THE SPINEL GROUP

A. N. WINCHELL,
University of Wisconsin, Madison, Wisconsin.

Twenty years ago E. S. Simpson[1] presented in graphic form the relations between $MgAl_2O_4$ and $FeCr_2O_4$. He considered that continuous variations are possible in all parts of the system. Since that time many

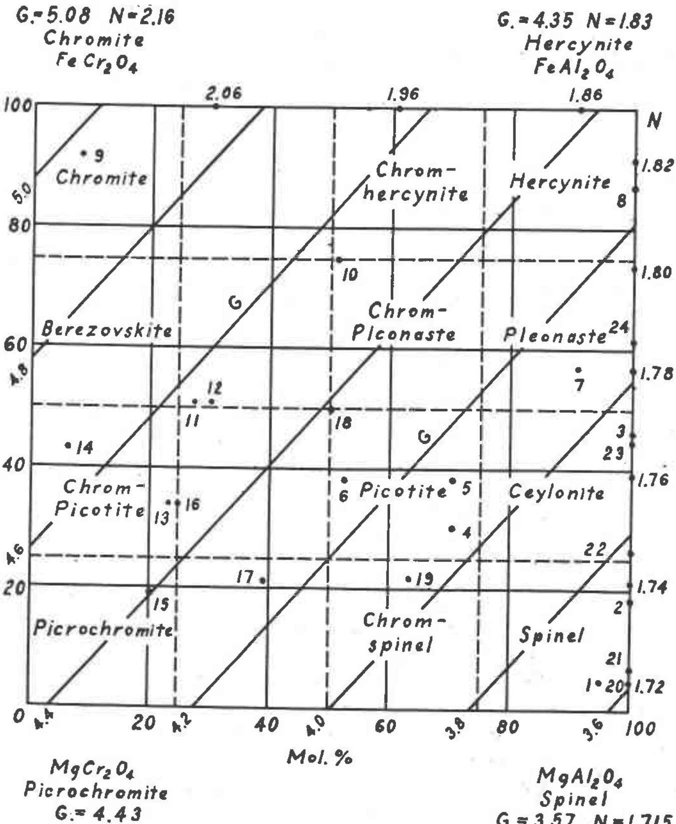

FIG. 1

more analyses have been made and it seems possible to present the facts in a diagram essentially like that of Simpson, but on a somewhat different basis. It is also possible now to add lines expressing approximately the

[1] A graphic method for the comparison of minerals with four variable components forming two isomorphous pairs: *Min. Mag.* **19,** 99 (1920).

variations in specific gravity which result from variations in composition. The continuity of the system seems to be beyond reasonable doubt in spite of the fact that certain areas still lack known examples.

Simpson gave names to certain portions of the system. His names are used in Fig. 1, except that he assigned the name picotite to the area between ceylonite and hercynite and alloted no names[2] to the squares adjoining these and spinel and hercynite. Since picotite is used by Lacroix for a member of this system characterized by $MgAl_2O_4$, $FeAl_2O_4$ and $FeCr_2O_4$, it seems better to assign it to some such position as shown in Fig. 1. Then perhaps the name pleonaste may be used for the area which Simpson assigned to picotite, although as a gem stone pleonaste doubtless contains less FeO than required by this area.

The diagram gives information as to the composition indicated by any point in a very simple way. Any outside line represents a binary series and, being divided into one hundred parts, the divisions represent (molecular) percentages of the two end-members. Thus, 22 represents 26% $FeAl_2O_4$ and 74% $MgAl_2O_4$. Inside the square, any point represents percentages of Fe and Mg in the vertical direction and percentages of Cr and Al in the horizontal direction. For example, 5 represents 38% Fe and 62% Mg, and also represents 70% Al and 30% Cr. Therefore 5 represents 38% $Fe(Al,Cr)_2O_4$, and 62% $Mg(Al,Cr)_2O_4$. Of this 38% $Fe(Al,Cr)_2O_4$, 70% (or 26.6% of the whole) is $FeAl_2O_4$ and 30% (or 11.4%) is $MgAl_2O_4$. And of the 62% $Mg(Al,Cr)_2O_4$, 70% (or 43.4%) is $MgAl_2O_4$ and 30% (or 18.6%) is $MgCr_2O_4$.

Of course the diagram assumes the absence of any other constituents than those which are shown. This assumption is frequently untrue, but in many cases is a very close approximation. Probably the commonest additional constituent is $FeFe_2O_4$, but spinel can apparently take only about 15 per cent of this into its structure. Accordingly, magnetite and spinel can probably form simultaneously from a magma, whereas chromite and spinel cannot.

By a study of spinel gem stones from Ceylon, Anderson and Payne[3] proved that $ZnAl_2O_4$ is miscible with $MgAl_2O_4$, at least to 35 per cent. Analyses of gahnite show that $FeAl_2O_4$ is miscible with it at least to 30 per cent, and it seems probable that $ZnAl_2O_4$ is miscible in all proportions with both $MgAl_2O_4$ and $FeAl_2O_4$.[4] Such a system is shown in Fig. 2 with lines to indicate the refractive index for all proportions. The binary series, $MgAl_2O_4$ to $ZnAl_2O_4$ is shown in Fig. 3.

[2] Except "magnochromite," which seems undesirable to the writer.

[3] *Min. Mag.*, **24,** 547 (1937).

[4] Brauns, R.: *Cent. Mineral.*, **1927 A,** 265.

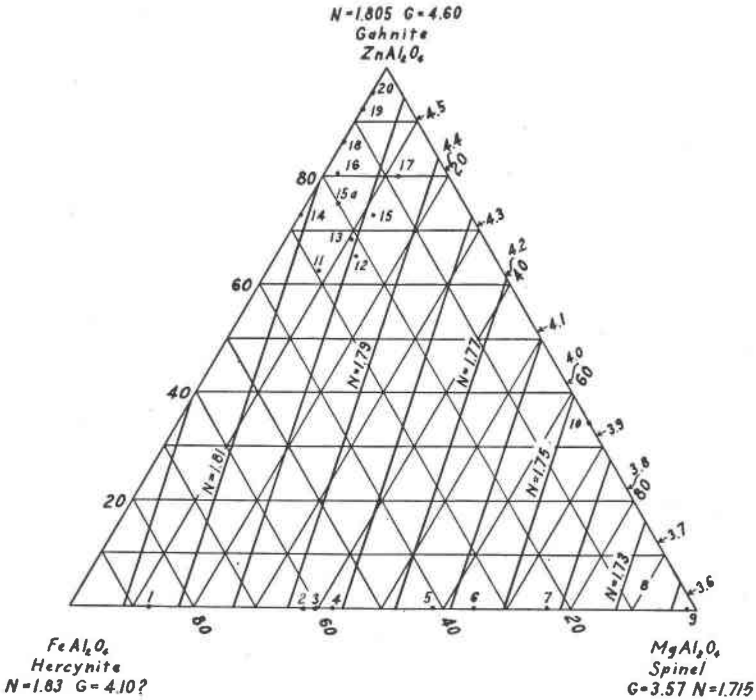
N=1.805 G=4.60
Gahnite
$ZnAl_2O_4$
FeAl$_2$O$_4$
Hercynite
N=1.83 G=4.10?
MgAl$_2$O$_4$
Spinel
G=3.57 N=1.715
N=1.81
N=1.79
N=1.77
N=1.75
N=1.73
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
20
40
60
80

FIG. 2

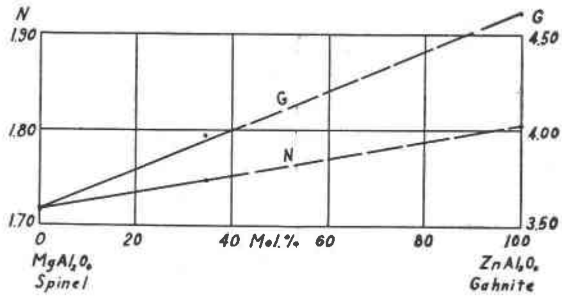
N
G
1.90
1.80
1.70
4.50
4.00
3.50
0
20
40 Mol.%
60
80
100
MgAl$_2$O$_4$
Spinel
ZnAl$_2$O$_4$
Gahnite

FIG. 3

Artificial spinel of gem quality has been made with varying amounts of excess Al_2O_3 (in crystal solution) up to 60 per cent. The limit seems to be about 68 per cent.[5] The relations between this variation in composition and the density and refractive index are shown in Fig. 4.

Many analyses point to the conclusion that $FeFe_2O_4$ in spinel can become Fe_2O_3 without destruction of the crystal structure, just as it can in magnetite. Accordingly, both Al_2O_3 and Fe_2O_3 can exist in the spinel crystal structure, though neither is possible in unlimited amount. Furthermore, this fact makes it reasonable to assume such changes of 2FeO to Fe_2O_3, or Fe_2O_3 to 2FeO as may be necessary to compute the spinel molecules from the analyses, and this assumption has been made in the computations.

Since the ferrites do not intercrystallize freely with the aluminates and chromates of the spinel group, they can be arranged on triangular dia-

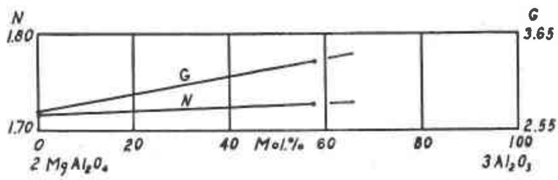

Fig. 4

grams, as shown in Fig. 5. All four end-members have been made artificially and it seems very probable that they can intercrystallize in all proportions at least in the two ternary systems which are shown, although this has not yet been demonstrated. Unfortunately the refractive indices are not well known in this system and no attempt is made to show them.

Of course, it should be remembered in using these diagrams that the natural minerals usually contain still other constituents (notably TiO_2) and therefore the specific gravity may vary from that shown by the diagram.

[5] Hägg, G., and Söderholm, G.: *Zeits. physik. Chem.*, *B*, **29**, 88 (1935).

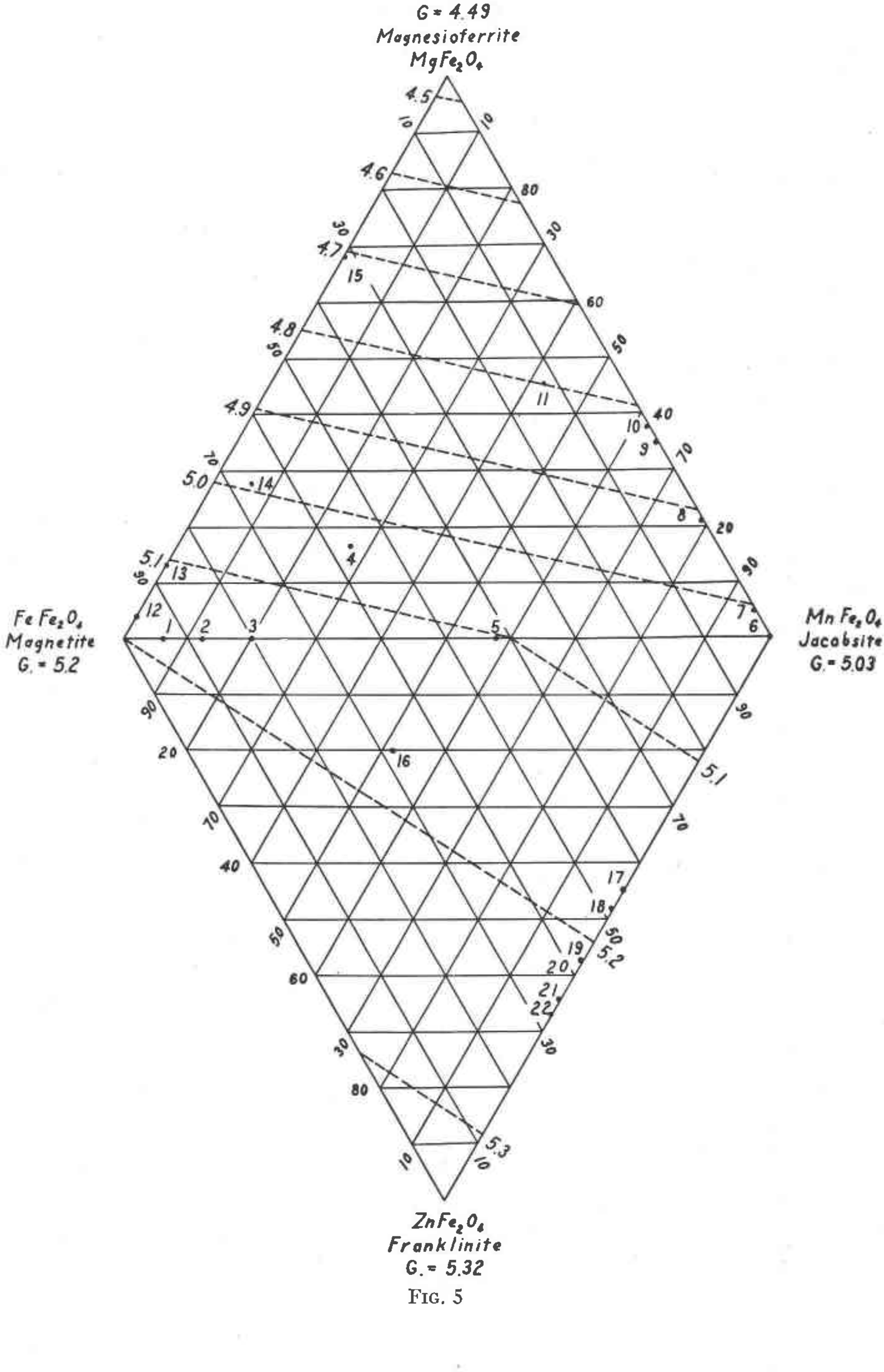
G = 4.49
Magnesioferrite
$MgFe_2O_4$
Fe Fe_2O_4
Magnetite
G. = 5.2
Mn Fe_2O_4
Jacobsite
G. = 5.03
$ZnFe_2O_4$
Franklinite
G. = 5.32
4.5
4.6
4.7
4.8
4.9
5.0
5.1
5.1
5.2
5.3

FIG. 5

REFERENCES FOR FIGURE 1

1–15. Same as Simpson's analyses (*Min. Mag.*, **19**, 99, 1920) except 10 and 12.
10. Chromhercynite, Madagascar, A. Lacroix: *Bull. Soc. Fr. Min.*, **43**, 69 (1920).
12. "Chromeisenstein," Serbia, E. Harbich: *Tsch. Min. Pet. Mit.*, **40**, 191 (1930).
16. Chromite, Mt. Rums, Albania, F. Rodolico: *Per. Min. Roma*, **2**, 5 (1931).
17. Chromite, Togoland. H. Arsandaux: *Bull. Soc. Fr. Min.*, **48**, 70 (1925).
18. Chromite, Moravia. J. Kokta: *Min. Abst.*, **6**, 155 (1935).
19. "Picotite," Finkenberg, Germany. R. Brauns: *Mineral. Niederr. Vulkangeb.*, 168 (1922).
20. Spinel, Vesuvius. Zambonini and Carobbi: *Min. Abst.*, **4**, 521 (1931).
21. Spinel, Trentino. C. Gottfried: *Min. Abst.*, **4**, 192 (1929).
22. "Ferropicotite," Haute-Loire. A. Lacroix: *Mineral. France*, **4**, 306 (1910).
23. Pleonaste, Lapland. A. Gavelin: *Bull. Geol. Inst. Upsala*, **15**, 289 (1916).
24. Spinel, Mull. H. H. Thomas: *Q. Jour. Geol. Soc. London*, **78**, 229 (1922). 17 others calculated but not included.

REFERENCES FOR FIGURE 2

1. Hercynite, Ronsberg. B. Quadrat: *Ann. Ch. Pharm.*, **55**, 357 (1845) (=8 of Fig. 1).
2. Hercynite, Hazlavy. J. Splichal: *Min. Abst.*, **3**, 353 (1925).
3. Spinel, Mull. H. H. Thomas: *Q. Jour. Geol. Soc. London*, **78**, 229 (1922) (=24 of Fig. 1).
4. Spinel, Virginia. T. L. Watson: *Econ. Geology*, **18**, 53 (1923).
5. Pleonaste, Lapland. A. Gavelin: *Bull. Geol. Inst. Upsala*, **15**, 289 (1916) (=23 of Fig. 1).
6. Spinel, Korea. Z. Harada: *Jour. Fac. Sci. Hokkaido Univ., Geol. Ser.* **3**, 221 (1936).
7. "Ferropicotite," Haute Loire. A. Lacroix: *Mineral. France*, **4**, 306 (1910) (=22 of Fig. 1).
8. Spinel, Trentino. C. Gottfried: *Min. Abst.*, **4**, 192 (1929) (=21 of Fig. 1).
9. Spinel, Vesuvius. Zambonini and Carobbi: *Min. Abst.*, **4**, 52 (1931) (=20 of Fig. 1).
10. Gahnospinel, Ceylon, B. W. Anderson and C. J. Payne: *Min. Mag.*, **24**, 547 (1937).
11. Gahnite, Finland. P. Eskola: *Geol. För. Förh. Stockholm*, **36**, 25 (1914).
12. Gahnite, W. Australia. E. S. Simpson· *J. Roy. Soc. W. Australia*, **23**, 17 (1936).
13. Gahnite, W. Australia. E. S. Simpson: *J. Roy. Soc. W. Australia*, **16**, 25 (1930).
14. Gahnite, Altyn-Taou, URSS. A. F. Sosedko: *Min. Abst.*, **6**, 305 (1936).
15. Gahnite, Sweden. P. Geyer: *Ars. Sver. Geol. Und.*, **1**, 1916.
16. "Zinc spinel," Carroll Co., Md. E. V. Shannon: *Am. Mineral.*, **8**, 147 (1923)
17. Gahnite, Ore Knob, N. C. C. S. Ross: *U. S. Geol. Surv. P. Paper*, **179** (1935).
18. Gahnite, Madagascar. A. Lacroix: *Mineral. Madagascar*, **1**, 327 (1922).
19. Gahnite, India. Christie and Coulson: *Rec. Geol. Surv. India*, **61**, 315 (1928).
20. Gahnite, W. Australia. E. S. Simpson: *J. Roy. Soc. W. Australia*, **17**, 137 (1931).

REFERENCES FOR FIGURE 5

1. Magnesioferrite, Vesuvius. C. F. Rammelsberg: *Min. Chem.*, 133 **(1875).**
2. Jacobsite, Jacobsberg. K. Johannson: *Zeits. Krist.*, **68**, 87 (1928).
3. Jacobsite, Jacobsberg. A. Damour: *C. R.*, **69**, 168 (1869).
4. Jacobsite, Bulgaria, F. Kovar: *Zeits. Kryst.*, **36**, 202 (1902).
5. Magnetite, New Zealand. A. H. Chester: *Min. Mag.*, **8**, 123 (1889).
6. Magnetite, Quebec. B. J. Harrington: *Min. Mag.*, **14**, 373 (1907).

7. Jacobsite, Langban. G. Lindstrom: *N. Jahrb. Min.*, 208 (**1878**).
8. Magnetite, Salzburg. E. Dittler and H. Hueber: *Ann. Nat. Mus. Wien*, **46,** 185 (1932).
9. Magnetite, near Rome. F. Zambonini: *Zeits. Kryst.*, **32,** 535 (1902).
10. Magnetite, Carolina. G. P. Tschernik: *Zeits. Kryst.*, **50,** 68 (1911).
11, 12. Mn-Magnetite, Wester Silfberg. M. Weibull: *Tsch. Min. Pet. Mit.*, **7,** 109 (1886).
13. Magnetite, Siegen. C. F. Rammelsberg: *Min. Chem.*, 132 (**1875**).
14. Jacobsite, Glakärn, Sweden. L. J. Igelström: *N. Jahrb. Min.*, **1,** 260 (1890).
15. Jacobsite, Nordmark. L. J. Igelström: *loc. cit.*
16. Franklinite, Sterling Hill, N. J. G. Seyms: *Am. Jour. Sci.*, **12,** 210 (1876).
17. Franklinite, Taylor Mine. G. C. Stone: *Sch. Mines Quart.*, **8,** 148 (1887).
18. Franklinite, Sterling Hill. G. C. Stone: *loc. cit.*
19. Franklinite, Taylor Mine. G. C. Stone: *loc. cit.*
20. Franklinite, Sterling Hill. G. C. Stone: *loc. cit.*
21. Franklinite, Hamburgh Mine. C. Palache: *Am. Jour. Sci.*, **29,** 177 (1910).
22. Franklinite, Mine Hill. G. Seyms: *Am. Jour. Sci.*, **12,** 210 (1876).

Many other analyses are given in *Trans. Sci. Res. Inst. Econ. Mineral, Fas.* **85** by S. A. Vakhromeev, J. A. Zimin, K. E. Kozhevnikov, A. N. Laskov and G. M. Mazaev: Chromite Deposits in the Urals, Moscow, 1936.