

*A graphic method for the comparison of minerals with four variable components forming two isomorphous pairs.*¹

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[Read November 9, 1920.]

GRAPHIC methods are often of the greatest assistance in bringing out the affinities of closely related minerals and particularly of members of isomorphous series. An illustration of the use of such a method in the case of a series involving three variables, all of them mutually replaceable, has already been given by the author in dealing with minerals of the tapiolite-mossite-rutile series.² Recently, in studying a mineral of the spinel group, occurring in serpentine country near Namban, in the South-Western Division of Western Australia, it was found convenient to use a graphic method to bring out its relationship to the type minerals spinel, hercynite, and chromite, and to the intermediate minerals previously described under the names of picotite, chrompicotite, magnesiochromite, and magnochromite.

In a series of minerals consisting of four components A , B , P , and Q , of which A and B form one isomorphous pair capable of mutual replacement, and P and Q a second similar pair, four pure compounds are possible, each worthy of separate specific names. These are AP , AQ , BP , and BQ . These species are often capable of co-crystallization to form a more or less complete series whose general formula is $wA \cdot xB \cdot yP \cdot zQ$, or expressed in conventional form $(A, B) \cdot k(P, Q)$. The possible values of w , x , y , and z in the first formula are limited by their necessarily conforming to the equation $(w+x) = k(y+z)$, k being a constant for the whole series. This constant is unity in the case of the spinels and the tantalite-manganocolumbite series, for example.

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² E. S. Simpson, On tapiolite in the Pilbara goldfield, Western Australia. Mineralog. Mag., 1917, vol. 18, pp. 118-121.

The constitutional affinities of such minerals are dependent upon the relative molecular preponderances of the different variables, and the physical and chemical affinities are closely related to the constitutional. It is, of course, possible to determine the relative preponderances mathematically and from a mere inspection of the figures to estimate their values. This is readily done in the case of two variables, but is more complicated in the case of four, and in such a case the graphical representation of the numerical results will indicate the affinities much more clearly than the figures, and in a form most suitable for further reference (see fig., p. 101).

Dealing with the minerals of the spinel-chromite series as a typical example, the four variables, which constitute two pairs, are MgO, FeO, Al₂O₃, Cr₂O₃. Four mineral species are possible, the pure forms of which are (1) MgO . Al₂O₃ spinel, (2) MgO . Cr₂O₃ picrochromite,¹ (3) FeO . Al₂O₃ hercynite, and (4) FeO . Cr₂O₃ chromite. And the general formula for the whole series is (MgO, FeO) . (Al₂O₃, Cr₂O₃) or as usually stated (Mg, Fe)O . (Al, Cr)₂O₃. In any mineral of this type, if *m*, *f*, *a*, *c* be the number of molecules of MgO, FeO, Al₂O₃, Cr₂O₃, respectively, then $(m+f) = k(a+c) = 1 \times (a+c)$.

The relative molecular preponderance of the components of each pair stated as a percentage of the maximum is given by the formulæ

$$x = \frac{100(m-f)}{m+f} \quad \text{and} \quad y = \frac{100(a-c)}{a+c}.$$

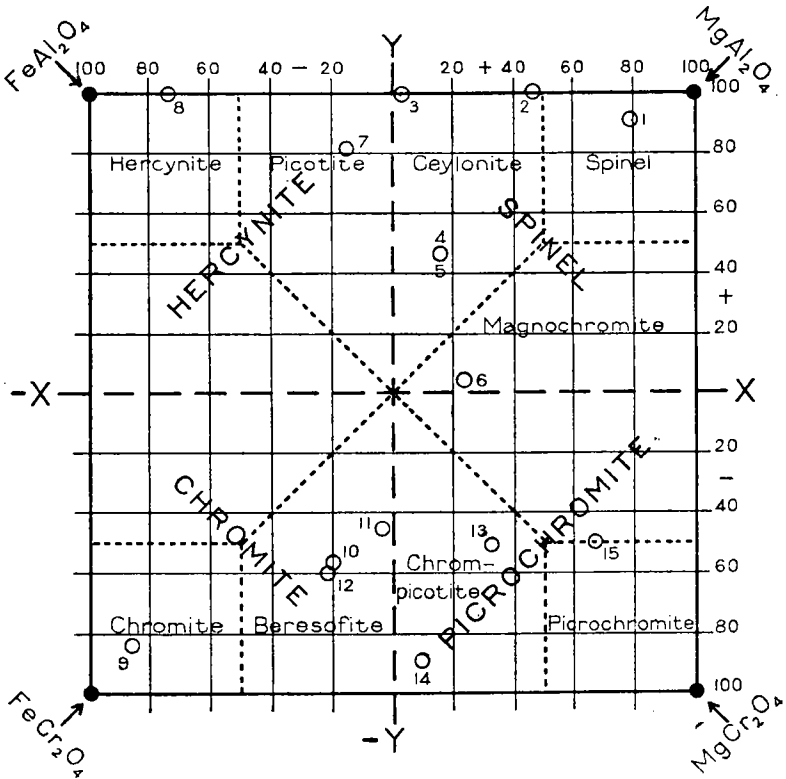
x will be positive when MgO preponderates over FeO, and negative when FeO preponderates over MgO. Similarly, *y* will be positive or negative according as Al₂O₃ does or does not predominate over Cr₂O₃. Such a relationship lends itself very conveniently to graphical representation by means of two rectangular co-ordinates, as shown in the accompanying figure. Working out the values of *x* and *y* for the four pure compounds we get:—

		<i>x</i>	<i>y</i>
Spinel, MgO . Al ₂ O ₃	...	+100	+100
Picrochromite, MgO . Cr ₂ O ₃	...	+100	-100
Hercynite, FeO . Al ₂ O ₃	...	-100	+100
Chromite, FeO . Cr ₂ O ₃	...	-100	-100

These are the four extreme values of *x* and *y*. If they are plotted and the four points joined by straight lines they give a major square divided

¹ New name required to complete the series and to designate already known minerals. Vide infra (p. 104).

into four equal minor squares by the two axes. All intermediate minerals corresponding to the general formula given above will, when plotted, be represented by points within the major square. The relative molecular preponderances of the various components will throw any



Graphical representation of the composition of minerals of the spinel-chromite series.

intermediate mineral into the minor square containing the pure compound with which it has the greatest affinity. Thus minerals most closely related to spinel will fall into the right-hand upper square, since all minerals with equal molecules of MgO and FeO will lie upon the *y* axis, and those with preponderating MgO will lie to the right of this axis; whilst all minerals with equal molecules of Al₂O₃ and Cr₂O₃ will lie upon the *x* axis, those with preponderating Al₂O₃ lying above it.

Similarly, all minerals most closely related to hercynite will lie within the left-hand upper square; those most closely related to chromite, within the left-hand lower square; and those most closely related to picrochromite within the right-hand lower square. The specific name to be applied to any intermediate mineral will be given by the square within which its locus lies when plotted, and the relative strength of its affinities by the measured distances of its locus from the pure compounds or complex minerals with which it is to be compared.

A number of typical minerals of this series have been plotted in this way. The figures on which the plottings are based are given in the accompanying table (p. 105), whilst the plottings are shown on the figure. Great difficulty was experienced in choosing and calculating suitable minerals owing to the serious imperfections detected in the published analyses when a close scrutiny of them was undertaken. Of some thirty-five analyses given by Rammelsberg,¹ Dana,² and Lacroix,³ only four or five are at all satisfactory. The chief imperfections are:—

(1) Failure to determine the proportions of a constituent known to be of importance, e.g. MgO (Baltimore chromite and others), Fe₂O₃ (Ceylon ceylonite and many others).

(2) Very imperfect balance between molecules of protoxides and sesquioxides. The ratio which should be 1 : 1 is as high as 2.5 : 1 in the only analysis of Bolton chromite, and in many others is close to 1.5 : 1. This in many cases can be corrected by calculating part of the FeO as Fe₂O₃, a process, however, which usually leads to a bad summation.

(3) Bad summation, ranging from 98 to 102.5.

(4) Impure mineral or reagents used for the analysis, as indicated by percentages of silica up to 4.75 per cent., and in one case 10.60 per cent.

The minerals given in the table were chosen as far as possible to avoid the worst of these defects, and the results obtained by plotting them enable the minerals to be systematically compared with one another, and grouped into species and sub-species. Four species are indicated; namely, spinel, picrochromite, hercynite, chromite. The normal boundary between any two of these species is the line at which equal numbers of the two molecules are present, e.g. MgO . FeO . 2Al₂O₃. These boundaries are marked in the graph by the two axes, which divide the whole figure into four equal squares, each defining the limits of one of the four species.

¹ C. F. Rammelsberg, *Handbuch der Mineralchemie*, 2nd ed., 1875, pt. 2, p. 142.

² J. D. Dana, *System of Mineralogy*, 5th and 6th eds., 1868 and 1892.

³ A. Lacroix, *Minéralogie de la France*, 1910, vol. 4, p. 312.

Many sub-species and varieties of the species have been recognized and described under individual names, but without rigid definition. In the case of minerals of such scientific and economic interest a systematic division into sub-species is desirable, and a logical division has been worked out by means of the graph, the boundaries being indicated by dotted lines. The division has been made at the points represented by the general formulae $\frac{3}{4}M'O . \frac{1}{4}M''O . R_2O_3$ and $MO . \frac{3}{4}R'_2O_3 . \frac{1}{4}R''_2O_3$. These points in the case of the simplest types of substitution are : $x = +50, y = +100$; $x = +100, y = +50$; &c. The boundaries have been drawn through these points parallel to the specific boundaries (i.e. to the axes) till they meet, whence they are carried direct to the origin. A little consideration of the graph will show that such a division gives due weight to the influence of all replacing molecules, whilst at the same time preserving as far as possible the ratio 3 : 1 as the divisional ratio for any pair of isomorphous components.

The names already in use by various authors have been retained as far as possible for the sub-species, but it will be interesting to note that these sub-species have not in the past, in all cases, been referred to the correct species.

The various species are divided as follows :

Species.	Sub-species.	Ratio MgO : FeO.	Ratio Al ₂ O ₃ : Cr ₂ O ₃ .	Ratio x : y ¹
Spinel	Spinel	> 3 : 1	> 3 : 1	-
"	Ceylonite	< 3 : 1	> 1 : 1	> 1 : 1
"	Magnochromite	> 1 : 1	< 3 : 1	> 1 : 1
Hercynite	Hercynite	< 1 : 3	> 3 : 1	-
"	Picotite	< 1 : 1	> 1 : 3	< 1 : 1
"	(Unknown)	< 1 : 1	< 3 : 1	> 1 : 1
Chromite.	Chromite	< 1 : 3	< 1 : 3	-
"	(Unknown)	< 1 : 1	< 1 : 1	> 1 : 3
"	Beresofite	< 1 : 1	> 1 : 3	< 1 : 1
Picrochromite	Picrochromite	> 3 : 1	< 1 : 3	-
"	Chrompicotite	> 1 : 1	< 3 : 1	< 1 : 1
"	(Magnesiochromite)			
"	(Unknown)	> 1 : 1	< 1 : 1	> 1 : 3

The arithmetical definition of the various sub-species, illustrated by this table, is plainly much more complex than the geometrical definition, illustrated by the graph.

The following points may be noted in connexion with this division of the series. In addition to the type mineral from Ceylon, ceylonite includes also the spinels from Peekskill, U.S.A., and Namban, W.A.

¹ Numerical ratio neglecting algebraic sign. Without this third ratio there would be overlapping of the second and third sub-species in each species.

The type picotite of Lherz is a sub-species of hercynite, not of spinel as usually assumed. Very few of the published analyses of chromite indicate a mineral of the type sub-species; a French chromite, however, appears to be typical. The few other chromites whose analyses are at all trustworthy belong to the sub-species beresofite of chromite: or the sub-species chrompicotite (magnesiochromite) of picrochromite. At least three previously described minerals, viz. chrompicotite of Dun Mt., New Zealand; magnesiochromite of New Caledonia; and 'chromite' of Lake Memphremagog in Quebec, are members of a new species for which the author proposes the name picrochromite as suitable from either the scientific or industrial standpoint.

The method of comparison outlined above is subject to an obvious limitation. In many minerals of the spinel-chromite series there is a fifth variable, viz. Fe_2O_3 . When this occurs to an extent which is small in molecular comparison with Al_2O_3 and Cr_2O_3 , it may conveniently and without appreciable error, be disregarded, and the method here outlined applied. When it exceeds this limit, however, it cannot be treated as negligible, and the method fails. Small quantities of MnO or NiO (under one per cent.) may be neglected or added to the FeO, with which they are most closely related, and the method applied as outlined. This has been done in the case of chrompicotite above.

Finally, the method is applicable also to a large number of series of minerals whose components consist of two pairs of isomorphous variables, associated with one or more invariable. Examples of this are to be found amongst the garnets where silica is the invariable, e.g. in the almandite-andradite series. The problem, however, is frequently complicated in the case of the garnets by the presence of a third or fourth isomorphous protoxide. Other mineral series susceptible of treatment in this way are:

Staurolite, $\text{H}_2\text{O} \cdot 2(\text{Fe}, \text{Mg})\text{O} \cdot 5(\text{Al}, \text{Fe})_2\text{O}_3 \cdot 4\text{SiO}_2$.
 Chloritoid, $\text{H}_2\text{O} \cdot (\text{Fe}, \text{Mn})\text{O} \cdot (\text{Al}, \text{Fe})_2\text{O}_3 \cdot \text{SiO}_2$.
 Alunite-natrojarosite, $(\text{K}, \text{Na})_2\text{O} \cdot 3(\text{Al}, \text{Fe})_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$.
 Apatite-mimetite, $3(\text{Ca}, \text{Pb})_3(\text{P}, \text{As})_2\text{O}_8 \cdot (\text{Ca}, \text{Pb})\text{Cl}_2$.
 Arsenopyrite-alloclasite, $(\text{Fe}, \text{Co})(\text{As}, \text{Bi})\text{S}$.
 Gersdorffite-ullmannite, $(\text{Fe}, \text{Ni})(\text{As}, \text{Sb})\text{S}$.
 and many others.

Note on the Western Australian Ceylonite. This mineral is found in very pure angular masses up to one kilo in weight scattered over the outcrop of a serpentine between the townships of Namban and Miling, Melbourne district. The mineral is dense and microgranular in structure, pure

Analyses of Minerals of Spinel-Chromite Series.

Diagram No.	1	2	3	4	5	6	7	8
Species	Spinel Mudgée	Spinel Ceylon	Spinel Ceylonite Peetskim	Spinel Ceylonite Namban	Spinel Ceylonite Namban	Magnochromite Grochlan	Hercynite Picoite I. Herz	Hercynite Ronsberg B. Quadrant, 1845
Sub-species								
Locality	A. University, 1888; J. F. Gmelin, 1825	C. A. Wollé, 1839	E. S. Simpson, 1923	E. S. Simpson, 1923	E. S. Simpson, 1923	G. M. Bock, 1868	A. Damour, 1862	
Analyst								
MgO	21.95	545	18.24	452	12.84	319	13.65	339
FeO	4.49	63	17.45	247	17.45	247	14.00	347
MnO	—	—	0.26	—	0.28	—	15.30	213
Fe ₂ O ₃	64.39	629	9.41	59	3.80	24	—	—
Al ₂ O ₃	4.62	30	60.79	595	42.09	412	29.92	293
Cr ₂ O ₃	2.75	—	—	—	22.76	150	40.78	268
SiO ₂	—	—	—	—	1.51	—	2.00	—
Total	88.10	100.04 ¹	100.63	100.01 ²	100.38 ³	100.00	101.20	99.76
x	+ 79	+ 46	+ 3	+ 16	+ 16	+ 24	- 15	- 74
y	+ 91	+ 100	+ 100	+ 47	+ 45	+ 5	+ 82	+ 100

Diagram No.	9	10	11	12	13	14	15	
Species	Chromite Chromite	Chromite Beresoffite	Chromite Beresoffite	Chromite Beresoffite	Chromite Beresoffite	Picrochromite Chrompicotite (Magnesiochromite)	Picrochromite Picrochromite L. Memphrenago	
Sub-species								
Locality	Maures Mts. C. Chabrie, 1910	Baltimore H. Abich, 1881	Baltimore H. Abich, 1881	Beresov A. Moberg, 1848	Dun MT. T. Petersen, 1869	New Caledonia E. Glasser, 1904	L. Memphrenago T. S. Hunt, 1849	
Analyst								
MgO	1.28	32	7.45	185	6.68	166	18.13	450
FeO	30.09	419	20.13	280	18.42	181	6.48	90
MnO	—	—	—	—	—	—	—	—
Fe ₂ O ₃	1.60	10	13.85	136	0.46	98	16.45	108
Al ₂ O ₃	3.72	38	54.91	361	12.13	119	11.30	110
Cr ₂ O ₃	61.58	405	0.83	—	36.54	372	49.75	327
SiO ₂	0.55	—	—	—	—	—	—	—
Total	99.12 ⁴	91.47	98.52	101.01	101.93 ⁵	99.89	102.17	—
x	- 86	- 20	- 3	- 22	+ 32	+ 89	+ 8	+ 67
y	- 84	- 55	- 45	- 60	- 52	- 88	- 88	- 50

¹ Original analysis shows iron as FeO 20.51. ² Also NiO trace. ³ Also H₂O 0.56. About 4% included serpentine. When this is allowed for, the peroxides and sesquioxides balance. ⁴ Also CaO 0.94. Original analysis shows iron as FeO 31.53. ⁵ Rammeisbergs and Dana's figures for this analysis differ throughout. Dana's Cr₂O₃ 44.91 is obviously incorrect, as also his total 98.25. ⁶ Original analysis shows iron as FeO 18.01. ⁷ Original analysis shows iron as FeO 21.28.

black to the naked eye, 'tawny-olive' (Ridgway's standard) in thin section under the microscope, the centres of some of the grains being notably darker, ranging to full black. The pure mineral (analysis 4, p. 105) has a density of 4.12. Some specimens (analysis 5) include a little serpentine, bringing the density down to 4.04 or even less. The analyses given were made in vessels only of quartz and platinum, with reagents of known purity, duplicate determinations being made of most of the constituents.
