

Heating experiments on some natural titaniferous magnetites.

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Summary. Chemically analysed samples of magnetites carrying exsolved ulvöspinel and ilmenite have been heated *in vacuo* at various temperatures without change in overall chemical composition and the changes occurring studied microscopically, magnetically, and by X-rays.

Magnetite with exsolution bodies of ulvöspinel can be homogenized probably below 600° C.; thermomagnetic curves and microscopic textures suggest that the solvus curve is very steep at the Fe_3O_4 end of the Fe_3O_4 - Fe_2TiO_4 series.

On heating magnetite containing ilmenite lamellae up to 950° C., some interchange of ions between the phases occurs ($\text{Fe}_3\text{O}_4 + \text{FeTiO}_3 \rightarrow \text{Fe}_2\text{TiO}_4 + \text{Fe}_2\text{O}_3$), the ilmenite lamellae taking Fe_2O_3 into solid solution. The accompanying host magnetite not only gains Fe_2TiO_4 , but at the same time dissolves some FeTiO_3 . Above 950° C. extensive decomposition takes place, with the production of pseudobrookite, and homogenization has not been achieved. It is suggested that under magmatic conditions extensive solid solution exists in which the FeTiO_3 component may be regarded as having a spinel (γ) structure; after exsolution, monotropic inversion may occur to yield a rhombohedral ferri-ilmenite (Chevallier *et al.*, 1955), which on slow cooling changes in composition towards FeTiO_3 .

Magnetite with exsolution bodies of both ulvöspinel and ilmenite shows on heating the features of both the above binary types.

THERE is still a lack of precise information concerning the solid solution relationships and unmixing of the various phases in the Fe-Ti-O system, including the important part involving magnetite, ulvöspinel, ilmenite, and hematite. A thorough knowledge of the behaviour of complex titanomagnetite solid solutions on cooling would be of great interest not only petrogenetically but also to the geophysicist, since these materials are the principal carriers of rock magnetism.

In previous papers (Vincent and Phillips, 1954; Chevallier, Mathieu, and Vincent, 1954) we have discussed relationships between bulk chemical composition, unmixing intergrowths, and simple magnetic properties of some Fe-Ti oxide minerals from the Skaergaard gabbroic intrusion,

and indicated how the chemical composition of the titanomagnetites and hence the mineralogical nature of the intergrowths produced on their slow cooling might depend rather delicately upon oxidation-reduction relationships between oxide minerals and magmatic liquids.

In the absence, so far, of any published detailed synthetic investigation of the Fe-Ti-O system, we have performed simple heating experiments with a few carefully selected, purified, and chemically analysed natural titaniferous magnetite intergrowths to see how the process of partial or complete homogenization varies with mineralogical and hence chemical composition. This in turn may allow us to predict some of the changes that will occur as a titanomagnetite crystallizes and cools in a magma.

The mineralogical changes occurring during these heating experiments were followed microscopically and by determining the changes in unit-cell dimensions of the various phases, and also by quantitative measurements of their magnetic properties. The magnetic measurements have been made by Chevallier and Mathieu at Nancy, the rest of the work has been done by Vincent and Wright at Oxford. The interpretation of the results has been done jointly, and one of us (E.A.V.) has been responsible for preparing this paper.

A fairly detailed study of this kind seems justified in view of such compilations of partial chemical analyses, X-ray, and magnetic data for titaniferous magnetites as those presented by Akimoto (1954, 1955) in which correlation between these various properties is often far from good, since the discrepancies may be partly explicable if the minerals described have unmixed to varying extents and in different ways according to their composition.

The majority of the unmixed titaniferous magnetites found in igneous rocks consist of cubic magnetite carrying exsolution lamellae of rhombohedral ilmenite arranged along the {111} directions of the host spinel; others carry both ilmenite and ulvöspinel in various proportions as exsolution bodies; while others—apparently rather few in coarse-grained rocks—carry only ulvöspinel. Homogeneous titanomagnetites of this last type (solid solutions along the Fe_3O_4 - Fe_2TiO_4 binary join) have been synthesized by Pouillard and Michel (1949) and by Kawai, Kume, and Sasajima (1954); the latter authors prepared an extreme solid solution with 80% Fe_2TiO_4 . Solid solutions in the binary join Fe_3O_4 - FeTiO_3 were synthesized by Chevallier and Girard (1950) with compositions ranging from pure Fe_3O_4 up to 37% FeTiO_3 ; these materials also all gave the spinel X-ray powder pattern.

The crystalline structures of these two distinct series of solid solutions have been discussed by Chevallier, Bolfa, and Mathieu (1955), who refer to them as titanomagnetites types I and II respectively. We have found that the behaviour of our natural unmixed intergrowths on heating *in vacuo* is quite different in the two binary series, while samples of intermediate composition show features of both types.

Various authors have previously given brief descriptions of heating experiments carried out on titaniferous magnetites, generally with a view to demonstrating the lamellae of ilmenite parallel to {111} to be of exsolution rather than of replacement origin. Among these may be mentioned Ramdohr (1926), Kamiyama (1929), Wilson (1953), and Roy (1954, 1955). In none of these experiments have carefully separated and chemically analysed materials been used; neither have any quantitative measurements been made of changes occurring in cell-dimensions or magnetic constants on heating. Mogensen (1946), however, reported the homogenization of the first magnetite-ulvöspinel intergrowth to be described in the literature by heat treatment at 600° C. *in vacuo*, to yield a spinel with $a = 8.43 \text{ \AA}$.

Materials and methods.

Titaniferous magnetites from coarse-grained igneous rocks were chosen for the present work, mainly because the exsolution of the various phases is complete or nearly so in such materials, which represent a close approach to the attainment of equilibrium conditions during crystallization and subsequent cooling.

Detailed experiments have been carried out with four samples, and a few observations made with five others. Three of the samples (designated C.S.L. 2, 3, and 5) are from titaniferous magnetite bodies (associated with Precambrian anorthosites) at Schmoor Lake, near Lac la Blanche, Comté du Saguenay, Quebec, Canada, kindly provided by Dr. J. P. Girault, who has already published a brief description of them (Girault, 1953), while the remainder (designated by E.G. nos.) are from the Skaergaard intrusion, East Greenland, kindly provided by Prof. L. R. Wager.

The magnetites for study were selected first on the basis of microscopic examination, and practically pure samples (better than 99.5% as checked microscopically) of grains passing 120-mesh bolting cloth were prepared chiefly by means of an A.C. electromagnet and simple elutriation.

Complete chemical analyses were made (table I), the overall compositions of the materials being plotted on the conventional Fe-Ti oxide triangular diagram (fig. 1), in which MgO, MnO, and CaO are added to

TABLE I. Chemical analyses of titaniferous magnetites.

Analysis no.	1.	2.	3.	4.	5.	6.	7.	8.	9.	
Sample no.	E.G. 2308.	C.S.L. 2.	E.G. 4359.	E.G. 2569.	C.S.L. 3.	E.G. 4355.	C.S.L. 5.	E.G. 4353.	E.G. 4430.	
<i>Weight %</i>										
MO	FeO ...	46.06	45.04	34.13	41.09	43.36	40.11	33.79	39.8	36.6
	MgO ...	2.29	3.61	1.84	1.05	2.58	2.34	1.49	0.9*	0.5*
	MnO ...	0.33	0.36	0.37	0.45	0.40	0.37	0.28	0.4*	0.4*
	CaO ...	0.06	0.13	0.49	0.15	0.20	0.40	0.20	0.7	0.7
R ₂ O ₃	Fe ₂ O ₃ ...	23.37	25.82	40.70	32.38	29.28	36.86	51.68	36.8	41.7
	Al ₂ O ₃ ...	1.39	2.70	2.54	2.98	2.28	2.77	2.91	3.1*	2.7*
	V ₂ O ₅ ...	1.97	0.42	1.52	0.40	0.48	0.64	0.58	2.1*	1.1*
TO ₂	Cr ₂ O ₃ ...	0.07	0.26	0.03	0.00	0.22	0.05	0.13	—*	—*
	TiO ₂ ...	19.42	21.87	18.55	21.17	21.31	16.56	9.36	15.6	15.3
	SiO ₂ ...	0.10	0.04	0.05	n.d.	0.03	0.08	0.05	0.1*	0.2*
	Total ...	100.06	100.25	100.22	99.67	100.14	100.18	100.47	99.5	99.2
<i>Molecular proportions</i>										
MO	...	61.0	60.8	50.6	54.8	58.6	57.1	52.0	55.6	52.5
R ₂ O ₃	...	17.8	16.2	27.4	21.2	18.2	23.9	36.1	25.9	28.6
TO ₂	...	21.2	23.0	22.0	24.0	23.2	19.0	11.9	18.5	18.9

Analysts: E. A. Vincent and J. B. Wright. Spectrographic determinations (*) in nos. 8 and 9 by S. R. Taylor.

Note: The analyses given above for E.G. 2308 and E.G. 2569 refer to completely new samples of these magnetites (in the case of E.G. 2569 separated from a different hand specimen), and differ slightly from those previously published (Vincent and Phillips, 1954, table 2) under the same sample numbers.

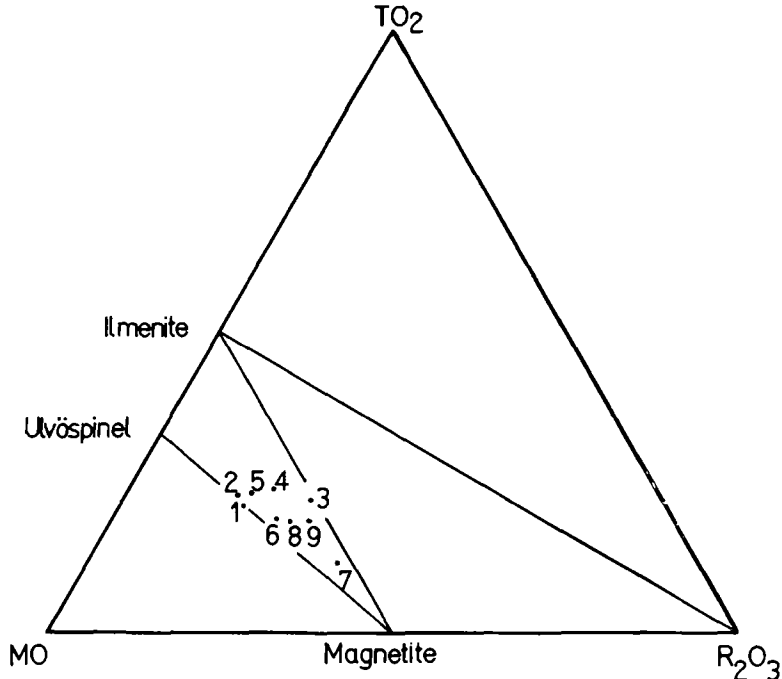


FIG. 1. Molecular composition of analysed titaniferous magnetites. MO = FeO + MgO + MnO + CaO; R₂O₃ = Fe₂O₃ + Al₂O₃ + V₂O₅ + Cr₂O₃; TO₂ = TiO₂ + SiO₂. The numbers refer to analyses in table I.

FeO; Al₂O₃, Cr₂O₃, and V₂O₃ are added to Fe₂O₃; and SiO₂ is added to TiO₂. Two of the titaniferous magnetites studied in some detail (C.S.L. 2 and E.G. 2308) lie almost precisely in the Fe₃O₄-Fe₂TiO₄ binary join; a

TABLE II. Normative compositions of titaniferous magnetites.

	1. E.G. 2308.	2. C.S.L. 2.	3. E.G. 4359.	4. E.G. 2569.	5. C.S.L. 3.	6. E.G. 4355.	7. C.S.L. 5.	8. E.G. 4353.	9. E.G. 4430.
Weight %:									
<i>Magnetite, &c.</i>									
FeO. Fe ₂ O ₃ ...	37.43	32.34	52.36	44.42	37.80	47.37	68.12	50.3	57.6
MgO. Fe ₂ O ₃ ...	2.86	3.99	4.33	1.75	3.46	4.25	4.64	1.8	1.2
MnO. Fe ₂ O ₃ ...	0.28	0.25	0.58	0.48	0.35	0.44	0.55	0.5	0.7
CaO. Fe ₂ O ₃ ...	0.06	0.11	0.88	0.19	0.22	0.56	0.50	0.9	1.1
FeO. Al ₂ O ₃ ...	2.15	3.99	3.83	4.80	3.48	4.20	4.50	4.9	4.4
MgO. Al ₂ O ₃ ...	0.16	0.47	0.30	0.17	0.30	0.36	0.28	0.1	0.1
MnO. Al ₂ O ₃ ...	0.02	0.03	0.03	0.05	0.03	0.03	0.03	0.2	—
CaO. Al ₂ O ₃ ...	—	0.02	0.06	0.02	0.02	0.05	0.03		
FeO. V ₂ O ₃ ...	2.64	0.53	2.00	0.55	0.64	0.84	0.80	2.9	1.6
MgO. V ₂ O ₃ ...	0.21	0.06	0.17	0.02	0.06	0.08	0.06	0.2	—
MnO. V ₂ O ₃ ...	0.02	—	0.02	—	—	0.02	—	—	—
CaO. V ₂ O ₃ ...	—	—	0.02	—	—	—	—	—	—
FeO. Cr ₂ O ₃ ...	0.09	0.34	0.04	—	0.27	0.07	0.18	—	—
MgO. Cr ₂ O ₃ ...	—	0.04	—	—	0.02	—	0.02	—	—
	45.92	42.17	64.62	52.45	46.65	58.27	79.71	61.8	66.7
<i>Ulvöspinel, &c.</i>									
2FeO. TiO ₂ ...	49.82	49.59	2.26	22.66	39.64	31.17	8.12	24.9	10.9
2MgO. TiO ₂ ...	3.18	5.09	0.16	0.74	3.02	2.32	0.47	0.6	0.2
2MnO. TiO ₂ ...	0.35	0.40	0.02	0.24	0.38	0.29	0.07	0.8	0.2
2CaO. TiO ₂ ...	0.08	0.15	0.04	0.10	0.21	0.35	0.06		
	53.43	55.23	2.48	23.74	43.25	34.13	8.72	26.3	11.5
<i>Ilmenite, &c.</i>									
FeO. TiO ₂ ...	—	2.31	29.83	22.65	9.19	6.90	10.74	11.2	20.7
MgO. TiO ₂ ...	—	0.26	2.26	0.82	0.77	0.56	0.67	0.3	0.5
MnO. TiO ₂ ...	—	0.02	0.32	0.24	0.09	0.06	0.09	0.3	0.2
CaO. TiO ₂ ...	—	0.01	0.49	0.10	0.05	0.08	0.07		
	—	2.60	32.90	23.81	10.10	7.60	11.57	11.8	21.8
Excess MO group	0.65	—	—	—	—	—	—	—	—
Limiting weight:									
% of Fe ₃ O ₄ ...	41.13	37.44	59.01	46.95	42.45	53.44	74.93	53.4	60.46
Molecular percentages:									
Magnetite, &c. ...	44.62	41.24	55.45	46.95	44.02	55.72	75.16	58.3	60.2
Ulvöspinel, &c. ...	53.34	54.97	2.18	21.46	41.74	33.39	8.42	25.2	10.5
Ilmenite, &c. ...	—	3.79	42.37	31.59	14.24	10.89	16.42	16.5	29.3
Excess MO group	2.04	—	—	—	—	—	—	—	—

third, E.G. 4359, lies almost precisely in the Fe₃O₄-FeTiO₃ binary join; while the fourth, E.G. 2569, lies in the field between the two principal series.

Normative mineralogical compositions have been calculated from the analyses (table II), the present norms (devised by Chevallier) differing from those previously published by one of us (Vincent and Phillips, 1954)

in that redistribution of the oxide molecules of the analysis is now made strictly according to their various molecular proportions, and not so arbitrarily. For instance, we assume that all the sesquioxides of the analysis enter into spinels of the type $MO.R_2O_3$. The group MO comprises FeO , MgO , MnO , and CaO in various proportions, while R_2O_3 comprises Fe_2O_3 , Al_2O_3 , V_2O_3 , and Cr_2O_3 . We calculate the fraction of molecules of the MO group that consists of FeO , and we combine this fraction with each of the R_2O_3 type molecules in turn, repeating the process with MgO , MnO , and CaO , until all the R_2O_3 group is combined with MO in spinel molecules. MO remaining is then similarly combined with TO_2 (TiO_2+SiO_2) by means of simultaneous equations in appropriate amounts to balance in the molecules $2MO.TO_2$ (ulvöspinel) and $MO.TO_2$ (ilmenite). The various constituents of the MO group are allotted proportionally in the same way as before.

Since our measurements of magnetic constants are on a weight basis, a detailed weight percentage norm, rounded off to 100 %, is given in table II as well as the totals of the main mineralogical groups in the molecular percentage norm. The table also gives a 'limiting' weight percentage of Fe_3O_4 for each sample, which would apply if all Fe_2O_3 in the analysis were present in the Fe_3O_4 molecule, which is probably the case in the materials that have been completely homogenized by heating.

For the heating experiments at temperatures up to $950^\circ C$. about 100 mg. portions of the purified samples were sealed under vacuum (around 10^{-5} cm. Hg) in transparent silica ampoules, with as little free space as possible. The ampoules were packed in sand in crucibles, placed in an ordinary muffle furnace with temperature control and pyrometer, and after heating for the required time were quenched by dropping into a dish of mercury.

The FeO contents of the heated samples were redetermined, showing in all cases that no significant oxidation or reduction had taken place under the simple experimental conditions adopted.

Small portions of the heated grains were mounted in a transparent cold-setting resin and polished for microscopic examination by reflected light.

Detailed X-ray investigation of the materials has not so far been attempted, but the lattice parameters of some critical samples, before and after heating, were measured by means of a Geiger-counter diffractometer, using filtered iron radiation.

Samples of unheated and heated grains were examined magnetically at Nancy, the constants determined being the value of the specific

saturation magnetization (per gram) of the sample at room temperature ($\sigma'_{\infty-20^{\circ}\text{C.}}$), and the Curie point ($\theta^{\circ}\text{C.}$). The symbol σ_{∞} is reserved to denote the specific saturation magnetization (per gram) of a *homogeneous* titanomagnetite solid solution, and is used in this sense later in the paper. The methods used have been described previously (Chevallier and Pierre, 1932; Chevallier and Mathieu, 1943; Chevallier, Bolfa, and Mathieu, 1955). The Curie temperature is derived from a photographic record of the change in magnetic moment of the sample with temperature, made with a thermomagnetic balance in a fairly small field. The profiles of these thermomagnetic curves can be analysed only qualitatively, but the Curie temperatures, where sharp, can be estimated with some accuracy.

Magnetite-ulvöspinel intergrowths.

These are structurally the simplest type of unmixed titaniferous magnetite, both phases being inverse spinels, and may be expected to show the simplest relationships during homogenization.

The two samples studied that lie to all intents and purposes in this binary series (E.G. 2308 and C.S.L. 2) are very similar in bulk chemical composition (tables I and II; fig. 1). Normative recalculation shows a slight excess of the *MO* group in E.G. 2308, and a slight excess of ilmenite in C.S.L. 2. Under the microscope both samples are seen at high magnification in oil to consist of a cloth-like intergrowth of magnetite and ulvöspinel, the ulvöspinel being arranged roughly parallel to $\{100\}$ and $\{110\}$ of the magnetite. In both samples a very occasional fine lamella (parallel $\{111\}$) or granule of ilmenite enclosed in the magnetite is visible. Irregular spindles of a transparent spinel, also arranged parallel to the cube face of the magnetite, are quite abundant in C.S.L. 2, but are not seen in E.G. 2308. They are often enclosed within the 'boxes' formed by the ulvöspinel lamellae, possibly indicating exsolution at an earlier stage in the cooling of the mineral.

The chief difference between the two samples lies in the size of the exsolution bodies of ulvöspinel. The intergrowth is very clearly visible at a magnification of about $\times 1000$ in C.S.L. 2, where it is exceptionally coarse, the rough lamellae of ulvöspinel being around 1 to 2 μ in width (fig. 2), while in E.G. 2308 the scale is finer, individual lamellae measuring 0.25 μ in average width.

The changes in texture on heating at various temperatures are shown for C.S.L. 2 in fig. 2; although the re-solution proceeds rather more readily in the finer-grained E.G. 2308, it was found impossible to

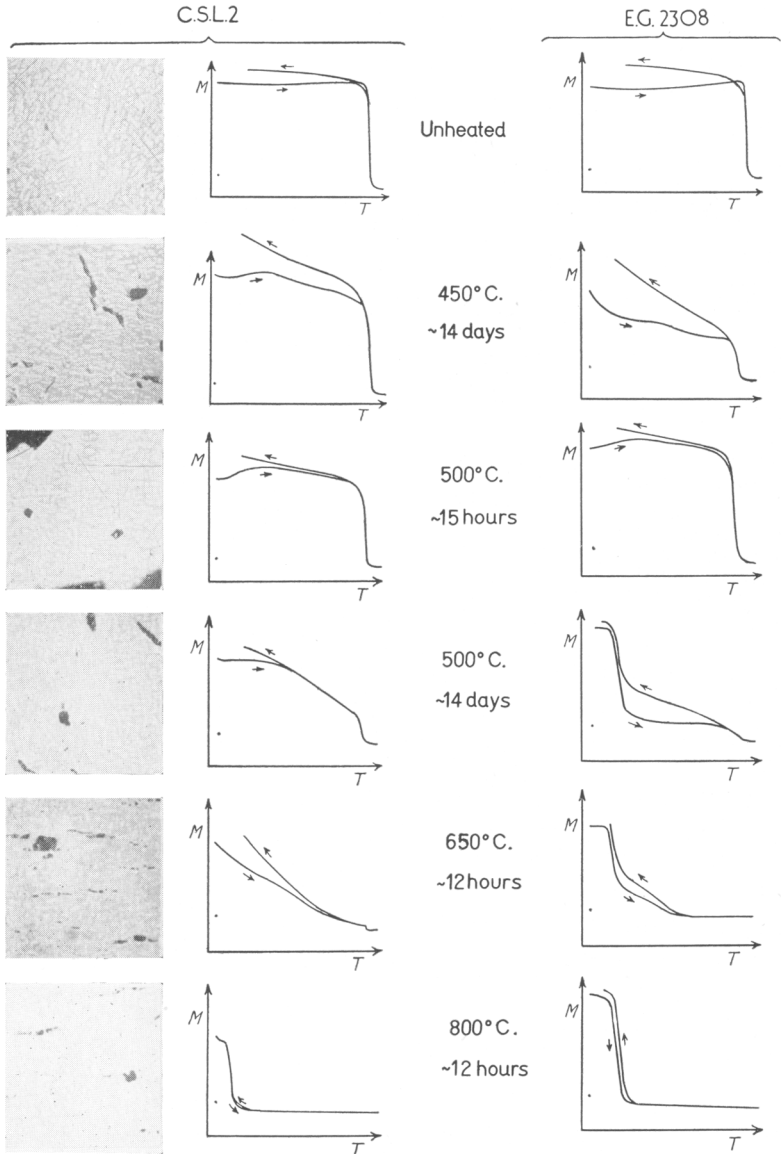


FIG. 2. Photomicrographs ($\times 420$, reflected light) and tracings of thermomagnetic curves of heated magnetite-ulvöspinel intergrowths.

produce satisfactory photomicrographs of the latter. The changes observed microscopically in both samples are, however, identical.

Heating for 15 hours at 500° C. causes little observable change, but heating for 14 days at 450° C. causes a general softening of the appearance of the intergrowth, and the areas of the darker ulvöspinel can be

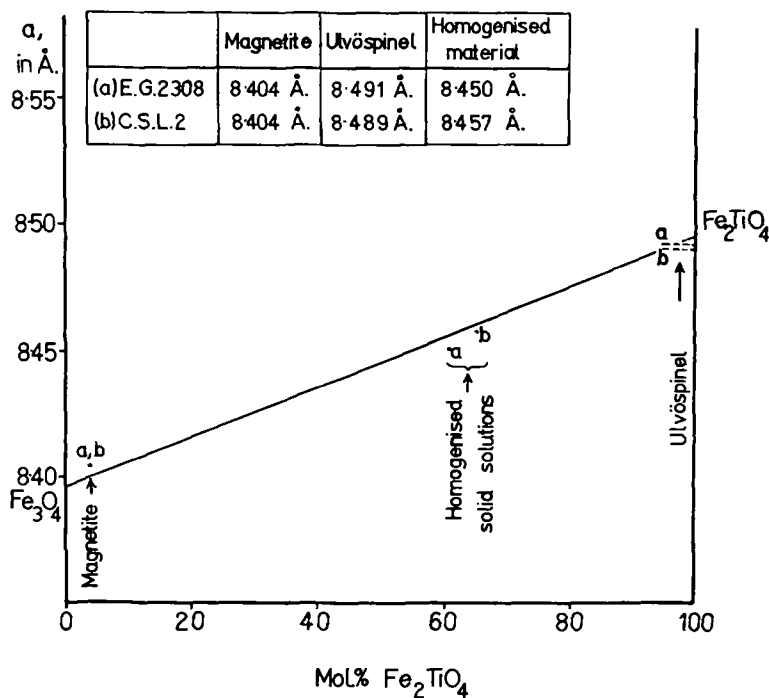


FIG. 3. Cell-dimensions of unheated and heated magnetite-ulvöspinel intergrowths.

seen to have grown slightly at the expense of the lighter magnetite. This continues on heating at 500° C. for 14 days, and at 550° C. and 650° C. for 12–17 hours. After heating at 800° C. for 12 hours, mutual solution of the magnetite and ulvöspinel can be seen to be complete, although rods of transparent spinel remain; these latter mostly disappear after treatment for 16 hours at 950° C.

The unit-cell dimensions determined for the unheated and homogenized samples are shown in fig. 3. The diffraction peaks measured on the unheated samples are broadened, particularly in the case of ulvöspinel, probably owing to strains set up in the lattices during the original separation of the mineral into two phases. The homogenized

samples yield quite sharp peaks, so that the probable error of the cell-edge determination in these cases is less than ± 0.001 Å.; in the case of the phases before heating, where the diffraction profiles had to be analysed geometrically to find the true position of the $K\alpha_1$ peak, the probable error for the magnetite is about ± 0.002 Å., for ulvöspinel ± 0.005 Å.

The compositions of the samples plotted in fig. 3 require explanation. The measured Curie points for the unheated samples are a little lower than for pure magnetite, indicating that about 4 % of some material remains in solid solution; this material seems most likely to be ulvöspinel. The compositions of the homogenized solid solutions are taken as the molecular proportions of Fe_3O_4 and Fe_2TiO_4 appearing in the normative recalculation of the analyses, reduced to a percentage and ignoring other molecules appearing in the norm. The ulvöspinel phase in fig. 3 has been indicated with a broken line near 100 % Fe_2TiO_4 , since it almost certainly in its turn contains some Fe_3O_4 in solid solution; in view of the chemical complexity of the samples, an attempt to calculate the composition of the ulvöspinel phase more precisely might be misleading. A straight line has been drawn between 8.396 Å., the cell edge for pure magnetite as determined by Basta (1953), and 8.495 Å., the mean of the values given for Fe_2TiO_4 by Barth and Posnjak (1932; 8.50 Å.) and by Ernst (1943; 8.49 Å.). Our determinations for unheated and homogenized materials fall fairly close to this line, indicating agreement with Végard's mixture law.

Our cell-dimensions for the magnetite phases of both unheated samples are rather larger than that of pure magnetite; this could be due to some Fe_2TiO_4 remaining in solid solution. Our values for ulvöspinel are in close agreement with those of Ernst and of Barth and Posnjak for synthetic material, and lower than Pouillard's (1950) value of 8.534 Å. It may be noted that Pouillard's value for magnetite (8.413 Å.) is also high (see also Nicholls, 1955, p. 132). Precise correlation between cell-dimensions and compositions of our samples is hardly to be expected, since the manner of distribution of ions other than Fe^{2+} , Fe^{3+} , and Ti^{4+} in the various lattices cannot be determined; this is the reason why we have adopted a form of normative recalculation of the analyses in which the minor elements are not assigned preferentially to any particular phase.

For each heated sample the saturation magnetization has been measured and a thermomagnetic curve recorded. Accurate tracings of some of the latter are reproduced in fig. 2. In each diagram the ordinate represents a non-linear scale of magnetic moment (not necessarily

precisely the same for each sample) and the abscissa the temperature scale. The spot in each tracing marks the position of the light spot of the thermomagnetic balance (Chevallier *et al.*, 1955, p. 357) before the sample was heated: it thus represents a temperature of about 20° C. The far ends of the traces represent a temperature of 620° C. Small arrows indicate the profiles of the thermomagnetic curves obtained on heating and then cooling the samples; the traces for temperatures below the Curie point are generally not coincident, due to thermoremanence.

TABLE III. Magnetite-ulvöspinel intergrowths: magnetic constants of heated samples. σ'_{∞} is given for 20° C., in electromagnetic units per gram.

Heated, ° C.	Original sample (unheated)	450	450	450	500	500	545	650	800	950
hrs.		12	336	504	15	336	12	12	12	16
C.S.L. 2										
θ° C.	563	562	558	—	557	550	—	*	80	80
σ'_{∞}	32.8	28.8	21.3	—	21.2	17.0	—	16.4	17.8	17.2
E.G. 2308										
θ° C.	562	550	546	550	552	*	*	*	130	130
σ'_{∞}	35.0	30.3	21.5	21.4	21.3	23.1	23.0	23.1	22.4	21.9

* indicates that the heated sample did not show a sharp Curie point.

The thermomagnetic curves of the unheated samples show a sharp Curie point at 563° C. (fig. 2; table III). Using the curve constructed by Chevallier *et al.* (1955, p. 364), relating Fe_3O_4 content with Curie point in homogeneous titanomagnetites, we may deduce that the magnetic spinel phase of the unheated complex titaniferous magnetite contains about 96 % Fe_3O_4 , the 4 % of material remaining in solid solution being probably ulvöspinel (Chevallier, Mathieu, and Vincent, 1954, pp. 30–31).

In samples heat-treated at temperatures up to 500° C. there is little change in the Curie point, which falls only to around 550° C. as can be seen from the curves in fig. 2. The *composition* of the ferromagnetic spinel phase thus changes but little on heating at moderate temperatures; the slight lowering of the Curie point indicates that about 3 % more ulvöspinel re-enters into solid solution.

The specific saturation magnetization (σ'_{∞}) is also a direct function of the Fe_3O_4 content in a homogeneous ferromagnetic spinel phase (Chevallier *et al.*, 1955, pp. 360–1). This parameter, unlike the Curie point, falls rapidly in the early stages of the heating process and then attains a constant value¹ (table III). Since the composition of the mag-

¹ A physical explanation of this phenomenon will be given in a further paper in the course of preparation by R. Chevallier.

netic phase changes very little at first, this initial drop in the saturation magnetization indicates a decrease in the *quantity* of the magnetic phase, which thus clearly begins to redissolve in the ulvöspinel, even at 450° C., the lowest temperature at which we have made experiments.

The thermomagnetic curves of C.S.L. 2 show the persistence of a limiting Curie point at about 550° C. in samples heated up to 650° C.; in E.G. 2308 up to 550° C. The profiles of the curves change steadily, however, and the presence in the samples of grains in varying stages of homogenization gives rise to long sloping portions on the traces (fig. 2). Changes in the profiles are seen more clearly and at lower temperatures of heating in E.G. 2308 than in C.S.L. 2; this is because the intergrowth of magnetite and ulvöspinel is very much finer in the former material, so that homogenization proceeds more rapidly. The equivalent effects of time and of temperature in the homogenization process are clearly shown by the curves for E.G. 2308 heated for 14 days at 500° C., and for 12 hours at 550° C. (not shown in fig. 2) which are practically identical, and not very different from that for 12 hours heating at 650° C. Further, the changes in thermomagnetic curve and in microscopic texture in samples of both materials heated at 500° C. first for 15 hours and then for 14 days are most striking.

The curve of E.G. 2308 heated for 14 days at 500° C. (fig. 2), while still showing a remnant of the original high Curie point, also shows clearly the low Curie point of the final solid solution; the thermomagnetic curve for a further sample heated for 3 weeks at 525° C. shows it to be sensibly homogeneous. If heated for long enough, even at 450°, the material would probably yield a curve identical with that of the samples heated at 800° C. and 950° C., where there is a single sharp Curie point at 130° C., representing the final spinel solid solution. C.S.L. 2 behaves similarly, but the homogenization proceeds more slowly.

The profiles of the thermomagnetic curves thus lend graphic expression to the process of homogenization in the Fe_3O_4 - Fe_2TiO_4 series. We may envisage that, as heating progresses, magnetite begins to dissolve in the ulvöspinel without itself taking much Fe_2TiO_4 into solid solution. A more or less heterogeneous mixture is thus formed, the Curie points of individual grains in which vary between that of magnetite and that of the final metastable solid solution. As long as any of the initial magnetite is left, the drop at 550° C. in the thermomagnetic curve will persist; when the last of the magnetite is dissolved this drop disappears; then, as the solid solutions in the various grains approach homogeneity,

the residual part of the curve gradually vanishes and we are finally left with the sharp drop of the final homogeneous solution.

The possible form of solvus in the Fe_3O_4 - Fe_2TiO_4 binary system has been discussed by Phillips (Vincent and Phillips, 1954) who, from an examination of microscopic textures, considers that magnetite and ulvöspinel probably form a sub-solidus eutectic; and by Kawai, Kume, and Sasajima (1954) and Kawai (1956), who, on the basis of some heating experiments and magnetic measurements, propose a simple hoop-shaped

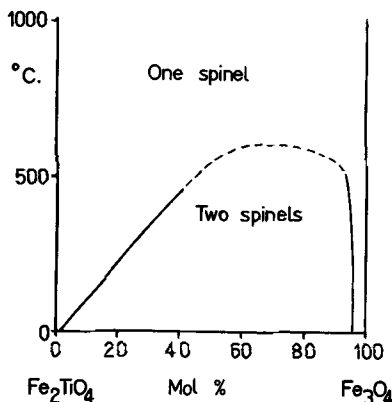


FIG. 4. Possible form of the solvus in the Fe_3O_4 - Fe_2TiO_4 binary series.

unmixing curve of the type found in the alkali feldspars. The present authors consider there is no real evidence for a eutectic, and prefer for the present to accept the interpretation of the Japanese workers.

Our clear observation, from magnetic measurements and microscopic examination, that magnetite dissolves in ulvöspinel on heating without itself taking much ulvöspinel into solution, leads us to modify somewhat the shape of curve from that proposed by Kawai *et al.* In fig. 4 the limb

of the solvus at the Fe_3O_4 end of the diagram leaves the composition abscissa at about 96% Fe_3O_4 ($\theta = 563^\circ \text{C.}$) at room temperature and rises steeply, passing through 93% Fe_3O_4 ($\theta = 550^\circ$) at about 500°C. The other limb of the curve is also drawn starting a little on the Fe_3O_4 side of pure Fe_2TiO_4 : we have no direct evidence for this, except perhaps the very slightly lower cell-dimensions of our ulvöspinel as compared with published values for the pure synthetic material. Kawai *et al.* (1954) put the crest of their solvus at about 37 mol. % Fe_2TiO_4 and 750°C. ; Kawai's (1956) diagram shows the crest temperature at 600°C. , but he does not comment on this discrepancy. In fig. 4 we have adopted Kawai's later value. The two materials we have investigated both contain around 60–65 mol. % Fe_2TiO_4 and 40–35 mol. % Fe_3O_4 (ignoring minor constituents) and would almost certainly homogenize completely at about 450°C. , if heated long enough. The solvus limb has therefore been sketched to pass through a temperature of about 450°C. at this composition.

A sample of C.S.L. 2, previously homogenized by heating at 800° C., was subsequently held at 300° C. for 6 weeks, to see whether any unmixing of the magnetite and ulvöspinel phases could be brought about. However, no significant change could be observed in the magnetic constants after this treatment, and X-ray diffractometer measurements confirmed that no unmixing whatever had taken place.

Magnetite-ilmenite intergrowths.

Only one sample (E.G. 4359) falling practically in the magnetite-ilmenite binary series has been studied in detail (analysis no. 3 in tables I and II and fig. 1).

This particular intergrowth of magnetite and ilmenite is on an extremely fine scale for the most part (fig. 5) and details of the texture are difficult to resolve with the microscope even at the highest magnifications. The majority of grains only carry ilmenite lamellae of such minute width that individual lamellae are not easily discernible, but a few of the magnetite grains also carry relatively broad ilmenite lamellae arranged along the usual octahedral directions. The reason for exsolution of ilmenite on such a fine scale in some magnetites is not entirely clear; it may sometimes be a matter of rapid cooling, or sometimes a matter of direct oxidation from already exsolved ulvöspinel (see also Ramdohr, 1953). In any event it is interesting to note in passing that such finely exsolved ilmenite in magnetite is a feature observed in most of the Skaergaard Middle Gabbros so far examined—rocks in which textural and other mineralogical evidence does not necessarily imply rapid cooling (see, for example, Brown, 1957). The magnetite grains of E.G. 4359 also carry myriads of minute transparent spinel grains, evenly distributed except where they form a beaded edge to large ilmenite lamellae. Their total bulk relative to the magnetite is small.

E.G. 4359 was selected for heating experiments because it was thought that its very fine scale of exsolution might facilitate the attainment of homogenization; this proved not to be the case, and its behaviour on heating is totally different from that of the magnetite-ulvöspinel intergrowths described above. Little or no change in the texture was discernible in samples heated at temperatures up to 600° C. for 12 hours. A sample heated for 12 hours at 750° C., however, showed that the rhombohedral lamellae had increased in width and organization, now showing clearly their relation to the octahedral planes of the magnetite (fig. 5). At the same time the reflectivity of the lamellae increased and they appeared whiter, though retaining reflection pleochroism; the magnetite,

E.G.4359

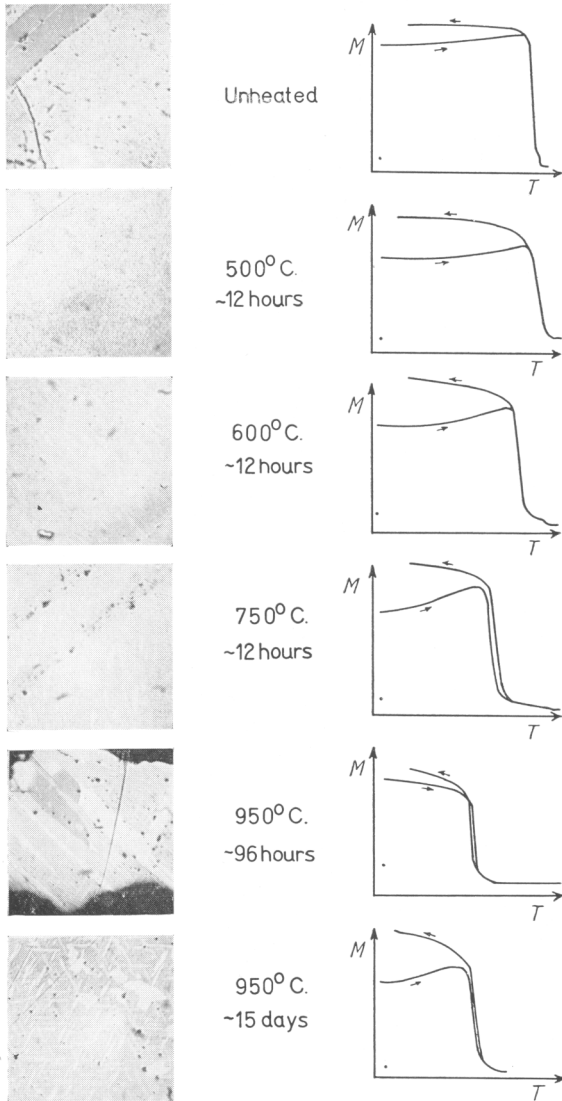


FIG. 5. Photomicrographs ($\times 420$, reflected light) and tracings of thermomagnetic curves of heated magnetite-ilmenite intergrowth E.G. 4359. (The photomicrograph of a grain heated for 96 hours at 950° C. shows the very rare development of (darker) pseudobrookite at the expense of portions of the ferri-ilmenite lamellae.)

on the contrary, appeared darker in tint. Similar features were observed by Ramdohr (1926) in his experiments with a Taberg magnetite, and interpreted qualitatively (Ramdohr, 1955, p. 137) in terms of migration of Fe_2O_3 from the spinel phase into the rhombohedral lamellae.

A sample of E.G. 4359 heated for 96 hours at 950°C . shows the process to have gone farther, the lamellae decreasing in area and beginning to resemble hematite in appearance. Heating for 3 weeks at 950°C . brought about no change in bulk chemical composition, but still failed to produce a homogeneous solid solution. The authors conclude that a reaction relationship exists between magnetite and ilmenite, so that on heating, the original lamellae of ilmenite change in composition towards hematite, and members of the $\text{FeTiO}_3\text{-Fe}_2\text{O}_3$ series of rhombohedral solid solutions are produced; the X-ray and magnetic measurements also support such an interpretation of the optical changes.

Attempts at homogenizing this sample by heating at high temperatures without change in bulk composition have so far failed. A sample heated at $1250\text{-}1300^\circ\text{C}$. for 5 hours in an evacuated silica ampoule showed slight oxidation; rhombohedral lamellae were still present, and patches of pseudobrookite were developed. Indeed, this latter phase has been observed very occasionally in samples heated at 950°C . for 96 hours, where it has been produced in the lamellae at the expense of the ilmenite-hematite solid solution (fig. 5); Ramdohr (1955, p. 785) has drawn attention to the spontaneous dissociation of ilmenite-hematite materials into pseudobrookite and magnetite on heating above 1100°C . As far as the authors are aware, none of the reports of successful homogenization of magnetite-ilmenite intergrowths in the literature confirm that the bulk composition of the samples remained unchanged.

The measured value of the cube edge of the magnetite component in the original unheated material agrees exactly with Basta's (1953) value for pure natural Fe_3O_4 , and is slightly smaller than the values obtained for the magnetite component of the magnetite-ulvöspinel intergrowths described above:

	Magnetic spinel phase.	Non-magnetic rhombohedral phase.		
		a , Å	a , Å.	c , Å. c/a
Unheated sample ...	8.396 ± 0.002	5.088 ± 0.001	14.092 ± 0.002	2.770
Heated 96 hours at 950°C	8.410 ± 0.001	5.068 ± 0.001	13.92 ± 0.01	2.749

The parameters a , c , and c/a (referred to the hexagonal cell) for the

ilmenite lamellae are all higher than the values generally quoted in the literature, of which Basta's (1953; see fig. 6) are typical. Our measurements have been repeated and thoroughly checked, but we can find no

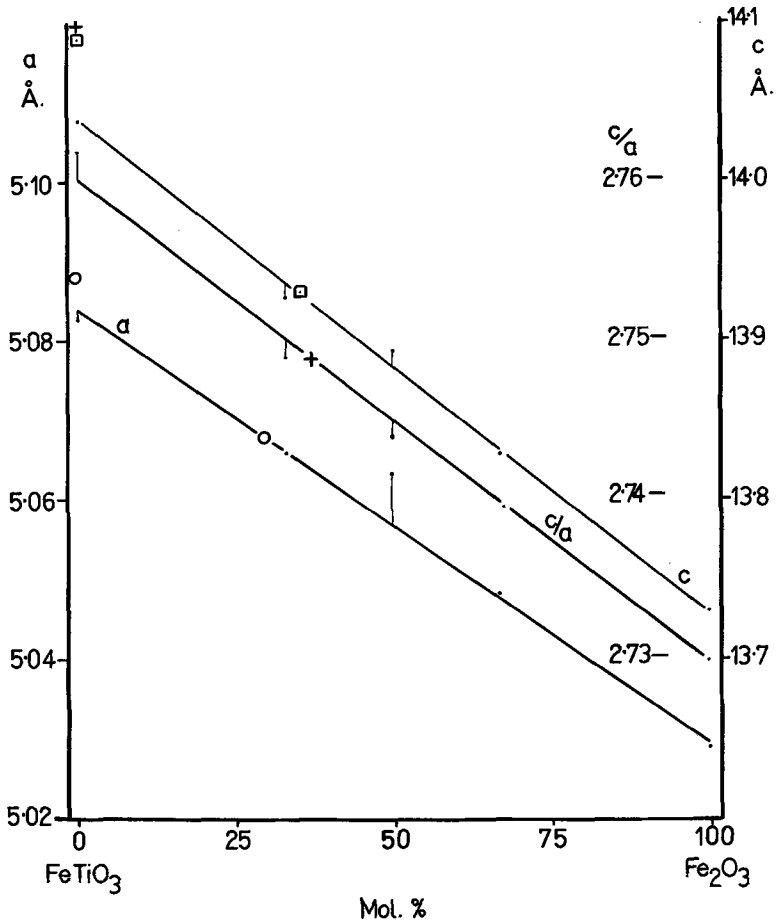


FIG. 6. Basta's (1953) lattice parameters (.) for α -FeTiO₃- α -Fe₂O₃ solid solutions. Parameters for rhombohedral phase of E.G. 4359, unheated, and heated for 96 hours at 950° C. inserted: ○ a; □ c; + c/a.

reason to change our values; Dr. R. St. J. Lambert (personal communication) informs us that he has obtained values very similar to ours for an ilmenite containing about 5 % Al₂O₃, but otherwise unremarkable in its composition. A possible reason for our high values might be that

most of the Mg and Mn revealed in the analysis of this ilmenomagnetite is concentrated in the ilmenite lamellae, since MgTiO_3 and particularly MnTiO_3 are generally reported to have rather larger cell-dimensions than FeTiO_3 . There is no direct evidence for this, but it was observed previously (Vincent and Phillips, 1954) that these two elements were significantly concentrated in discrete ilmenite crystals as compared with the accompanying ilmenomagnetite in rocks of the Skaergaard intrusion.

After heating for 96 hours at 950°C . the parameters of the rhombohedral phase have all fallen significantly, consistent with the entry of $\alpha\text{-Fe}_2\text{O}_3$ into solid solution. Such a decrease in lattice parameters of the rhombohedral component of a heated ilmenomagnetite was also observed by Basta (1953), who further gives values for the cell-dimensions of three solid solutions intermediate between FeTiO_3 and $\alpha\text{-Fe}_2\text{O}_3$ (quoted in Nicholls, 1955, p. 137). Basta's figures are plotted in fig. 6, where straight lines have been drawn to indicate the approximate variation in parameter with composition. The values of a , c , and c/a for original and heated samples of E.G. 4359 have been added; the parameters for the heated sample have been placed on the straight lines through Basta's points. The compositions of the final rhombohedral solid solution to be deduced from each parameter are in fair agreement, but some of Basta's points in this part of the series are somewhat aberrant (see fig. 6), so that the positions of the lines relating parameters with molecular composition are none too well defined. We may at least say that our observed parameters in the heated sample are consistent with a ferri-ilmenite carrying between 30 and 40 % Fe_2O_3 in solid solution.

We cannot be sure that it is strictly valid to refer our observed lattice parameters to the lines drawn through Basta's points, since our original ilmenite has a larger cell than his. On heating the sample, the reaction $\text{Fe}_3\text{O}_4 + \text{FeTiO}_3 \rightarrow \text{Fe}_2\text{O}_3 + \text{Fe}_2\text{TiO}_4$ proceeds to some extent, and it may be that any Mg or Mn replacing Fe" in the ilmenite tends to react to form an ulvöspinel-type 'molecule' before the iron. In this way, the solid solution with Fe_2O_3 may approach Basta's line more closely as reaction progresses.

The cubic magnetic spinel phase arrived at concurrently on heating for 96 hours at 950°C . gives a value $a = 8.410 \pm 0.002 \text{ \AA}$. for the cube edge, as against $8.396 \pm 0.002 \text{ \AA}$. for the unheated material.

Nicholls (1955, p. 149), in the course of an excellent theoretical discussion of the phase-change relationships during unmixing of a homogeneous crystal in the $\text{Fe}_3\text{O}_4\text{-FeTiO}_3$ series, points out that attempts

to rehomogenize magnetite-ilmenite intergrowths are unlikely to succeed because 'the solid solutions from which the intergrowths formed are probably metastable intermediates between magnetite and a cubic form of FeTiO_3 ($\gamma\text{-FeTiO}_3$) which cannot be produced by heating rhombohedral FeTiO_3 (ilmenite)'. Mason's (1943) discussion of the monotropic nature of the hematite-maghemite inversion should also be borne in mind in this connexion.

The possible existence of a spinellid form of FeTiO_3 , having a defect lattice structure analogous with that of maghemite, $\gamma\text{-Fe}_2\text{O}_3$, has occurred to various mineralogists interested in the iron-titanium oxides, but only recently have any firm proposals been put forward for its possible structure (Chevallier, Bolfa, and Mathieu, 1955; Nicholls, 1955), and it has not yet been found in nature¹ or prepared synthetically. It may be that $\gamma\text{-FeTiO}_3$ can have no stable independent existence, but may be regarded only as entering into solid solution with magnetite over an extensive compositional range at high temperatures. Chevallier *et al.* and Nicholls discuss its possible structure in view of the magnetic properties of its solid solutions with magnetite, but unfortunately little precise X-ray data are available for such solid solutions. Chevallier and Girard (1950) observed that the cell-dimensions of their synthesized cubic $\text{Fe}_3\text{O}_4\text{-FeTiO}_3$ solid solutions appeared very similar to magnetite up to a composition of 37 mol. % FeTiO_3 . Basta (1953) gives the value 8.3475 Å. for the cube edge of a titanomaghemite from the Transvaal, containing 19.45 % TiO_2 . If the homogeneous titanomaghemites are accepted as solid solutions between $\gamma\text{-Fe}_2\text{O}_3$ and $\gamma\text{-FeTiO}_3$, which seems the most feasible structure (Nicholls, 1955, p. 143), Basta's measurement allows us to extrapolate to a cube edge of around 8.39 to 8.40 Å. for $\gamma\text{-FeTiO}_3$, provided that Vegard's mixture law is followed in the series.

The very slight increase in the cell-dimension of the spinel phase in E.G. 4359 on heating at 950° C., as contrasted with the appreciable decrease in the cell-dimensions of the accompanying rhombohedral phase, could thus be visualized as due to a one-way migration of Fe^{2+} , Ti^{4+} , and O^{2-} ions from the lamellae into the spinel host, giving rise to a cubic solid solution between Fe_3O_4 and (γ) FeTiO_3 , at the same time as an exchange of ions ($2\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+} + \text{Ti}^{4+}$) between cubic and rhombohedral phases, which would in effect add some Fe_2TiO_4 to the cubic solid solu-

¹ In an abstract of a paper by I. A. Yudin, Some minerals of meteorites, *Зан. Всесоюз. Мин. Общ.*, 1956, vol. 85, p. 403 [Chem. Abstr. vol. 51, no. 5, 3376], mention is made, however, of 'isometric forms of ilmenite . . . observed in the meteoric iron of Sevryukovo'.

tion. This is doubtless a somewhat artificial picture of the process, but will suffice for our purposes.

Fig. 5 shows that each of the heated samples of E.G. 4359 has a sharp Curie point, falling steadily through the series as the Fe_3O_4 becomes diluted with paramagnetic materials, and a completely homogeneous magnetic spinel phase is produced at every stage of the heating experiments. This is consistent with the mechanism of ionic migration and exchange outlined above, and is in striking contrast to the simple homogenization process in the magnetite-ulvöspinel binary series described earlier (p. 635; fig. 2). At the same time the value of the specific saturation magnetization decreases steadily with heating (table IV; fig. 7), and does not reach a constant value early in the process as it does in the magnetite-ulvöspinel binary series.

Fig. 7 shows saturation magnetization plotted against Curie point for the magnetite-ulvöspinel sample C.S.L. 2 (see p. 634), the magnetite-ilmenite sample E.G. 4359, and the magnetite-ulvöspinel-ilmenite sample E.G. 2569 (p. 649), at the various stages of heat-treatment to which they have been subjected. The difference in profile between the curves for C.S.L. 2 and E.G. 4359 is very striking, while that for E.G. 2569 is of the same form as for C.S.L. 2 until the ulvöspinel has redissolved, when it continues in the form of E.G. 4359 as reaction between spinel and rhombohedral phases take place.

This diagram shows clearly the inherent difficulty in correlating Curie point and saturation magnetization in a titaniferous magnetite unless its mineralogical composition and state of exsolution are accurately known, which can seldom be the case.

Each thermomagnetic curve for E.G. 4359 (fig. 5) shows but a single Curie point; the ferri-ilmenite lamellae produced on heating are thus not of the ferromagnetic type (Chevallier *et al.*, 1955; Nicholls, 1955, pp. 139–141). Hence we may as a first approximation use the Curie point to deduce the proportion (f) of Fe_3O_4 in the magnetic spinel phase at each stage of the heating experiments (Chevallier *et al.*, 1955, p. 364). This proportion of Fe_3O_4 may then be referred to the graph prepared by Chevallier *et al.* (1955, p. 361) connecting Fe_3O_4 content with specific saturation magnetization for homogeneous magnetic spinels. Comparison of this saturation (σ_∞) for the spinel phase with the saturation measured on the total heterogeneous intergrowth (σ'_∞) gives the approximate weight percentage ($100 \sigma'_\infty/\sigma_\infty$) of magnetic spinel. Knowing now the approximate percentage of magnetic spinel in the heated samples and the Fe_3O_4 content of that spinel it is easy to calculate correspondingly the amount of

Fe_2O_3 that must have entered the rhombohedral phase at each stage of the heating, and by difference (knowing that the overall bulk chemical

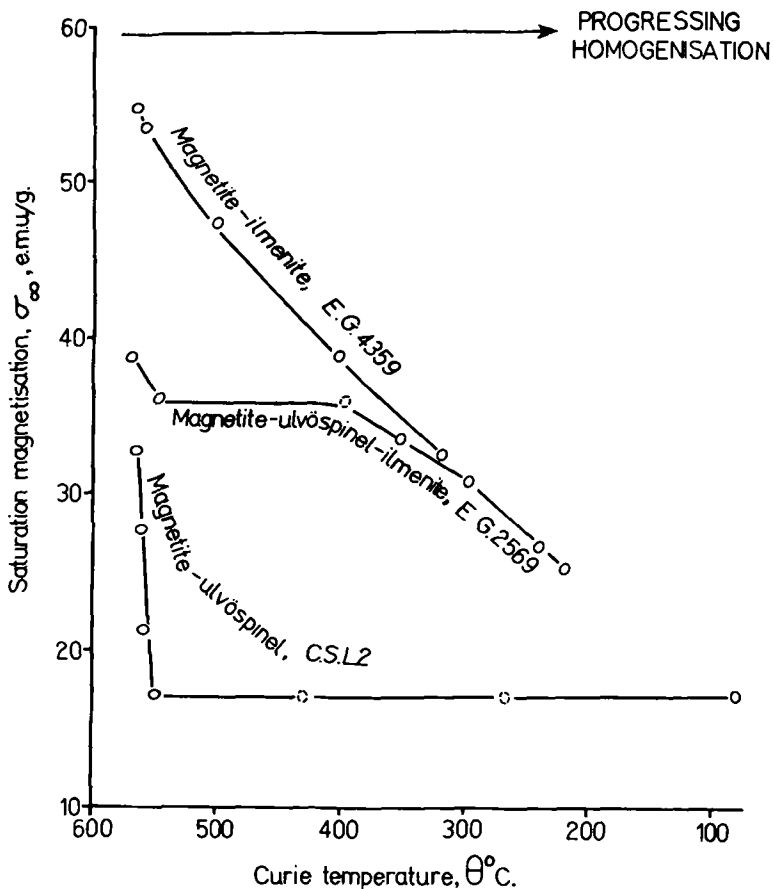


FIG. 7. Saturation magnetization (σ'_{∞}) for unheated and heat-treated samples plotted against Curie point (θ). Note the characteristic differences in profile for the various types of exsolution assemblage. Broken rings indicate that the sample showed no sharp Curie point.

composition of the samples remains unchanged) the composition of the accompanying spinel phase (table IV). In making such calculations the assumption is made that all the ferric ions made available by the reduction in the quantity of Fe_3O_4 in the spinel phase at each stage of heating enter the ilmenite lamellae to yield an $\text{FeTiO}_3\text{-Fe}_2\text{O}_3$ solid solution; this

is borne out by microscopic and X-ray results. It is further assumed, as a simplification, that the ilmenite lamellae in the original unheated sample contained no Fe_2O_3 in solid solution.

Since the specific saturation magnetization is determined on a weighed sample of heterogeneous intergrowth, calculations of this kind are made on a weight percentage basis. The results for the heated samples of

TABLE IV. Magnetite-ilmenite intergrowth, E.G. 4359: magnetic constants of heated samples, and approximate compositions of phases deduced therefrom (weight %). σ'_{∞} and σ_{∞} are given for 20° C., in electromagnetic units per g. The total magnetic phase is taken as 100 $\sigma'_{\infty}/\sigma_{\infty}$. The numbers in column 1 refer to fig. 8.

No.	Heated.		Measured magnetic constants of sample.				Deduced from magnetic constants.				Magnetic spinel phase.			Rhombohedral phase (non-magnetic).		
	° C.	hrs.	θ° C.	σ'_{∞}	f (%)	σ_{∞}	Total.	$M\text{Fe}_2\text{O}_4$		$M_2\text{TiO}_4$	MTiO_3	Total.	MTiO_3		Fe_2O_3	
1	unheated		565	54.8	95.5	89	61.2	58.5	2.5	—	(0.2)	32.7	32.7	—		
2	500	12	557	53.5	94.0	88	60.8	57.1	3.7	—	—	33.1	32.2	0.9		
3	600	12	495	47.5	84.0	74.5	63.7	53.5	7.4	—	2.8	30.2	26.8	3.4		
4	750	12	400	38.8	71.5	56.5	68.7	49.1	11.5	—	8.1	25.2	18.7	6.5		
5	950	96	316	32.8	63.0	44	74.5	47.0	13.7	—	13.8	19.4	11.5	7.9		
	950	360	317	35.0	—	—	—	—	—	—	—	—	—	—		

Note: In order to achieve closer agreement between normative magnetite, &c., and percentage magnetic phase in the unheated material as deduced from magnetic constants, 0.3 % normative other spinels have been added to normative ferrites to give ferrites 58.5 %; ulvöspinel, &c., 2.5 %; ilmenite, &c., 32.9 %; other spinels 6.1 % (cf. table II).

The 6.1 % of other spinels have been ignored in the above table, so that magnetic spinel and non-magnetic rhombohedral phases total 93.9 % in each case.

E.G. 4359, recalculated to molecular percentages, are presented graphically in fig. 8.

The deduced composition 60 % FeTiO_3 , 40 % Fe_2O_3 , for the rhombohedral phase after heating at 950° C. is compatible with the observed decrease in cell-dimensions (fig. 6) as compared with the unheated intergrowth. From its composition the associated spinel (57 % Fe_3O_4 , 26 % FeTiO_3 , 17 % Fe_2TiO_4) might be expected to have a cubic cell edge of about 8.41 Å., the value actually found by measurement, provided the increase above that of magnetite were due to the 17 % of Fe_2TiO_4 taken into solid solution and there were no appreciable change in cell-dimensions in a pure binary solid solution series between Fe_3O_4 and $\gamma\text{-FeTiO}_3$, as suggested above.

Optical, magnetic, and X-ray observations, then, all indicate compositional changes rather as shown in fig. 8 in the two coexisting phases

when an almost pure magnetite-ilmenite intergrowth is heated at temperatures up to 950° C.; it will be noted in table IV that magnetic properties show little appreciable change in samples heated for 4 days and for 15 days at that temperature. In all experiments we have carried out above 950° C. some decomposition of the phases into pseudobrookite and magnetic

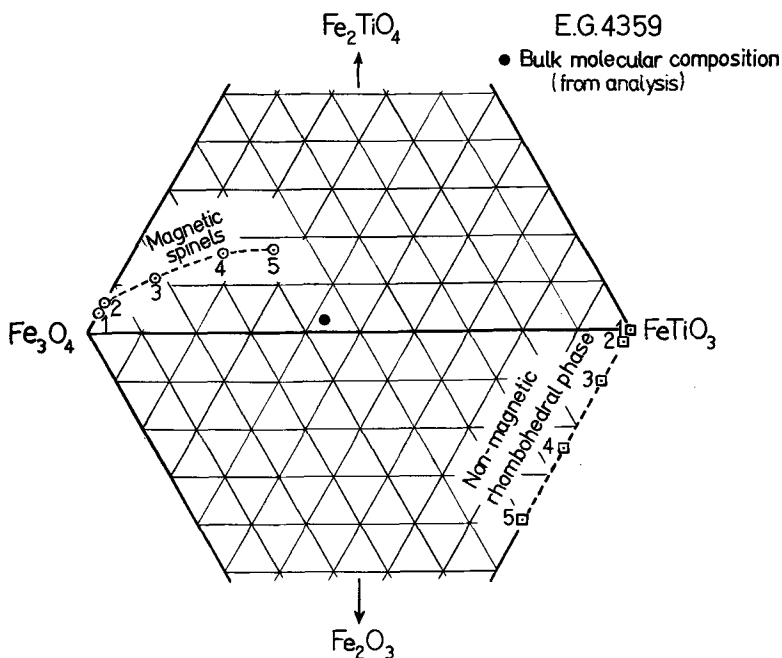


FIG. 8. Approximate compositional changes (mol. %) in coexisting phases of heated magnetite-ilmenite intergrowth E.G. 4359, deduced from magnetic properties. (Numbers refer to stages of heating in table IV.)

spinel has occurred, so that the experiments at 950° C. have probably yielded very nearly the last stage possible in reaction and rehomogenization of the two phases that can be reached without such decomposition.

Our results appear to confirm the general form of the solvus surface in the Fe_3O_4 - Fe_2TiO_4 - FeTiO_3 - Fe_2O_3 part of the system proposed by Nicholls (1955, fig. 13), but do not justify our proposing modifications in detail, while the compositional changes observed on heating agree more or less with this author's predictions of the course of unmixing in an Fe_3O_4 - FeTiO_3 solid solution. We may visualize a homogeneous spinel on or near the Fe_3O_4 - FeTiO_3 join unmixing, first probably into two spinels, the one in or

very close to the Fe_2O_3 - FeTiO_3 binary series rapidly undergoing a monotropic inversion to a rhombohedral ferri-ilmenite. Ionic migration on further cooling would cause the rhombohedral phase to continue changing in composition towards FeTiO_3 and the spinel phase towards Fe_3O_4 .

Magnetite-ulvöspinel-ilmenite intergrowths.

One example of an intergrowth of all three phases, from a ferrogabbro (E.G. 2569) of the Skaergaard intrusion, has been studied in some detail. Its analysis and norm are given in column 4 in tables I and II, and it will be seen that in bulk composition it falls midway between the two principal binary series.

In reflected light this magnetite is seen to carry very well-defined ilmenite lamellae parallel to $\{111\}$ and at high magnification the spaces between these lamellae are seen to contain fine thread-like lamellae of ulvöspinel and ilmenite—the latter possibly having originated by oxidation of some of the pre-existing ulvöspinel rather than representing a second generation of direct exsolution bodies (fig. 9).

On heating, we may say that broadly the material first behaves as a magnetite-ulvöspinel intergrowth and then, when all the original ulvöspinel has been taken back into solid solution, reaction takes place in the manner of the magnetite-ilmenite intergrowth E.G. 4359. This can be well seen from the form of the thermomagnetic curves in fig. 9, which in the earlier stages of the heating experiments show the sloping traces characteristic of the re-solution of magnetite and ulvöspinel, and later show the sharp but steadily falling Curie points of the magnetite-ilmenite reaction and re-solution.

The measured magnetic constants of the heated series of samples of E.G. 2569 are given in table V. The approximate compositions of the coexisting spinel and rhombohedral phases may be calculated from the norm and the magnetic constants in the same general manner as outlined above (pp. 643-4) for E.G. 4359: the results, recalculated to molecular percentages, are shown graphically in fig. 10.

Measured lattice parameters for the magnetite and ilmenite phases before and after heating are given below (reflections from the ulvöspinel phase were too broad to permit any reasonable estimation of its cell edge):

	Magnetic spinel.	Ilmenite.		
		a , Å.	a , Å.	c/a .
E.G. 2569, unheated	... 8.403 ± 0.001	5.087 ± 0.001	14.09 ± 0.01	2.770
Heated 12 hours at 650° C.	... 8.420 ± 0.002	5.087 ± 0.001	14.09 ± 0.01	2.770
Heated 96 hours at 950° C.	... 8.431 ± 0.001	5.082 ± 0.001	14.04 ± 0.01	2.760

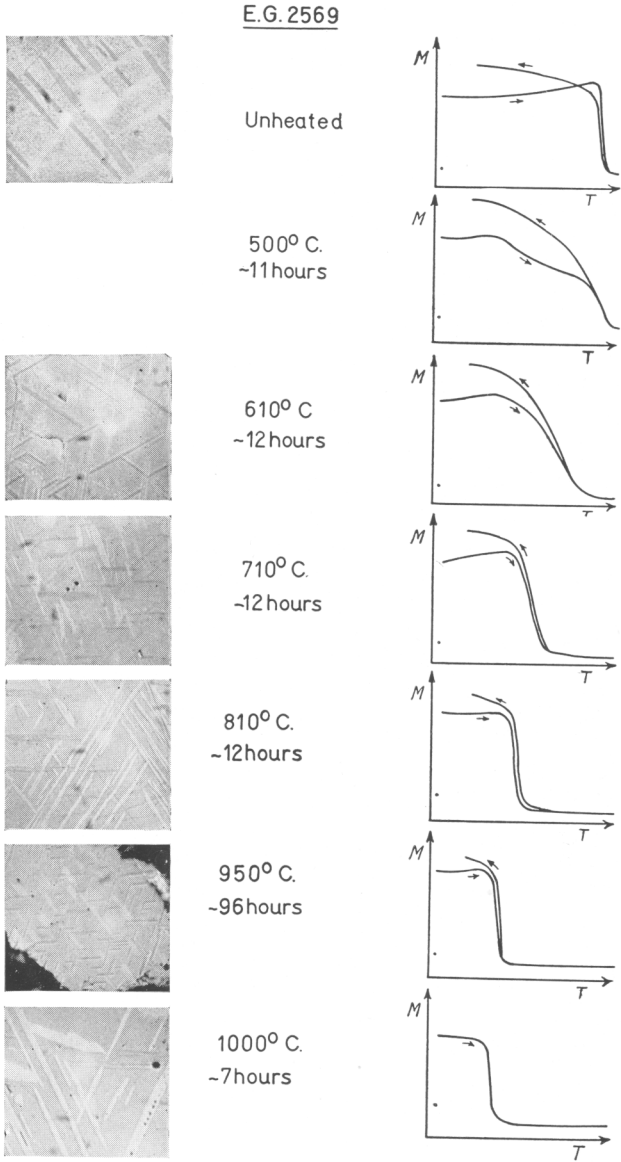


FIG. 9. Photomicrographs ($\times 420$, reflected light) and tracings of thermomagnetic curves of heated magnetite-ulvöspinel-ilmenite intergrowth E.G. 2569.

TABLE V. Magnetic properties of magnetite-ulvöspinel-ilmenite intergrowth, E.G. 2569, before and after heat-treatment. σ'_{∞} is given for 20° C., in electro-magnetic units per gram. The numbers in column 1 refer to fig. 10.

No.	Heated.		θ° C.	σ'_{∞}
	$^{\circ}$ C.	hrs.		
1	unheated		567	38.8
2	500	11	547	36.1
3	610	12	*	36.1
—	650	12	*	34.3
4	710	12	349	33.4
5	810	13	292	30.7
6	950	96	236	26.8
—	950	96	240-50	27.7
7	1000	7	220	25.5

* Indicates that the heated sample did not show a sharp Curie point.

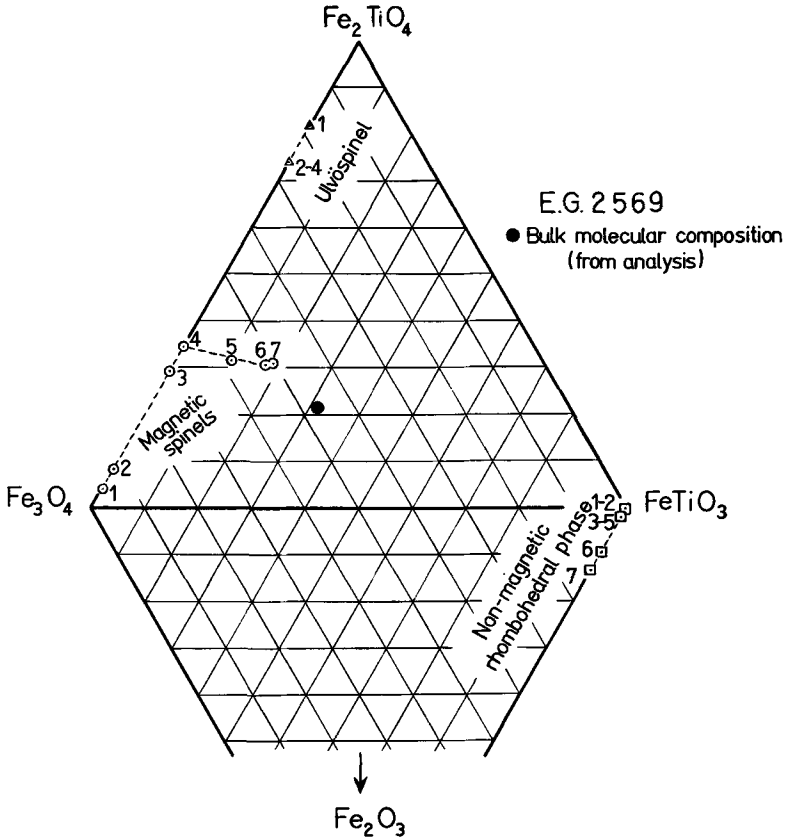


FIG. 10. Approximate compositional changes (mol. %) in coexisting phases of heated magnetite-ulvöspinel-ilmenite intergrowth E.G. 2569, deduced from magnetic properties. (Numbers refer to stages of heating in table V.)

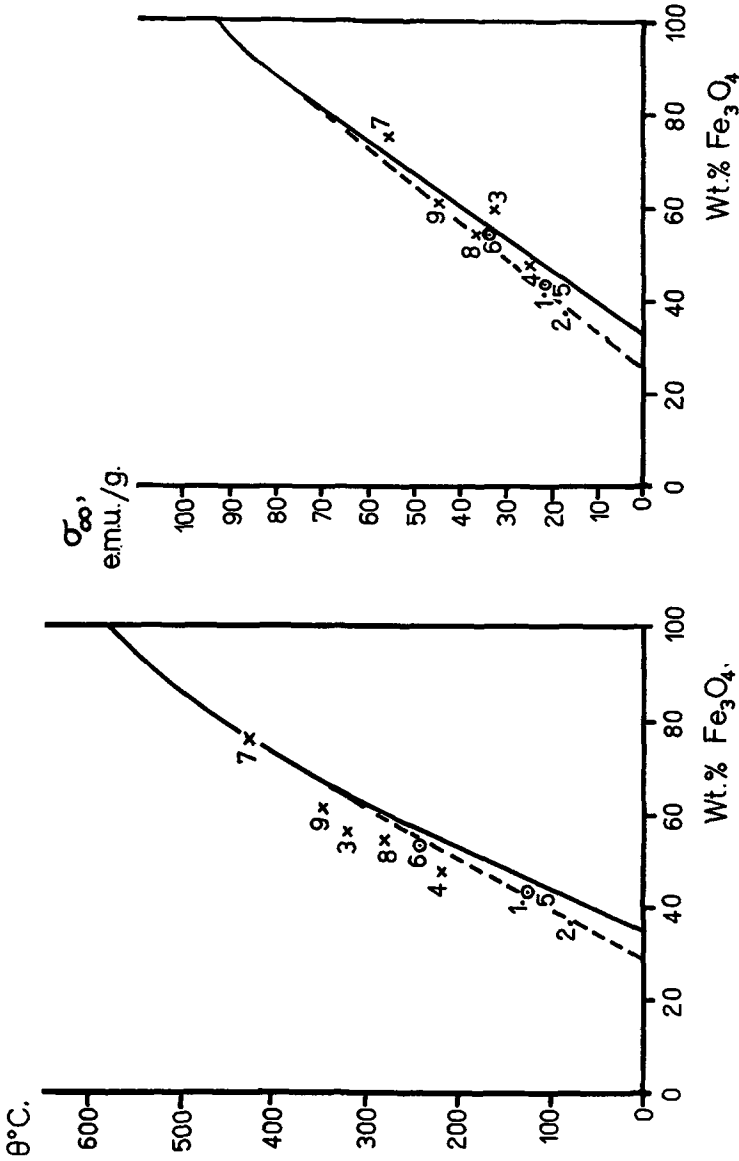
As in the case of the pure magnetite-ilmenite intergrowth E.G. 4359, the changes in lattice parameters on heating agree quite well with the changes in composition of the phases deduced magnetically. The value $a = 8.431 \text{ \AA.}$ for the spinel phase after heating at 950° C. is appropriate for the content of around 30–35 mol. % Fe_2TiO_4 , assuming once again that the (γ) FeTiO_3 component of the final solid solution has little or no effect upon the cell-dimensions.

The cell-dimensions of the rhombohedral phase of E.G. 2569 have changed much less on heating than the corresponding phase in the pure magnetite-ilmenite intergrowth E.G. 4359, the final parameters indicating an ilmenite with perhaps about 10 % Fe_2O_3 in solid solution. This again is in fair agreement with the magnetic deductions (fig. 10) and with microscopic observation, since the rhombohedral lamellae in this heated sample retain a darker tint and far more marked reflection pleochroism than the ferri-ilmenite lamellae developed in E.G. 4359 when heated to the same temperature.

Materials not studied in detail.

As well as the four intergrowths already described in detail, heating experiments and some magnetic measurements have been carried out on five other titaniferous magnetites (Analyses nos. 5–9 in tables I and II and fig. 1). The results are set out in table VI. The original materials are all intergrowths of all three phases: magnetite, ulvöspinel, and ilmenite, in varying proportions, and in no case has absolute homogeneity (as observable microscopically) been attained by heating at 950° C. , although two samples (C.S.L. 3 and E.G. 4355, lying near the Fe_3O_4 – Fe_2TiO_4 join) closely approach homogeneity.

Figs. 11 and 12 show curves constructed by one of us (R.C.) relating Curie point and specific saturation magnetization respectively with weight percentage (f) of Fe_3O_4 in homogeneous natural titanomagnetites. These curves are slightly revised from those already published (Chevallier *et al.*, 1955), being improved at the magnetite-rich end by the inclusion of magnetic data recently obtained on titanium-poor magnetite-ulvöspinel solid solutions separated from East African carbonatites and chemically analysed (E.A.V.). In the region of low Curie points, however, the curves are based only upon samples from Ankaratra (Madagascar), which contain between 8 and 10 % Al_2O_3 and 3.7 to 6.7 % MgO (Chevallier *et al.*, 1955, pp. 338–9). Naturally occurring, structurally homogeneous titanomagnetites with such low Curie points are somewhat rare, and the curves are perhaps less well defined in this region than in the regions closer to Fe_3O_4 .



Figs. 11 (left) and 12 (right). Curves relating weight percentage (f) of Fe_3O_4 in homogeneous titanomagnetites with Curie point (θ) and saturation magnetization (σ_∞) respectively. θ and σ_∞ for samples heated at 950° C. inserted: \circ completely homogenized; \times homogenization almost complete; \times homogenization incomplete. (Numbers refer to analyses in table I.)

The observed values of θ and σ'_{∞} for our nine samples heated to 950° C. have been inserted in figs. 11 and 12, using as the value for the abscissa in each case the limiting weight percentage of Fe_3O_4 (table II), i.e. the Fe_3O_4 percentage corresponding to the total Fe_2O_3 revealed by analysis, since in completely homogeneous titanomagnetites all the Fe^{III} ions may be regarded as contributing towards the formation of Fe_3O_4 .

TABLE VI. Magnetic properties of various titanomagnetites before and after heating. σ'_{∞} is given for 20° C., in electromagnetic units per gram.

Anal. no.	Sample.	Normative mol. %.			Heated.		Measured magnetic constants.	
		Fe_3O_4 &c.	Fe_2TiO_4 &c.	FeTiO_3 &c.	° C.	hrs.	θ ° C.	σ'_{∞} .
5	C.S.L. 3	44.0	41.7	14.3	unheated		563	53.2
					450	12	558	29.0
					500	12	556	25.4
					950	16	120	22.1
					unheated		565	48.6
6	E.G. 4355	55.7	33.4	10.9	unheated		565	48.6
					450	12	557	41.9
					500	12	556	38.7
					550	12	551	36.8
					650	12	*	36.9
					950	16	247	33.6
7	C.S.L. 5	75.2	8.4	16.4	unheated		563	68.8
					950	16	429	55.0
8	E.G. 4353	58.3	25.2	16.5	unheated		552	50.0
					450	336	550	43.2
					950	96	286	36.5
9	E.G. 4430	60.2	10.5	29.3	unheated		564	56.0
					950	18	350	44.9

* Indicates that the heated sample did not show a sharp Curie point.

After heating at 950° C. C.S.L. 3 and E.G. 4355 appear at least 95 % homogeneous under the microscope, a very few rods and small granules of ferri-ilmenite remaining. C.S.L. 5 and E.G. 4353 appear about 90 % homogeneous, E.G. 4430 80 % homogeneous, lamellae of ferri-ilmenite remaining.

The samples that have been completely homogenized (analyses nos. 1 and 2) or very nearly homogenized (5 and 6) by heating tend to define a (broken) line deviating from the original curve (fig. 11) at Curie points below about 300° C. This modified curve may prove to be more accurate than the original, although the latter has been used in this paper for calculating the approximate compositions of the coexisting phases in the heated magnetite-ilmenite intergrowths described in earlier sections. It is likely that titanomagnetites homogenized by heating to a high temperature and suddenly quenched, as in our experiments, will have

somewhat disordered structures with regard to the distribution of Fe^{2+} , Fe^{3+} , and Ti^{4+} between the available lattice sites. It has been found by Gorter (1954) and commented upon by Nicholls (1955, p. 134) that such disorder in certain ferrites may lead to some increase in both Curie point and saturation magnetization over the values to be anticipated were the substances in stable structural equilibrium (e.g. in the case of Fe_3O_4 - Fe_2TiO_4 solid solutions, having the true inverse spinel structure).

We do not assert at present, therefore, that the broken curves in figs. 11 and 12 should be substituted for the original ones, even though the latter are based upon magnetites with rather high contents of Al and Mg. The true relationships between Fe_3O_4 content and magnetic constants may well be represented by curves lying somewhere in between the two cases.

Conclusions.

At high temperatures fairly extensive solid solution probably exists over much of the magnetite-ulvöspinel-ilmenite compositional field, and homogeneous titanomagnetites of widely varying composition and magnetic properties may persist without unmixing in some rapidly cooled lavas. The composition of the titanomagnetite is sensitive to changes in oxidation-reduction relationships between crystals and magma, and a magnetite that remains strongly reduced during cooling (i.e. in or near the Fe_3O_4 - Fe_2TiO_4 binary spinel series) may be expected to remain homogeneous down to much lower temperatures than one in the Fe_3O_4 - FeTiO_3 binary series. Once it unmixes, however, the magnetic phase will always be rather close to Fe_3O_4 (see fig. 4), which can be expected to cause a rather sudden rise in the Curie point of the mineral as exsolution commences. The lack of a sharp Curie point observed in some lavas may be due to varying degrees of exsolution in different grains of titaniferous magnetites in or near the Fe_3O_4 - Fe_2TiO_4 series.

A titanomagnetite solid solution crystallizing with an original composition in or near the Fe_3O_4 - FeTiO_3 binary series, or which changes its composition towards this series by oxidation, may be expected to exsolve an FeTiO_3 - Fe_2O_3 solid solution which may at first be a spinel, but which rapidly inverts to a rhombohedral ferri-ilmenite. The initial exsolution will take place at a much higher temperature than in the Fe_3O_4 - Fe_2TiO_4 series, but we have no data to suggest a possible temperature. On further cooling both rhombohedral and spinel phases change in composition until they closely approach FeTiO_3 and Fe_3O_4 respectively. Experience of the ore minerals commonly occurring in igneous rocks suggests that the

exsolution and this compositional change take place rather rapidly, since few rocks have been described in which ferri-ilmenite lamellae have been identified in the magnetite. It is of interest, however, that Nagata (1953) and Uyeda (1955) describe an intergrowth of magnetic ferri-ilmenite and inverse magnetic spinel in the celebrated reversely magnetized Haruna (Japan) dacite pumice. This type of intergrowth may well have originated by exsolution and incomplete ionic migration in a member of the Fe_3O_4 - FeTiO_3 series. The ferri-ilmenites produced in our heating experiments are not ferromagnetic, but this could well be due to structural disorder in the rapidly quenched samples.

The reaction relationship observed between spinel and rhombohedral phases in our heating experiments leads to the spinel phase always showing a sharp Curie point—in contrast to intermediate heated samples in the magnetite-ulvöspinel series; partly unmixed non-equilibrium minerals in the magnetite-ilmenite series may thus equally be expected to show sharp Curie points and successively greater saturation magnetization as final equilibrium is approached.

Microscopic study and magnetic behaviour of a sample containing exsolved ulvöspinel as well as ilmenite suggest that exsolution and organization of broad ilmenite lamellae parallel to {111} was complete before exsolution of ulvöspinel occurred, and that a second period of ilmenite exsolution or partial oxidation of the exsolved ulvöspinel at still lower temperatures may lead to a second generation of less well-organized ilmenite lamellae.

In conclusion it must be emphasized that the variations observed in thermomagnetic curve, Curie point, and saturation magnetization with degree of homogenization in our experiments (and hence of exsolution) depend very much on whether the mineral is a member of the Fe_3O_4 - Fe_2TiO_4 series, or the Fe_3O_4 - FeTiO_3 series, or is intermediate between the two. This is of great importance to the geophysicist concerned with rock magnetism, and adequate correlation between magnetic constants, lattice parameters, and chemical composition will only be attained in those cases where the magnetic minerals have been separated from the rocks in a very high state of purity, examined carefully with the microscope, and the chemical analysis carried out accurately and in detail (not merely confined to FeO , Fe_2O_3 , and TiO_2), so that the position of the mineral relative to the two main binary series can be established. The assumption that is sometimes made that the apparently homogeneous titaniferous magnetites of lavas are always essentially Fe_3O_4 - Fe_2TiO_4 solid solutions cannot be supported.

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References.

- AKIMOTO (S.), 1954. *Journ. Geomagn. Geoelectr.*, vol. 6, no. 1, p. 1.
 — 1955. *Japan Journ. Geophys.*, vol. 1, no. 2, p. 1.
 BARTH (T. F. W.) and POSNJAK (E.), 1932. *Zeits. Krist. Min. Petr.*, A, vol. 82, p. 325 [M.A. 5-179].
 BASTA (E. Z.), 1953. Ph.D. Thesis, Bristol.
 BROWN (G. M.), 1957. *Min. Mag.*, vol. 31, p. 511.
 CHEVALIER (R.) and PIERRE (J.), 1932. *Ann. Physique*, ser. 10, vol. 18, p. 383.
 — and MATHIEU (S.), 1943. *Ibid.*, ser. 11, vol. 18, p. 258.
 — and GIRARD (J.), 1950. *Bull. Soc. Chim. France*, ser. 5, vol. 17, p. 576 [M.A. 11-368].
 — MATHIEU (S.), and VINCENT (E. A.), 1954. *Geochimica Acta*, vol. 6, p. 27 [M.A. 12-499].
 — BOLFA (J.), and MATHIEU (S.), 1955. *Bull. Soc. Franç. Min. Crist.*, vol. 78, pp. 307 and 365.
 ERNST (T.), 1943. *Zeits. angew. Min.*, vol. 4, p. 394 [M.A. 11-198].
 GIRAULT (J. P.), 1953. *Naturaliste Canadien*, vol. 80, p. 307 [M.A. 12-447].
 GORTER (E. W.), 1954. *Philips Research Reports*, vol. 9, pp. 295, 321, 403.
 KAMIYAMA (M.), 1929. *Journ. Geol. Soc. Tokyo*, vol. 36, p. 12 (in Japanese).
 KAWAI (N.), 1956. *Proc. Japan Acad.*, vol. 32, p. 464.
 — KUME (S.), and SASAJIMA (S.), 1954. *Ibid.*, vol. 30, p. 588.
 MASON (B.), 1943. *Geol. För. Förh.*, vol. 65, p. 97 [M.A. 9-32].
 MOGENSEN (F.), 1946. *Ibid.*, vol. 68, p. 578 [M.A. 10-101].
 NAGATA (T.), 1953. *Nature*, vol. 172, p. 850.
 NICHOLLS (G. D.), 1955. *Phil. Mag.*, suppl., vol. 4, p. 113.
 POUILLARD (E.), 1950. *Ann. Chimie*, ser. 12, vol. 5, p. 164.
 — and MICHEL (A.), 1949. *Compt. Rend. Acad. Sci. Paris, Cl. Sci. math. phys.*, vol. 228, p. 1232.
 RAMDOHR (P.), 1926. *Neues Jahrb. Min., Abt. A, Beil.-Bd.* 54, p. 320.
 — 1953. *Econ. Geol.*, vol. 48, p. 677 [M.A. 12-388].
 — 1955. *Die Erzminerale und ihre Verwachsungen*. Akademie Verlag, Berlin.
 ROY (S.), 1954. *Proc. Nat. Inst. Sci. India*, vol. 20, p. 691.
 — 1955. *Ibid.*, vol. 21, B, p. 222.
 UYEDA (S.), 1955. *Journ. Geomagn. Geoelectr.*, vol. 7, p. 9.
 VINCENT (E. A.) and PHILLIPS (R.), 1954. *Geochimica Acta*, vol. 6, p. 1 [M.A. 12-499].
 WILSON (H. D. B.), 1953. *Econ. Geol.*, vol. 48, p. 370.