

Some further heating experiments on natural titaniferous magnetites.

(With Plate III.)

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Summary. Samples of magnetite containing exsolution bodies of ilmenite, or of ulvöspinel and ilmenite, were heated at 1,250–1,300° C. under oxidizing and under reducing conditions.

In the former case, the product consisted of magnetite, ferri-ilmenite, and pseudobrookite. In the latter, loss of oxygen converted a magnetite-ilmenite intergrowth into a homogeneous Fe_3O_4 - Fe_2TiO_4 spinel solid solution, while a magnetite sample originally carrying ulvöspinel in addition to ilmenite yielded a spinel phase with surprisingly low cell dimension, together with some metallic iron.

IN a recent paper (Vincent, Wright, Chevallier, and Mathieu, 1947)² were described results of heating experiments, at temperatures up to 950° C., on a series of titaniferous magnetites, in which the over-all chemical compositions of the samples were unchanged after heat treatment. In the experiments briefly described here, the titaniferous magnetites were heated to between 1250° and 1300° C. One series of samples, heated in insufficiently degassed platinum sheaths sealed *in vacuo*, became oxidized; samples of another series, heated under continuous evacuation, or in argon at 1 atmosphere pressure, lost oxygen and were reduced. The results of these experiments, although not intentionally produced, are sufficiently interesting to merit brief description.

Two of the titaniferous magnetites investigated by Vincent *et al.* (1957) were used: E.G. 4359 and 4353, respectively magnetite-ilmenite and magnetite-ulvöspinel-ilmenite intergrowths. The changes in these minerals, produced by heating, were followed microscopically, chemically, and by X-rays. Quantitative data for unheated and three representative heated samples are given in table overleaf I, p. 34.

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² E. A. Vincent, J. B. Wright, R. Chevallier, and S. Mathieu, *Min. Mag.*, 1957, vol. 31, p. 624 [M.A. 13-556].

Series 1. Oxidized samples. Microscopic examination of both samples after heating showed considerable coalescence and growth of the original very small ilmenite lamellae (pl. III, A, B, c), which had also become

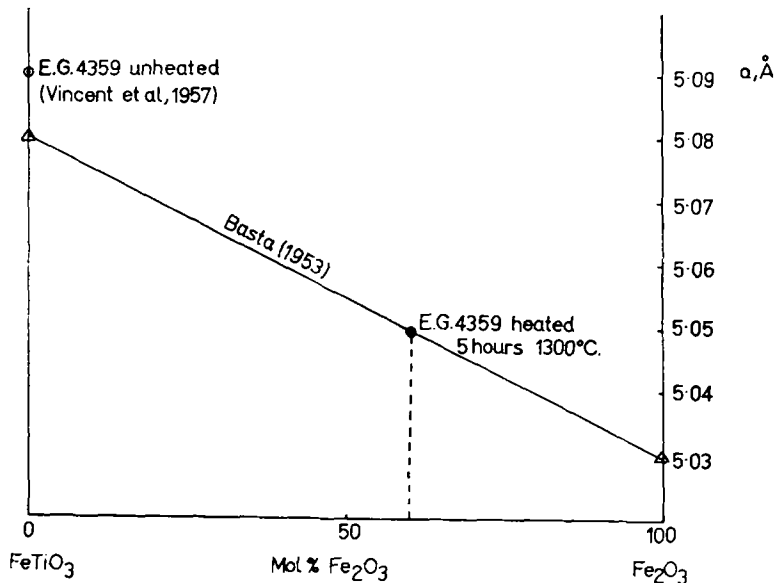
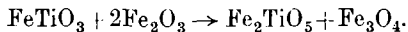


FIG. 1. Diagram showing approximate Fe_2O_3 content of rhombohedral phase in E.G. 4359, heated 5 hours, at 1300°C . under oxidizing conditions, as deduced from the a cell dimension (hexagonal axes).

much whiter in reflected light due to the intake of Fe_2O_3 (Vincent *et al.*, 1957): about 60 mol. % of Fe_2O_3 is indicated by the a cell dimension of the rhombohedral phase of the heated sample E.G. 4359 (fig. 1). Pseudobrookite is well developed in these oxidized samples (plate III, B and c) and can be identified in the X-ray powder patterns. It is probably developed from the rhombohedral FeTiO_3 - Fe_2O_3 solid solution produced on heating, by the reaction:



In the previous series of heating experiments (Vincent *et al.*, 1957) it was shown that Fe_2O_3 can enter the rhombohedral phase of a heated magnetite-ilmenite intergrowth in appreciable amounts without over-all compositional changes occurring in the complex mineral. Heat treatment under oxidizing conditions has encouraged the formation and entry

of considerable amounts of Fe_2O_3 into the rhombohedral ilmenite phase, and also the formation of pseudobrookite.

A homogeneous titaniferous magnetite could probably never be produced by heating under neutral or oxidizing conditions, because Fe_2O_3 in an exsolved rhombohedral phase apparently cannot invert to the cubic $\gamma\text{-Fe}_2\text{O}_3$ form (Mason, 1943;¹ Vincent *et al.*, 1957). Under reducing conditions, however (series 2, below), a completely homogeneous cubic titaniferous magnetite can readily be produced.

Series 2. Reduced samples. Microscopic examination of E.G. 4359, after heating under reducing conditions, showed that the original magnetite-ilmenite intergrowth had become a uniform pale yellow in colour in reflected light (plate III, D); while X-ray and chemical data indicate that the sample has been reduced to an almost pure magnetite-ulvöspinel solid solution (table I).

TABLE I.

	<i>E.G. 4359 unheated, Vincent et al., 1957</i>	<i>E.G. 4359 heated 5 hrs., 1300° C. Series 1. Oxidation</i>	<i>E.G. 4359 heated 24 hrs., 1250° C. Series 2. Reduction</i>	<i>E.G. 4353 heated 24 hrs., 1250° C.</i>	<i>E.G. 4353 unheated, Vincent et al., 1957</i>
<i>Chemical data</i>					
FeO	34.13	31.1 (det.)	43.5 (det.)	58.6 (det.)	39.8
MgO	1.84	} assumed unchanged	} assumed unchanged	} assumed unchanged	0.9
MnO	0.37				0.4
CaO	0.49				0.7
Fe_2O_3	40.70	44.1 (calc.)	30.3 (calc.)	15.9 (calc.)	36.8
Al_2O_3	2.54	} assumed unchanged	} assumed unchanged	} assumed unchanged	3.1
V_2O_5	1.52				2.1
Cr_2O_3	0.03				—
TiO_2	18.55				15.6
SiO_2	0.05				0.1
	100.22	100.6	99.2	97.4	99.5
<i>Calculated norms Very approximate</i>					
	<i>Approx.</i>				<i>Approx.</i>
$\text{MO.Fe}_3\text{O}_3$...	58.2	57	44	22	53.5
$\text{MO.R}_2\text{O}_3$...	6.5	6	7	8	8.3
2MO.TiO_2 ...	2.5	—	44	44	26.3
MO.TiO_2 ...	32.8	31	5	—	11.8
$\text{R}_2\text{O}_3.\text{TiO}_2$...	—	6	—	—	—
Excess MO ...	—	—	—	26	—
	100.0	100	100	100	99.9
<i>X-ray data Powder films</i>					
	<i>Diffractometer</i>				<i>Estimated</i>
Mag: <i>a</i>	8.40 Å.	8.40 Å.	8.44 Å.	8.39 Å.	c. 8.40 Å.
Im: <i>a</i>	5.09 Å.	c. 5.05 Å.	c. 5.08 Å. (weak lines)	no lines	c. 5.08/9 Å.

The mineral E.G. 4353, originally in a more reduced state than E.G.

¹ B. H. Mason, *Geol. För. Förh.*, 1943, vol. 65, p. 97 [M.A. 9-32].

4359 (since it contains exsolved ulvöspinel, Pl. III, E), has been further reduced to such an extent that metallic iron has separated and the colour of the remaining spinel phase is dark brown, similar to that of pure ulvöspinel (pl. III, F).

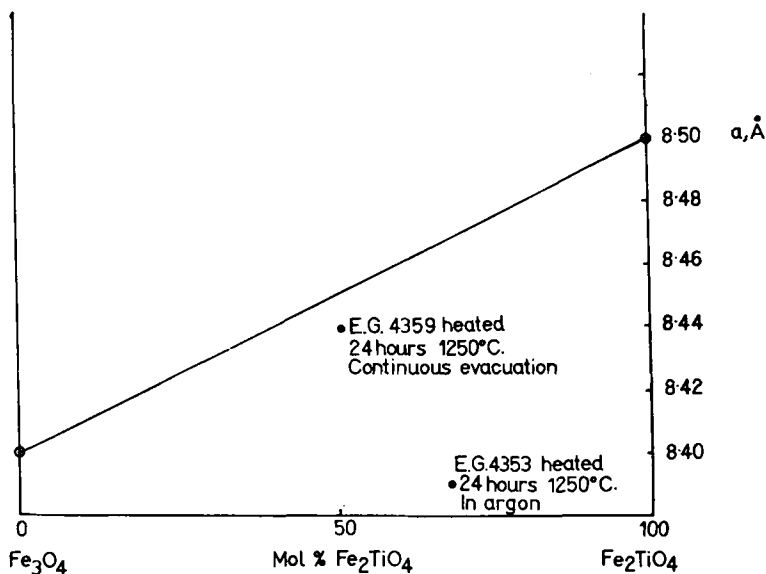


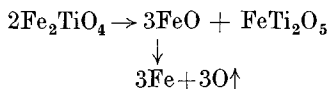
FIG. 2. Diagram illustrating variation in cell-dimension with approximate estimated compositions of spinel phases, in reduced titaniferous magnetite samples. It is very unlikely that E.G. 4353, after heating, is a normal magnetite-ulvöspinel solid solution.

In fig. 2 are plotted values of the spinel cell-dimensions for the reduced samples of E.G. 4359 and 4353, against their approximate normative compositions in terms of ulvöspinel and magnetite. The point representing E.G. 4359 lies close to the Végard line joining the end members, but the point for E.G. 4353 lies well below it; i.e. the cell-dimension of the spinel phase is far too small for a material which both chemical and optical data indicate as being very rich in ulvöspinel.

The spinel phase in this reduced sample of E.G. 4353 thus appears not to be a normal solid solution of magnetite and ulvöspinel. It may be a transitional stage between cubic ulvöspinel and the orthorhombic series Fe_2TiO_5 - FeTi_2O_5 , recently synthesized by Akimoto *et al.* (1957).¹ The

¹ S. Akimoto, T. Nagata, and T. Katsura, *Nature*, 1957, vol. 179, p. 37.

FeTi_2O_5 member of this series might be produced together with metallic iron from ulvöspinel by the reaction:



Mason (1943) showed that a gradual increase in cubic cell-dimension occurred in the solid-solution series Fe_3O_4 – Mn_3O_4 , before a symmetry change from cubic Fe_3O_4 , with a unit-cell volume of $592 \text{ \AA}^3$, to tetragonal Mn_3O_4 , with a unit-cell volume of $617 \text{ \AA}^3$. For the reduced spinel phase of E.G. 4353, therefore, a reduction in cell-dimension might perhaps be expected if it were prior to a symmetry change from cubic ulvöspinel, with a unit-cell volume of $613 \text{ \AA}^3$, to orthorhombic FeTi_2O_5 , with the smaller unit-cell volume of $368 \text{ \AA}^3$.

Finally, it is of interest to note that, in contrast to grains of the separated mineral, the magnetite-ilmenite intergrowths in a whole rock chip of E.G. 4359, sealed *in vacuo*, became completely homogeneous after heating to only 940°C. , and are very similar, microscopically, to the titaniferous magnetite grains separated from this rock and heated at higher temperatures under reducing conditions.

Previous workers (Ramdohr, 1926;¹ Kamiyama, 1929;² Wilson, 1953;³ Supriya Roy, 1955⁴) have reported homogenization of magnetite-ilmenite intergrowths in heated rock samples. The experiments discussed here strongly suggest that such homogenization can only have occurred because reducing conditions were brought about by volatile substances released from the rock during heating. This process was originally suggested by Ramdohr (1926), as one of the possible explanations for his experimental results; but hitherto there has been no further experimental data to confirm his suggestion.

EXPLANATION OF PLATE III.

Photomicrographs of titaniferous magnetites before and after heat treatment.

A. E.G. 4359, Middle Gabbro, Skaergaard Intrusion, E. Greenland. Magnetite carrying an exceedingly fine network of ilmenite lamellae arranged parallel to $\{111\}$ and some much broader ilmenite lamellae with which are associated granules of a transparent spinel (black in photograph). Note the development of larger ilmenite

¹ P. Ramdohr, Neues Jahrb. Min., Abt. A, 1926, Beil.-Bd. 54, p. 320.

² M. Kamiyama, Journ. Geol. Soc. Tokyo, 1929, vol. 36, p. 12.

³ H. D. B. Wilson, Econ. Geol., 1953, vol. 48, p. 370.

⁴ S. Roy, Proc. Nat. Inst. Sci. India, 1954, vol. 20, p. 691; *ibid.* 1955, vol. 21, B, p. 222.

lamellae on either side of veinlets at the top of the photograph. Reflected light, oil immersion, $\times 410$.

B. E.G. 4359, Separated titaniferous magnetite grains heated 5 hours at *c.* 1300° C. under oxidizing conditions. The ilmenite has taken Fe_2O_3 into solid solution and has coalesced into large lamellae and irregular masses (white in photograph). Pseudobrookite (Ps) is seen as darker irregular areas in the spinel phase. Reflected light, oil immersion, $\times 410$.

C. E.G. 4359, Separated titaniferous magnetite grains heated at *c.* 1300° C. under oxidizing conditions. The process shown in fig. B has continued further, the ferri-ilmenite (white) now forming large irregular masses covering several sintered grains, (Irregular curved cracks are former grain boundaries; darker grey areas, Ps, are pseudobrookite.) Reflected light, oil immersion, $\times 410$.

D. E.G. 4359, Separated titaniferous magnetite grains heated for 24 hours at 1250° C. under continuous evacuation, causing loss of oxygen. Completely homogenized, rounded and sintered spinel grains bordered by a fine network of (?) titanomagnetite and transparent material. Reflected light, oil immersion, $\times 410$.

E. E.G. 4353, Middle Gabbro, Skaergaard Intrusion, E. Greenland. Magnetite carrying ilmenite lamellae with which are associated (black) granules of transparent spinel. A further set of very much finer exsolution bodies—partly ilmenite, partly ulvöspinel—is seen in the spaces between the larger ilmenite lamellae. Reflected light, oil immersion, $\times 410$.

F. E.G. 4353, Separated titaniferous magnetite grains heated for 24 hours at 1250° C. in argon at 1 atmosphere pressure. Loss of oxygen has reduced the sample to a homogeneous dark brown spinel in sintered grains cemented by a fine-grained lamellar mass of transparent material. Note also the development of metallic iron (white in photograph). Reflected light, oil immersion, $\times 410$.

