Canadian Mineralogist,
Vol. 11, pp. 930-939 (1973)

A NATURAL OCCURRENCE OF TWO-PHASE CHROMIUM-BEARING SPINELS

J. E. MUIR * AND A. J. NALDRETT

Department of Geology, University of Toronto, Toronto, Ontario

ABSTRACT

Microprobe analyses of two-phase chromium-bearing spinels from utramafic rocks at the Giant Nickel Mine, Hope, B.C. coupled with petrographic observations suggest that "unmixing" of originally homogeneous, magmatic spinels has taken place.

Analyses indicate that the inferred solvus in the magnetite-chromite-hercynite system appears to project outwards from the magnetite-hercynite join and to terminate at approximately 15 mole percent chromite at the temperature (unknown) at which unmixing stopped. Both Ti and Ni appear to be partitioned more strongly into the magnetite-rich phase whereas Mg is concentrated in the hercynite-rich phase.

INTRODUCTION

In a study of the '4600' orebody at the Giant Nickel Mine, Hope, B.C. « inhomogeneous-looking » chromium-bearing spinel grains were observed in olivine-bearing ultramafic rock (Muir 1971). This paper deals with an optical description of these spinels and offers analytical evidence supported by textural observations to substantiate the existence of a limited solvus between magnetite-rich and hercynite-rich chromium-bearing spinels.

Opaque oxides are common accessory minerals in numerous rock types. Until approximately ten years ago their phase relationships remained obscure, particularly those of spinels [1] whose composition lay in the system $MgO\text{-}FeO\text{-}Cr_2O_3\text{-}Al_2O_3\text{-}Fe_2O_3$. Recent investigators including Irvine (1965, 1967), Thayer (1970), Turnock & Eugster (1962), Cremer (1969), and Ulmer (1969) have provided from experimental work and/or investigations of natural occurrences, insight into the complex nature of these spinels.

In the above system six end-members are presently recognized. Table 1 summarizes current knowledge of the phase relations in each of the nine possible binary joins (Irvine 1965) with particular emphasis on the existence or absence of solid solutions.

It is apparent from Table 1 that extensive solid solutions exist in all geologically significant binary spinel systems at high temperatures (i.e.

---

* Present address : Falconbridge Metallurgical Laboratories, Thornhill, Ontario,

[1] Throughout this paper the terminology of Irvine (1965) is used.

$\sim$> 900° C) but that at lower temperatures miscibility gaps occur. Cremer (1969) has constructed a theoretical ternary solvus from experimental work on the binaries in the system magnetite-hercynite-chromite, but to date no analytical data on naturally occurring spinels are available to support his postulation. However, on the basis of an optical study, Ramdohr (1969) has reported a few natural occurrences of « unmixing » between magnetite and hercynite.

PETROGRAPHY

Within the area of the '4600' orebody there are essentially four distinct ultramafic rock types (Muir 1971) : (i) peridotite — defined as containing more than 20 modal per cent olivine with variable amounts of Ca-poor pyroxene and hornblende ; (ii) olivine pyroxenite — containing less than 15 modal per cent olivine and variable amounts of Ca-poor pyroxene, hornblende and Ca-rich pyroxene ; (iii) hornblende pyroxenite — containing variable amounts of Ca-poor pyroxene, hornblende and Ca-rich pyroxene ; and (iv) hornblendite — composed mainly of hornblende and lesser amounts of plagioclase.

TABLE 1. COMMENTS ON BINARY JOINS IN SYSTEM MgO-FeO-Cr_2O_3-Al_2O_3-Fe_2O_3

Binary Join	
Fe_3O_4-$FeAl_2O_4$	complete miscibility above ~860°C, limited below ~860°C[1].
$MgAl_2O_4$-$MgCr_2O_4$	complete miscibility between 510°-1600°C[2], phase relations unknown at lower temperatures.
$MgFe_2O_4$-Fe_3O_4	complete miscibility at 1400°C[3], phase relations unknown at lower temperatures.
$FeCr_2O_4$-$MgCr_2O_4$	complete miscibility at 1300°C[4], phase relations unknown at lower temperatures.
$FeAl_2O_4$-$MgAl_2O_4$	complete miscibility at 1300°C[4], phase relations unknown at lower temperatures.
$FeAl_2O_4$-$MgAl_2O_4$	complete at all temperatures [5].
$FeAl_2O_4$-$FeCr_2O_4$	complete at all temperatures [5].
Fe_3O_4-$FeCr_2O_4$	complete miscibility at > 900°C[7] (at > 400°C[6]), limited between 500-900°C[7].
$FeCr_2O_4$-$FeAl_2O_4$	complete miscibility at > 900°C[7], limited between 500°-900°C[7].

1. Turnock & Eugster (1962). — 2. Warshaw & Keith (1954). — 3. Muan & Osborn (1956). — 4. Ulmer (1964). — 5. Deer, Howie & Zussman (1962). — 6. Muan & Somiya (1960). — 7. Cremer (1969). References 1 to 6 inclusive are as reported in Irwine (1965).

Spinels are in general ubiquitous in all of the above rocks (1 – 3% of the rock) and occur either interstitially, or poikilitically enclosed in olivine and/or Ca-poor pyroxene. Where enclosed in olivine the spinels are sometimes rimmed by Ca-poor pyroxene.

Three optically different varieties of spinel have been identified: (1) homogeneous-looking, euhedral, isotropic grains; (2) woven or rippled-looking, subhedral to euhedral, isotropic grains; and (3) inhomogeneous-looking (mottled), subhedral, isotropic grains.

The first variety shows no preferential development in any particular rock type whereas the second and third types are found almost exclusively in olivine-bearing rocks.

An inhomogeneous-looking spinel grain is shown in Figure 1. The spinel grain is composed of two irregular, optically distinct, isotropic light and dark grey phases. In some spinel grains of this type, lamellae of ilmenite surrounded by a medium grey spinel rim can also be observed enclosed by both phases (see Fig. 2). Generally the light grey phase in these inhomogeneous-looking grains is woven-looking. Figure 3 is a photomicrograph of a woven-looking variety of spinel which owes its texture to minute, oriented (3 directional), exsolution(?) lamellae of another oxide, possibly ilmenite. Those spinel grains which contain ilmenite lamellae partly resemble ilmenite-bearing chromites from the Merensky Reef as described by Legg (1969).

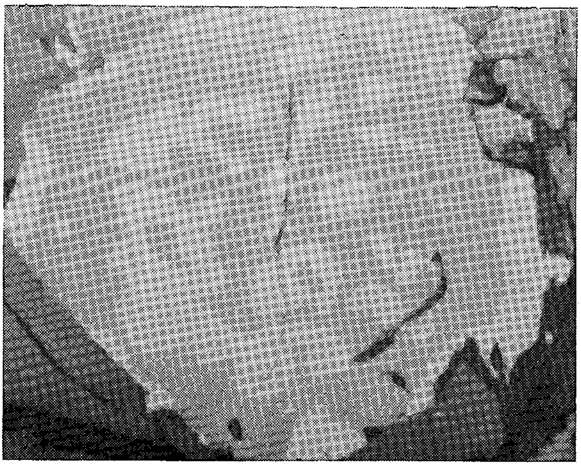


FIG. 1. Photomicrograph (465X) of an inhomogeneous-looking spinel grain.

CHEMISTRY OF THE SPINELS

Analytical procedure

Individual grain analyses were performed on an ARL model EMX electron microprobe in the Department of Geology at the University of Toronto. A sample current of 0.15 μamps with an accelerating potential

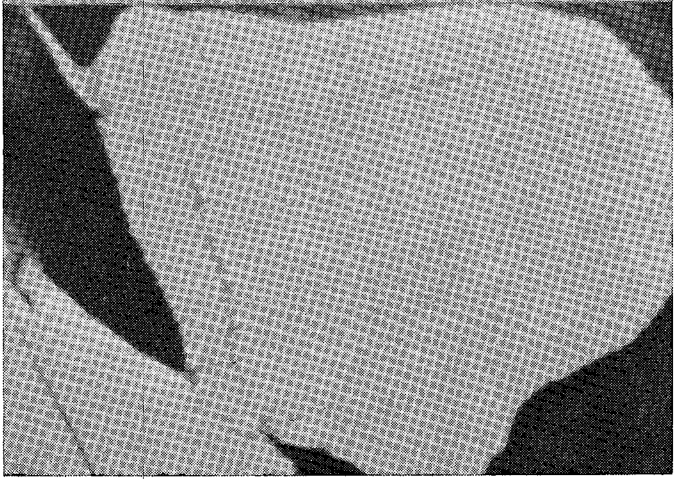


FIG. 2 (top). Photomicrograph (610X) of an inhomogeneous-looking spinel grain containing an ilmenite lamella.

FIG. 3. Photomicrograph (1000X, under oil) of a woven-looking spinel grain.

TABLE 2. AVERAGE COMPOSITION (± STANDARD DEVIATION) IN WEIGHT % OF SPINEL GRAINS FROM MICROPROBE ANALYSES

Sample	Grain Type	TiO_2	Al_2O_3	Cr_2O_3	MgO	NiO	Fe_2O_3	FeO	No. of Grains
29-30	H	1.4 ± .2	14.8 ± .9	31.7 ± 1.0	3.2 ± .3	.12 ± .05	19.2 ± 1.4	30.8 ± .2	9
(HP)*	cores	1.2 ± .1	15.4 ± .8	32.7 ± .2	3.4 ± .1	.09 ± .01	17.9 ± .8	30.5 ± .1	3
	rims	1.4 ± .1	14.8 ± 1.0	31.1 ± .7	3.3 ± .2	.16 ± .07	19.7 ± 1.8	30.8 ± .1	3
29-47	H	.7 ± .2	16.2 ± 3.4	37.0 ± 2.7	5.3 ± .7	.07 ± .02	15.3 ± 3.8	27.6 ± .8	15
(P)	cores	.6 ± .1	15.6 ± 3.8	38.7 ± 2.8	5.3 ± .9	.06 ± .02	14.3 ± 3.8	27.4 ± .9	5
	rims	.7 ± .3	16.2 ± 4.9	35.7 ± 1.6	5.4 ± .9	.06 ± .02	16.3 ± 5.2	27.4 ± 1.0	5
29-11	H_1	.7 ± .1	15.5 ± 1.6	36.6 ± 4.7	3.3 ± .6	.10 ± .05	14.3 ± 2.9	30.1 ± 1.0	4
	H_2	1.6 ± .5	3.5 ± .6	12.4 ± 1.8	1.1 ± .1	.40 ± .14	50.0 ± 2.8	31.7 ± .7	5
(OP)	W	1.3 ± .2	3.3 ± 1.1	12.1 ± 3.9	1.2 ± .2	.50 ± .04	51.2 ± 5.6	31.3 ± .1	5
	IH dk	.1 ± .1	38.0 ± 4.8	20.8 ± 2.2	9.1 ± 1.0	.16 ± .04	7.3 ± 3.3	23.9 ± 1.0	3
	lt	1.6 ± .4	4.3 ± .3	16.3 ± 1.4	1.4 ± .2	.60 ± .05	44.2 ± 2.6	31.8 ± .2	3
29-37	H	.7 ± .1	14.7 ± 3.5	32.8 ± 6.5	2.5 ± .8	.15 ± .01	18.9 ± 7.6	31.1 ± 1.0	5
(HP)	W	.8 ± .2	16.4 ± 1.7	30.1 ± 3.0	2.4 ± .7	.16 ± .04	19.4 ± 2.0	31.6 ± 1.0	1
29-76	H	.8 ± .2	4.1 ± .4	19.8 ± 1.0	2.2 ± .2	.23 ± .07	44.6 ± 1.7	29.8 ± .3	6
(P)	W	1.0 ± .3	5.0 ± 1.2	19.6 ± 2.2	2.4 ± .2	.18 ± .06	43.1 ± 2.0	29.7 ± .4	1
7-560 (P)	H	.8 ± .2	2.5 ± 1.0	23.0 ± 4.1	.4 ± .1	.11 ± .01	40.7 ± 5.3	31.7 ± .2	10
29-7 (OP)	H	.7 ± 1.0	1.2 ± .1	1.2 ± .1	.2 ± .3	.17 ± .03	65.5 ± 2.2	31.8 ± .3	3
29-65 (P)	H_1	.7 ± .2	18.8 ± 2.0	30.3 ± 2.1	6.3 ± .7	O	19.9 ± 3.0	26.6 ± .8	5
	H_2	1.0 ± .6	2.4 ± .9	11.4 ± 3.7	1.4 ± .4	.01 ± .05	54.2 ± 5.1	30.8 ± .8	11
	W	.5 ± .1	17.2 ± 1.5	28.9 ± 2.0	4.9 ± .8	O	22.9 ± 1.9	28.1 ± .3	1
	IH dk	.1 ± .1	41.7 ± 7.0	19.5 ± 3.4	11.4 ± 2.0	O	7.2 ± 4.1	21.8 ± 2.2	7
	lt	2.2 ± .2	3.3 ± .5	13.4 ± 2.7	1.6 ± .2	.07 ± .03	50.4 ± 2.8	31.3 ± .3	6
29-62	IH dk	.2 ± .2	35.8 ± 5.3	22.1 ± 2.2	9.6 ± 1.5	.07 ± .04	11.1 ± 3.1	24.0 ± 1.7	7
(P)	lt	2.3 ± .3	4.0 ± .5	18.4 ± 1.4	1.8 ± .2	.28 ± .02	42.4 ± 1.8	32.1 ± .6	7

* P - peridotite; OP - olivine pyroxenite; HP - hornblende pyroxenite; H - homogeneous-looking; W - woven-looking; IH - inhomogeneous-looking; dk - dark grey, hercynite-rich; lt - light grey, magnetite-rich.

of 15 kv was consistently used on all samples. Pure elements were used as standards. Counting times were controlled electronically using a current digitizer. Raw data were processed using EMPADR VII, an IBM 360/65 computer program written by Rucklidge (1969).

Analytical results

Averaged microprobe results appear in Table 2. Since only total iron (*i.e.* $Fe^{2+} + Fe^{3+}$) could be measured on the microprobe using the above technique it was necessary to recalculate in terms of Fe^{2+} and Fe^{3+} using the procedure outlined by Carmichael (1967). In the recalculation the oxides were assumed to be stoichiometric (see Irvine 1965 for discussion)

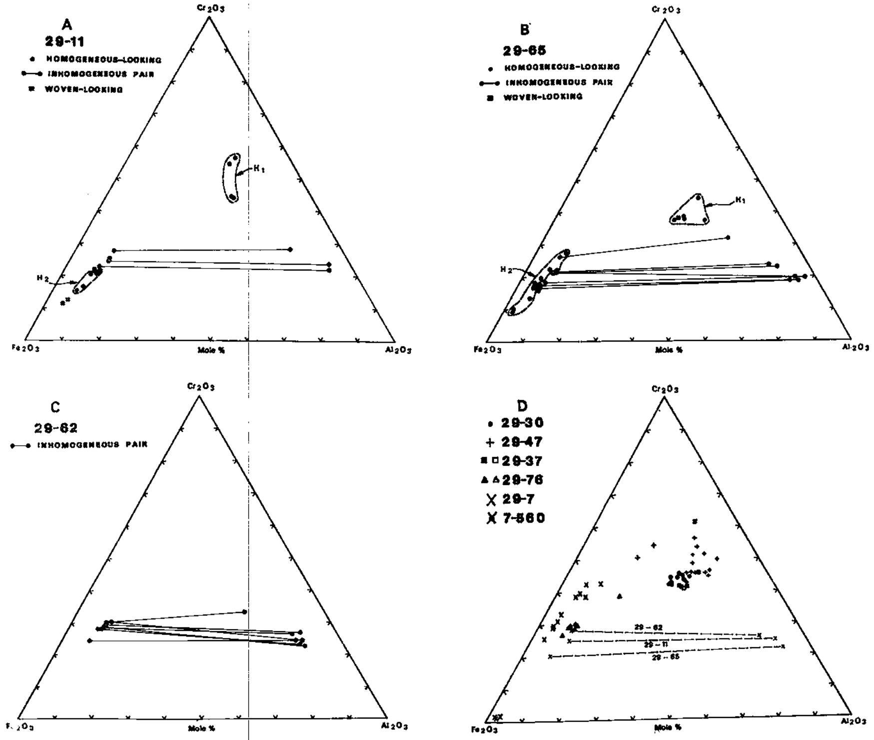


FIG. 4A, B, C & D. Composition (in mole %) in the system Cr_2O_3-Fe_2O_3-Al_2O_3 of individual grains in samples 29-11, 29-65, 29-62, and 29-30, 29-47, 29-37, 29-76, 29-7, 7-560 respectively. Average compositions of inhomogeneous spinel pairs from samples 29-11, 29-65 and 29-62 are plotted in 4D as well for comparison. Open symbols in 4D represent woven-looking grains. The symbols H_1 and H_2 are explained in the text.

having the general spinel formula $R^{2+}R_2^{3+}O_4$ where R^{2+} = Mg, Ni, Fe^{2+} and R^{3+} = Fe^{3+}, Cr, Ti, Al. Individual grain analyses were then recalculated on a basis of the number of moles of Cr_2O_3, Fe_2O_3 and Al_2O_3, respectively, and plotted in Figs. 4A, B, C and D.

Individual homogeneous-looking grains are slightly zoned from core to rim. Cores are generally richer in chrome and alumina and poorer in titanium, nickel and ferric iron. Within any one sample and between different samples the composition of the grains as a whole varies, the major variant being the $Cr_2O_3 : Fe_2O_3$ ratio. The diameter of the microprobe beam was too large to distinguish the different phases in the « woven-looking » grains which are found to be on the average similar in composition to homogeneous-looking grains. The inhomogeneous-looking grains (samples 29-11, 29-65 and 29-62) consist of two compositionally and optically different phases; the light grey phase is a spinel rich in chrome and ferric iron and poor in alumina (*i.e.* magnetite-rich similar in composition to some of the homogeneous and woven-looking grains; the dark grey phase is a ferric iron-poor and chrome-magnesia-alumina-rich spinel (*i.e.* hercynite-rich), compositionally unlike any other of the analysed grains. Both Ti and Ni appear to be partitioned more strongly into the magnetite-rich spinel than into the hercynite-rich spinel, whereas the opposite is true for Mg.

Two samples (29-11 and 29-65) contain homogeneous-looking grains which fall into two compositionally distinct groups (labelled H_1 and H_2 in Table 2).

DISCUSSION

It is apparent from Figure 4 that a gap exists in the series of spinel analyses from the '4600' orebody ultramafic rocks. These same rocks are fresh and it is doubtful that the inhomogeneous-looking spinel grains are the result of alteration, such as that proposed by Beeson & Jackson (1969) for chromite from their study of chromite-ferritchromit pairs in the Stillwater complex.

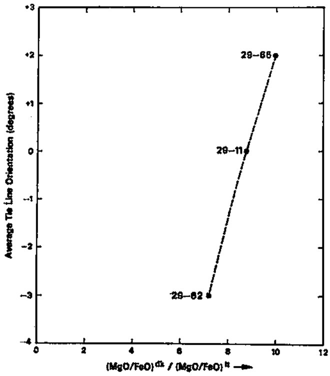
As an alternative it is postulated that these inhomogeneous-looking spinel grains are the result of « unmixing » of originally homogeneous, single phase magmatic oxide grains. A solvus similar to that found between magnetite and hercynite by Turnock & Eugster (1962) appears to be present in the chromium-bearing system, at least as far as bulk compositions with 10-15 mole per cent chromite.

The homogeneous-looking grains with a high chromium content (*i.e.* grains labelled H_1) in samples 29-11 and 24-65 are interpreted as grains which did not undergo «unmixing»; however, it is not known whether the low chromium, low alumina grains (*i.e.* H_2) are also original homogeneous grains (a result of increased fractionation?), or the products of complete « unmixing ».

In some samples at least two generations of ilmenite are observed associated with the chromium-bearing spinels. Relatively large ilmenite lamellae, as illustrated in Figure 2, are believed to have formed by 'exsolution' from originally homogeneous titaniferous chromium-bearing spinel. At lower temperatures and after « unmixing » of the homogeneous spinels into « hercynite-rich » and «magnetite-rich » phases ilmenite again 'exsolved' (by oxy-exsolution?) as minute, oriented lamellae from the latter (see Fig. 3).

It is interesting to compare the shape of the solvus suggested by the present study with that proposed by Cremer (1969) who suggested that in the system magnetite-chromite-hercynite a solvus projects into the system from the chromite-hercynite join. Although the exact shape of the solvus and the temperature at which it appears are unknown at present, the solvus clearly projects into the system from the Fe_2O_3-Al_2O_3 join and appears to be quite incompatible with Cremer's. However, Cremer's solvus is purely hypothetical and since Mg-bearing spinels were not considered in his study a direct comparison of the two may be invalid.

There appears to be a correlation between average orientations (arbitrarily measured as the angle (+ or −) that the tie-line makes with a line drawn parallel to the Fe_2O_3-Al_2O_3 join) of tie-lines in Figure 4D



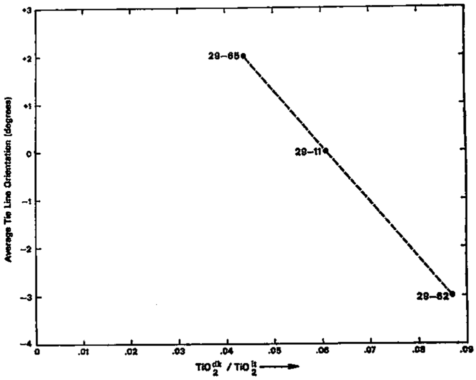


FIG. 5 (left). Variation of average tie-line orientation with the average $(MgO/FeO)^{dk}$: $(MgO/FeO)^{lt}$ ratio in inhomogeneous-looking pairs.

FIG. 6 (right). Variation of the average tie-line orientation with the average $(TiO_2)^{dk}$: $(TiO_2)^{lt}$ ratio in inhomogeneous-looking pairs.

and both the distribution of magnesium and ferrous iron and the partitioning of TiO_2 between the « hercynite-rich phase (dark grey spinel) » and the « magnetite-rich phase (light grey spinel) » (see Figs. 5 and 6). If tie-line orientation can be assumed to be a function of equilibrium temperature (*i.e.* the more « negative » the orientation the lower the temperature) then it would appear that with decreasing temperature the MgO:FeO ratio decreases and the TiO_2 content increases in the « hercynite-rich phase » relative to the « magnetite-rich phase » .

ACKNOWLEDGEMENTS

The authors wish to thank Dr. A. R. Graham and R. Buchan of Falconbridge Nickel Mines for their constructive criticism during the preparation of the manuscript. This study was supported in part through Geological Survey of Canada Grant No. 23-68.

REFERENCES

BEESON, M.H. & JACKSON, E.D. (1969): Chemical composition of altered chromites from the Stillwater complex, Montana. *Amer. Mineral.* **54,** 1084-1100.

CARMICHAEL, I.S.E. (1967) : The Fe-Ti oxides of salic volcanic rocks and their associated ferromagnesian silicates. *Contrib. Mineral. Petrol.* **14,** 36-64.

CREMER, V. (1969) : Die Mischkustallbildung im System Chromit-Magnetit-Hercynit zwischen 1000° und 500°C. *Neues Jahrb. Mineral., Abh.* **111,** 184-205.

DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1962) : *Rock-Forming Minerals.* Vol. 5. *Non-silicates.* Longmans, London.

IRVINE, T.N. (1965) : Chromian spinel as a petrogenetic indicator. Part. I. Theory. *Can. J. Earth Sci.* **2,** 648-672.

———— (1967) : Chromian spinel as a petrogenetic indicator. Part II. Petrologic applications. *Can. J. Earth Sci.* **4,** 71-104.

LEGG, C.A. (1969) : Some chromite-ilmenite associations in the Merensky Reef, Transvaal. *Amer. Mineral.* **54,** 1347-1354.

MUAN, A. & OSBORN, E.F. (1956) : Phase equilibria at liquidus temperatures in the system $MgO\text{-}FeO\text{-}Fe_2O_3\text{-}SiO_2$. *J. Amer. Ceram. Soc.* **39,** 121.

MUAN, A. & SOMIYA, S. (1960) : Phase relations in the system iron oxide-Cr_2O_3 in air. *J. Amer. Ceram. Soc.* **13,** 204.

MUIR, J.E. (1971) : The petrology and ore genesis of the Giant Nickel '4600' orebody, Hope, B.C. *M.Sc. thesis, University of Toronto.*

RAMDOHR, P. (1969) : *The Ore Minerals and Their Intergrowth,* 3rd edit. Pergamon Press.

RUCKLIDGE, J.C. (1969) : Specifications of a Computer Program for Processing Electron Micro-probe Analytical Data — EMPADR VII. Department of Geology, University of Toronto.

THAYER, T.P. (1970) : Chromite segregations as petrogenetic indicators. *Geol. Soc. S. Africa,* Spec. Paper **1,** 380-390.

TURNOCK, A.C. & EUGSTER, H.P. (1962) : Fe-Al oxides : Phase relationships below 1000°C, *J. Petrol.* **3,** 533-565.

ULMER, G.C. (1964) : Lattice parameters and compositions of synthetic defect spinels for the spinel solid solution series $FeCr_2O_4$-$MgCr_2O_4$ and $FeAl_2O_4$. *Geol. Soc. Amer. Abstr. Ann. Mtg., Miami Beach, Florida,* 210.

——— (1969) : Experimental investigations of chromite spinels, *Econ. Geol., Mono.* **4,** 114-131.

WARSHAW, I. & KEITH, M.L. (1954) : Solid solution and chromium oxide loss in part of the system MgO-Al_2O_3-Cr_2O_3-SiO_2. *J. Amer. Ceram. Soc.* **37,** 161.

Manuscript received November, 1971.