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CHROMITE: ITS MINERAL AND CHEMICAL COMPOSITION¹

LLOYD W. FISHER, *Johns Hopkins University.*

INTRODUCTION

The mineral called chromite is a member of the spinellid group of minerals which crystallize in the isometric system. The spinellids have the general formula $R''O \cdot R'''_2O_3$. Chromite, however, is seldom found as a pure double oxide. Replacement of FeO by MgO and Cr_2O_3 by either or both Al_2O_3 and Fe_2O_3 gives rise to varietal types and chief among these are chrompicotite, chromhercynite, magnesiochromite (mitchellite), picotite and chromiferous spinels. The mineral called chromite can seldom be expressed by a definite formula. It is usually a mixture of the varietal types cited. There is a strong probability that the spinellids, magnetite, magnesioferrite and others enter into its chemical makeup.

The spinellids have been classified by various investigators and it is not necessary to go into the details of subdivision of the group. There are four major sub-groups: the aluminates, chromates, manganates and ferrates, represented by spinel, chromite, jacobsite and magnetite, respectively

The physical properties of chromite are, briefly stated: lustrous to pitchy black color, fine grained granular to crystallized octahedra, rarely truncated by the cube or beveled by the rhombic dodecahedron; M.W. 223.84; S.G. 4.32-4.57; M.V. 50.3; $n = 2.07$ to 2.16; fusibility 2180°C.

STUDY OF THE PUBLISHED ANALYSES

More than 150 published analyses of supposed chromite have been collected in order to ascertain the formula of the mineral. Various lines of attack might be followed to gain this goal. Among these are:

¹ An abstract of a portion of a dissertation submitted to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy.

- (1) Study of ratios between the bivalent and trivalent oxides.
- (2) Study of methods in which the various oxides are combined in the mineral.
- (3) Deduction of formula from individual analyses.
- (4) Calculation of ratios that exist between the various oxides listed in the analyses.

RATIOS

It has been suggested that the spinellids are double oxides and they may be represented by the general formula set forth above. A study of analyses indicates that the ratio of 1:1 between bivalent and trivalent oxides is not the general rule in the species chromite. No analysis of chromite shows the presence of zinc, and since chromite is considered to be an isomorphous mineral closely related to other spinellids, the absence of zinc eliminates relationship to zinciferous spinels.

An effort is first made to correlate ratios of the bivalent to trivalent oxides. This leads to the following result:

Ratio of $R_2'''O_3$ to $R''O$
(molal amounts)

	av.
Lowest ratio	1:0.53
"Subnormal" (less than 1:0.90)	1:0.774
"Normal" (between 1:0.90 and 1:1.00)	1:0.998
"Abnormal" (greater than 1:1.00)	1:1.340
Highest ratio	1:3.69

All the analyses termed "subnormal" and "normal" fall below the average of the entire number of analyses, namely, 1:1.13. The average ratio of the subnormal and normal groups is 1:0.934. The terms used in the above tabulation will be used throughout this discussion in the sense designated.

A comparison between the relative percentages of true spinels and chromite that fall within the three normality ranges is shown below.

	RATIOS					
	Lowest	Subnormal	Normal	Abnormal	Highest	Average
Spinel	1:0.64	1:0.707 (12.6%)	1:0.980 (76.7%)	1:1.23 (10.7%)	1:1.47	1:0.97
Chromite	1:0.53	1:0.774 (15.2%)	1:0.998 (38.3%)	1:1.34 (46.3%)	1:3.69	1:1.13

Note: average ratio of groups is given; per cent indicates total number of analyses represented that falls within group.

Ratios between the total bivalent and trivalent oxides reported in mineral analyses depend entirely on two features. First: It is necessary to reduce and eliminate, by some arbitrary method, oxides which do not enter into the composition of the spinellid. Second: Improper and incomplete methods of analyses are often causes of abnormal or subnormal ratios (*i.e.* such analyses are sometimes detected where all iron of chromite is reported as either all ferrous or all ferric). If all iron is determined as ferrous the mineral species will probably fall in the abnormal group.

From a comparison of the relative percentages of spinel and chromite that fall within the normal group it is noted that less than 40% of the chromite analyses are normal. In attempting to solve the reason for this, certain subtractions are made from the abnormal analyses. In a heavy gravity separation it is impossible to secure absolutely pure material for analysis, for chromite is often fractured and contains much serpentine, kämmererite, and other hydrous minerals. Hence, water, carbon dioxide, silica, excess magnesia, etc., must be eliminated. Oxides have been subtracted on the following basis: Serpentine— $2\text{H}_2\text{O} \cdot 3\text{MgO} \cdot 2\text{SiO}_2$; Enstatite— $\text{MgO} \cdot \text{SiO}_2$; Magnesite— $\text{MgO} \cdot \text{CO}_2$; Uvarovite— $3\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot 3\text{SiO}_2$; Ilmenite— $\text{FeO} \cdot \text{TiO}_2$; and Rutile— TiO_2 .

Titanium minerals are nearly restricted to those chromites which occur in chromiferous magnetites or in the chromiferous serpentines that carry rutile. In some of the analyses no oxides other than those really essential to the spinellid have been reported and such analyses allow no correction.

MUTUAL REPLACEMENT OF OXIDES

Another classification, purely chemical in nature, is suggested and is to be used in connection with the ratio classification. The various analyses of chromite are grouped according to their contained oxides and comparisons between such groupings are thus afforded. The collected analyses fall into the following chemical groups:

Type		No. of anal.	% of total
I.	$\text{FeO} \cdot \text{Cr}_2\text{O}_3$	3	2.0
"	IIa. $\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$	12	8.0
"	IIb. $\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$	1	0.6
"	IIc. $\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$	0	0.0
"	III. $\text{FeO} \cdot \text{MgO} \cdot \text{Cr}_2\text{O}_3$	2	1.2
"	IIIa. $\text{FeO} \cdot \text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$	96	64.0

"	IIIb.	FeO · MgO · Fe ₂ O ₃ · Cr ₂ O ₃	0	0.0
"	IIIc.	FeO · MgO · Fe ₂ O ₃ · Al ₂ O ₃ · Cr ₂ O ₃	31	20.6
"	IIIId.	FeO · MgO · Mn ₂ O ₃ · Fe ₂ O ₃ · Al ₂ O ₃ · Cr ₂ O ₃	5	3.3
"	IV.	MgO · Al ₂ O ₃ · Cr ₂ O ₃	1	0.6

The most prominent types are IIa, IIIa and IIIc. The discussion will be based chiefly on these types and the nomenclature cited above will be used with that adopted for the ratios.

RELATED SPECIES

Many of the analyses of so-called chromites contain varying amounts of ferrous iron and magnesia. Varietal types arise because of such replacements. The common varietal species of chromite are:

	Al ₂ O ₃	Cr ₂ O ₃	FeO	MgO	Sp. Gr.
Chrompicotite	12.13	56.54	18.01	14.08	4.115
Magnochromite	29.92	40.78	15.30	14.00	4.02
Mitchellite (a)	29.28	39.95	13.19	17.31	—
Mitchellite (b)	7.82	57.80	18.18	11.62	—
Chromhercynite	27.12	38.64	27.00	5.33	4.415 (c)
Picotite	56.00	8.00	24.90	10.30	4.08

(a) from Corundum Hill, N. C.; (b) from Price Creek, N. C.; (c) contains 0.61% Fe₂O₃, 1.10% MnO, 0.28% SiO₂, and 1.25% H₂O.

The formulas are next calculated on the basis of magnesia replacing ferrous iron, and alumina replacing chromic oxide..

Chrompicotite	1:1.17	(42 Fe · 58Mg)O · (24 Al · 76Cr) ₂ O ₃
Magnochromite	1:1.01	(38 " 62 ") (52 " 48 ")
Mitchellite (a)	1:1.12	(30 " 70 ") (52 " 48 ")
Mitchellite (b)	1:1.24	(47 " 53 ") (17 " 83 ")
Chromhercynite	1:0.98	(74 " 26 ") (51 " 49 ")
Picotite	1:1.00	(58 " 42 ") (92 " 8 ")

(Note:—Formula computed on basis of 100 R'′O · 100 R''O₃).

Chrompicotite and magnochromite have approximately the same amount of bivalents, although the ratio of alumina to chromic oxide varies. This suggests that magnochromite is nearer the aluminates than the chromates. There is little difference between magnochromite and the Corundum Hill mitchellite (a). The varieties, magnochromite, mitchellite and chromhercynite are closely related to the aluminates. Chrompicotite and mitchellite (b)

carry the most chromic oxide but there does not appear to be enough difference chemically to warrant the name mitchellite. Approximately 30% of the collected analyses show as much or more chromic oxide as the type chrompicotite. This mineral species has 12.13% alumina, and 34% of the analyses studied carry more than 10% alumina. Of these, only 12% show more than 55% chromic oxide. Less than 30% of the so-called chromites analyzed are richer in chromic oxide than chrompicotite. These four predominating chromic-spinels have only four oxide variants and accordingly fall within type IIIa.

Magnochromite is listed with 40.78% chromic oxide and 29.9% alumina. Four of the collected analyses show more than 25% alumina and none of these contain more than 45% chromic oxide.

Chromhercynite is reported as showing 38.53% chromic oxide and 27.12% alumina. These percentages overlap those cited for magnochromite. Picotite, more strongly hercynitic than chromitic, carries only 8% chromic oxide and 56% alumina. None of the analyses studied carry as much alumina and only 2 have less than 10% chromic oxide.

If the limits of alumina are set at 15% and 25% only 37 chromite analyses fall within the range, and 8 of these analyses show between 45 and 55% chromic oxide. Alumina less than 10% is encountered in 68 analyses. Most of the chemical analyses of chromite are really representative of chrompicotite or closely related to it.

A STUDY OF CHEMICAL TYPES

Type IIa.

This is the closest approximation to the pure chromite molecule. Eight analyses of normal ratios are considered. The formula for the group is: $100\text{FeO} \cdot (23\text{Al} \cdot 77\text{Cr})_2\text{O}_3$. The range in ratios of the oxides are: alumina to chromic oxide—from 1:1.4 to 1:22; alumina to ferrous iron—from 1:2.4 to 1:20; chromic oxide to ferrous iron—from 1:0.9 to 1:1.7. The limits of the oxides and their relative abundance is shown in figures 1 and 1a. The acid radicle in IIa corresponds to chrompicotite, (See Fig. 5) with FeO slightly higher than normal. It is believed that ferric iron was not determined in these analyses.

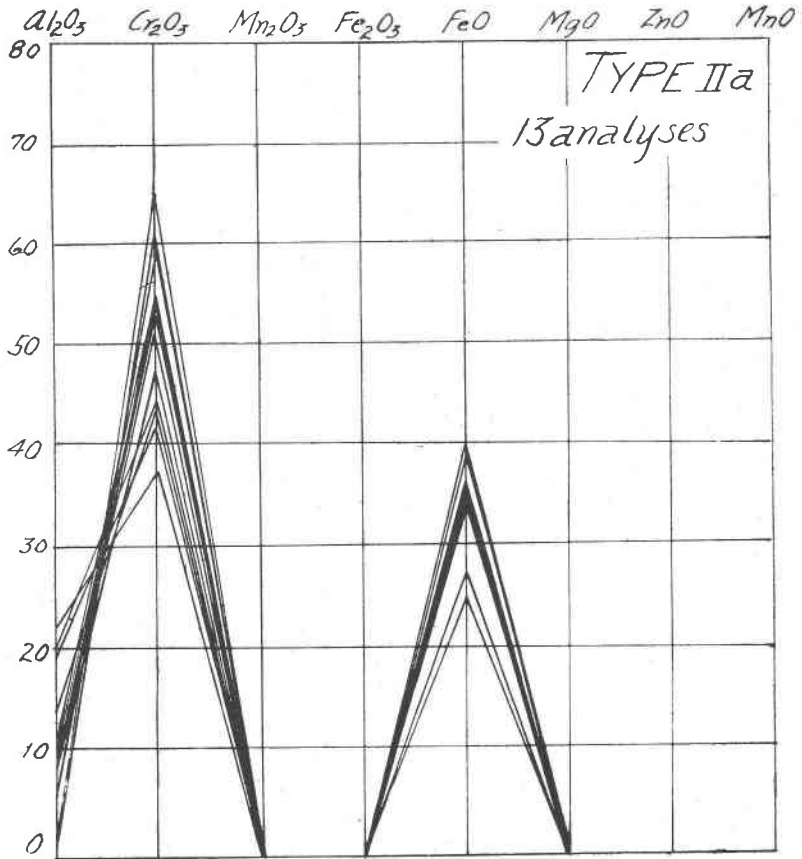


FIG. 1.

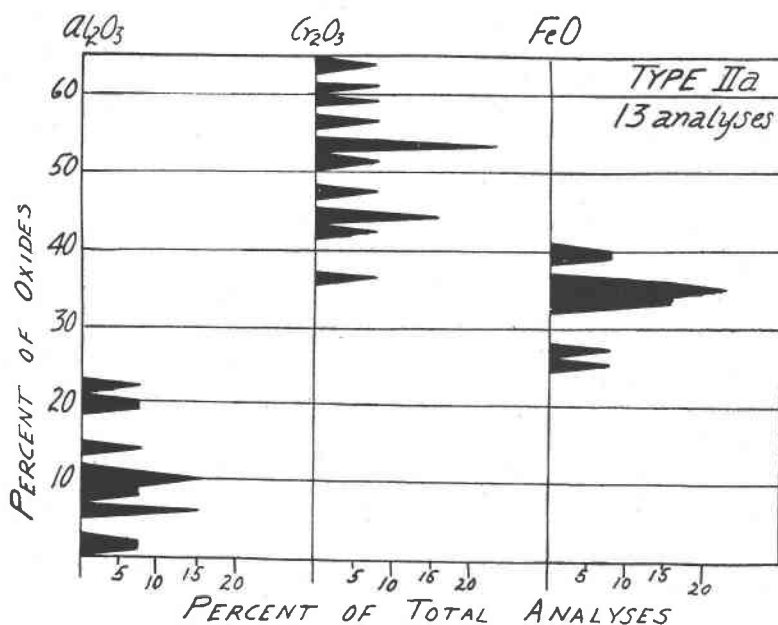


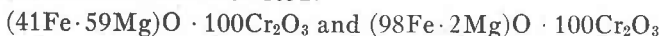
FIG. 1a.

Type IIb.

One analysis of this type is included and is expressed by the formula $100FeO \cdot 15 Fe_2O_3 \cdot 85 Cr_2O_3$. No deductions are made from this analysis.

Type III.

Two analyses fall in this type and because of the wide variation in their formula both are listed:

*Type IIIa*

The same as type III with alumina added. This is the largest group in the study and includes 64% of all the analyses. This type is compared with the varietal types cited earlier. Subnormal ratios occur in 15% of the analyses, 27% are normal and 58% are abnormal. The normal group will be discussed in full.

The average formula of the 25 normal analyses is: $(64Fe \cdot 36Mg)O \cdot (28Al \cdot 72Cr)_2O_3$. The acid radicle is nearer chrompicotite but the base is closely related to chromhercynite (See Fig. 5).

The abnormal group of this type includes more than 33% of the collected analyses. There is a range in ratios of trivalent to bivalent oxides from 1:1.10 to 1:1.94, with such analyses rather uniformly distributed throughout the range. The ratio of alumina to chromic oxide varies slightly despite the great range in the group ratio. The alumina to ferrous iron ratio remains practically the same. There is little difference in the ratios between chromic oxide and ferrous iron. It appears that the high group ratios are due to magnesia. The ratio of the latter to alumina is 2.3:1 in the lowest abnormal analysis and 4:1 in the highest.

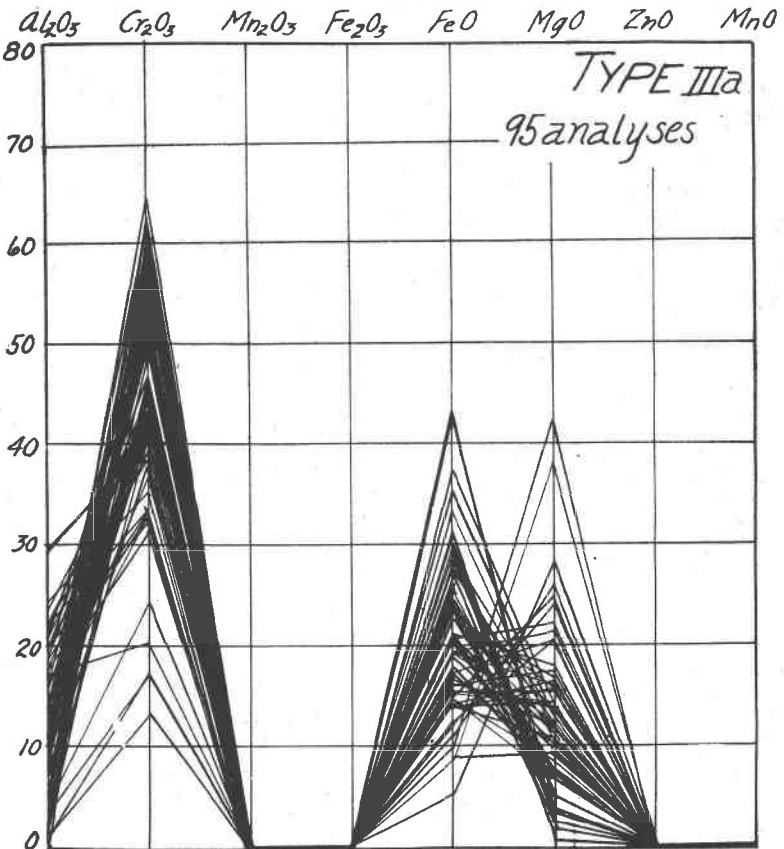


FIG. 2.

The average percentage composition of the divisions of this type, based on normality are:

	Al ₂ O ₃	Cr ₂ O ₃	FeO	MgO	Ratios
Subnormal group	15.7	57.8	19.4	7.1	1:0.77
<i>NORMAL GROUP</i>	13.7	54.9	23.3	7.1	1:1.02
Abnormal group	10.4	55.2	22.5	11.8	1:1.37
Average of type	11.9	54.4	21.8	11.6	1:1.8

Alumina decreases more rapidly than chromic oxide. This increase in ratio is apparently expressed by an increase in magnesia. When total trivalents are higher than total bivalents alumina is usually higher with respect to chromic oxide than when conditions are reversed. The ratio between ferrous iron and magnesia shows the latter increasing in amount as the sum of the bivalents becomes greater than the sum of the trivalents. This indicated effect of magnesia is suggestive of undetermined ferric iron. Figures 2 and 2a show the limits of the various oxides and their relative distribution.

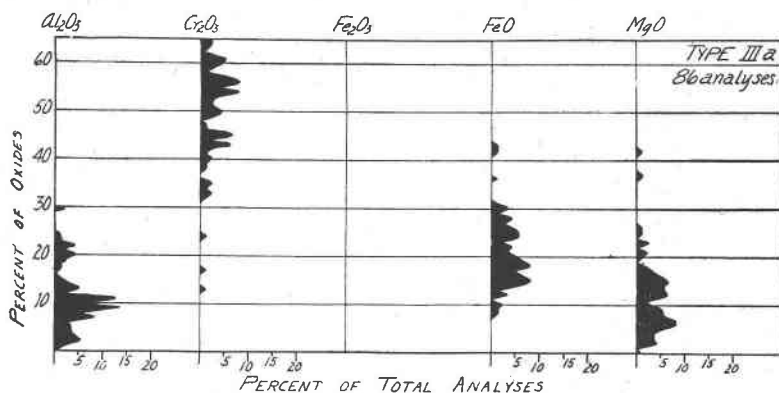


FIG. 2a.

Type IIIc.

This is the second largest group of analyses and includes 15 normal ratios. The average formula of these analyses is: (37Fe'' · 67Mg)O · (7Fe''' · 33Al · 60Cr)₂O₃. The outstanding feature here indicated is that magnesia is higher than ferrous iron. The type is more closely related to magnochromite than to any other. Alumina increases with respect to ferrous iron but decreases with respect to chromic and magnesia oxides. The ratio of ferric to

ferrous iron, compared with the subnormal group, has doubled.

If the abnormal group of this type is compared with the abnormal group of IIIa it is noted that the proportion of alumina to chromic oxide remains about the same. The introduction of ferric iron has not visibly affected this ratio. A comparison of figure 3 with figure 2 shows the peak of alumina has moved upward. The ratio of alumina to ferrous iron is not greatly changed but magnesia has gained fully 20% with respect to alumina of type IIIa. The ratios of chromic oxide to ferrous iron and magnesia remain much as they were in type IIIa. The entire 31 analyses of this type give an average formula of $(43\text{Fe} \cdot 57\text{Mg})\text{O} \cdot (8\text{Fe} \cdot 29\text{Al} \cdot 62\text{Cr})_2\text{O}_3$.

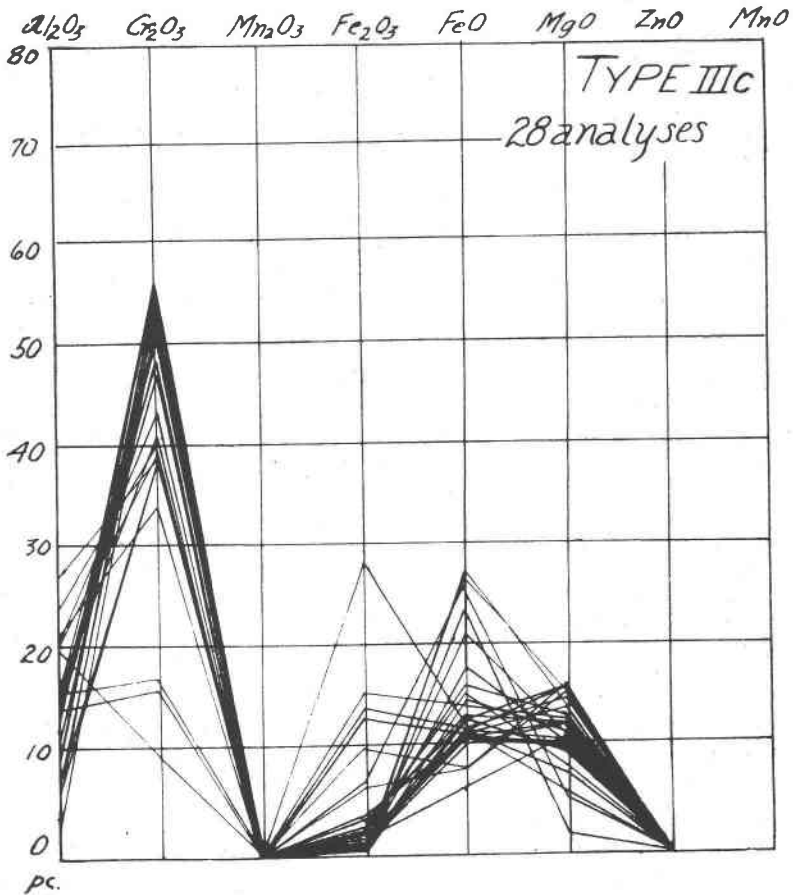


FIG. 3.

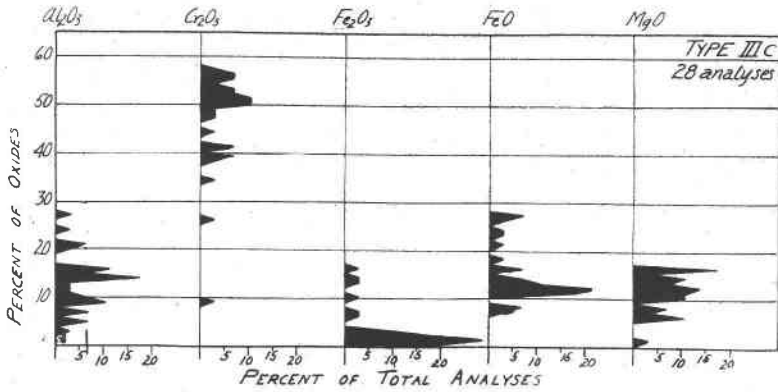


FIG. 3a.

SUMMATION OF TYPE IIIc.

1. By analyses

	Al ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃	FeO	MgO
Subnormal group	14.0	49.2	12.4	15.2	9.2
NORMAL GROUP	17.7	47.1	6.0	14.4	14.8
Abnormal group	11.4	52.8	1.8	22.5	11.2
Average of type	17.2	49.0	66.3	15.8	11.7

2. By formula

Subnormal group (48Fe · 52Mg)O · (14Fe · 25Al · 51Cr)₂O₃

NORMAL GROUP (37Fe · 67Mg)O · (7Fe · 33Al · 60Cr)₂O₃

Abnormal Group (52Fe · 48Mg)O · (4Fe · 23Al · 73Cr)₂O₃

The outstanding relations shown in Type IIIc are: magnesia continually increases toward the extremes of abnormal ratios. The mineral called chromite moves toward magnesiochromite as abnormal ratios are reached.

Type III d

Four of the 151 analyses show this combination. No effort is made to correlate results. The analyses follow:

No.	Al ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃	Mn ₂ O ₃	FeO	MgO
149	9.40	55.40	1.78	1.10	16.39	12.72
150	17.00	37.31	3.80	1.12	35.12	3.08
151	17.23	37.03	0.71	1.16	23.95	9.94
152	0.48	31.20	27.72	4.18	14.79	10.92
153	10.23	43.76	—	1.95	21.27	15.25

SUMMATION OF OXIDE RELATIONSHIPS

In figure 4 the frequency of percentages of oxides is plotted for all analyses considered. The bulk of the analyses show chromic oxide well above 40%, but alumina is massed around 10%. Ferrous iron extends over a considerable range although magnesia is somewhat restricted and is most abundant between 8 and 12%.

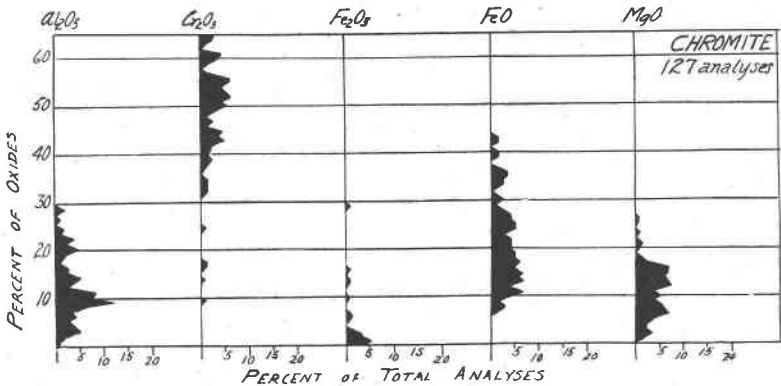


Fig. 4.

A comparison of figures 1a and 2a shows interesting facts. When magnesia replaces ferrous iron, in part, the majority of analyses show less alumina, the peak of the latter being in the neighborhood of 10%. Chromic oxide reaches its high point when magnesia is not present. (This is not shown in figure 2). It is natural that the peak of ferrous iron should drop as magnesia increases. Ferric iron is in all probability replacing chromic oxide and not alumina. This indicates that these analyses are more closely related to the ferrate spinellid than to the aluminate variety. It is inferred from a study of the graphs that magnesioferrite enters into those chromites that contain ferric iron in substantial amounts.

Figure 5 shows a graph representing varietal species superimposed on figures 1, 2, and 3, illustrating variations in oxides. A study of this figure gives the following results:

1. Alumina is highest in type IIIa, although all types show the same lower limits.
2. High values of chromic oxide occur in types IIa and IIIa. In the former there is no magnesia.
3. High and low values of ferric iron are not restricted to any particular type.

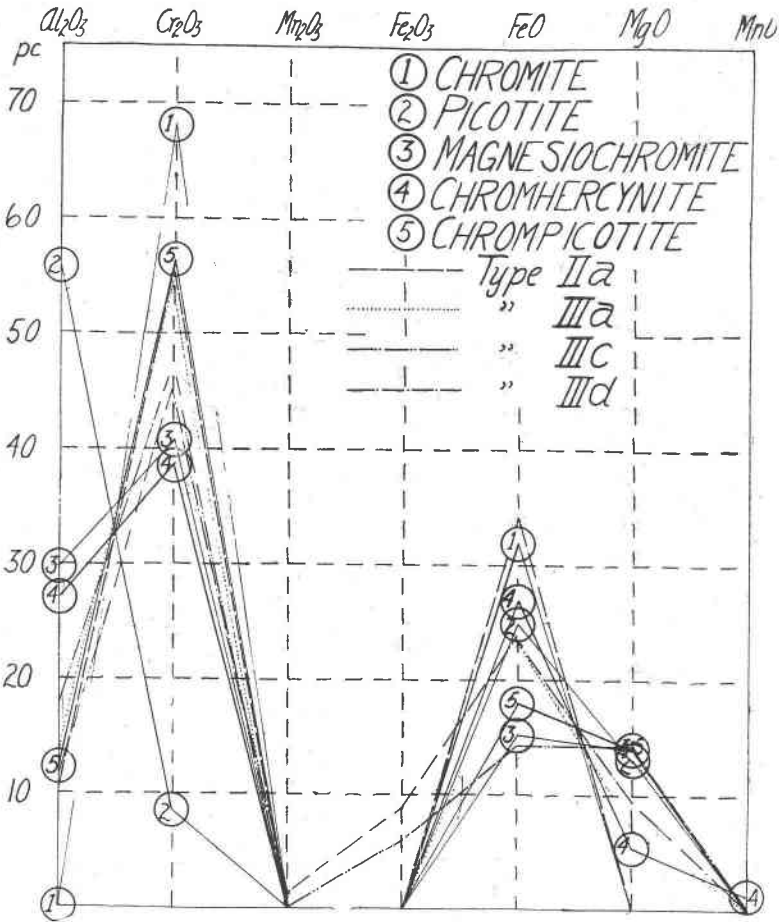


FIG. 5.

The analyses as a whole show that some correlative value may be attached to the replacement of iron by magnesia and chromic oxide by alumina and ferric iron. Application of such values to individual analyses fails. As a rule, however, when ferric iron is present, magnesia will dominate ferrous iron. When ferric iron replaces a trivalent element, chromic oxide is more affected. From these facts it follows that magnesioferrite must enter the composition of chromites.

In figure 5 where the averages of the four prevailing chemical types of chromite are plotted against the analysis of the original varietal type another comparison is afforded. Some of the deduced facts are:

1. No type average approaches the high chromic oxide of the theoretical chromite, although in type IIa ferrous iron is higher than in the pure chromite molecule. Ferric iron must have been present in those analyses.

2. There is considerable variation in average oxide content of the so-called chromites.

3. The majority of all chromite analyses recorded are closely related to the varietal types, magnesiochromite, chromhercynite and chrompicotite.

(a) Type IIIa corresponds closely to chrompicotite acid radicle and picotite-chromhercynite base.

(b) Type IIa is related to chrompicotite acid radicle and to a chromite base.

(c) Type IIIc bears a closer relation to the alumina of chrompicotite and chromic oxide of magnesiochromite when the acid radicle is considered, but to a magnesiochromite base.

Therefore, the majority of chromites are considered as intermediate members between chrompicotite and magnesiochromite.

MINERAL ANALYSIS OF CHROMITE

To ascertain the mineral analysis of chromite it is necessary to record some previously deduced values.

Normal ratios only are given. These are expressed in molar amounts.

	Al ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃	FeO	MgO
Type IIa	109	390	none	505	none
Type IIb	none	439	75	486	none
Type III	none	422	none	238	341
Type IIIa	135	359	none	324	178

Picotite	457	43	none	290	214
Magnochromite	260	237	none	190	312
Chromhercynite	257	244	none	365	129
Chrompicotite	108	340	none	227	320
Type IIIc	163	293	none	187	320

Two methods of computing mineral analyses from the above may be followed:

(1) Regard all FeO or Cr₂O₃ as entering the molecule chromite. Excess of either is then distributed in proportion among the remaining oxides.

(2) Distribute all bivalents on a proportionate basis to the trivalents.

Alumina is in excess in type IIa and in chromhercynite when the first method is used, likewise ferric iron is in excess in IIb, and magnesia in III, IIIa, IIIc, in picotite and chrompicotite. Ferrous iron is in excess only in picotite.

When the second method of calculation is used the following excesses are noted: chromic oxide in IIa and chromhercynite; ferric oxide in IIa; alumina in picotite and chromhercynite; magnesia in III, IIIa, magnesiochromite, chrompicotite and IIIc; and ferrous iron in the same types and varietal species as magnesia.

The study of either method shows that the mineral called chromite is not a simple mineral expressible by a definite formula. There is no relationship between the ratios of the bivalent or trivalent oxides in one specimen of chromite owing to the lack of uniformity of mixing of the spinellid molecules to form the mineral. The simplest formula that may be used to express the mineral composition is: 4 Chromite + 1 Hercynite, and the most complex variations are shown in IIc. Chromite is usually a combination of the pure chromite molecule plus the so-called magnesiochromite of Bock, hercynite and spinel. Magnesiochromite represents a spinellid that stands between spinel and chromite. The varietal types plotted with spinel and chromite show a transitional series—spinel-magnesiochromite-chromhercynite-chrompicotite-chromite. Chromite, as a mineral, represents varying proportions of these species and none of the latter may be represented by a definite chemical formula.

The study of the analyses indicates the probable presence of a pure magnesium chromite to which the name magnochromite

might be given to differentiate it from the chromite sub-species, magnesiochromite.

Spinel, hercynite, supposedly pure chromite and magnochromite are the end members of a four component diagram and within the limits of this diagram all non-ferric chromite will fall. When ferric iron is present, magnesioferrite must be added to the series.

CONCLUSIONS

I. *Chemically*

1. Chromite as a pure $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ occurs only in meteorites.
2. There is a wide variation in the amounts of oxides that enter into both the acid and base of the mineral called chromite.
3. Practically all chromites analyzed show one or more oxides in excess. This excess may be caused by:
 - (a) Improper separation of chromite from gangue.
 - (b) Incomplete analysis.
 - (c) Solid solution of oxides within the chromiferous spinellid.

II. *Mineralogically*

4. Various members of the spinellid group are isomorphous with each other, but all the members cannot be arranged in a definite isomorphous series.
 - (a) According to Rettger's law one of the proofs of isomorphism between related species is that the physical properties of such mixtures are continuous functions of percentage composition.

The spinellids, taken as a group, do not show such a relationship when chromic oxide, alumina, ferric iron, ferrous iron, or total iron are plotted with index of refraction, specific gravity, etc.

- (b) Chromite does not contain zinc and cannot be a true variant of a series which contains gahnite.
- (c) The following isomorphous series are indicated within the spinellid group:

- I. Spinel-Magnochromite-Chromite.
- II. Magnetite-Kreitonite-Dysluite-Gahnite.
- III. Spinel-Magnesioferrite-Magnetite.
- IV. Gahnite-Spinel-Franklinite.

- (d) The atomic volumes of the oxides of the spinellids are:
- | | | | |
|-------------------|------|---------------------|------|
| alumina..... | 9.98 | zinc oxide..... | 9.50 |
| chromic oxide.... | 7.50 | manganous oxide.... | 7.10 |
| manganic oxide... | 7.40 | ferrous oxide..... | 6.80 |
| ferric oxide..... | 7.10 | magnesia..... | 6.70 |

On the basis of exchange of acid radicles the series would be aluminates-chromates-manganates-ferrates. Dividing such a series by the bases there would be:

- (1) aluminates: gahnite-manganspinel-hercynite-spinel.
- (2) chromates: chromite-magnochromite.
- (3) manganates: heterolite-hausmannite-ferromanganate.
- (4) ferrates: franklinite-jacobsite-magnetite-magnesioferrite.

Chromite is related to the mafic end of the aluminate series, and apparently is not related in any way to the manganates. It is related to the ferrates only by way of magnetite and magnesioferrite.

5. The spinellids, which have always been regarded as an isomorphous series, have variants that are predominantly manganiferous and zinciferous. The chemical analyses of the mineral called chromite do not harmonize chromite with these two types of spinellids.
6. Finally the mineral called chromite is not a definite mineral and cannot be regarded as a member of a definite isomorphous series, although the three, four, five or six spinellids which make up chromite are interrelated.

III. *Optically*

7. The chemical composition of the mineral called chromite is roughly indicated by the color of the mineral in thin section. Low chromic oxide content as in picotite, is characterized by a yellowish brown translucency, and high chromic oxide content by a deep cherry red to coffee brown color.
8. Anastomosing black, opaque lines traverse translucent chromite grains and indicate either: (1) the presence of a foreign substance which may be present as a solid solution in the mineral, or (2) iron oxide deposited as a cement along narrow or incipient fractures.