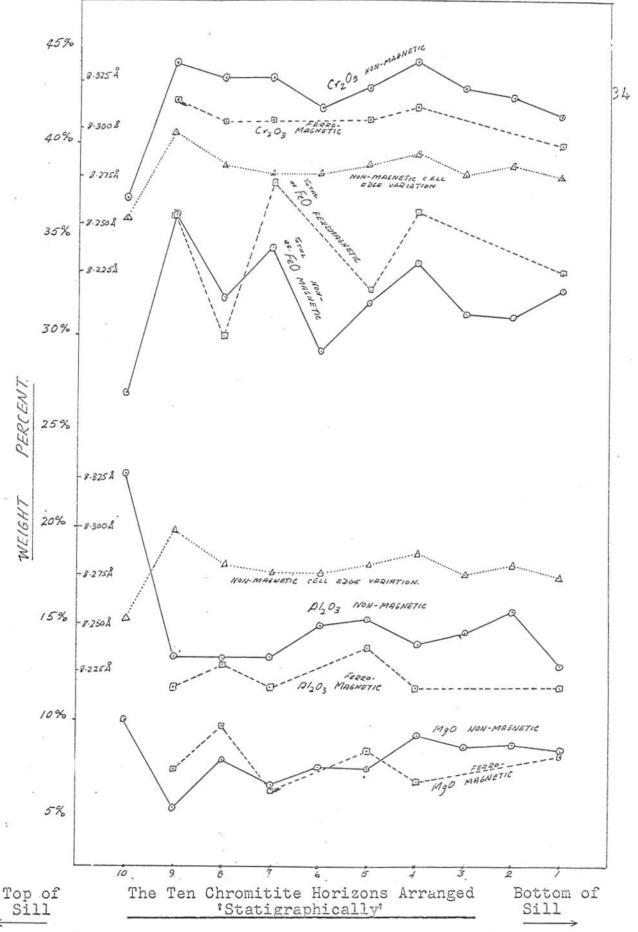


FIGURE 6. Variation in Composition and Cell Edge of Nonmagnetic and Ferromagnetic Concentrates.

in the next chapter, two identical curves of the 'stratigraphic' variation of cell edge of the non-magnetic and the ferromagnetic fractions are inserted in two arbitrary positions suitable for easy comparison with the variation in composition. The non-magnetic cell edge curve should be compared only with the compositional variation of the non-magnetic fractions. A separate section in Chapter VI is reserved for discussing variation in composition with 'stratigraphy'.

The non-magnetic fractions are noticably different from the ferromagnetic fractions. Cr_2O_3 and Al_2O_3 are higher and total iron is lower in the non-magnetic fraction. MgO varies considerably but no overall difference can be recognised. TiO_2 (Fig. 7) is, within the limit of analytical error, almost equal in both concentrates. The pairs of curves in Fig. 5 generally follow each other, however, the ferromagnetic curves are less variable than the non-magnetic curves (Table IV). This suggests that the ferromagnetic fraction may have to have a more precise chemical formula to account for its magnetism than the non-magnetic variety which has a highly variable composition.

Table V shows total iron as FeO for the non-magnetic as well as the ferromagnetic fraction proportioned between FeO and Fe_2O_3 according to the requirements of the spinel structure (Appendix IV). Fig. 8 shows curves for total iron

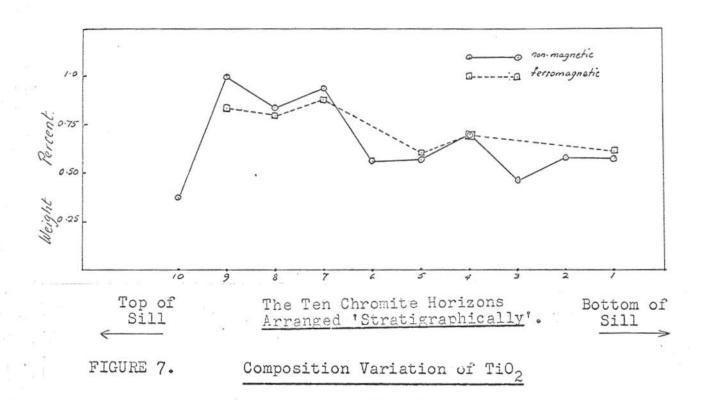


TABLE IV DEGREE OF VARIATION IN COMPOSITION BETWEEN

NON-MAGNETIC & MAGNETIC CONCENTRATES

NON-MA	GNETIC CONCENTRATES	FERROMAGNE	TIC CONCENTRATES
	OVERALL DIFFERENCE IN CONCENTRATION		ERALL DIFFERENCE N CONCENTRATION
Cr ₂ 0 ₃	2.6%	Cr ₂ O ₃	2.4%
Al ₂ 0 ₃	2.8%	A1 ₂ 0 ₃	2.2%
FeO	6.8%	FeO	5.5%
MgO	3.7%	MgO	3.4%
TiO ₂	0.54%	TiO ₂	0.28%

TABLE V TOTAL IRON

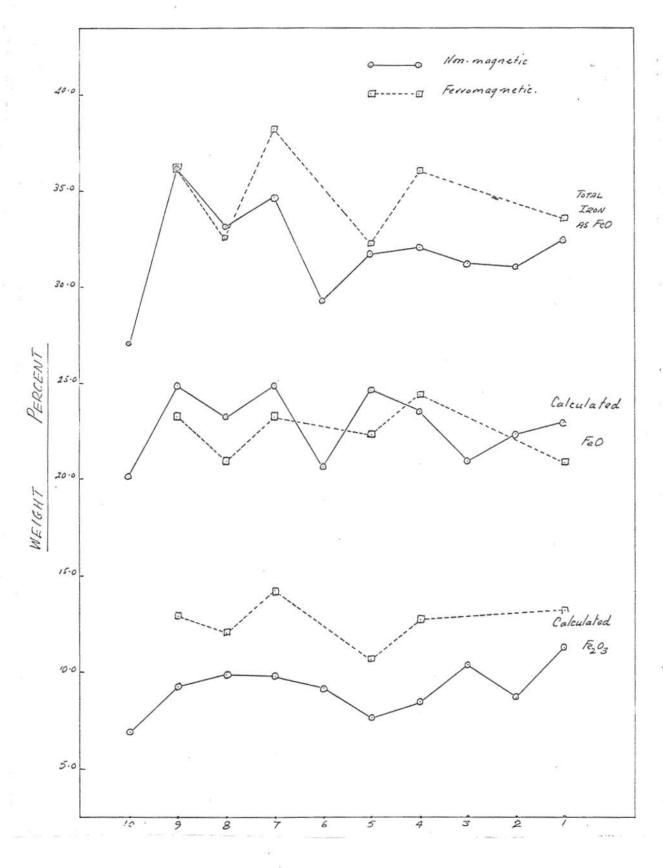
PROPORTIONED BETWEEN FeO AND Fe₂O₃ (APPENDIX IV)

A. THE NON-MAGNETIC CONCENTRATES

Specimen Number	Total Fe as FeO.	FeO%	Fe ₂ 0 ₃ %
Cl	32.4	22.9	11.2
C 2	31.0	22.3	8.7
C 3	31.2	20.9	10.3
C 4	32.0	23.5	8.5
C 5	31.7	24.6	7.6
c 6	29.3	20.6	9.2
C 7	34.6	24.8	9.8
C 8	33.1	23.2	9.9
C 9	36.1	24.8	9.3
C 10	27.0	20.1	6.9

B. THE FERROMAGNETIC CONCENTRATES

Specimen Number	Total Fe as FeO.	FeO%	Fe ₂ 0 ₃ %	
Ml	33.5	20.9	13.1	
M 4	36.5	24.4	12.6	
M 5	32.3	22.3	10.7	
M 7	38.0	23.8	14.2	
M S	32.5	20.9	12.1	
M 9	36.1	23.3	12.8	



Top of The Ten Chromite Horizons Bottom of Arranged *Stratigraphically*

FIGURE 8. Variation of Total Iron (as FeO), Calculated FeO and Fe₂O₃

as FeO, true FeO and Fe₂O₃ plotted 'stratigraphically' so that they may be compared.

Concentrate 10 is anomalous and will be mentioned here as it is ignored in the following discussion of the more general relationships. $\mathrm{Cr}_2\mathrm{O}_3$ and total iron are low compared to the other concentrates. (37.3% and 27.0% respectively) whereas Al 0 is high (22.8%). MgO is a little higher than the average and TiO_2 is the lowest of all the samples (0.37%). Concentrate 10 does not have a ferromagnetic fraction. As its composition is anomalous, so is its cell edge which is the lowest of the group (8.25%) bringing it well into the range of the aluminate group of spinels (Thayer, 1956). It should be noted that specimen 10 is the topmost member of the horizons studied. Its radically different composition indicates a sharp change in the crystallising conditions between horizon 9 and 10. There would have to have been a deficiency of iron and chrome with alumina in excess, as one would expect at the end of a long period of crystallisation with chromite settling out.

From Fig. 8 it can be seen that the shape of the curves for FeO are very similar for those for total iron while the Fe_2O_3 curves are very different; since most of the iron is present as FeO this is to be expected. Fe2O3 and Cr_2O_3 vary together and inversely to Al_2O_3 . This

shows the affinity of chromium and ferric iron whereas aluminium can replace them both. MgO and FeO vary inversely with one another indicating that they can substitute for one another in the bivalent part of the "molecule". TiO₂ (Fig. 7) closely follows the curves for FeO in Fig. 8 implying their close relationship in the structure.

CaO, SiO₂ and K₂O which are present in the rock analyses would not be expected in a pure chromite concentrate. CaO and SiO₂ in the latter can be accounted for as impurities in the concentrates due to the inclusions of gangue material within some of the chromite crystals. K₂O occurs in small amounts, O.1 to O.2%, in five of the six ferromagnetic concentrates but none is present in the non-magnetic concentrates.

Table VI shows the Cr:Fe ratio calculated for the ten non-magnetic fractions and the six ferromagnetic fractions. The Cr:Fe ratio varies from 0.96:1 to 1.22:1, and all these chromites exsolved hematite on heating. The non-magnetic concentrates average Cr:Fe of 1.16:1 whereas the ferromagnetic concentrates average 1.02:1. This ratio usually expresses the commercial value of the chromite ore, and determines its suitability for the various processes in which it is used. The average value for all the Bird River chromite concentrates, 1.1:1, is considered low from a



commercial viewpoint and it is this fact which is primarily responsible for making the deposit uneconomic at the present time.

TABLE VI THE CHROME : IRON RATIO FOR THE BIRD RIVER CHROMITE

A. NATURAL NON-MAGNETIC CONCENTRATES

				Total Fe as				
Speci	men	No.	Cr203	FeO	Cr	Fe		Cr:Fe
C	1		41.5	32.4	28.39	25.	19	1.13:1
C	2		42.5	31.0	28,65	24.	10	1.19:1
C	3		42.6	32.2	29.15	25.0	03	1,16:1
C	4		44.5	32.0	30.45	24.8	88	1.22:1
C	5		43.0	31.7	29.42	24.6	54	1.19:1
C	6		42.0	29.3	26.96	22.6	55	1.19:1
C	7		43.5	34.6	29.76	26.9	90	1.11:1
C	8		43.5	33.1	29.76	25.	73	1.16:1
C	9		44.1	36.1	30.17	28.0	06	1.07:1
C	10		37.3	27.0	25.52	20.9	99	1.22:1
						AVERAGE	Cr:Fe	1.16:1

B. NATURAL FERROMAGNETIC CONCENTRATES

Speci	imen	No.	Cr ₂ O ₃	Total Fe as FeO	Cr	Fe	Cr:Fe
M	1		40.0	33.5	27.37	26.04	1.05:1
M	4		42.0	36.5	28.74	28.37	1.01:1
M	5		41.5	32.3	28.39	25.11	1.13:1
M	7		41.2	38.0	28.33	29.54	0.96:1
M	8		41.4	32.5	28.33	25.26	1.12:1
M	9		42.4	36.1	29.01	28.06	1.03:1

AVERAGE Cr:Fe 1.02:1

OVERALL AVERAGE Cr:Fe 1.1:1

CHAPTER V

X-RAY DIFFRACTION STUDIES

i. General Statement

X-ray diffraction work on the Bird River chromites was done on the Phillips X-ray diffraction unit under the guidance of Dr. R. B. Ferguson. The X-ray diffraction powder photographs were taken on large cameras (diam. 114 mm.) using the fine collimators. The large camera and fine collimators were used to enhance accuracy in the measurement of the 'd' spacings and hence the accuracy of the cell edge. The fine collimator ensures fine lines on the photograph but increases the exposure time. The most satisfactory results were obtained using iron radiation with a manganese filter for an exposure time of thirty hours on portals one and three. The specimens were made into thin collodion rollings rather than using a glass fibre to mount the powdered mineral, which is important in defining the lines on the photograph more sharply. Careful centering of the specimen is necessary.

The first X-ray diffraction powder photographs taken were of heated specimens. Hematite was positively identified. Further work determining the cell edges of the remaining chromites was performed in the hope of establishing a relation between cell edge, composition

and exsolution characteristics. These relationships are discussed mainly in Chapter VI.

The Nies scale was used to 'read' the spacings of the reflecting planes on the photographs and the cell edges were then calculated from the formula;

$$a_0 = d / h^2 k^2 1^2$$
.

The results are shown in Table VII. The standard line spacings and hkl values were compared with those for a type example in Berry and Thompson (1962, p. 195). The line of maximum theta angle and sharpness, used to calculate the cell edge was (044). All the cell edge calculations were done using this line whose 'd' spacing is about 1.473 Å (Berry and Thompson, 1962, p. 195).

ii. The cell Edges of the Natural Chromites

The cell edges of the Bird River chromites are compared with Thayer's (Thayer, 1956) three groups in Fig. 9. The Bird River specimens may be described as ranging from the aluminate group into the true chromite group. The cell edges of the ferromagnetic group are greater than those of the non-magnetic fraction (Fig. 10). In some chromites, especially the ferromagnetic variety, two phases of spinel are clearly seen on the X-ray diffraction powder photographs. These will be briefly discussed later. The cell edges of the non-magnetic

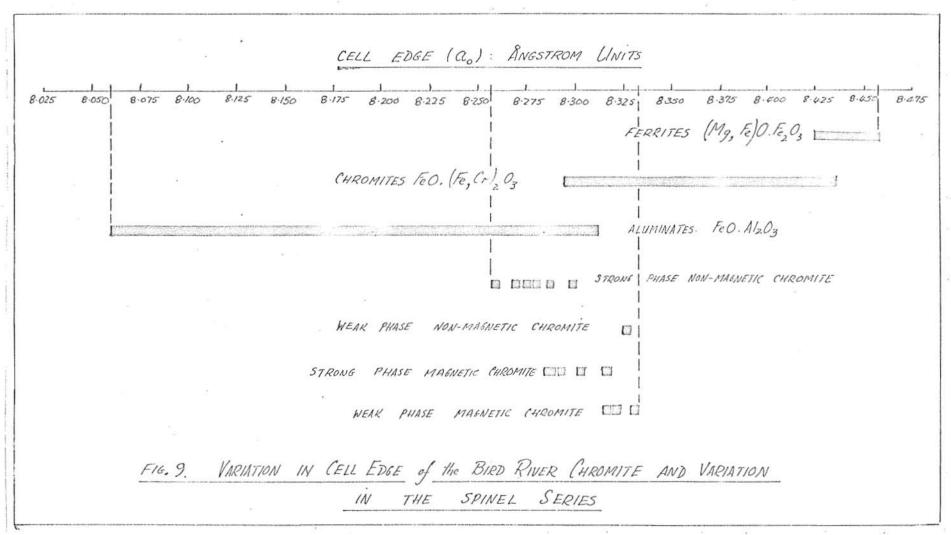
TABLE VII CELL EDGES IN A CF

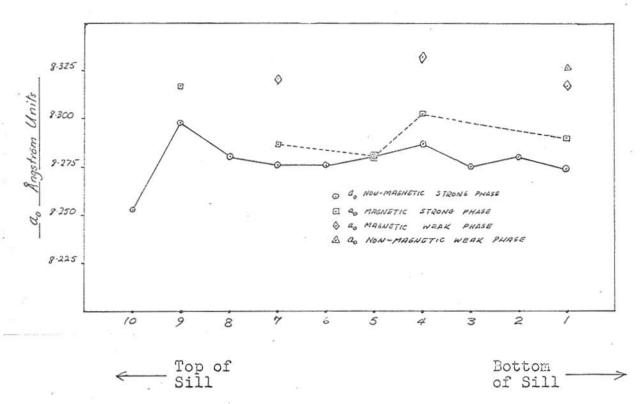
A. NATURAL NON-MAGNETIC CONCENTRATES

Specimen '	No. Film Number	Phase I (strong)	Phase II (weak)
C 1	A-1053	8.2705	8.3275
C 2	A-1021	8.2818	none
C 3	A-1056	8.2760	none
C 4	A-1062	8.2875	none
C 5	A-1067	8.2818	none
c 6	A-1064	8.2760	none
C 7	A-1066	8.2760	none
C 8	A-1055	8.2818	none
C 9	A-1063	8.2988	none
C 10	A-1065	8.2592	none

B. NATURAL FERROMAGNETIC CONCENTRATES

Specimen No.	Film Number	Phase I (strong)	Phase II (weak)
M 1	A-1052	8.2931	8.3157
M 4	A-1057	8.3044	8.3328
M 5	A-1068	8.2818	none
M 7	A-1058	8.2875	8.3214
M &			
M 9	A-1069	8.3157	none





The Ten Chromitite Horizons Arranged 'Stratigraphically'

FIGURE 10. 'Stratigraphic' Variation of Cell Edge

fraction show little variation, and are paralleled by the curve for the ferromagnetic fraction. Concentrate 10 is anomalous and has a small cell edge of 8.2592 Å.; this is a consequence of its high Al₂O₃ content.

In relating cell edge to composition, the problem becomes more complex. Figure 6 (page 34) should be referred to where the variation in cell edge is plotted against the variation in composition. The cell edge curve parallels the curve for Cr2O3 in the non-magnetic concentrates. The relationship of cell edge to the ${\rm Al}_2{\rm O}_3$ content is inverse, in a general way, high Al 03 corresponding to a small cell edge. A similar relationship is to be seen for MgO but again is only general. With FeO the curves follow a general pattern, high FeO indicating a large cell edge. This is applicable to both the nonmagnetic and the ferromagnetic fractions. FeO in sample 5 is nearly equal in both fractions and the cell edges are the same. As expected the cell edge and composition are related in a complex way and any more precise statements should be supported by a larger number of cell edge determinations and analyses.

Of the ten chromites, four showed two spinel phases occurring in the same specimen (Table VII). This may be related to the prominence of the altered rims in some of the chromite crystals described in Chapter III. Specimens

1, 4, 7 and 9 have noticable rims compared to the other specimens and each show two phases. Except in specimen 1 the two spinel phases occur only in the ferromagnetic fraction of the concentrates. In the X-ray diffraction photographs one phase is strong (Phase I) while the other is much weaker (Phase II). The weaker phase is less abundant than the stronger phase and may be representative of the crystal rims which are small in size. Since the cell edges of the rims are noticably higher than those of main crystal, and since the cell edge increases with increasing iron, it is reasonable to assume that the rim phase is iron-rich. This is further supported by the fact that the spinel group as a whole have increasing cell edges as they approach the iron-rich, magnetic ferrites (Fig. 9). This substantiates the earlier suggestion that hematite exsolution may be expected to begin in iron-rich areas on heating,

CHAPTER VI

INTERPRETATION OF DATA

i. Exsolution and Composition

Exsolution developed in all ten specimens on heating in air for seventy two hours at 1000°C. Hematite was proved to be the solute mineral with chromite as the solvent mineral. Exsolution appears to be crystallographically aligned along the (111) planes of the crystals in a true Widmanstätten pattern. The iron content of the natural chromites is considered to be the main factor governing the development of exsolution, since hematite is the solute mineral. All the specimens are rich in iron compared to true chromites. The ferromagnetic variety produces a stronger exsolution pattern on heating than the non-magnetic variety. Again the iron content is generally higher in the former thereby accounting for the stronger development of the exsolution. The weak phase, in the rims of the crystals, is the first part to develop exsolution, and was shown, on the basis of the size of their cell edge, to be iron-rich. The other elements are in some way dependent on the $\mathrm{Cr}_2\mathrm{O}_3$ and FeO content but no relation between them and the exsolution could be established. The iron therefore seems to be the main factor controlling the development of hematite as an exsolution mineral from chromite.

ii. 'Stratigraphic' Variation of the Parameters

The 'stratigraphic' variation of the parameters is not clearly defined. Only generalisations may be made and these are not of great value since the local variation is erratic. For convenience all the figures showing the parameters determined on each specimen are plotted in 'stratigraphic' order. With the exception of Fig. 3 the 'stratigraphic' sequence is plotted without regard to scale. Fig. 3 is plotted to scale and serves as a 'stratigraphic' column representing the chromitite horizons. Fig. 5 shows the variations of MgO, Cr_2O_3 , Al_2O_3 and total iron as FeO of the rock analyses across the 'stratigraphic' section. Because of the variation of concentration of chromite in these layers no trends can be demonstrated.

The composition of the chromite concentrates is also considered in relation to the 'stratigraphic' variation. Since the non-magnetic and ferromagnetic fractions vary in similar ways, and since taken together they represent the total composition of the chromite in each horizon, the trends will refer to the pairs of curves in Fig. 6. Specimen 10 has a very different composition to the other horizons and will not enter the general discussion. Cr_2O_3 and total iron as FeO tend to increase upwards in the sill; Al_2O_3 remains constant while MgO decreases towards the top of the sill. Generally the cell edge increases in size

towards the upper horizons in sympathy with Cr203 and total iron as FeO and decreasing MgO, while Al2O3 remains constant. Specimen 10 is from the uppermost horizon studied and has reverse relationships to the general trends in composition, that is to say, low $\operatorname{Cr}_2\operatorname{O}_3$ and iron as FeO and high MgO and Al_2O_3 . This horizon is at the top of the main zone (Fig. 3) and represents a deficiency of Cr203 and iron as FeO after a long period of crystallisation of Cr203 and iron-rich spinels, at which time one would expect a surfeit of MgO and Al₂O₃ in the remaining liquid. earlier chromites to crystallise are lower in $\operatorname{Cr}_2\operatorname{O}_3$ and iron as FeO than those in the main zone excluding Specimen 10. It may be suggested that Cr203 and iron as FeO crystallized in increasing amounts as conditions approached an optimum, after which a sharp change in the crystallisation pattern occurred to account for specimen 10.

From Fig. 8 it can be seen that any trend in true FeO or Fe_2O_3 is very slight, although possibly the latter decreases slightly with increasing 'stratigraphic' order. The Fe_2O_3 curve is smoother than that for FeO suggesting that MgO varies widely while Al_2O_3 and Cr_2O_3 only change slightly throughout the sequence. This is found to be true (Fig. 6).

The 'stratigraphic' variation in the amount of ferromagnetic to non-magnetic spinel in each sample is

shown in Fig. 3. There is no progressive variation so it is unlikely that magnetism in these minerals is dependent on the usual course of crystallisation.

The parameters do not vary in a regular way across the sill, though general trends may be recognised. From one horizon to the next the variation is erratic obscuring the trend if one actually exists.

CHAPTER VII

SUMMARY AND CONCLUSIONS

The Bird River chromites are described with special reference to the phenomenon of exsolution. To this end, heating experiments were conducted on ten chromites from different horizons, and the optimum conditions for maximum exsolution were found to be heating in air at 1000°C for 72 hours at one atmosphere. Polished section work was carried out in conjunction with the heating experiments and hematite was found to exsolve from all the ten specimens. Analyses of the chromitites and the concentrates were done on the A. R. L. Vacuum X-ray Quantometer at the University of Manitoba. Six of the concentrates were found to have a ferromagnetic fraction and these were analysed separately. Several differences between the ferromagnetic and nonmagnetic concentrates can be seen. The non-magnetic fraction has more Cr_2O_3 and Al_2O_3 and less iron as FeO than the ferromagnetic fraction. Exsolution is more pronounced in the ferromagnetic fraction and this indicates that exsolution of hematite is dependent on the total iron content of the chromian spinel. X-ray diffraction powder photographs were taken of both types of concentrates and the cell dimensions determined. The ferromagnetic fraction have larger cell edges than the non-magnetic fractions. A general relation between the compositions and cell edges

can be seen, but not enough samples zould be examined to give a statistical comparison. Cell edge seems to increase with increasing iron. 'Stratigraphic' trends are noticable in the composition curves and the cell edge variation curve, but the amount of magnetic spinel in the concentrates does not seem to be related to the 'stratigraphic' position of the horizons. Two spinel phases occur in certain chromites, the weak phase representative of the altered rims of the crystals and the strong phase representative of the central areas of the crystals. The rims were concluded to be iron-rich due to deuteric alteration at late stage of the crystallisation process, rather than zoning since they occur along fractures within crystals as well as in the rims.

Exsolution develops with heating, first in the ironrich areas of the rims and it is resolved into a
Widmanstätten pattern under high power magnification (X850).
With further heating, tiny rods and plates gradually appear
at the centres of the crystals and ultimately after 72 hours
at 1000°C the exsolution is complete across the crystal.
From the data collected it seems likely that hematite will
exsolve in any iron-rich chromite which has a Cr:Fe ratio
comparable to the Bird River chromites of about 1.2:1 or
less.

APPENDIX I

PREPARATION OF THE CONCENTRATES

Concentrates of the chromite were required for the analyses and the X-ray diffraction work. The Haultain Super-panner was used to concentrate the chromite from the gangue minerals. For the best concentration of grains large enough to study, the chromitites were crushed to -150 to \$\frac{200}{200}\$ mesh. In this size range no small particles of gangue could be seen adhering to the chromite grains under the binocular microscope, as was the case with the larger mesh sizes. Nevertheless, the analyses indicate some impurities, and it is felt that they are due to gangue inclusions within the chromite crystals themselves.

APPENDIX II

PREPARATION OF THE SAMPLES FOR X-RAY FLUORESCENCE ANALYSES

The sample for analysis was pulverised to -200 mesh, and then fused into a bead using the following mixture:

- 0.5 gm. pulverised sample.
- 0.5 gm. lanthanum oxide.
- 1.0 gm. lithium tetraborate.

This mixture was fused to a bead for 20 minutes at 1800°F. To make up the required weight of 2.1 gms., boric acid was added to the bead and this mixture was then pulverised and, using a 30 ton press, made into a pellet with a boric acid base. The resulting pellet was then ready for analysis.

APPENDIX III

PREPARATION OF PLASTIC GRAIN MOUNTS FOR POLISHED SECTION EXAMINATION

With a brass ring on a piece of glass, 'Quickmount' plastic solution was moulded into a pellet and allowed to set. Since four fractions of the concentrate were required for comparison, four small holes were drilled in the pellet and the grains of each fraction mixed with a little plastic solution and poured into each hole. When set, the plastic mount could be ground to expose some grains of each fraction and then polished for study.

APPENDIX IV

PROPORTIONING TOTAL IRON IN THE CHROMITES BETWEEN

FeO AND Fe₂O₃

(See TABLE V p. 38)

According to the requirements of the molecular structure of spinel 33% of the cations must be bivalent and 67% trivalent. Hence by adjusting the total composition to 100% it is possible to proportion total iron available into FeO and Fe₂O₃ by adding the trivalent components and making up the deficiency with Fe₂O₃. The remaining iron would then be present as FeO. This method, though not precise, is adequate for this study as the general relationships become clear. It should be kept in mind that some of the chromite showed exsolution of hematite before heating and that this would represent excess iron in the analysis rather than iron as a part of the spinel structure. However, this amount would be small.

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