MINERALOGICAL ASPECTS OF THE SYSTEM Fe_3O_4—Mn_3O_4—$ZnMn_2O_4$—$ZnFe_2O_4$

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ABSTRACT

The phase relations in the system Fe_3O_4—Mn_3O_4—$ZnMn_2O_4$—$ZnFe_2O_4$ have been determined at temperatures up to 1300° C. by the study of synthetic preparations and natural minerals. The equilibrium diagram shows complete mutual miscibility of the components at temperatures above 1000° and a considerable field of incomplete miscibility at ordinary temperatures. Mix-crystals rich in iron have a cubic lattice, those rich in manganese a tetragonal lattice. Diagrams are given showing the variation with composition in dimensions and volume of the unit cell, and in the axial ratio for tetragonal phases. Analyses of magnetite, jacobsite, franklinite, vredenburgite, hetaerolite and hausmannite are plotted on a composition diagram, and composition limits for these mineral species are proposed. The use of vredenburgite as a geologic thermometer is suggested.

INTRODUCTION

This paper presents the results of an experimental study of the system Fe_3O_4—Mn_3O_4—$ZnMn_2O_4$—$ZnFe_2O_4$, using both synthetic preparations and natural minerals. This system is important mineralogically for the number of distinct species which have been recognized within it: magnetite, Fe_3O_4; jacobsite, $MnFe_2O_4$; franklinite $ZnFe_2O_4$; hetaerolite, $ZnMn_2O_4$; hausmannite, Mn_3O_4; and vredenburgite, which is generally an oriented intergrowth of jacobsite and hausmannite, but which has been recorded in a homogeneous state. This investigation was undertaken mainly in order to study the mutual relationships of these individual minerals, and their conditions of formation, and to define their range in composition as far as possible in relation to the physico-chemical conditions under which they occur as stable phases. Other interesting phenomena within the system are the change in crystal lattice from one with cubic symmetry for the iron-rich members to one with a tetragonal symmetry for the manganese-rich members, and the occurrence of complete mutual miscibility in the solid state of the components at high temperatures (in spite of lattice differences) and a wide field of incomplete miscibility at lower temperatures. The variation in magnetic properties, from strong ferromagnetism for Fe_3O_4 to paramagnetism for the other components, is also striking but was only partly studied.

The experimental work upon which this paper is based was carried out during 1942 and 1943 at the University of Stockholm. It was abruptly terminated by my departure from Sweden in 1943; the essential parts of the experimental work had been completed by that time, but further investigations were intended with a view to studying more closely the change from a cubic to a tetragonal lattice within the system, and making detailed measurements of variation of magnetic properties with composition. Since that time it has not been possible to continue with these experiments, and this paper does not deal as fully with these aspects as might be wished.

In this connection it is my pleasant duty to acknowledge my indebtedness to those I was associated with at the University of Stockholm, especially Professor Percy Quensel, of the Mineralogical Institute, and Professor Arne Westgren, of the Institute of Inorganic Chemistry, for the hospitality I received while working as a foreign guest in their Institutes. Their advice and encouragement, together with the many kindnesses which I received from all quarters during my enforced stay in Sweden, are gratefully remembered.

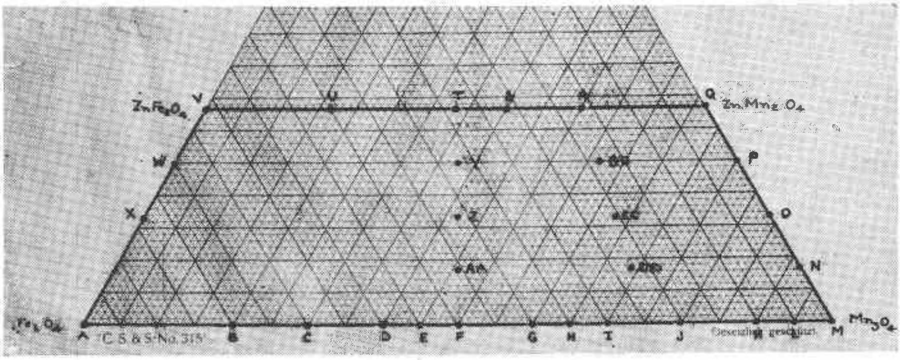

FIG. 1. Synthetic preparations within the system.

THE NATURE OF THE SYSTEM

The system here studied clearly falls within the four-component system Fe—Mn—Zn—O. By plotting the components Fe_3O_4, Mn_3O_4, $ZnMn_2O_4$, $ZnFe_2O_4$ on a tetrahedron with Fe, Mn, and Zn as the corners of the base and O as the apex it can readily be seen that these components all lie in a plane parallel to the base and situated $\frac{4}{7}$ of the distance towards the apex, since the ratio of oxygen atoms to the total number of atoms in all these components is 4:7. The system Fe_3O_4—Mn_3O_4—$ZnMn_2O_4$—$ZnFe_2O_4$ is thus part of the three-component system whose components are Fe_3O_4, Mn_3O_4, and a hypothetical Zn_3O_4. All compositions within this system can therefore be represented on a truncated equilateral triangle with the Fe_3O_4—Mn_3O_4 join forming the base and the $ZnFe_2O_4$—$ZnMn_2O_4$ join truncating the triangle one-third of the distance towards the apex (Fig. 1). Such a truncated triangle is used throughout this paper for representing compositions within this system, compositions being plotted as atom percentages of Fe, Mn, and Zn.

TABLE 1

Prep.	Composition				Phases	Cubic	Tetragonal			Remarks
	Fe	Mn	Zn	T		a	a	c	c/a	
A					C	8.381				Natural magnetite, analyzing 99.2% Fe_3O_4
B	80	20		1170	$C+R_2O_3$					
				1220	$C+R_2O_3$					
				1300	C	8.444				
C	70	30		1050	$C+R_2O_3$					
				1220	C	8.455				
D	60	40		1220	C	8.483				
E	55	45		1150	C	8.501				
F	50	50		1100	C	8.505				
G	40	60		1150	C	8.515				
H	35	65		1200	T		8.378	8.827	1.054	
				750	T					In vacuo, unchanged
I	30	70		1150	T		8.307	8.972	1.080	
				990	T					In vacuo, unchanged
				750	T					In vacuo, unchanged
J	20	80		1150	T		8.235	9.180	1.115	
				950	T					In vacuo, unchanged
				750	$T+T_1$		8.194 8.284	9.281 9.030	1.133 1.090	In vacuo
				650	T					In vacuo, unchanged
K	10	90		1150	T		8.190	9.310	1.137	
				750	T					In vacuo, unchanged
L	5	95		1100			8.162	9.410	1.153	
M		100		1100			8.140	9.435	1.159	
N		91.7	8.3	890	T		8.123	9.391	1.156	
O		83.3	16.7	710	$T+(Mn_2O_3)$					Brackets indicate small amount
				890	T		8.107	9.341	1.152	
P		75	25	890	T		8.084	9.286	1.149	
Q		66.7	33.3				8.076	9.225	1.142	
R	16.7	50.0	33.3	890	T		8.162	8.991	1.102	
				800	$T+(T_1)$		8.120 (8.204)	9.107 8.872)	1.121 (1.081)	Brackets indicate small amount
				710	T+(C)	(8.423)	8.114	9.115	1.123	Brackets indicate small amount
				590	T+(C)	(8.422)	8.111	9.139	1.127	Brackets indicate small amount
				515						2 or 3 very faint lines only
S	26.7	40.0	33.3	920	T		8.217	8.869	1.080	
				810	T		8.214	8.861	1.079	
				700	C+T	8.424	8.125	9.099	1.120	
				600	C+T	8.422	8.117	9.121	1.124	
T	33.3	33.3	33.3	920	T		8.253	8.790	1.065	
U	50.0	16.7	33.3	890	C	8.426				
W	75		25	1000	$C+R_2O_3$					
X	83.3		16.7	1000	$C+R_2O_3$					
Y	37.5	37.5	25	1000	T		8.282	8.780	1.060	
				920	T		8.287	8.780	1.059	
Z	41.7	41.7	16.6	1000	C	8.494				
AA	45.8	45.8	8.4	1000	C	8.498				
				920	$C+R_2O_3$					
BB	18.8	56.2	25	1000	T		8.181	9.065	1.108	
				920	$T+T_1$		8.138 (8.183)	9.143 (9.025)	1.124 (1.103)	Brackets indicate small amount
				810	$T+T_1$		8.137 (8.212)	9.136 (8.953)	1.123 (1.090)	Brackets indicate small amount
				710	$T+T_1$		8.133 (8.250)	9.136 (8.934)	1.123 (1.083)	Brackets indicate small amount
				600	C+T	8.433	8.129	9.169	1.128	
CC	20.8	62.5	16.7	920	T		8.194	9.114	1.112	
				810	$T+T_1$		8.158 8.193	9.195 9.016	1.127 1.100	
				710	$T(+T_1)$		8.156	9.165	1.124	Lines of second phase hardly visible
				600	$T+R_2O_3$					
DD	22.9	68.8	8.3	890	T		8.215	9.111	1.109	
				810	$T+R_2O_3$					

EXPERIMENTAL PROCEDURE

Synthetic preparations were made covering a wide range of compositions within this system (Fig. 1 and Table 1). From Fig. 1 it would appear that the coverage was somewhat irregular, but the concentration of synthetic preparations towards the manganese side of the composition diagram is on account of the closer study of the change from a cubic to a tetragonal lattice, and the region of limited miscibility, both of which are situated on this side of the diagram.

These synthetic preparations were made in the following way. Manganous sulphate, ferrous sulphate, and zinc sulphate (analytical reagent quality) were weighed out in the desired proportions and dissolved in hot water; the solution was precipitated by a small excess of sodium hydroxide solution for those containing manganese and iron only, or sodium carbonate solution for those containing zinc also, the precipitate washed first by decantation and then on a filter until free from sulphate, and dried by heating in an oven with free access of air at 165° for 24 hours. The products thereby obtained were semi-amorphous, giving few or no lines on an x-ray powder photograph. In order to assure that the proportions of iron, manganese, and zinc in the products corresponded to the amounts of parent materials taken, the percentages of iron, manganese, and zinc in some of the products were confirmed by chemical analysis.

These synthetic preparations were converted into the AB_2O_4 type compounds by heating in an electric furnace at temperatures up to 1300° C. for periods varying from 12 to 24 hours. Syntheses containing more than 80% of the Fe_3O_4 component could not be prepared in this way without exceeding 1300°, beyond the capacity of the furnaces available; in this composition range at temperatures below 1300° the products contained Fe_2O_3 as well as the AB_2O_4 compound.

All these heatings were carried out with free access to the air, with the exception of some of the preparations along the Fe_3O_4—Mn_3O_4 join, which were heated in sealed evacuated tubes at temperatures between 650° and 1000°, the sealed evacuated tubes being necessary for these compositions and at these temperatures in order to prevent oxidation to the corresponding R_2O_3 type compound. With these exceptions, which are indicated in Table 1, the system was thus investigated under a partial pressure of oxygen of approximately 159 mm.

The phase relations in the products obtained by heatings at different temperatures were investigated by means of x-ray powder photographs. The cameras used for making the powder photographs were of the Seeman-Bohlin focussing type as designed by Phragmén. Chromium radiation was employed. The lattice dimensions of the various phases were also determined from the powder photographs, and the relationship between lattice dimensions and chemical composition in the solid solution series thereby obtained. These relationships made it then possible to determine the composition of any phase within the system from the determination of its lattice dimensions. This was extensively used for determining the composition of the separate phases for samples falling within the region of incomplete miscibility, and thereby building up the boundaries of this region at different temperatures. This technique for opaque materials corresponds with the utilization of the relations between refractive index and chemical composition so extensively employed in the elucidation of phase relationships in silicate systems.

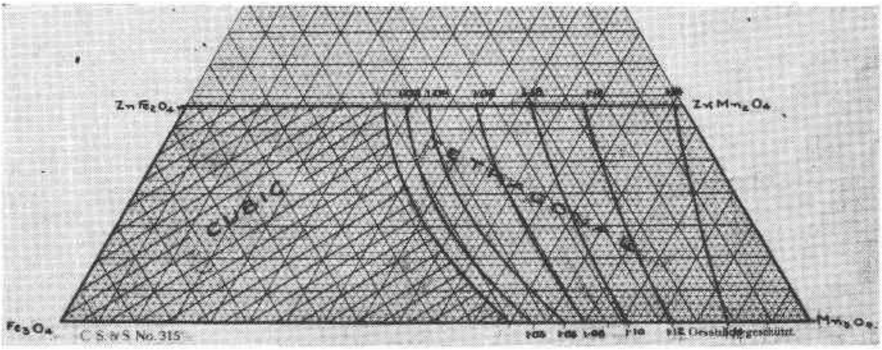

Fig. 2. Cubic and tetragonal lattices and variation of the axial ratio (c/a) with composition.

In routine work the accuracy of measurement of the lattice dimensions from powder photographs was ±0.1% or better. For determining the relationship between lattice dimensions and chemical composition special precautions were taken, and the measurements for this purpose have an accuracy of ±0.05%. All temperatures are in degrees Centigrade.

RESULTS OBTAINED

The results obtained from the experiments with synthetic preparations are set out in Table 1, and are expressed by the curves in Figs. 2, 3, 4, and 5.

Figure 2 shows the composition regions within which the cubic lattice and the tetragonal lattice are respectively stable, and also shows the change in axial ratio with composition for the tetragonal phase. The axial ratio reaches a maximum of 1.16 for pure Mn_3O_4.

It has been suggested by Eckermann (2), on the basis of earlier work on the Fe_3O_4—Mn_3O_4 system by Montoro (10) and the writer (8), that the change from a cubic to a tetragonal lattice in that system is dependent not only on composition but also on temperature. Systematic experiments to test this suggestion have not been carried out. However, it may be pointed out that preparation 1 (Fe 30, Mn 70), which according to Eckermann's tentative phase diagram should possess cubic symmetry between 700° and 1000° and tetragonal symmetry above 1000°, was uniformly tetragonal between 750° and 1150° (Table 1). Another feature of Eckermann's diagram for the change from cubic to tetragonal symmetry is that this change is shown to take place for any one composition with increasing temperature, whereas a change of this type is usually to a lattice of greater symmetry with increasing temperature—e.g., leucite, α-β quartz, low-high tridymite and cristobalite, monoclinic pyroxene—orthorhombic pyroxene; changes to a lattice of lower symmetry with increasing temperature are, however, known (e.g., α-β sulphur).

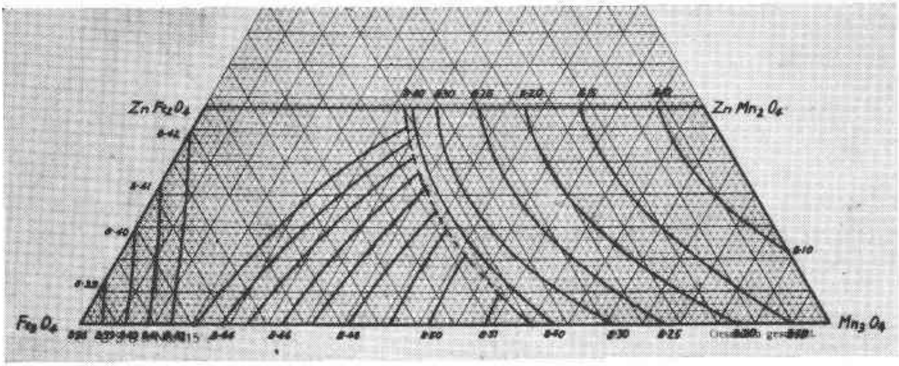

FIG. 3. Relationship between composition and *a* for cubic and tetragonal lattices.

Figure 3 shows the variation in *a* with chemical composition for both the cubic and tetragonal phases. It will be seen that a relatively large area of the cubic field is enclosed between the curves for 8.42 Å and 8.43 Å; within this area the lattice dimensions change relatively slightly with composition, and a value for *a* between 8.42 Å and 8.43 Å does not indicate any very precise chemical composition, particularly if zinc is present in considerable amount. For the tetragonal phase *a* decreases rapidly away from the boundary between the two fields, reaching a minimum of 8.076 Å for pure $ZnMn_2O_4$.

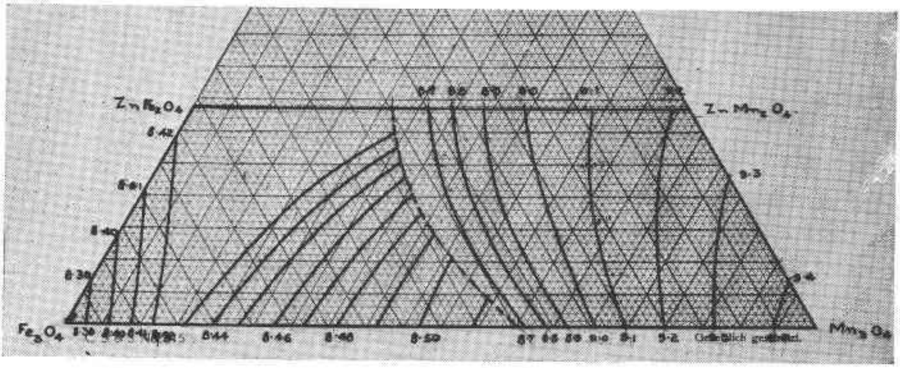

FIG. 4. Relationship between composition and *a* for cubic lattices and *c* for tetragonal lattices.

Figure 4 shows the variation with chemical composition of *a* for the cubic phase and *c* for the tetragonal phase. For the tetragonal phase, *c* increases rapidly away from the boundary between the two fields, reaching a maximum of 9.435 Å for pure Mn_3O_4.

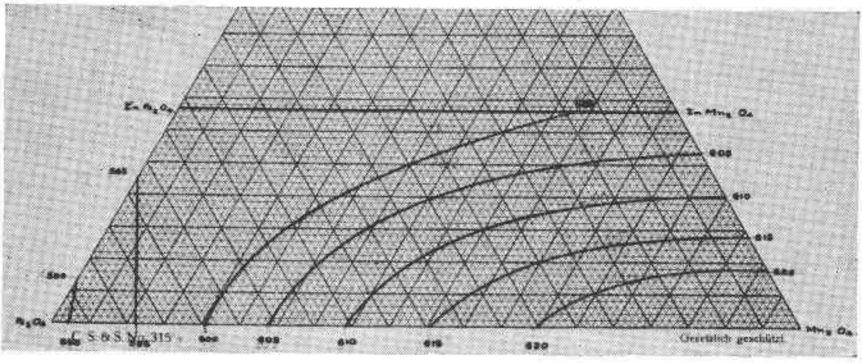

FIG. 5. Variation in unit cell volume (in Å^3) with composition.

Figure 5 shows the variation in the unit cell volume with chemical composition. The unit cell volume varies from a minimum of 588 Å^3 for pure Fe_3O_4 to a maximum of 625 Å^3 for pure Mn_3O_4. It is evident that the manganese ions are the principal determining factor in the increase of cell volume, substitution of zinc for iron having relatively little effect, whereas substitution of manganese for iron or for zinc is reflected by a relatively rapid increase in cell volume.

THE EQUILIBRIUM DIAGRAM

Figure 6 is a partial equilibrium diagram for the system, showing conditions between ordinary temperatures and the highest temperatures reached during this investigation, viz. 1000°–1300°. It has been constructed from the results of experimental work on synthetic preparations (Table 1), and from the study of mineral specimens.

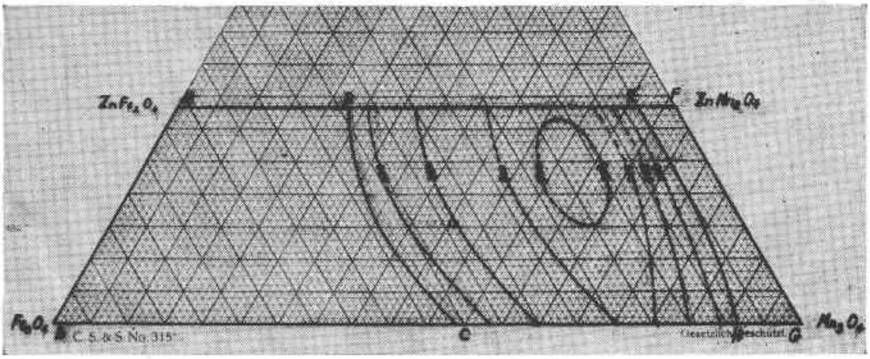

FIG. 6. Equilibrium diagram for the system. *ABCD* is the field of cubic mix-crystals. *EFGH* is the field of tetragonal mix-crystals. *CDEH* is the field of incomplete miscibility; isotherms show the boundaries of the field of incomplete miscibility at different temperatures.

In Fig. 6 the field *ABCD* is one of complete miscibility in the solid state, the single phase present being a solid solution of the respective components and having a cubic lattice. The field *EFGH* is also one of complete miscibility in the solid state, the single phase present being also a solid solution of the respective components but having a tetragonal lattice. Separating these two fields is the field *CDEF*, which is a field of incomplete miscibility in the solid state. For any composition within this field at ordinary temperatures two phases coexist in stable equilibrium. As the temperature rises the field of solid immiscibility contracts and finally disappears between 900° and 1000°. The isotherms in Fig. 6 indicate the boundaries of the field of incomplete miscibility at different temperatures.

The boundaries of the field of incomplete miscibility at temperatures between 600° and 1000° were determined by holding synthetic preparations at definite temperatures for a sufficient time for equilibrium to be attained. Under these conditions powder photographs of preparations whose composition fell within the field of incomplete miscibility for that temperature showed the presence of two phases; the composition of these two phases, which are points on the boundaries of the field of incomplete miscibility at that temperature, were determined by measuring the lattice dimension, axial ratios, and cell volumes of these phases and correlating these with the diagrams giving variation of lattice dimensions, axial ratios, and cell volumes with composition (Figs. 2, 3, 4, and 5). For tetragonal phases the variation of these properties with composition was sufficiently rapid for the compositions of unknown phases to be determined with a probably uncertainty of about ±2%; for cubic phases the uncertainty was too great for useful information concerning composition to be obtained; however, above 700° the field of limited miscibility lies almost entirely within the region of tetragonal lattices, so above this temperature the isotherms bounding the field of limited miscibility could be directly established. Below this temperature the isotherms within the region of cubic lattices were established by extrapolation and the study of mineral specimens.

For the synthetic preparations rich in zinc it was only necessary to take portions of the original preparations and heat them in air at the respective temperatures for one to two days. The stable phase in air from 590° upwards was the AB_2O_4 compound, and there was no tendency for the iron or manganese to form the R_2O_3 type oxides. Below 590° these preparations gave either blank photographs or a few very faint and diffuse lines, indicating a lack of crystallinity. As the amount of zinc in the preparations was decreased, however, there was an increasing tendency for the iron and manganese to form the R_2O_3 type oxides, and along the Fe_3O_4-Mn_3O_4 join the R_3O_4 oxides were not stable in air below 1000°, being oxidized to the sesquioxides. For preparations in this region it was therefore necessary first to heat them at a sufficiently high temperature to convert them to the R_3O_4 oxide, and then to reheat them in sealed evacuated tubes at the temperatures below 1000°. It was found, as might be expected, that equilibrium was reached much less readily than in those preparations which could be heated directly from their original semi-amorphous condition to the temperature required, the readjustment to falling temperature being much more sluggish than that to rising temperature. Thus preparation J (Fe 20, Mn 80) was converted into the R_3O_4 oxide by heating at 1150° and then heated in a sealed evacuated tube at 750° for three days, when it was found to have disintegrated into two phases; on heating at 650° under similar conditions, however, it showed no signs of any change, the rate of readjustment at this temperature evidently being practically zero.

Thus it was not possible to determine the isothermal boundaries of the region of incomplete miscibility for temperatures below 600° by laboratory experiments on synthetic preparations. The limiting curves for the region of incomplete miscibility were established from a study of natural minerals—whether homogeneous or showing intergrowths of the vredenburgite type, and in the latter case, the determination of the composition of the two phases of the intergrowth from measurements of the lattice dimensions. This was possible with a fair degree of accuracy for the Fe_3O_4—Mn_3O_4 tie-line, as a number of specimens of vredenburgite whose composition fell on this tie-line were available for study. Only one specimen of a zincian vredenburgite was available for study, so the extension of these limiting curves towards the $ZnFe_2O_4$—$ZnMn_2O_4$ tie-line is subject to some degree of extrapolation.

The results of measurements of lattice dimensions on the phases present in different specimens of vredenburgite are given in Table 2.

TABLE 2. LATTICE DIMENSIONS OF THE PHASES PRESENT IN DIFFERENT SPECIMENS OF VREDENBURGITE

Locality	a_{cubic}	$a_{\text{tetr.}}$	$c_{\text{tetr.}}$
Långban 1	8.504	8.167	9.345
Långban 2	8.502		
Jakobsberg 1	8.496	8.158	9.342
Jakobsberg 2	8.487	8.152	9.339
Jakobsberg 3	8.503	8.165	9.349
Kodur 1	8.483	8.162	9.369
Kodur 2	8.480	8.157	9.371
Kodur 3	8.478	8.171	9.333
Franklin (zincian)	8.422	8.115	9.190

Analyses of the vredenburgites from Långban, Jakobsberg, and Kodur show no zinc. The variation in lattice dimensions of the respective phases for the different specimens, while not great, is beyond the margin of error of the measurements, and is probably largely due to the presence of small and variable amounts of magnesium substituting iron and manganese. Analyses of vredenburgite from Jakobsberg show up to 1.25% MgO (7). The presence of magnesium in solid solution will have the effect of reducing the lattice dimensions below those for the pure iron-manganese compounds.

For the Fe_3O_4—Mn_3O_4 tie-line the figures given in Table 2 indicate a figure of 91% Mn_3O_4 (±2%) for the position of the bounding curve of the limited miscibility field on the manganese side of the diagram. The composition of naturally occurring hausmannites confirms this to some extent, in that the most iron-rich hausmannite so far recorded contains 6.91% Fe_3O_4, close to the bounding curve determined above. On the iron side of the diagram the position *C* of the bounding curve was determined from the specimen recorded as Långban 2 in Table 2. It is listed as a vredenburgite although the powder photographs did not show any lines corresponding to the tetragonal phase. Examination of polished sections of this specimen under the microscope showed however the presence of a few very narrow lamellae of the tetragonal phase, less than 5% in amount and evidently insufficient to give the characteristic lines on a powder photograph. An analysis of this specimen gave $Mn_3O_4 = 55.9\%$. The position *C* of the bounding curve is therefore put at 54% Mn_3O_4.

The use of minerals to establish the limits of the field of incomplete miscibility in the solid state rests on the assumption that these minerals are actually in a condition of chemical equilibrium. There are reasonable grounds for this assumption, in that the rate of changes in physical conditions, i.e., temperature and pressure, in nature is in general so extremely slow in comparison to that which can be attained in laboratory experiments that the chances for equilibrium to be continuously maintained are good. For the conditions of metamorphism under which these zinc-manganese-iron spinels have originated this must be particularly true. A further argument in favor of this concept can be adduced. From Table 2 it can be seen that the two phases in zinc-free vredenburgites, whether from different localities or different specimens from the same locality, show a marked constancy of lattice dimensions, especially when allowance is made for small quantities of magnesium in solid solution. This would indicate a constancy in chemical composition for these phases, suggesting that these specimens have reached a state of equilibrium which is the same in all.

The study of mineral specimens can thus contribute greatly to the knowledge of equilibrium conditions in chemical systems, since the time factor available for reactions under geological conditions is so vastly greater than that attainable in the laboratory. Although much has been done along these lines, the closer study of minerals will undoubtedly greatly advance our present knowledge of chemical equilibria.

Mineralogical Applications

In Fig. 7 analyses of minerals which fall within his system are plotted on the composition diagram. For this purpose the atom proportions of iron, manganese, and zinc were calculated from each analysis, converted to percentages, and plotted in the usual way. All the analyses were checked from the original publications, except for those of franklinite, which were taken from the table of collected analyses published in Palache's memoir on the minerals of Franklin and Sterling Hill (12).

On the basis of the phase relations within this system and this collection of mineral analyses an attempt has been made to define the valid mineral species within this system in terms of composition fields, as set out in Fig 7.

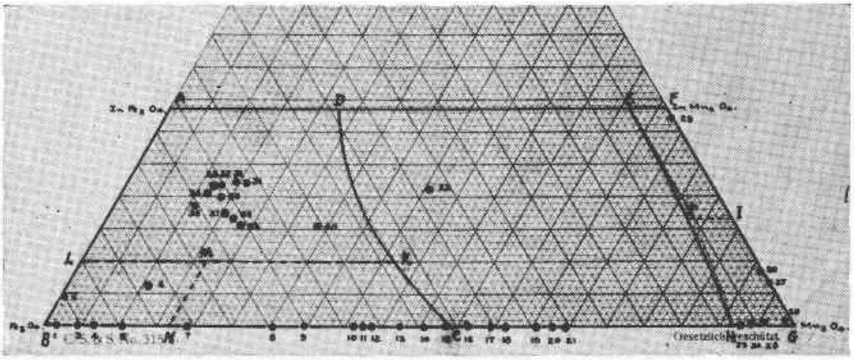

FIG. 7. Analyses of minerals falling within the system, and suggested composition limits for the different species. Magnetite *BNML;* jacobsite *NMKC;* franklinite *ADKL;* vredenburgite *DEHC;* hetaerolite *EFIJ;* hausmannite *GHIJ.*

Key to analyses for Fig. 7

1. Magnetite, Tongue, Scotland. *Mineral. Mag.*, **5,** 150 (1884).
2. ———, Franklin, New Jersey. *U. S. Geol. Survey, Prof. Paper* **180,** 44 (1935).
3. ———, Väster Silvberg, Sweden. *Mineral. petrog. Mitt.*, **7,** 110 (1886).
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5. ———, St. Joseph du Lac, Quebec. *Mineral. Mag.*, **14,** 373 (1907).
6. ———, Franklin, New Jersey. *U. S. Geol. Survey, Prof. Paper* **180,** 47 [anal. 10] (1935).
7. Jacobsite, Siegen, Germany. *Rammelsberg, Mineral.-Chem.*, 132 (1875).
8. ———, Debarstica, Bulgaria. *Zeits. Kryst.*, **36,** 202 (1902).
9. ———, Nordmarken, Sweden. *Bull. soc. franç. minéral.*, **10,** 185 (1885).
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11. ———, Beldongri, India. *Trans. Nat. Inst. Sci. India*, **1,** 108 [779a] (1936).
12. ———, Sjögruvan, Sweden. *Bull. soc. franç. minéral.*, **10,** 172 (1887).
13. ———, Beldongri, India. *Trans. Nat. Inst. Sci. India*, **1,** 108 [779*b*] (1936).
14. ———, Beldongri, India. *Records Mysore Geol. Dept.*, **34,** 82 [no. 1] (1935).
15. ———, Sjögruvan, Sweden. *Bull. soc. franç. minéral.*, **10,** 173 (1887).
16. Vredenburgite, Långban, Sweden. *Nyt. Mag. for Naturvidenskaberne*, **29,** 304, 1885 (Manganomagnetite).
17. ———, Devada, India. *Records Mysore Geol. Dept.*, **34,** 82 [no. 2] (1935).
18. ———, Kodur, India. *Records Mysore Geol. Dept.*, **34,** 82 [no. 3] (1935).
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20. ———, Garividi, India. *Mem. Geol. Survey India*, **37,** 44 (1909).
21. ———, Jakobsberg, Sweden. *Zeits. Krist.*, **68,** 116 (1928).
22. ———, Franklin, New Jersey. *Geol. Fören. Förh.*, **68,** 55 (1946) (zincian vredenburgite).
23. Hausmannite, Långban, Sweden. *Geol. Fören. Förh.*, **65,** 159 [no. 27] (1943).

24. ———, Jakobsberg, Sweden. *Bull. soc. chim.* (3), **29,** 1110 (1903).
25. ———, Långban, Sweden. *Bull. soc. chim.* (3), **29,** 1110 (1903).
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Physico-chemical considerations divide the diagram into three fields, by means of the two lines *CD* and *EH* limiting the field of incomplete miscibility in the solid state. Thus we have at the left of the diagram a field of cubic solid solutions, the magnetite-jacobsite-franklinite field, in the center the vredenburgite field, and on the right the field of tetragonal solid solutions, the hausmannite-hetaerolite field.

Only the field of vredenburgite is precisely determined in this way. Division of the field of magnetite-jacobsite-franklinite and that of hausmannite-hetaerolite into areas for the respective minerals cannot be made on the basis of clearly defined phase boundaries but must depend upon a more or less arbitrary procedure.

In an earlier paper (8) the writer suggested that the division between jacobsite and magnetite be drawn according to the dominance or otherwise of $MnFe_2O_4$, the formula usually ascribed to jacobsite, although it has not been shown that this formula represents more than a point in a mix-crystal field. If this procedure be followed then the point of division on the Fe_3O_4-Mn_3O_4 tie-line is at the point representing 16.7% Mn_3O_4. It is now suggested that a line—*NM* in Fig. 7—be drawn from this point parallel with the Fe_3O_4-$ZnFe_2O_4$ tie-line (i.e., keeping the percentage of manganese in the relative percentages of iron, manganese and zinc at 16.7) until it meets the boundary of the franklinite field, thereby separating the field of magnetite from that of jacobsite.

The field of franklinite might be defined in a similar way, by considering the boundary between franklinite and magnetite as being determined by the dominance or otherwise of $ZnFe_2O_4$ and drawing a line from the point thus determined parallel to the base of the diagram until it met the bounding curve of the vredenburgite field. This would, however, lead to a clustering of the points representing analyzed franklinites on either side of this line. In order to keep the compositions generally recognized as franklinite within one field it is therefore suggested that the boundary of the franklinite field be a line corresponding to 10% of zinc in the relative percentages of iron, manganese, and zinc shown by an analysis.

Thus the field of stable cubic solid solutions is divided into the following areas: *BLMN*, that of magnetite; *NMKC*, that of jacobsite; and *ADKL*, that of franklinite.

Turning now to the hausmannite-hetaerolite field the division here can well be made on the dominance or otherwise of $ZnMn_2O_4$. In the diagram this is indicated by a line *IJ* representing 16.7% zinc in the relative percentages of zinc, iron, and manganese. Thus *EFIJ* is the field of hetaerolite, and *GHJI* that of hausmannite.

Finer distinctions within these mineral species can be made by the use of the adjectival qualifiers suggested by Schaller (14), and adopted by the authors of the new (7th.) edition of Dana's *System of Mineralogy* (13).

In an earlier paper on the Fe_3O_4-Mn_3O_4 system (8), the writer devoted considerable space to the discussion of the nature and systematic position of vredenburgite, the essential points of which may be repeated here. Vredenburgite was originally described by Fermor (3), who gave it the formula $3Mn_3O_4 \cdot 2Fe_2O_3$ on the basis of analyses made at that time. Some years later the examination of polished sections of vredenburgite under the microscope, by Schneiderhöhn and Ramdohr (15), Orcel and Pavlovitch (11), and Dunn (1)—the latter on Fermor's original specimens showed that vredenburgite was an oriented intergrowth of jacobsite and hausmannite. Schneiderhöhn and Ramdohr pointed out that the structure was typical of exsolution on cooling of a mix-crystal formed at high temperatures, and showed that the excess oxygen over the simple $(Fe,Mn)_3O_4$ formula in the original analyses of vredenburgite was due to the selective replacement of the hausmannite lamellae by pyrolusite and psilomelane, probably the result of supergene processes.

Further analyses of the Indian vredenburgite were made by Iyer (5, 6). Iyer's analyses show an excess of oxygen over the simple $(Fe,Mn)_3O_4$ formula, but later microscopic examination (8, pp. 163–165) has shown that this is due to the presence of pyrolusite and psilomelane. However, Fermor (4) has extensively discussed Iyer's analyses and correlated them with those given in the original description of vredenburgite. On the basis of the variation in manganese and iron content of vredenburgites from different localities he has suggested two new names, devadite and garividite, for the originally homogeneous material from which vredenburgite was formed by unmixing. On account of the excess oxygen over the simple $(Fe,Mn)_3O_4$ formula shown by analyses of these Indian vredenburgites he also argues that this originally homogeneous material was not a spinellid, and that on unmixing it broke down not into jacobsite and hausmannite alone, but into jacobsite, hausmannite, and free MnO_2, the latter appearing as pyrolusite and psilomelane. Neither of Fermor's proposals are, however, valid; firstly microscopic examination of specimens of the Indian vredenburgite has shown that the MnO_2 is a secondary product, resulting from the selective replacement of the hausmannite lamellae; and secondly the variation in iron and manganese in vredenburgite is continuous, vredenburgites being members of a continuous mix crystal series, and therefore no real grounds exist for the division of vredenburgite into distinct species on the basis of relative content of iron and manganese.

From the nature of the equilibrium diagram it is evident that a homogeneous phase for any composition within the vredenburgite field can exist at ordinary temperatures and pressures only in a metastable condition. Arguments have been advanced above against the occurrence of such metastable phases as natural minerals. However, the writer has recently described (9) a homogeneous vredenburgite from Långban (anal. 19, Fig. 7). This material had however originated under rather special circumstances. It was pseudomorphous after bixbyite, $(Mn,Fe)_2O_3$, having been produced by a process of reduction probably at a comparatively low temperature. Evidently the first product of the reduction was this metastable homogeneous vredenburgite, and the temperature at which the reduction took place was so low that the rate of readjustment was effectively zero. As a result it has remained in this metastable condition. Primary vredenburgite, on the other hand, seems always to show the typical intergrowth of jacobsite and hausmannite produced by unmixing of the originally homogeneous solid solution.

Comparison of the positions of analyzed specimens of vredenburgite (Fig. 7) with the equilibrium diagram (Fig. 6) reveals an interesting grouping. All the analyses lies on the left side of the vredenburgite field. While this may be due partly to proportions between iron and manganese in the environment in which they originated, an important factor has probably been the temperature at which they formed; comparison with the equilibrium diagram shows that these analyses all fall below the 800° isotherm, and most of them are grouped about the 600° isotherm. The absence of analyzed vredenburgites lying within the higher isotherms suggests that the metamorphosed manganese ores from which vredenburgite has been recorded have never been subjected to these higher temperatures, and that recrystallization took place at temperatures below 800° and in some cases considerably lower. Vredenburgite can thus be used as a geologic thermometer for indicating minimum temperatures of formation, and detailed study of the variation in its composition in any ore-body may give useful evidence as to the thermal history of that ore-body.

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