MINERALOGICAL ASPECTS OF THE SYSTEM $FeO - Fe_2O_3 - TiO_2$.

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I. Introduction.

The advances in physical chemistry and in X-ray structural analysis in the past thirty years have revolutionised and revitalised mineralogy. The study of mutual relationships between the phases and components of a chemical system has led to new concept of a mineral species. A mineral species is fundamentally an independent phase of a physico-chemical system, occurring in the earth's crust.

The present study of the system FeO - Fe_2O_3 - TiO_2 has been made by means of chemical, physical, and mineralogical investigations for the purpose of obtaining a clearer insight into the nature of the different mineral species and their interrelations, especially the limits of isomorphous replacements. This system is one of the most important metal oxide systems, not only from a purely scientific point of view, but also on account of its industrial applications: extraction of the metal from the ore, reactions at high temperature in furnaces, catalysts, mineral pigments, slags, etc. In addition to being common rock forming minerals and ore minerals, the constituents of the system FeO - Fe_2O_3 - TiO_2 provide the main source of ferromagnetism in volcanic rocks. Yet it is only in the past twenty years that any study of its phase relations has been made, which even today is not sufficient to enable a reliable phase diagram to be drawn. This is largely due to the serious practical difficulties which are inherent in a systematic investigation of the iron oxides - partly on account of the difficulty in controlling the degree of oxidation, and partly because of the lack of a suitably inert enclosing material which can withstand the attack at high temperatures of these chemically reactive oxides.

In the case of the natural minerals of the system $FeO - Fe_2O_3 - TiO_2$, the fact that most of these ores show very fine, often submicroscopic, intergrowths, together with the lack of a sufficiently reliable technique for the identification of the mineral phases present, have led to much disagreement in the literature as to both the nature and the limit of solid solutions. Among the numerous analyses of such ores which have been published, many are of material so rich in silicates that no further conclusions can be drawn as to the combination of the ore minerals. Of the remainder, only few have been made with material examined in polished sections. These analyses, even when prepared from individual crystals, show great departure from the theoretical formulae. The question then arises: are these departures due to a fundamental solid solution, or are they the result of extremely fine intergrowths which are not detectable under the microscope? No satisfactory answer to such a question has so far been given, which is astonishing considering the importance and wide distribution of the minerals which we are dealing with. There has also been no definite agreement as to the origin of the intergrowths which are commonly observed between the different minerals. The well known intergrowths of ilmenite and magnetite were generally considered to be due to the unmixing on slow cooling of an originally homogeneous solid solution. Such magnetite - ilmenite solid solution - the so-called titanomagnetite - has never been separated or determined with certainty from natural occurrences or from synthetic preparations.

In the present work, in order to determine the original solid solution, it has been essential to study the ore minerals in volcanic and other fine-grained rocks which by cooling rapidly left no opportunity for unmixing to take place. Mineral separation was made of a large collection of about 120 specimens, partly igneous rocks (especially the volcanic representatives), and partly ores, from different parts of the world. X-ray powder photographs were taken of the separated ore-minerals, and were used to identify the different phases, to determine the relationship between lattice dimensions and composition in the various systems, and to delimit the phase boundaries. Twenty one new chemical analyses of pure samples - the homogeneity of which was determined by X-ray powder photographs - were made, together with about 12 semiquantitative spectrochemical analyses. A number of polished sections of certain ore specimens were examined in order to determine the different types of structure and intergrowth relationships of the constituents. To confirm the results obtained from the study of natural minerals, and to complete the solidification diagram, a number of high temperature experiments were made on different mixtures of the artificial oxides, and on natural ex-solution intergrowths.

As a result of the present study, it has been possible to give a certain quantitative expression to the limits of the various systems and to effect some simplification and clarification in the nomenclature of this group, from which a dozen or more minerals have been described as individual species. Some of these so-called individual species have proved to be invalid. At the same time it has been possible from investigations of natural minerals and synthetic materials to reach a satisfactory conclusion as to the nature and composition of titanomagnetite. Finally, the relations between the different phases have been represented in a ternary diagram, $FeO : Fe_2O_3 : TiO_2$.

II. Previous Work.

The literature on the system $FeO-Fe_2O_3-TiO_2$ and its constituents is very extensive. For clarity, the work made by the previous investigators is divided into two main parts: 1) Systems of iron oxides, 2) Systems of iron-titanium oxides.

1) Systems of iron oxides:

Sosman and Hostetter (1916) studied the dissociation pressures at 1200°C of the system $Fe_3O_4-Fe_2O_3$, and came to the conclusion that at this temperature there was continuous solid solution between Fe_2O_3 and Fe_3O_4. This paper was followed by another by the same authors on natural occurrences of Fe_2O_3 and Fe_3O_4, which they claimed supported their laboratory results (1918). However, subsequent workers on magnetite and haematite, and investigations on polished sections, have shown that the material considered by Sosman and Hostetter to be solid solution of two minerals was undoubtedly heterogeneous (Broderick, 1919; Gruner, 1922; Gilbert, 1925). They were all convinced that solid solutions between Fe_2O_3 and Fe_3O_4 are either very rare or do not exist.

Palmunen (1925), describing the ilmenite-magnetite-olivinite associated with a hornblende-biotite gabbro from Susimäki, found that the analyses showed a remarkable excess of FeO over magnetite and ilmenite molecules. As analyses of almost pure ilmenite showed no such excess, he thought that the high FeO content was apparently associated with magnetite for which he suggested the formula $3FeO.2Fe_2O_3$. Foslie (1928) described a specimen of magnetite - from Storgangen, Norway - the chemical analysis of which also showed an excess of FeO. He also considered this excess FeO to be in the magnetite molecule.

Sosman and Posnjak (1925) established the similarity in magnetic susceptibility and X-ray pattern between magnetite and ferromagnetic ferric oxide (γ-Fe_2O_3). Wagner (1927) discovered large quantities of ferromagnetic ferric oxide in the so-called titaniferous magnetite segregations in the upper part of the norite zone of the Bushveld igneous complex in Transvaal, and proposed the name maghemite for the mineral. Hägg (1935) determined the structure of γ-Fe_2O_3 as a spinel with empty Fe positions, the unit cell content being $Fe_{21\ 1/3}O_{32}$ compared to $Fe_{24}O_{32}$ for magnetite. He also showed that the oxidation of Fe_3O_4 to γ-Fe_2O_3 is a continuous process, the cell edge decreasing continuously from 8.380 A for Fe_3O_4 to 8.322 A for γ-Fe_2O_3.

The most thorough work on the system Fe_2O_3-Fe_3O_4 is that by Greig and his co-workers (1935). Their results indicate that the solubility of Fe_3O_4 in Fe_2O_3 is very small at all temperatures up to 1450°C, whereas the solubility of Fe_2O_3 in Fe_3O_4 is small but noticeable at low temperatures and rapidly increases at high temperatures, reaching 30 wt. % at about 1450°C. As compared with previous workers, they found generally a much smaller solubility of Fe_3O_4 in Fe_2O_3 and a greater solubility of Fe_2O_3 in Fe_3O_4. These results have since been largely confirmed by the investigations of White (1938) and of Schmahl (1941). There is almost complete agreement on the shape of the solubility curve of Fe_2O_3 in Fe_3O_4. White, however, found a somewhat greater solubility of Fe_3O_4 in Fe_2O_3 than did Greig and his co-workers, but Schmahl has pointed out certain defects in White's work sufficient to account for such high solubility.

Ex-solution intergrowths of magnetite and haematite have been described by Edwards (1949) in a small pebble from Cairns, Queensland, Australia, and in grains from beach sands at Viti Levu, Fiji. Another example of such rare intergrowths has been recently recorded by Baker (1952) in amphibolite from Matapau, and occasionally in peridotite from Babiang, New Guinea.

2) Systems of iron-titanium oxides:

In the extensive literature on the relationships between the oxides of iron and titanium, highly divergent observations and conclusions are expressed. Singewald (1913) described magnetite which contained intergrowths of ilmenite as tablets, lines or dots with nearly circular outline, which are oriented parallel to the octahedral faces of magnetite. He chemically analysed the microscopically homogeneous material and found it to contain a maximum of 6.6% TiO_2, a result which he stated "tends to prove the existence of a mineral titanomagnetite". Brunton (1913) has little to say on the subject of Singewald's work, having come to much the same conclusions.

Warren (1918) described different types of titanic iron ores from various localities and gave a number of chemical analyses. He classified them into four main types: 1) Ilmenite-haematite solid solutions, 2) Ilmenite-haematite intergrowths, 3) Ilmenite-magnetite intergrowths, 4) Ilmenite-magnetite solid solutions. However, later investigations have proved that most of his so-called solid solutions are actually heterogeneous mixtures of two or more minerals.

The apparently constant Fe:Ti ratio in the total mass of the magnetite-ilmenite intergrowths has led both Singewald and Warren to suggest a eutectic crystallisation.

In 1925, Lindley, describing iron ores in basalts under the reflecting microscope, remarked that magnetite and ilmenite can form a continuous series of solid solutions which may remain homogeneous if cooled sufficiently rapidly, although under ordinary conditions of cooling in plutonic rocks, unmixing takes place. He noted the variation in properties of magnetite with increase in ilmenite; magnetite with high percentage of ilmenite in solid solution is red brown under polarised light, it is weakly anisotropic, and is more resistant to acids than normal varieties. He also believed that there is a continuous mutual solubility between haematite and ilmenite.

The most extensive work on the relationships between iron and titanium oxides was made by Ramdohr (1926), who studied microscopically a very large number of specimens from different localities, especially ores from Taberg. He formed the opinion that at the temperature of separation of the ore, there is very extensive mutual solubility of magnetite and ilmenite. In two equally composed meltings, either a cubic titanomagnetite or a hexagonal "magneto-ilmenite" may be formed. However, the "magnetoilmenite" is not so frequent as the titanomagnetite, and he was able to describe only three cases. The mixed crystals of titanomagnetite can be preserved if the cooling takes place quickly. With slow cooling, helped perhaps by mineralisers, ex-solution takes place giving rise to intergrowth of ilmenite in magnetite. To determine the ex-solution temperature, he made a number of experiments on the homogeneisation of naturally ex-solved material and found it to begin at 600-700°C. In the case of the system Fe_2O_3 -$FeTiO_3$, Ramdohr found a continuous mutual solubility at high temperatures. The mixed crystals can also be preserved on rapid cooling, while on slow cooling haematite forms lamellae in ilmenite. The earlier formed ex-solution bodies are always distinctly larger than the others and occur more or less in rows. This, and the fact that on heating such an ex-solution intergrowth the finer bodies dissolved in the ilmenite at temperatures between 500-600°C, while the coarser bodies did not appear to dissolve until about 700°C, led Ramdohr to postulate that the ex-solution takes place in two stages, the second stage coinciding with the inversion of the ilmenite to tetartohedral symmetry. This view was challenged by Greig (1932) and by Edwards (1938) who showed that the difference in size of the "two generations" of lamellae is due to the decrease in the rate of solid diffusion as the temperature fell.

Goldschmidt (1926) emphasised that extensive formation of mixed crystals between rhombohedral $FeTiO_3$ and isometric Fe_3O_4 is improbable on crystallographic grounds. He also showed that Mg_2TiO_4 which crystallises into a spinel type can form mixed crystals with $MgAl_2O_4$. Similarly, he suggested that titanomagnetites are mixed crystals of magnetite and a Ti mineral of the spinel type, which may be Fe_2TiO_4 or $FeTi_2O_4$ or both.

Foslie (1928) gave a precise account of some titaniferous ores from Storgangen, in the Ekersund-Soggendal area, Norway. He made magnetic and heavy liquid separations of pure magnetite and ilmenite and analysed both. For the magnetite, which contained 1.48% TiO_2, a FeO surplus of 4.49% was obtained and he suggested that Fe_2TiO_4 may enter into the spinel structure concerned. According to him, ilmenite and magnetite show very little miscibility at all temperatures; on the other hand, the orthotitanate Fe_2TiO_4 is isomorphous with magnetite at high temperatures and can form a very varied mixed crystals. He observed that when intergrowth lamellae of haematite occur in ilmenite, the magnetite is poor in TiO_2. Foslie (p.13) suggested that the following rules govern the factors which determined these intergrowths:

a) If excess of Fe_2O_3 occurs, Fe_2TiO_4 cannot be formed because of the low solubility of $FeTiO_3$ and the resulting magnetite is poor in TiO_2:

$$Fe_2TiO_4 + Fe_2O_3 \longrightarrow FeTiO_3 + FeFe_2O_4.$$

b) If there is only a little excess, or insufficient, Fe_2O_3 present, Fe_2TiO_4 can form and go into solution with magnetite. On cooling, it separates as $FeTiO_3$ and intergrowths immediately appear by sufficiently long cooling, giving the actual titanomagnetite:

$$Fe_2TiO_4 \longrightarrow FeTiO_3 + FeO.$$

FeO entering into solid solution in magnetite and so giving the excess that has been remarked upon.

Kamiyama (1929) described some heating experiments on titaniferous magnetites from Korea; his results differ somewhat from those of Ramdohr. He distinguished two varieties of titaniferous magnetite. On heating the one variety, the typical magnetite-ilmenite intergrowths became more pronounced up to 1150°C, but then diminished to 1390°C, at which point melting commenced and homogeneisation took place. In the second variety the intergrowths were absent but appeared on heating. He concluded that at ordinary temperature titaniferous magnetite is in a metastable state, and on heating there is an easier molecular diffusion to attain the stable state and a more complete separation of magnetite and ilmenite takes place.

Gruner (1929), in discussing the general question of the orientation of intergrowths, found that intergrowths take place only on those crystallographic planes in which the atomic arrangement and spacing are almost alike. Ilmenite and haematite have closely related structures in which the distribution of oxygen atoms is practically identical, every third plane parallel to the base (0001) consists of oxygen ions. The oriented intergrowth is made possible by the sharing of one oxygen plane by both crystals.

Schwartz (1930) described the intergrowths in the magnetite of the Duluth gabbro, U.S.A., and later on (1942) reaffirmed in detail the significance of these textures, but offered no new explanation of their origin.

Walker (1930) investigated a specimen of maghemite from Bon Accord, Transvaal, and made a chemical analysis. This analysis was similar to those published by Wagner (1928), and also showed the presence of a considerable amount of titanium. Although the analysis could be satisfactorily interpreted on the assumption that the analysed material was a mixture of Fe_2O_3 and ilmenite, Walker assumed that titanium was present as Ti_2O_3 in solid solution with Fe_2O_3. He gave the formula of this mineral as $(Fe,Ti)_2O_3$ and suggested that Wagner's name 'maghemite' should be applied to a substance of this composition rather than to ferromagnetic ferric oxide, γ-Fe_2O_3.

Barth and Posnjak (1932, p. 333), by heating together in vacuum TiO_2, Fe_2O_3, and metallic iron in proper molecular proportions at 1150°C, were the first to prepare Fe_2TiO_4. They determined its structure as a spinel with variate atom equipoints, having the character of a double oxide $2FeO \cdot TiO_2$; the edge of the unit cube was 8.5±0.01 A. Somewhat later, the same authors (Posnjak & Barth, 1934) studied the system Fe_2O_3-Ti_2O_3 by heating appropriate mixtures sealed in evacuated silica glass tubes at 1200°C. They were able to prepare ilmenite, and a solid solution midway between ilmenite and haematite, but beyond this, i.e. between ilmenite and Ti_2O_3, repeated grinding and heating did not result in the formation of a homogeneous phase.

Jouravsky (1936) found that homogeneous titanomagnetite from basalts of Madagascar possess a reflection power which is notably much lower than both magnetite and ilmenite, and which has an abnormal dispersion. He also described some grains of titanomagnetite in which the nucleus is homogeneous while the border shows microperthitic structures. These properties cannot be explained by the presence of a homogeneous solid solution of magnetite and ilmenite, the unmixing of which depends on the rate of cooling (Ramdohr's view). He suggested that the abundance of Mg and Al oxides play an important part in helping the formation of homogeneous titanomagnetites.

Dunn and Dey (1937), in a detailed work on vanadium-bearing titaniferous iron ores from Singhbhum and Mayurbhanj, India, doubted whether true solid solution of ilmenite and magnetite exists under normal temperature and pressure conditions. According to them, any supposed natural solid solution between magnetite and ilmenite is actually an extremely fine intergrowth, the nature of the original titanomagnetite from which this separated out is still doubtful. They also questioned Foslie's theory of Fe_2TiO_4 on the grounds that in their analysed ores they found a decided deficiency of FeO. Dunn and Dey (p. 160) offered two explanations:

a) It is assumed that much of the Ti in the titanomagnetite is present as TiO_2 as well as Fe_2TiO_4, and with falling temperature the following redistribution takes place:

$$TiO_2 \quad + \quad Fe_3O_4 \longrightarrow FeO.TiO_2 \quad + \quad Fe_2O_3$$

b) In their second explanation they supposed an excess of oxygen to be present in the original titanomagnetite molecule giving maghemite instead of magnetite. They suggested the possibility that a Ti atom can take the place of a Fe atom in the γ-Fe_2O_3 cubic lattice at high temperature, i.e. at high temperature $FeTiO_3$ can assume a cubic symmetry isomorphous with magnetite and maghemite; a stable solid solution of the three compounds represents the original titanomagnetite.

Edwards (1938) made two chemical analyses of haematite which showed up to 10% TiO_2 in solid solution. He found its properties to be quite distinct from ordinary haematite, and therefore suggested the name "titanhaematite". He also described (p. 54)-in ore specimens from different Australian localities - fine ex-solution lamellae of rutile arranged along the rhombohedral directions of ilmenite-haematite ex-solution intergrowths.

Ramdohr (1939), in another paper on the ilmenite-haematite-magnetite-rutile relationships, altered some of his earlier views on the subject. He found that

Fe_3O_4 is slightly soluble in ilmenite, and that in cases where "magnetoilmenite" seems to contain 50% or more of Fe_3O_4 the magnetite in them was formed out of original haematite lamellae.

Grieve and White (1939) constructed the solidification diagram of the system TiO_2-FeO which showed three eutectic points. X-ray powder photographs confirmed the formation of two crystalline compounds: $2FeO.TiO_2$ (which they erroneously called pseudobrookite) and $FeO.TiO_2$.

Ernst (1943) also prepared $2FeO.TiO_2$ by melting TiO_2 and FeO, and found it to be the spinel ferrotitanate with $a = 8.494 \pm 0.005$ A and not pseudobrookite. He also studied the system Fe_2O_3-TiO_2, by similar melting experiments in sealed quartz tubes. This was found to be a double eutectic system. Besides haematite and rutile, only one compound, pseudobrookite ($Fe_2O_3.TiO_2$) was separated from the melt. "Arizonite", described by Palmer (1909) as $Fe_2O_3.3TiO_2$, had to be rejected as an independent mineral.

Evrard (1944) gave chemical analyses of separated ilmenite and titanomagnetite from the deposits of Håaland in the Norwegian district of Ekersund. These analyses can be compared with Foslie's analyses, and they also show an excess of FeO in the titanomagnetite molecule. The ilmenite showed an excess of Fe_2O_3 which segregates in the form of haematite lamellae, but near the contact with the titanomagnetite these are absent. Evrard suggested that this is due to the migration phenomenon which allows the departure of Fe_2O_3 from titanomagnetite, and its segregation in the ilmenite.

Mogensen (1946) was the first to discover natural "ferro-ortho-titanate" Fe_2TiO_4,from Sodra Ulvön, Sweden. The polished sections of the original ore showed, under high magnification, very fine intergrowths of two minerals, one of which was magnetite. Chemical analyses of the concentrated ore disclose a surplus of FeO lying 15-20% above the value which would have been obtained had the concentrate been composed of magnetite and ilmenite alone. X-ray powder photographs were taken which showed two spinels which compare fairly well with Fe_2TiO_4 and Fe_3O_4. After recalculation of the mineral composition of the ore on the condition that all the TiO_2 of the analysis is in the spinel Fe_2TiO_4, an excess of 3% FeO still remains. Mogensen (p. 588) supported Foslie's view on the origin of titanomagnetites, and suggested that "if FeO has in no way been removed, the formation of FeO will counteract the decomposition of Fe_2TiO_4, so that a surplus of FeO may always be anticipated in primary Fe_2TiO_4 ores".

Pouillard and Michel (1949) were able to synthesize titanomagnetite in two ways: 1) By action of TiO_2 on Fe_3O_4 at high temperature in absence of air; 2) By reduction of Fe_2O_3 by hydrogen in presence of TiO_2. They found that there is a complete solid solution of Fe_2TiO_4 in Fe_3O_4 accompanied by increase in the size of the cubic unit cell and a rapid lowering of the Curie point. The mechanism of substitution is as follows:

$$2Fe^{+3} \rightleftharpoons Ti^{+4} \quad Fe^{+2}$$

and they gave the following formula for the titanomagnetite:

$$\left[Fe^{+3}_{2-2x},\ Ti^{+4}_{x},\ Fe^{+2}_{1+x}\right] O_4$$

They also studied the system $FeTiO_3$-Fe_2O_3, by heating mixtures of ilmenite and haematite in evacuated silica glass tubes at 950°C for two hours. They did not find a total solid solution, but two series of limited solid solutions: one with base Fe_2O_3, limited at ($2Fe_2O_3$, $FeTiO_3$), and the other with base $FeTiO_3$, limited at ($2FeTiO_3$, Fe_2O_3).

In a recent work (1950), Chevallier and Girard prepared another type of titanomagnetite, by heating mixtures of Fe_2O_3 and TiO_2 with borax at 1000°C first in nitrogen, and then in a determined amount of hydrogen, and finally cooling in nitrogen. The mixture of titanomagnetite, ilmenite, haematite, pseudobrookite, and rutile was separated magnetically. Separation of titanomagnetite from the ferromagnetic ilmenite was carried out at 250°C, the temperature at which the ilmenite loses all its ferromagnetism. Chemical analysis of six samples of the titanomagnetite confirmed the formula: $yFe_3O_4 . (1-y)FeTiO_3$. X-ray powder photographs showed it to be homogeneous, and to have a unit cell which is almost that of magnetite. However, they could not explain how $FeTiO_3$ which is rhombohedral is placed in the magnetite lattice.

Ramdohr (1950, p. 660), in his recent book on ore minerals, although still keeping to his view of extensive solubility of ilmenite in magnetite at high temperature, suggests that on cooling of a solid solution of Fe_2TiO_4 in Fe_3O_4, it is possible that the ex-solved Fe_2TiO_4 may change afterwards into ilmenite intergrowths, perhaps the net unmixing of ilmenite in magnetite may be interpreted altogether in this way.

III. Materials Used.

Besides the investigations on natural minerals, the present work includes high temperature experiments on artificial compounds. The materials which have been used, therefore, consist of two types: 1) Natural minerals, 2) Materials used for the thermal work.

1) Natural minerals.

A large number of specimens from different parts of the world was studied consisting of about 45 specimens of igneous rocks and 75 ore specimens. Table A in the Appendix shows the localities, occurrences and the results of x-ray analysis of all the specimens which have been used in the present work. More attention was given to volcanic rocks, especially the basic types, owing to the fact that rapidly cooled rocks offer the best chance for the study of thd original solid solutions of the different phases. A number of gabbros, anorthosites, norites, diorites, dolerites, and essexites - where slow cooling has caused unmixing of the originally homogeneous solid solution - has also been studied. The ore collection included various types of iron and titanium oxides, e.g. magnetite, titanomagnetite, Ulvö spinel, maghemite, haematite, ilmenite, titanhaematite, rutile, iserine, and nigerine. Many of these ore minerals have been chosen from their described localities.

The bulk of the material was obtained from the collection of the Geology Department of Bristol University. From his own interesting collection, Professor P. Ramdhor lent me a number of valuable specimens which he has previously used in his work on the system $FeO-Fe_2O_3-TiO_2$ (1926). A number of specimens of the Ulvö ore - showing all kinds of transitions to dolerite - came from the Höganäs-Billesholms Aktiebolag, the owners of the Ulvö mines in Sweden. These specimens were taken from the same locality whence Mogensen (1946) described his "ferro-ortho-titanate". Dr. E. A. Vincent of Oxford University sent me an interesting sample of "magnetite" - which he separated from a gabbro occurring at the base of the Skaergaard intrusion, East Greenland - and which, after examination, proved to be similar to the Ulvö ore. A sample of maghemite, from Bon Accord, Transvaal, was furnished by Professor W. H. Newhouse of the University of Chicago, such as he has previously used in his study on iron ores (1936). It was of the same material as that chemically analysed by Walker (1930). Professor A. B. Edwards, of Melbourne University, supplied me with a polished section of his original titanhaematite from Mount Monger, W. Australia (1938), as well as samples of Fiji beach sands which showed the rare magnetite-haematite ex-solution intergrowths (1949). Mr. G. Baker, also of Melbourne University, sent me three samples from his collection of gabbros and amphibolites from New Guinea, one of which showed the only example of ilmenite-rutile ex-solution intergrowth (1952).

It has also been possible to obtain a number of samples from different other sources, including the Geological Department of the Imperial College of London, the Geological Department of Liverpool University, and the Geological Department of Fouad I University, Cairo. Some of the material has been purchased from private firms.

2) Materials used for the thermal work:

a. FeO: This was prepared by the slow decomposition in vacuum of pure (Analar) recrystallised ferrous oxalate. The ferrous oxalate was heated at about 700°C in silica bulbs after evacuation, but before sealing off.

b. TiO_2: Sample 'E', obtained from the British Titan Products Co., was used. Its chemical analysis showed: TiO_2 98.5, Sb_2O_3 0.03, FeO 0.006, P_2O_5 0.55, soluble salts 0.35, moisture 0.30.

c. Fe_2O_3: Calcined iron oxide, obtained from the British Drug Houses Ltd., was used; it contained 99.3% Fe_2O_3. Before being used this oxide was heated in air at 400°C to drive off moisture.

d. Fe_3O_4: Bisperg magnetite from Bisperg, Säter, S. Sweden, was used after magnetic separation of the finely powdered sample to remove the small amount of non-magnetic and of slightly magnetic material. Chemical analysis (Appendix, Table B, Col. 1) showed 31.43% FeO, 67.55% Fe_2O_3; it contains therefore 98.5% Fe_3O_4.

e. $FeTiO_3$: Two samples of ilmenite were used:
Sample (1) was obtained by heating FeO and TiO_2 in equal molecular proportions at 1100°C for 24 hours. Sample (2) consisted of the magnetically separated ilmenite from Taranaki, New Zealand. X-ray powder photographs of this material showed pure homogeneous ilmenite; the unit cell was exactly that of $FeTiO_3$.

IV. Mineral Separation.

In order to obtain pure minerals for X-ray and chemical analyses, mineral separation of the different components of the system $FeO-Fe_2O_3-TiO_2$ was carried out, for most of the specimens studied. This proved to be a tedious and difficult procedure for three reasons: 1) The extreme fine grain size of some of the rocks, 2) The presence of fine ex-solution intergrowths, 3) The subordinate amounts of the minerals studied, in normal igneous rocks, so that large rock specimens have had to be used for separation.

Preparation of the powder.

In the case of the igneous rock specimens, about 200-400 grams were crushed into fragments of about 2 cm. diameter. Preliminary trials for further crushing, using an especially hardened percussion steel mortar, resulted in iron contamination, which although of negligible quantity relative to the amount of rock used, became concentrated in the magnetite fraction after magnetic separation. To avoid such contamination, the small rock fragments were crushed between two horizontal discs of hard, nonmagnetic copper-beryllium alloy under a pressure of about 3 to 4 tons per square inch. A 10-ton "Denison" vertical-compression, mechanically operated machine was used. This method had the advantage of causing the least amount of friction with the rock in comparison with that caused by the heavy blows of a hammer or a mallet if a percussion mortar is used. The material was then transferred to an 80-mesh sieve and, after sieving, the coarse part was returned to the crusher without loss. The process was repeated over and over again, additional material being added as required. The crushing was continued until the last residue passed through the sieve, because it was in this residue that the hardest and the most resistant particles, including the iron and titanium oxides, were concentrated. In the case of the smaller ore specimens, a hardened diamond mortar was found satisfactory.

To disaggregate the composite grains and the coarse intergrowths of the ore minerals, the fraction which passed through the 80-mesh sieve was further ground to less than 0.1 mm. This was done in an agate mortar, using small amounts at a time. Contamination of silica from the agate pestle and mortar, if any, was removed during the separation procedure. The sieving was done through a series of 40, 60, 80, 125, and 200-mesh brass sieves.

After disaggregation was complete, it was essential to free the powder from the clay fraction before satisfactory separation was possible. This was accomplished by pouring the powder into a one-litre beaker nearly filled with water, making certain that the powder was thoroughly wetted and dispersed. Usually the fine powder had to be dampened with alcohol before adding water, in order to hasten thorough wetting. After the muddy liquid had settled for about 90 seconds, 750 mls. of the supernatant liquid were carefully decanted. The process was repeated until, after a settling period of 90 seconds, the supernatant liquid no longer remained cloudy. The powder was then thoroughly dried in an electric oven at 110°C for two hours, immediately before separation.

Procedure during separation.

Two methods of separation were used: 1) Magnetic separation; 2) Heavy liquid separation. When preparing samples for chemical analysis, the following scheme of work was generally adhered to, while in the case of samples for X-ray study, magnetic separation alone was usually found satisfactory.

1) Magnetic separation using an A.C. electromagnet:

The ferromagnetic minerals, e.g. magnetite, titanomagnetite, maghemite and pyrrhotite were separated by an A.C. electromagnet. The use of an alternating current instead of direct current has three distinct advantages: 1) The rapid agitation of the grains makes for a clean separation; 2) Since the pole-pieces are completely demagnetised the moment the circuit is broken, no ferromagnetic grains remain attached thereto; 3) The ferromagnetic grains are not themselves magnetised in the process and hence there is no coalescence of the grains.

A simple A.C. electromagnet was used, and was supported by a wooden retort stand on which a simple make-and-break switch was attached. It was also connected to a Variac transformer which provided a range of voltage and, in actual practice, a range from 10 to 24 volts has been found most satisfactory.

The sample was spread out thinly on a shallow aluminium tray, and the magnet, with the switch closed, was moved steadily over the grains at a distance from them that would just allow attraction of the ferromagnetic material, but would cause the somewhat less susceptible material such as ilmenite to agitate vigorously; the attracted material was quickly carried aside and dropped in a porcelain evaporating dish by a movement of the thumb on the switch and the process repeated until all the ferromagnetic grains were separated. The ferromagnetic fraction was then ~~more~~ ground further and magnetic separation repeated until no further purification was possible.

2) Magnetic separation using a permanent magnet:

The last stages of purification of the ferromagnetic fraction were sometimes effected by using a permanent magnet of the type used in the radar sets. Each limb was about 12 cm. in length, the pole-pieces being pointed upwards, and the distance between their tips about 1.5 cm. The maximum distance at which the ferromagnetic minerals were attracted was 10 to 12 cm., while ilmenite was not attracted except in direct contact with the poles. The impure ferromagnetic fraction was placed, in small amounts at a time, in a tube of strong glass with a diameter of about 2.5 cm., and a length of about 9.5 cm. By putting the glass tube horizontally and tapping it strongly between the two limbs of the magnet, it was possible to make the ferromagnetic minerals come to the top, while the less magnetic ones remained at the bottom, and were removed with a brush while the tube was in the magnetic field. By repeating the process, using small amounts of material, and by strong agitation, it was possible to obtain a pure ferromagnetic fraction.

3) <u>Separation by heavy liquids:</u>

Ilmenite and haematite were separated from the non-ferromagnetic fraction by using heavy liquids. Centrifuging methods had to be used, on account of the very fine nature of the material. Two tubes were used simultaneously, each having a total capacity of about 60 mls. The material was first concentrated using bromoform of Sp. Gr. 2.9. Samples (about 10 grams in each tube) were usually centrifuged for 2 to 5 minutes, at a speed ranging from 1500 to 3500 revolutions per minute. After centrifuging the light fraction was carefully decanted or siphoned out, the tubes containing the heavy fraction were refilled with bromoform, and the process was repeated. In this way it was possible to free the non-ferromagnetic fraction from quartz and all felspars.

The heavy mineral fraction (containing ilmenite, haematite, and the ferromagnesian silicates) was washed free from all traces of bromoform, using alcohol, and thoroughly dried at 110°C. The centrifuging was then repeated in the same manner using Clerici solution of Sp. Gr. 4.1 at room temperature. All the remaining silicates were thus removed, and an almost pure fraction of ilmenite, haematite, or both, was left.

4) Magnetic separation using a D.C. magnet:

If both ilmenite and haematite were present, their separation from each other was effected by using a direct current electro-magnet. It was designed to operate directly on 20-110 volts current and could carry a range of 2-20 amps. To obtain the maximum magnetic flux, the reluctance had to be as low as possible. The cores were thus made short, but with a large cross sectional area (about 8 cm. diameter and 20 cm. length). They were horizontal, with tapering, cone-shaped pole-pieces.

By means of a micrometer screw, made of hard bronze and a graduated knob, the horizontal distance between the poles could be varied and duplicated, within 0.1 mm., from 0 to 15 mm. The electro-magnet was connected to a sliding resistance, up to 9 ohms, and an ammeter. A range of 5-8 amps. was found quite satisfactory. The separation was readily effected in a glass tube in the same way as that previously described for the permanent magnet. On applying a current of about 7.5 amps., ilmenite was attracted to the top of the tube at a distance of about 4 cm. below the poles which were 2 cm. apart. Haematite was separated by increasing the current to 8 amps., by decreasing the distance between the poles, or by putting the tube in contact with the poles.

5) If any sulphide minerals were present (detected in the powder photographs), they were removed by hand-picking with a needle under a binocular microscope.

V. General remarks on the methods and techniques of analysis.

a. X-ray analysis.

Owing to the fact that the minerals studied were of high symmetry - cubic, hexagonal or trigonal - all the X-ray work was done by means of powder photographs. These were used for the identification of the different phases in both natural and synthetic materials, for testing the degree of purity of samples for chemical analysis, for the determination of the relationship between lattice dimensions and composition in various systems, and for the fixing of phase boundaries. For certain simple mixtures (usually of two minerals only), semiquantitative determinations of the constituents were carried out by making comparisons of line-intensities with photographs of standard mixtures.

Philips X-ray diffraction apparatus (type 11704) was used, with two cameras having diameters of 57.3 and 114.6 mm. In these cameras, described by Parrish and Cisney (1948), errors due to film shrinkage and inexact knowledge of the camera radius can be easily eliminated. The small powder camera was used only when a rapid identification was required; an exposure time of ½ to ¾ hour was sufficient, when 35 KV and 17 MA current was applied. To obtain good resolution, however, use was made of the large powder camera, and exposures were usually of about 1½ to 2 hours. The change of temperature of the camera during this period did not exceed 2°C. under operating conditions; the room in which the apparatus was housed was well ventilated. In almost all cases, filtered cobalt K_α radiation (iron filter) was used. Occasionally, however, copper K_α radiation (nickel filter) was used in order to obtain the extremely high-angle reflections (important for measurements of the unit cell), although the film becomes slightly fogged due to absorption by the iron present in the minerals. The wave-length values used, were:

CoK_{α_1}	1.78890 A	CuK_{α_1}	1.54050 A
CoK_{α_2}	1.79279 A	CuK_{α_2}	1.54434 A
CoK_α	1.79020 A	CuK_α	1.54180 A

Sharp unspotted X-ray powder patterns were obtained when the particle-size of the powder was about 10^{-4} cm. Gum tragacanth was mixed with the powdered material, both to act as an adhesive, and to reduce the absorption error. In order to counteract the effect of absorption, the rod-like samples were kept as thin as possible (0.2 to 0.3 mm. in diameter) and were about 1.5 cm. in length.

Ilford G. Industrial X-ray film was used and, after processing, was allowed to dry for a week before being measured. The measurements were done by means of the Hilger Measuring Device specially designed for powder photographs ~~([illegible] and Turner, [illegible])~~. This has a measuring scale with vernier; an ordinary lamp which did not create undue heat was used. By interpolation,measurements to a precision of 0.02 mm. could be duplicated. Films were at first measured twice using different parts of the scale,but no added accuracy resulted,nor were any variations in results found. For each reading, the mean of two or three separate ones was taken, which should agree to within 0.03 cm. The diffraction rings were measured on either side of the entrance and exit holes of the X-ray beam; the determination of the centers of these holes on the scale gave two valuable check-points, one of which could be used for each pair of measurements. As the Ievinš-Straumanis method of film mounting (Henry, Lipson, & Wooster, 1951,

p. 171) was used in the camera, the difference between these two points enabled the "shrinkage correction" to be applied accurately and simply.

The tabulated powder data include the observed relative intensities which were determined visually; the glancing angles for cobalt or copper radiation, together with the measured spacings in A; and in certain cases the indices of the powder lines and the calculated spacings. The lines were indexed using Bunn charts (Bunn, 1945). To eliminate systematic errors, the lattice parameters calculated from the high angle lines were extrapolated, according to the method adopted by Nelson and Riley (1945), against the function $\frac{1}{2}(\cos^2\theta/\sin\theta+\cos^2\theta/\theta)$. The best straight line was then drawn through the points, and the value of 'a', at $\frac{1}{2}(\cos^2\theta/\sin\theta+\cos^2\theta/\theta) = 0$, is recorded.

The accuracy of measurement of the lattice dimensions was 0.001%, but with special precautions a higher accuracy of 0.0005% was attained (see Section VI, a).

b. Chemical and spectrochemical analysis.

Many of the published chemical analyses of minerals in the system $FeO-Fe_2O_3-TiO_2$ are old, and have been made on material not examined under the reflecting polarizing microscope. The remainder have been proven homogeneous in polished sections only. Owing to the fact that these ore minerals usually form extremely fine intergrowths, which it may not be possible to detect with the microscope, the purity of the material used is open to question. Of the many analyses found in the literature, only two were supported by X-ray diffraction data. As far as the author is aware, no analysis has been published on material separated from volcanic rocks.

In the present work, after the magnetic and heavy liquid separation, the identity and the homogeneity of each sample was examined by X-ray powder photographs. Only from those which proved homogeneous were samples taken for chemical analysis, with the exception of two cases where completely pure samples were unobtainable, due to the fineness of the grains. For these exceptions the amount and composition of the small percentage of impurities present were determined with a fair degree of accuracy, by both microscopic and X-ray methods, and the analyses were recalculated minus these constituents. Each sample was also tested, by X-ray methods, for iron contamination. In the few cases where the iron lines appeared, cold dilute hydrochloric acid (1:5) was added to the powder for two to three hours. The acid did not affect the magnetite, titanomagnetite, or maghemite, but dissolved the iron completely.

Chemical analyses of 21 samples were made, and were used to determine the composition of the main phases, to fix the extent of solid solution, and to establish the relation between the composition and the unit cell dimensions. In a few cases (Appendix, Table B, Cols. 1, 5, 7, 15, 21), owing to the small amount of material available (about 0.5 to 1 gram), some of the rare elements present were determined spectroscopically (V, Cr, Al, Si, & Ca).

The tables of the chemical analyses show the recalculation of the percentages of oxides in the ore after the substraction of the silicate impurities, the molecular proportions, and the percentages of mineral components. Some data are given in the notes on each analysis concerning the impurities present, their amount, and the accuracy with which this is known.

c. Polished section technique.

Polished sections were made of some of the natural specimens, as well as of a few artificial preparations, in order to determine the mutual relationships of the different ore minerals, and to interpret their textures.

The specimens were mounted in the "Marco Resin" embedding solution, which was also used for impregnating the porous, crumbly artificial preparations. This transparent solution was used in the cold, under low vacuum, and hardened in a period of 24 hours.

Fine grinding was done on a phosphorus-bronze lap, using 303 emery in the case of soft minerals, or on a cast iron lap, using 600 carborundum in the case of hard minerals. This step was usually accomplished by hand, the average time of grinding being 20 minutes.

Polishing was done on rotating laps with a speed of about 100 revolutions per minute, using a "Cook Troughton & Simms" ore polishing machine. Spirally grooved plastic laps were used, these being prepared by pouring the above-mentioned "Marco Resin" on to a cast iron lap, and then inducing the spiral grooves with a lathe after the plastic had hardened. During polishing, three specimens were rotated automatically so as to be polished at the same time. The abrasive, used as a suspension in distilled water, was added to the rotating lap and, after a few minutes, became partly embedded inthe surface of the lap. This method is more advantageous than the normal method of polishing using impregnated soft metal laps (Short, 1940), owing to its being much faster than the latter. This is due to the fact that the abrasive is not entirely embedded in the plastic lap, but is partly free-rolling in a thin film on the surface. However, this technique of polishing produced surfaces of almost no relief, even when the specimens were composed of minerals of different hardness. The average time of polishing three specimens was about 90 minutes. In polishing magnetites, graded rouge was used as abrasive, while for the harder ilmenites and magnetites, chromic oxide was used. The final polishing was done by means of "Gamma Alumina" obtained from Griffin & Tatlock Ltd.

A "Leitz Panphot" photographic apparatus was used for taking the photomicrographs.

d. Thermal work.

To investigate the extent of solid solution between the different phases of the system, and to check the results obtained from the work on natural minerals, a number of experiments were made by heating mixtures of known composition at temperatures ranging from 1000° to 1200°C and then quenching. To prevent any change in composition, the materials were heated in evacuated tubes of transparent silica glass (Vitreosil). The products were examined by X-ray powder analysis, and in certain cases by means of the ore-microscope.

A Johnson-Matthey platinum-wound electric furnace (J.M.G., type T) shown in Fig. 1, was used. The ends of the furnace were plugged by loosely fitting "Alundum" tubes filled with calcined powdered magnesia. For convenience one of these is extended to form a cradle in which the silica glass tubes enclosing the oxides are carried. To prevent damaging the thermocouple and the heating elements, in the event of the bursting of the silica tubes, the other "Alundum" tube is extended to form a cover to the cradle. When the furnace, with these "Alundum" tubes in place, is running at the desired temperature, the former "Alundum" tube may be quickly slipped out, the silica tube dropped in the cradle, and the "Alundum" tube slipped back to position, without greatly disturbing the temperature or temperature distribution in the furnace. For rapid quenching the furnace was used in the horizontal position, the "Alundum" tube carrying the silica tube being rotated as it is withdrawn so that the silica tube will drop into the vessel containing the quenching medium. The temperature of the furnace was controlled automatically using an A.C. pyrometer.

Two important requirements in working with sealed tubes are: first, that the composition of the charge should not change significantly during the heat treatment; second, that it should be readily determinable, from an examination of the charge - whether by X-ray analysis or under the microscope - what phases had been present in it before quenching.

That the first of these requirements has been met will be evident from the following considerations. The silica tubes were evacuated to a pressure of 10^{-4}mm. Hg using a mercury pump. The volume of these tubes is so small - the largest had a volume of 2 cc. which enclosed a charge of 1 gram - that the amount of oxygen left is negligible.

Tube should be central

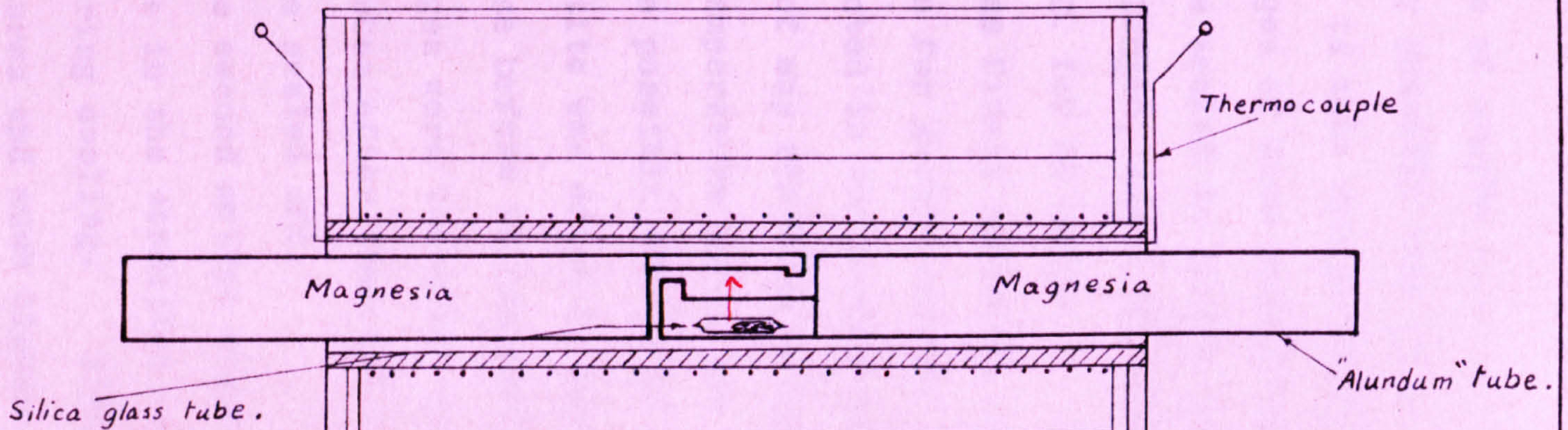

Fig. 1. Diagram of platinum-wound electric furnace used for heating charges in sealed silica glass tubes.

Diffusion of oxygen from the air through the silica glass may possibly take place at 1100°C., but, if so, the rate is slow enough to be ignored in this work. Two charges of pure magnetite weighing about 0.5 gram each were sealed in silica glass tubes of 4.5 mms. bore, 50 mms. length, and 1 mm. wall thickness, then heated at 1100°C. for 48 hours. After the run the whole charge was finely powdered, and a representative sample was taken for X-ray analysis. No change in composition was detected in the powder photographs. Furthermore, no sign of any reaction between the silica and the oxides, at the temperature used, was observed.

The possible effect of moisture was also investigated. If magnetite was dried by being heated in air it begins to oxidize before it has given up all its water. All the charges were therefore dried by being heated in the silica tubes after they had been evacuated, but before they were sealed off.

The second matter requiring consideration is that no change in the condition of the charge should take place during cooling. Although in experiments at high temperatures and much higher oxygen pressure dissociation often occurs during cooling, it evidently does not take place in these experiments, so any haematite present in the charge remains. Since the charge was protected by the tube from the air, and no oxygen is supplied by dissociation, oxidation does not occur during cooling, so any magnetite present also remains. Unmixing of solid solutions did not occur, when the charges in silica tubes of 4.5 mm. bore were quenched in water. All the runs were carried out in such tubes. Two experiments were made, one on ilmenite from Hamata, Egypt (ex-solution intergrowths of titanhaematite and ilmenite), and another on the Ulvö ore from Sodra Ulvön, Sweden (ex-solution intergrowths of magnetite and Fe_2TiO_4). Each charge was heated at 1050°C in evacuated silica glass tubes for 24 hours, and then quenched in water. In both cases, X-ray powder photographs showed only one mineral which was the homogeneised solid solution; no unmixing was detected.

VI. Results of investigations on natural and synthetic material:

a. Accurate determination of the cell dimensions of magnetite.

Many oxides have been described with formulae between FeO and Fe_2O_3, but the only homogeneous phase is Fe_3O_4, known under the name magnetite. There is little reliable evidence for the occurrence of polymers of Fe_3O_4, although there are some strange discontinuities in several curves which require further investigation. Schlaepfer and Niggli (1914), in experiments on mineral synthesis, obtained some orthorhombic crystals which they thought to be probably an unstable chrysoberyl modification of Fe_3O_4. However, it was in no way shown that the composition of these crystals was actually Fe_3O_4, and no further evidence for a chrysoberyl modification has been published.

It may, therefore, be said that only one form of Fe_3O_4 is known to exist. This form is cubic, a member of the spinel group, the unit cell containing 8 Fe_3O_4 molecules. Its crystal structure was one of the first to be investigated, being analysed in 1915, independently by Bragg in England and Nishikawa in Japan. However, it is surprising to find that, despite the comparative simplicity of determining the lattice dimensions of cubic minerals, only three measurements of the cell-edge of naturally occurring magnetite have been published. Holgersson (1927) gave measurements of two natural magnetites from Sweden: one from Dalarna with a cell-edge of 8.400 ± 0.003 A, and the other from Nordmarken with a cell-edge of 8.412 ± 0.003 A. However, he did not give any chemical analyses. Newhouse and Glass (1936, p. 703), in their study of some physical properties of iron oxides, gave 8.379 A for the cell-edge of magnetite from Lovers' Pit, Mineville, N.Y.; chemical analysis showed nearly pure Fe_3O_4 (Appendix, Table B, Col. 22). This figure was obtained by averaging all values calculated from the different lines recorded on their film. Unfortunately, they did not give the values of the lattice spacings, nor any details of the method they used. The cell-edge of magnetite is better known however for the artificial compound, and the measurements by different workers range from 8.36 to 8.45 A.

It is evident that there is a need for reliable and accurate data on the lattice dimensions of such a common mineral as magnetite. Determination of such data is important before starting the study of magnetite solid solutions with other compounds. A specimen of magnetite from Bisperg, Säter, Dalecarlia, S. Sweden, was found by chemical and spectrochemical analysis (Appendix, Table B, Col. 1) to be exceedingly close to the ideal stoichiometric composition Fe_3O_4. A portion of the analysed sample was studied by the X-ray diffraction method; X-ray powder patterns (Plate 1, Fig. 3) were obtained on the 114.6 mm. diameter powder camera. Although the low θ values were indicated by sharp lines, the important large angle ones, i.e. the back-reflection lines, were diffuse. This results from induced dislocation or strain of the crystal structure as is commonly found in metals. Guided by the fact that annealing is customarily done to metallurgical powder samples and also to radioactive minerals to obtain better X-ray photographs, the powdered magnetite sample was heated to between 300 and 400°C for a few minutes. To safeguard against oxidation, the heating was carried out in evacuated silica glass tubes. The remarkable improvement in definition is apparent from Figs. 1 & 2, Plate 1, which show the same sample before and after annealing. The decrease in fuzziness on annealing is actually equivalent to recrystallisation. It could readily be established that it was the grinding process which mainly, if not wholly, caused the lattice distortion for, if the annealed powder was again ground, the sharp lines gave place to diffused ones in the X-ray pattern.

The interplanar spacings and indexing of eight lines of the X-ray powder pattern for higher diffraction angles on the large camera are given in Table 1, together with the lattice parameter calculated from each spacing. The table shows in the back-diffraction region a slight but definite increase of the cell-edge calculated from the lines of the powder pattern with increasing angle of diffraction. As is well known, this arises from systematic offsetting of the diffraction lines, and the error in the lattice parameter measurement can be greatly lowered by extrapolation back to $\theta = 90°$. The parameter values calculated from the high-angle lines of the pattern were extrapolated, according to the method adopted by Nelson and Riley (1945), against the function $\frac{1}{2}(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$. A straight line was obtained (Fig. 2), and the parameter determined by this extrapolation was 8.3963 A. The measurements were made for the specimen at 18°C, using a cobalt target and an iron filter. The wavelengths of the X-rays from the cobalt target were taken as $K\alpha_1$=1.78890 A, $K\alpha_2$=1.79279 A, $K\alpha$=1.7902A. Doublets were resolved for the lines having θ ranging between 60° and 80°.

Table 1

Magnetite, Bisperg, S. Sweden. Stronger lines at higher diffraction angles of the X-ray powder pattern on the 114.6 mm diameter camera. Co target, Fe filter.

θ	d(measured)	hkl	a(A)	$\frac{1}{2}(\cos^2\theta/\theta + \cos^2\theta/\sin\theta)$
54.992	1.0922 α_1	(731),(553)	8.3873	0.3720
58.519	1.0489 α_1	(800)	8.3896	0.2940
64.730	0.9890 α_1	(822),(660)	8.3918	0.1800
65.003	0.9890 α_2		8.3922	0.1770
67.344	0.9692 α_1	(751),(555)	8.3929	0.1435
67.640	0.9692 α_2		8.3930	0.1396
72.353	0.9386 α_1	(840)	8.3943	0.0846
72.763	0.9386 α_2		8.3944	0.0805

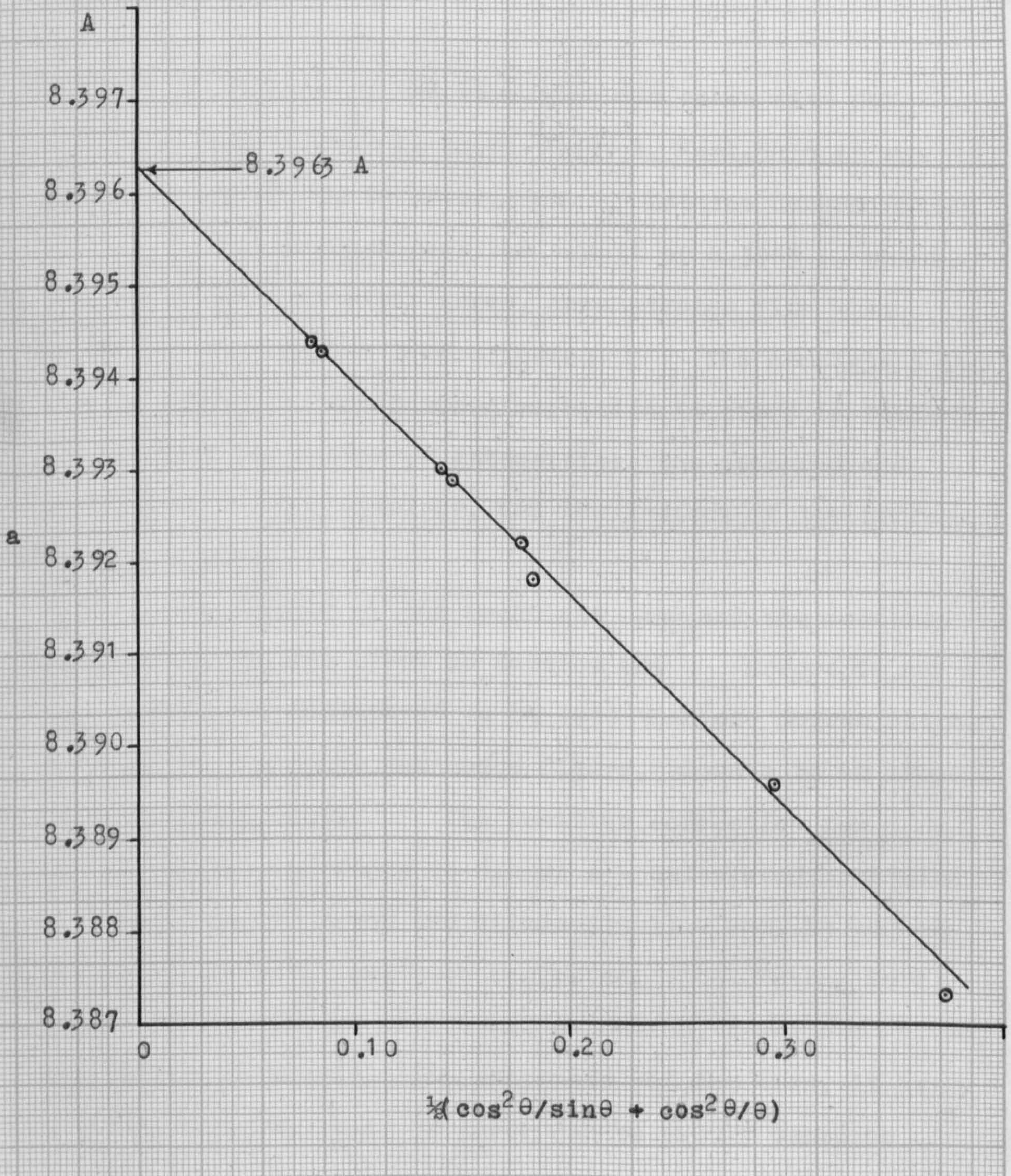

Fig. 2. Extrapolation curve for the accurate determination of the lattice parameter of magnetite at 18°C.

Another photograph of the same specimen taken with CuK$_{\alpha}$ radiation (Kα_1=1.5405 A, Kα_2=1.54434 A, Kα=1.5418 A) was somewhat fogged due to absorption. Lattice determination from such a photograph gave the result of 8.3965 A, which, despite a small possible error, demonstrates with what precision results can be duplicated. The complete X-ray powder pattern of the Bisperg magnetite is given in Table 2, which shows the estimated intensities, the measured and calculated lattice spacings, and the indices of the different crystal planes.

A description of the technique used, and the accuracy of measurement, was given in Section V,a. Errors in temperature are considered to be less than one degree which, in terms of the final cube-edge figure, amounts to an error of less than 0.0001A. The positive correction for refraction for magnetite is 0.0001 A - calculated according to the method of Lipson and Wilson (1941) - and, in common with other workers, has been neglected. Taking into consideration factors of thermal expansion, X-ray absorption, elimination of strain, line sharpness and the like, it is believed that the limit of error can be safely taken as 0.0005 A.

Table 2

Magnetite, Bisperg, S. Sweden. X-ray powder data.
(Co K_α radiation); a = 8.3963 ± 0.0005 A.
Comparison with spacings from two A.S.T.M. index cards.

I	d(meas.)	hkl	d(calc.)	d 1-1120	d 3-0877
30	4.847	(111)	4.847	4.85	4.7
70	2.966	(220),(202)	2.968	2.97	2.96
100	2.530	(311),(113)	2.532	2.53	2.53
10	2.419	(222)	2.423	2.42	2.41
60	2.096	(400),(004)	2.098	2.10	2.09
40	1.712	(422),(224)	1.714	1.71	1.71
80	1.614	(511),(333)	1.616	1.61	1.60
90	1.483	(440),(404)	1.484	1.48	1.49
15	1.327	(620),(602)	1.328	1.33	1.33
20	1.279	(533),(335)	1.281	1.28	1.28
10	1.264	(622)	1.266		
15	1.2112	(444)	1.2120	1.21	1.22
20	1.1214	(642)	1.1220	1.12	1.13
40	1.0922 α_1	(731),(553)	1.0930	1.09	1.10
25	1.0489 α_1	(800)	1.0495	1.05	1.05
10	0.9890 α_1	(822),(660)	0.9895		
5	0.9890 α_2	(822),(660)	0.9895		
30	0.9692 α_1	(751),(555)	0.9695	0.97	
20	0.9692 α_2	(751),(555)	0.9695	0.97	
20	0.9386 α_1	(840)	0.9387	0.94	
15	0.9386 α_2	(840)	0.9387		
25*	0.8794 α_1	(931)	0.8800	0.88	
35*	0.8565 α_1	(844)	0.8589	0.86	
20*	0.8565 α_2	(844)	0.8589	0.85	
30*	0.8113 α_1	(951)	0.8115	0.81	
15*	0.8113 α_2	(951)	0.8115	0.81	

* Measurements of these five lines were obtained from a photograph taken with CuK_α radiation.

Four other samples of practically pure magnetite, which have also been chemically analysed (Appendix, Table B, Cols. 2, 4, 5, 6), were examined in the same way and their unit cell dimensions were found to range from 8.3960 to 8.3970 A. In view of the fact that the Bisperg magnetite was the purest sample examined here, it is proposed to take its value as representative of pure natural magnetite until such time as a purer specimen is measured:

Magnetite, Bisperg, S. Sweden, at 18°C.
$a_0 = 8.3963 \pm 0.0005$ A.

The accurate determination of the unit cell of magnetite now allows a check of the "d-spacings" given in the A.S.T.M. X-ray cards; Table 2 shows the fairly good agreement obtained between the calculated and observed spasings recorded on two of the cards.

Many elements may substitute either the divalent or the trivalent atoms in Fe_3O_4, and as a result pure magnetite is the exception and not the rule. It is astonishing to see the variation in qualitative and quantitative data on the physical properties of magnetite. Thus figures for the specific gravity vary between 4.96 and 5.3 . From the present X-ray data on the Bisperg magnetite, its specific gravity was calculated to be 5.192. The formula (Bragg, 1947): $\rho = 1.66020\Sigma A/V$, was used, where ρ is the density, ΣA is the sum of the atomic weights of the atoms in the unit cell, and V is the volume in A^3 of the unit cell.

Comparison of the cell-edge obtained for naturally occurring magnetite with that given by other investigators on artificial preparations is difficult because of striking variations among the latter. The following measurements[*] have been collected from the literature, with errors as estimated by the respective authors:

8.3963 ± 0.0005 A	naturally occurring, this thesis.
8.361 ± 0.003 A	Clarke, Ally & Badger (1931).
or 8.389 ± 0.003 A	Clarke, Ally & Badger (1931).
8.373 ± 0.002 A	Bénard (1939).
8.380 A	Hägg (1935).
8.3940 ± 0.0005 A	Tombs & Rooksby (1951).
8.3940 ± 0.0005 A	Abrahams & Calhoun (1953).

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[*] Throughout this thesis measurements are given in angstrom units, converted when necessary from the original values in the references cited. In the absence of a statement of the wave-length used, particularly before 1943, the measurements, although usually specified as being in A, were presumed to be in kX.

8.41 A	Gaglioti & D'Agostino (1936).
8.413 A	Pouillard (1949).
8.417 A	Holgersson (1927).
8.42 A	Frank-Kamenecky (1939).
8.441 ± 0.0043 A	Van der Marel (1951).

The values given by the earlier workers up to 1940 may not be quite as precise as indicated for, at the time when these measurements were made, the nature of the systematic errors was not fully known. The wave-length values for the various radiations differ appreciably from the present values. The measurement of the unit cell dimensions was usually determined by taking the average of the values calculated from all the lines of both low and high angle θ. In most cases there was no resolution of K_{α_1} and K_{α_2} radiations. Thus the measurement of Clarke, Ally and Badger (1931), which is that given in the 7th edition of Dana's System of Mineralogy (1944, p. 698), needs further consideration. In their original paper the value of 8.374 ± 0.003 A is given. This figure was obtained by averaging all values calculated from all the lines recorded on their film, which was measured with a scale reading directly in lattice spacings. This averaged result, which has no pretensions to high accuracy and which was determined 20 years ago, is also adopted by the well known "Handbook of Chemistry and Physics, 33rd edition" (1951-52). The two values listed above were obtained by conversion, firstly to angstrom units from the wave-length 0.712 "A" stated for the Mo radiation used, secondly, from the wave-length 0.70783 kX then known for MoK in which the scale may have been calibrated. As to the exceptionally high value that was obtained by Van der Marel (1951), this is most probably due (as the author also indicated) to impurities in the samples. The unit cell of magnetite is augmented by small amounts of titanium or manganese as was proved by the experiments of, respectively, Pouillard (1949), and Bénard and Chaudron (1937).

The only result which deserves serious consideration is that given by Tombs & Rooksby (1951). Exactly the same value - $a = 8.3940 \pm 0.0005$ A at 22°C - was determined in a recent paper by Abrahams & Calhoun (1953). Their results, obtained from measurements on synthetic Fe_3O_4, show a very satisfactory agreement with the value for natural magnetite, determined in the present work.

Another possibility which has to be considered in this respect is the variation in chemical composition, as shown by the presence of oxygen in excess of the stoichiometric formula requirements. The spinel structure has long been known as capable of existing with a deficiency of metal constituents below the requirements of the formula AB_2O_4. With this there is a commensurate replacement of the A or lower valency cation to maintain over-all electrostatic neutrality, and a corresponding decrease in cell dimensions (see Section VIc, on the System $Fe_2O_3 - Fe_3O_4$). Hägg (1935) found that magnetite, when oxidised at up to 300°C, may vary continuously in composition from Fe_3O_4 to $Fe_{8/3}O_4$, retaining the same structure but with a uniform decrease in the cell-edge from 8.38 to 8.32 A. Furthermore, from the work of Greig and his co-workers (1935), magnetite was found to be capable of containing about 30% Fe_2O_3 at 1452°C. The product would give an X-ray powder pattern of the spinel type but with slightly lower cell dimensions than that of composition Fe_3O_4. The artificial preparations of Fe_3O_4 on which the cell dimensions quoted in the above list were measured, were made either from slags, the so-called hammer-scale (Holgersson, 1927); or by heating at up to 1300°C preparations containing Fe^{2+} and Fe^{3+} in the atomic ratio 1:2 (Clark, Ally, and Badger, 1931); or by reduction of haematite at high temperatures up to 1400°C. with hydrogen.

In none of these preparations was a check made on the $Fe^{2+} + Fe^{3+}$: O ratio after heating. An increase of oxygen beyond the formula requirement may well have occurred, and may be the reason for the low values of the cell-edge as observed in some of the preparations.

The presence of such defects in the lattice may be determined from the chemical analysis. The atomic ratio of total cations to oxygen will be 3:4 for a structure without vacant cation positions. The analysis of the Bisperg magnetite (Appendix, Table B, Col. 1) was recalculated in atomic ratios relative to O = 4.000, and gave the formula: $Fe^{2+}_{1.024}Mg^{2+}_{0.010}Fe^{3+}_{1.984}O_{4.000}$. The ratio of total cations to oxygen was 3.018: 4.000, which, within the limits of error of analysis, is close to 3:4. The lattice parameter for this material therefore represents that of Fe_3O_4 without vacant cation positions.

Finally, the influence of the structure type on the cell dimensions of magnetite remains to be considered. In the normal structure of an AB_2O_4 spinel (Bragg, 1915), the unit cell with 32 O contains 8 A cations occupying the equiposition 8(a), in tetrahedral coordination with the oxygen, and 16 B cations in the 16(d) equipositions, in octahedral coordination with the oxygen. In some spinels, the so-called inversed spinels, (Barth and Posnjak, 1932), the cations occupy the same two equi-positions, but 8 B cations fill the 8(a) positions, and 8A + 8B are distributed at random through the 16(d) positions. In the case of magnetite, the scattering power is the same and, therefore, the intensities of the X-ray diffraction beams do not enable a distinction to be made between the two structures. However, Verwey and Boer (1936) have proposed an inversed arrangement for Fe_3O_4 on account of its high electron conductivity - in comparison with that of similar compounds (Mn_3O_4,γ-Fe_2O_3) - which they explained on the basis of continuous interchange of electrons between Fe^{3+} and Fe^{2+} at the 16-fold position. Verwey and Heilmann (1947) also classified Fe_3O_4 as inversed 2-3 spinel $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$, on the basis of the values of unit cell of a large number of spinels. They found that, in going from the spinel series (aluminates) through the chromite series (chromites) to the magnetite series (ferrites), there is a regular increase in cell dimensions. For ferrites with normal structure, there is an increase of about 0.12 A above the cell dimensions of the corresponding chromites (Table 3), while for ferrites with inverse structure, there is a much smaller increase (of about 0.05 A). In the series $FeAl_2O_4$-$FeCr_2O_4$-$FeFe_2O_4$ the increases 0.22 A and 0.05 A respectively were therefore taken by Verwey and Heilmann to indicate the inverse structure of magnetite. This is contrary to the electrostatic rules (normal 2-3 spinels are more stable than the inversed 2-3 ones), but is found to be in complete accordance with other physical properties of magnetite.

At elevated temperatures where the thermal vibrations in the lattice are relatively large, a more general random distribution of the cations in magnetite, or a partial change to the normal type structure may occur. If this were the case, small variations in the lattice dimensions may occur in Fe_3O_4 after heating, varying with the heating and rate of cooling or quenching of the material. A similar change in cation arrangement at high temperatures has been deduced for other members of the spinel group e.g. Fe_2AlO_4 and $MnFe_2O_4$.

Table 3. Lattice dimension differences in the spinels.

B r(B^{3+})	Al 0.57		Cr 0.64		Fe 0.67	Structure of the ferrite.
A						
Zn	8.07	0.23	8.30	0.12	8.42	normal
Cd	-	-	8.57	0.12	8.69	normal
Cu	8.07	(0.24	-	0.06)	8.37	inverse
Mg	8.07	0.24	8.31	0.05	8.36	inverse
Ni	8.05	0.25	8.30	0.06	8.36	
Mn	8.26	0.23	8.49	0.06	8.55	
Fe	8.12	0.22	8.34	0.05	8.39	
				0.06	8.40*	

Modified from Verwey and Heilmann (1947).

*The value of cell-edge for magnetite as determined in this thesis, simplified to three significant figures.

b. The system FeO - Fe_3O_4.

In discussing the ferrous oxide it must first be emphasised that a stable solid phase with a composition corresponding to the formula FeO does not exist.

This fact was first discovered by Schenck and Dingmann (1927), who showed that the so-called FeO always contains less iron than the formula requires. Their results indicated that the homogeneous phase FeO which was named by them "wüstite" contained 75.76% - 76.59% Fe at 600°C, increasing to 75.22% - 77.33% Fe at 1100°C (for pure FeO, Fe = 77.73%). The most thorough and satisfactory investigation of the wüstite solid solution is that of Jette and Foote (1933), who fixed the homogeneity limits of this phase by means of X-ray studies, and gave an adequate explanation of its structure. According to their results, wüstite has the NaCl type of lattice; the lattice dimensions decrease rapidly with decrease in iron content from 4.3023A (76.79%Fe) to 4.2722A (75.72%Fe). By extrapolation of their measurements, the lattice dimensions of the theoretical FeO were found to be 4.332A. The values given by many investigators for the lattice dimensions of FeO - 4.27

to 4.3A - all refer to wüstite. In addition, however, most of the methods used for the preparation of ferrous oxide are misleading; the supposed FeO sold commercially is generally formed of metallic iron and Fe_3O_4, which can be readily established by testing with a magnet, wüstite being nonmagnetic. In the present work, homogeneous wüstite was prepared by the slow decomposition in vacuum of pure recrystallised ferrous oxalate (see Section 111). Measurements on X-ray powder photographs (Plate 1, Fig. 6), gave a unit cell of 4.295 ± 0.001 A.

Wüstite is unstable at ordinary temperatures, the reaction

$$4FeO \rightleftharpoons Fe_3O_4 + Fe$$

proceeding to the right below 575°C. and to the left above this temperature. Thus the triple point at which Fe, wüstite, and magnetite are in equilibrium lies at 575°C. By rapid cooling, wüstite can be obtained at room temperatures, at which the rate of disintegration into Fe_3O_4 and Fe is practically nil. Sufficiently slow cooling, however, results in the complete disintegration of wüstite.

The occurrence of FeO (wüstite) as a mineral has only once been indicated, by Brun (1924) who named it "iozite". His description is far from convincing, and has never been confirmed. According to him, "iozite" often occurs in recent iron-rich lavas, as swarms of minute granules up to 0.01 mm. in diameter surrounding microlites of feldspar and pyroxene. However, the properties of "iozite", especially its ferromagnetism, are not those of wüstite, but of magnetite; and it appears very probable that Brun's "iozite" is actually magnetite, possibly with excess FeO in solid solution. The analyses on which Brun based his arguments were made on the rock as a whole. During X-ray examination of the heavy fractions separated from a great number of iron-rich basalts, the author has not been able to distinguish the FeO lines in any of the powder photographs taken. At present it may safely be concluded that wüstite does not occur as a mineral, and therefore the name iozite should be rejected.

As to the possibility of solid solution of FeO in magnetite, there is practically no conflict between the various investigations on artificial preparations. All agree in giving a very low figure - not more than 3wt.%FeO - for the limiting solid solution, below 1200°C. Thus it appears that in magnetites whose analyses show a considerable excess of FeO, the excess is accounted for either by the presence of foreign elements, especially titanium in solid solution, or by the possibility that the analysed material was not homogeneous. The few more or less convincing descriptions of magnetites with excess FeO, such as that of Palmunen (1925) which led him to suggest the formula $3FeO.2Fe_2O_3$, are all of magnetites from titanium-rich igneous rocks. It is almost certain that this excess FeO was present in the spinel $2FeO.TiO_2$, which enters in solid solution with the magnetite molecule, forming titanomagnetite (see Section VI, h).

In the homogeneous, non-titanium magnetites analysed in the present work, as well as those from the literature, not more than 2% FeO was found in solid solution, which agrees well with the results obtained with artificial preparations. In Table 4, new chemical analyses of two specimens of magnetite are given which show an excess of 1.2% and 1.9% FeO respectively, in solid solution. X-ray powder photographs (Plate 1, Fig. 4) show exactly the same pattern as that of pure magnetite.

Table 4

Chemical Analyses of Fe_3O_4 - FeO solid solutions.

		% High grade concentrate	Ore		Mineral component		
			%	Mol	Mol		%
1.	TiO_2	Traces			407	$FeFe_2O_4$	94.4
	Fe_2O_3	66.54	68.59	428	9	$MnFe_2O_4$	2.0
	Al_2O_3	Traces			12	$MgFe_2O_4$	2.4
	V_2O_3	-					
					18	FeO	1.2
	Cr_2O_3	Nil					100.0
	FeO	29.72	30.64	425			
	MnO	0.26	0.27	9			
	MgO	0.49	0.50	12			
	SiO_2	2.02			Impurities 2.3%:quartz.		
	Total	99.03	100.00				
2.	TiO_2	Traces			413	$FeFe_2O_4$	95.8
	Fe_2O_3	65.42	67.66	423	7	$MnFe_2O_4$	1.6
	Al_2O_3	Traces			4	$MgFe_2O_4$	0.7
	Cr_2O_3	Nil					
					27	FeO	1.9
	FeO	30.64	31.69	440			100.0
	MnO	0.49	0.51	7			
	MgO	0.14	0.14	4			
	SiO_2	2.48			Impurities 2.5%:quartz.		
	Total	99.17	100.00				

1. Magnetite. Binnental, Germany. Analyst, W. H. Herdsman. S 609.
2. Magnetite. Forola, Sweden. Analyst, W. H. Herdsman. S 610.

c. The System Fe_2O_3 - Fe_3O_4.

1) The two forms of Fe_2O_3:

Two distinct forms of Fe_2O_3 are known: α-Fe_2O_3 (haematite), and γ-Fe_2O_3 (maghemite). It is evident on reviewing the literature, that the significance of the relationship between these two forms, whether enantiotropic or monotropic, has not been fully appreciated. Many investigators have given a transition point for the change from γ-Fe_2O_3 to α-Fe_2O_3, but there is a lack of agreement on the temperature of such a change (200°C. to 700°C.). It is possible that this supposed transition point is merely the temperature at which the rate of change becomes noticeable; this temperature is largely dependent on the previous history of the sample, its method of preparation, and the presence or absence of impurities. The change from γ-Fe_2O_3 to α-Fe_2O_3 is irreversible, a fact which suggests that the two forms are monotropic. As γ-Fe_2O_3 changes to α-Fe_2O_3 with evolution of heat, and the density of the γ-form is considerably less than that of α-form, the evidence for the metastable nature of the γ-form is conclusive. However, at ordinary temperatures the rate of inversion of γ-Fe_2O_3 is so slow that it can be easily prepared and studied, and can also occur naturally as the mineral maghemite.

Note on the nomenclature of maghemite.

The occurrence of γ-Fe_2O_3 as a mineral was first noted by Sosman and Posnjak (1925) in a specimen from Iron Mountain, Shasta County, California. In 1927, **Wagner** announced the discovery of very large quantities of this substance in the so-called titaniferous magnetite segregations in the upper part of the norite zone of the Bushveld igneous complex, Transvaal, and proposed the name maghemite for the mineral. Later Walker (1930, p. 18) gave the formula $(Fe,Ti)_2O_3$ for a specimen from Bon Accord, Transvaal (also in the Bushveld complex), and suggested that Wagner's name maghemite should be applied to a substance of this composition rather than to ferromagnetic ferric oxide, γ-Fe_2O_3. However, X-ray powder photographs and chemical analyses (Newhouse, 1936; and the present work) show that natural minerals quite identical in structure and composition with those of artificial γ-Fe_2O_3 do exist. Therefore, it is suggested that the name maghemite should be restricted, as originally intended by Wagner, to natural γ-Fe_2O_3, while for those minerals with composition approaching $(Fe,Ti)_2O_3$ (e.g. the Bushveld maghemites) I propose the new name "titanomaghemite" (see Section VI, d).

The name maghemite has now become generally accepted, but not without opposition. Schneiderhöhn and Ramdohr (1931), who thoroughly discussed this mineral in their "Lehrbuch der Erzmikroskopie", considered maghemite an unsuitable name on the grounds that it suggested a magnetic haematite, and would have prefered to call it "sosmanite", but conformed with the laws of priority and adopted the name maghemite. However, Winchell (1931) rejected maghemite as indicating either a substance between magnetite and haematite (homogeneous substances of this kind are unknown) or haematite which had become magnetic, and suggested the name "oxymagnite", an abbreviation for "oxydized magnetite". Apart from the fact that Wagner clearly stated that the name maghemite was intended for the naturally occurring γ-Fe_2O_3, and that it would be a gross and unnecessary breach of priority to rename it "oxymagnite", Winchell's name can be justifiably rejected on the grounds that natural γ-Fe_2O_3 can be formed not only by the oxidation of magnetite, but also by the dehydration of lepidocrocite.

2) <u>Maghemite - magnetite solid solutions</u>:

Before establishing the relationship between magnetite and maghemite it would be preferable to discuss the maghemite structure. Sosman and Posnjak (1925) showed by powder photographs that its structure is practically identical with that of magnetite, and thus quite distinct from haematite α-Fe_2O_3. As soon as this fact was realised, attempts were made to find out the positions of the atoms in the unit cell. It was first thought that the problem consisted of fitting in four extra oxygen atoms within the magnetite unit, according to the scheme

$$\underset{\text{(unit cell of magnetite)}}{Fe_{24}O_{32}} + 4O \longrightarrow \underset{\text{(unit cell of } \gamma\text{-}Fe_2O_3)}{Fe_{24}O_{36}}.$$

On this assumption Welo and Baudisch (1925), and Twenhofel (1927), proposed a structure in which the four extra atoms were accommodated. However, there are strong objections to such a structure; firstly it is difficult to see how four extra oxygen ions, with their large radius, could be fitted into the already close-packed structure of magnetite; secondly, it gives rise to the improbable co-ordination number 5; and thirdly, the density of γ-Fe_2O_3, instead of being less, is made to be greater than that of α-Fe_2O_3. A structure of γ-Fe_2O_3 free from these objections was published independently and almost simultaneously in 1935 by Hägg, by Verwey, and by Kordes, who all came to the conclusion that the excess of oxygen in the spinel lattice of γ-Fe_2O_3, compared with Fe_3O_4, is due to empty iron positions, 1/9 of the metal positions in the magnetite lattice being vacant in γ-Fe_2O_3. Thus the unit cell of maghemite is not $Fe_{24}O_{36}$, but $Fe_{21\frac{1}{3}}O_{32}$. This structure is in good accord with both X-ray and physical data and is undoubtedly correct in principle, although Haul and Schoon (1939) have observed a number of weak additional lines in powder photographs of γ-Fe_2O_3, which they suggest indicate either a lower symmetry, or a larger unit cell than has been postulated for this substance. Another possible explanation is that the vacant positions are arranged regularly in the lattice. Some of these additional lines, especially two lines with spacings of about 5.9 and 4.1 A (Table 6, Col. 5), appeared in the X-ray photographs of all the maghemite samples which the author has examined (Plate 2, Figs. 5,6).

The analyses of maghemite which have been published all show a certain percentage of FeO (Table 5). This FeO is probably combined with the TiO_2 present, as ilmenite, especially in specimens from the Bushveld occurrences.

Table 5.

Chemical Analyses of Magnetite-maghemite Solid Solutions.

	1	2	3	4	5	6	7	8
TiO_2	0.16	0.84	0.49	Traces	2.54	19.45	0.35	-
Fe_2O_3	69.88	70.46	69.88	75.26	80.63	64.92	73.75	85.30
Al_2O_3	0.34	Traces	0.16	Traces	0.30	<0.01	2.96	-
V_2O_3	0.02	-	0.18	-	0.12	2.40	0.31	-
Cr_2O_3	0.07	-	<0.01	-	<0.01	<0.01	-	-
FeO	27.93	26.08	22.90	24.48	12.75	7.87	15.30	2.40
MnO	0.07	0.58	0.10	-	0.18	0.24	1.43	-
CaO	0.03	-	1.00	Traces	0.76	0.70	0.43	-
MgO	0.14	0.18	1.88	0.10	0.91	1.05	0.30	-
SiO_2	1.07	1.24	2.20	0.53	0.84	1.60	2.35	-
H_2O	-	-	-	-	-	-	3.01	3.10
Rem.	-	-	-	-	-	-	-	4.30
Total	99.71	99.38	98.79	100.37	99.03	98.23	100.19	95.10

1. Magnetite-maghemite. Devon. Analyst, H. B. Milner (new analysis). S 172.
2. Magnetite-maghemite. Mt. Blagodot, Urals, U.S.S.R. Analyst, W. H. Herdsman (new analysis). S 391.
3. Magnetite-maghemite. Mourne, Co. Down, Ireland. Analyst, H. B. Milner (new analysis). S 407.
4. Magnetite-maghemite. Windpass Mine, British Columbia. Analyst, Keyes. (Newhouse and Glass, 1936, p. 701).
5. Maghemite-magnetite. From basalt. Co. Antrim, Ireland. Analyst, H. B. Milner (new analysis). S 456.
6. Titanomaghemite-magnetite. Bon Accord, N. Pretoria, Transvaal. Analyst, H. B. Milner (new analysis). S 542.
7. Maghemite-magnetite. Bukusu Hill, Uganda. Analyst, H. J. Broughton. (Broughton, Chadwick, and Deans, 1950, p. 263).
8. Maghemite-magnetite. Iron Mountain, Shasta Co., California. Analyst, Hostetter. (Sosman and Posnjak, 1925, p. 333).

It may also be present as remnants of magnetite, but in some cases it occurs in the homogeneous γ-Fe_2O_3. Hägg (1935, p. 98) showed that the oxidation of Fe_3O_4 to γ-Fe_2O_3 is a continuous process, the cell-edge decreasing continuously from 8.380 A for Fe_3O_4 to 8.322 A for γ-Fe_2O_3. It is therefore conceivable that all stages in the oxidation of magnetite to maghemite may take place, and consequently the optical properties, as seen in polished sections, would also vary continuously from magnetite to maghemite.

These intermediate substances have not been previously recognised, but in the present work their existence is proved with certainty. Table 6 shows the results of X-ray measurements of five such samples. The powder photographs (Plate 2, Figs. 2-6) show the pattern of either magnetite or maghemite, but not a mixture of the two. These five samples were chemically analysed (Table 5). Samples 5 and 6 showed - after allowing for ilmenite - 45 and 25 wt.% Fe_3O_4 respectively, together with the maghemite. As the powder photographs did not show any magnetite lines, the excess Fe_3O_4 must be present in solid solution in the maghemite. Similarly, samples 1, 2 and 3 showed 4.5, 12, and 13 wt.% Fe_2O_3 respectively, in solid solution in the magnetite lattice (Table 8).

Table 6.

Magnetite-maghemite solid solutions. X-ray powder data
Co target, Fe filter.

I	1	2	3	4	5	hkl
	d(meas.)	d(meas.)	d(meas.)	d(meas.)	d(meas.)	
30	4.8373	4.8351	4.8328	4.8240	5.9170 4.8073 4.1150	(111)
				3.7206*	3.712 *	
70	2.9648	2.9614	2.9608	2.9567	2.9491	(220)
10	2.6841**			2.7372*	2.735 *	
100	2.5269	2.5265	2.5242	2.5218	2.5148	(311)
15	2.4172	2.4149			2.4040	(222)
					2.222 *	
65	2.0956	2.0937	2.0908	2.0898	2.0840	(400)
35	1.7116	1.7104	1.7112	1.7073	1.7026	(422)
80	1.6136	1.6132	1.6110	1.6084	1.6047	{(511) (333)}
90	1.4822	1.4819	1.4801	1.4781	1.4736	(440)
15	1.3255		1.3238	1.3213	1.3198	(620)
25	1.2788	1.2785	1.2767	1.2753	1.2721	(533)
20	1.2100		1.2092	1.2070	1.2037	(444)
20	1.1209		1.1199	1.1182	1.1148	(642)
40	1.0919	1.0919	1.0902	1.0892	1.0862	{(731) (553)}
25	1.0486	1.0483 α_1	1.0476 α_1	1.0457	1.0423	(800)
10	0.9887	0.9885	0.9879	0.9854	0.9829	{(822) (660)}
30	0.9689 α_1	0.9687 α_1	0.9680 α_1	0.9660 α_1	0.9638 α_1	{(555)
20	0.9689 α_2	0.9687 α_2	0.9680 α_2	0.9660 α_2	0.9638 α_2	(751)}
15	0.9384 α_1	0.9382 α_1	0.9374 α_1	0.9356 α_1	0.9332 α_1	(840)
10	0.9384 α_2	0.9382 α_2	0.9375 α_2	0.9358 α_2	0.9332 α_2	

1. **Magnetite with 4.5% maghemite in solid solution. Devon.** a = 8.394 ± 0.001 A.
2. **Magnetite-with 12% maghemite in solid solution. Mt. Blagodot, Urals, U.S.S.R.** a = 8.390 ± 0.001 A.
3. **Magnetite with 13% maghemite in solid solution. Mourne, Co. Down, Ireland.** a = 8.3860 ± 0.001 A.
4. **Maghemite with 45% magnetite in solid solution. Co. Antrim, Ireland.** a = 8.369 ± 0.001 A.
5. **Titanomaghemite with 25% magnetite in solid solution. Bon Accord, Transvaal, S. Africa.** a = 8.3475 ± 0.001A.

* **Ilmenite lines.** ** **Haematite lines.**

It was also possible to follow the decrease in the size of the unit cell of magnetite with the progressive increase of its oxidation to maghemite. The curve in Fig. 3 shows the relationship between the cell-edge and the composition of the magnetite-maghemite solid solutions. Newhouse and Glass (1936, p. 701), gave the chemical analysis of a specimen of magnetite - from Windpass mine, British Columbia - which was almost free of oxides other than those of iron (Table 5, Col. 4). The analysis shows an excess of about 20.5% Fe_2O_3 over that which is necessary for the formation of magnetite. In spite of the fact that their X-ray powder photograph did not show any maghemite pattern, and that the cell-edge was 8.369 A (lower than pure magnetite), they erroneously considered it to be a heterogeneous mixture of magnetite and maghemite. This is no doubt a case of magnetite containing maghemite in solid solution.

It is possible that the occurrence of partially oxidized magnetites may be much more widespread than hitherto believed. This would account for some of the contradictory statements on the appearance of magnetite in polished sections. In many of the samples examined by the author, the somewhat lower value of the cell-edge than that of pure magnetite may be due to partial oxidation to maghemite (See Appendix, Table A). The X-ray measurements should be supplemented by chemical analysis, as the cell dimensions of magnetite can also be lowered by other elements replacing iron. However, most replacements in magnetite - by manganese, zinc, titanium, - result in an increase in the size of the unit cell, and replacement by magnesium has little effect, since the cell edge of $MgFe_2O_4$ is about 8.37 A, within 0.02 A of pure magnetite. A magnetite from Kropferberg, Saxony, which contains about 9% $MgFe_2O_4$ (chemical analysis in Table 7) gave the same X-ray pattern as pure magnetite (Plate 1, Fig. 5).

Before leaving the subject of magnetite-maghemite solid solutions, it is perhaps desirable to discuss their relationship to martite. The conversion of magnetite to haematite, often known as "martitisation", is a distinct process from that which gives rise to maghemite. Martitisation usually follows the crystallographic directions in the magnetite, spreading along the octahedral planes, from grain boundaries, cracks, and twinning lines, whereas conversion to maghemite appears to be completely independent of the crystallographic form.

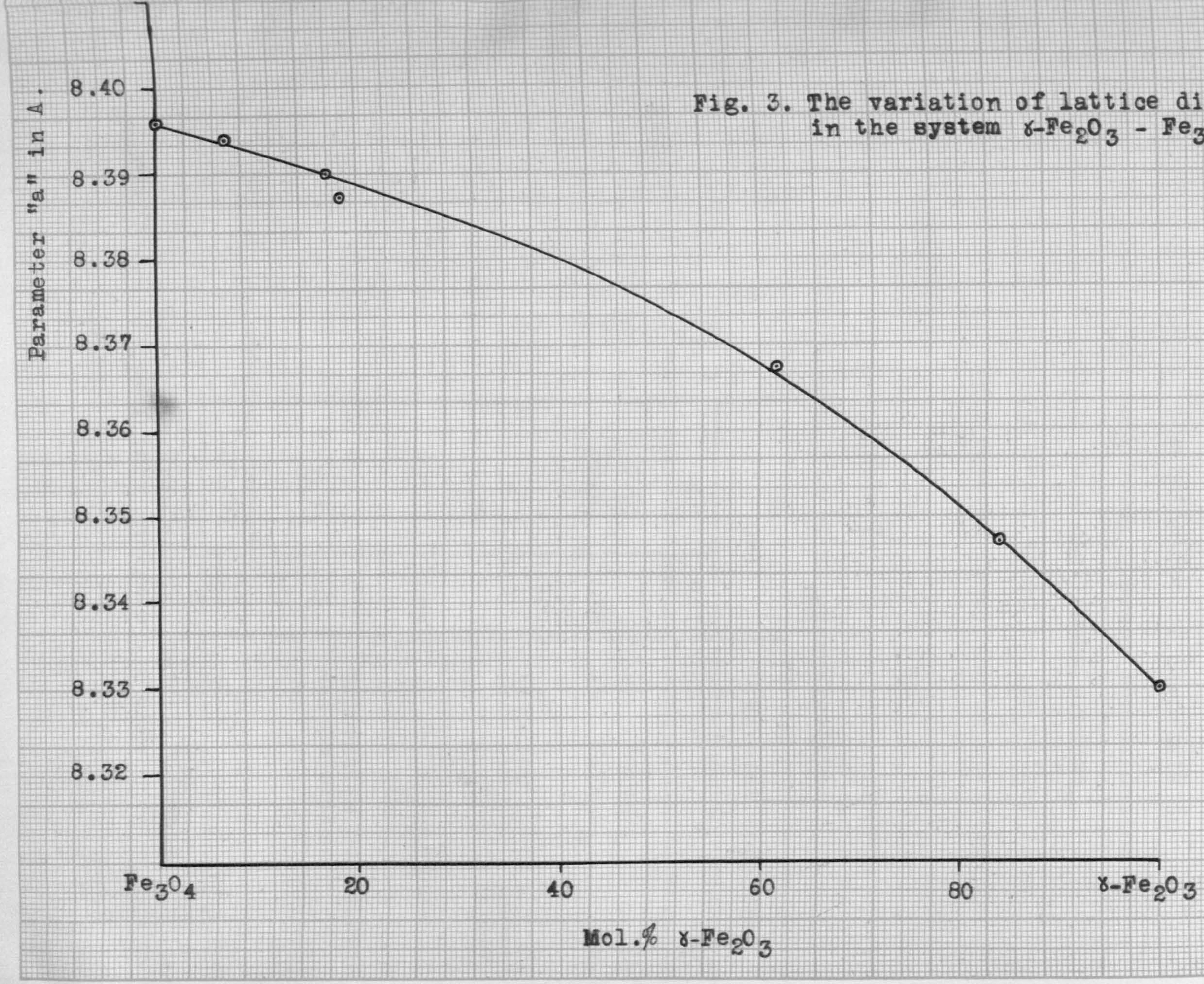

Fig. 3. The variation of lattice dimensions in the system γ-Fe_2O_3 - Fe_3O_4.

This distinction reflects the difference in the nature of the two processes: the oxidation of magnetite to haematite must be discontinuous, whereas the oxidation of magnetite to maghemite is a continuous process, oxygen atoms being continuously added to (or rather iron atoms being continuously removed from) the crystal lattice of magnetite.

Table 7

Chemical analysis of magnesomagnetite.*

	% High grade concentrate	Ore		Mineral component		
		%	Mol	Mol		%
TiO_2	0.05	0.05		390	$FeFe_2O_4$	90.5
Fe_2O_3	67.57	69.21	0·433	43	$MgFe_2O_4$	8.6
Al_2O_3	0.14					
V_2O_3	Nil			13	FeO	0.9
Cr_2O_3	Nil					100.00
FeO	28.40	29.01	403			
MnO	0.06					
CaO	Nil			Impurities 2%: quartz and chlorite.		
MgO	1.85	1.73	43			
SiO_2	1.55					
Total	99.62	100.00				

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* Magnesomagnetite. Kropferberg, Saxony, Germany. Analyst, Milner. (new analysis). S 448.

Table 8

Calculation of the Chemical Analyses of magnetite - maghemite solid solutions.

		% High grade concentrate	Ore		Mineral component		
			%	Mol	Mol		%
1.*	TiO_2	0.16	0.16	2	393	$FeFe_2O_4$	91.2
	Fe_2O_3	69.88	71.13	444	1	$MnFe_2O_4$	0.2
	Al_2O_3	0.34			3.5	$MgFe_2O_4$	0.7
	V_2O_3	0.02			2	$FeTiO_3$	0.3
	Cr_2O_3	0.07	0.07				
					47	Fe_2O_3	7.5
	FeO	27.93	28.43	395			99.9
	MnO	0.07	0.07	1			
	CaO	0.03					
	MgO	0.14	0.14	3.5			
	SiO_2	1.07			Impurities 3%:Haematite		
	Total	99.71	100.00				
2.	TiO_2	0.84	0.86	11	359	$FeFe_2O_4$	83.3
	Fe_2O_3	70.46	71.75	448	8	$MnFe_2O_4$	1.85
	Al_2O_3	Traces			4.5	$MgFe_2O_4$	0.9
	Cr_2O_3	Nil			11	$FeTiO_3$	1.7
	FeO	26.08	26.62	370	76.5	Fe_2O_3	12.25
	MnO	0.58	0.59	8			100.00
	MgO	0.18	0.18	4.5			
	CaO	Nil					
	SiO_2	1.24					
	Total	99.38	100.00				

Table 8 (contin.)

		% High grade concentrate	Ore		Mineral component		
			%	Mol	Mol		%
3.	TiO_2	0.49	0.51	6.4	6.4	$FeTiO_3$	1
	Fe_2O_3	69.88	73.24	458	327.6	$FeFe_2O_4$	76.0
	Al_2O_3	0.16			49	$MgFe_2O_4$	9.8
	V_2O_3	0.18	0.18	1.2			
					82.6	Fe_2O_3	13.2
	Cr_2O_3	0.01					100.00
	FeO	22.90	24.00	333			
	MnO	0.10	0.10	1			
	CaO	1.00					
	MgO	1.88	1.97	49			
	SiO_2	2.20					
	Total	98.79	100.00				
4.	TiO_2	2.54	2.59	32	32	$FeTiO_3$	4.9
	Fe_2O_3	80.63	82.52	516	23	$MgFe_2O_4$	4.6
	Al_2O_3	0.30			11	$CaFe_2O_4$	2.4
	V_2O_3	0.12	0.12	1	151.5	$FeFe_2O_4$	35.1
	Cr_2O_3	0.01					
					331.5	Fe_2O_3	53.0
	FeO	12.75	13.05	181			100.0
	MnO	0.18	0.18	2.5			
	CaO	0.76	0.61	11	Impurities 5%: ilmenite.		
	MgO	0.91	0.93	23			
	SiO_2	0.84					
	Total	99.03	100.00				

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* Numbers 1, 2, 3, 4 correspond to the same numbers in Table 5.

3) Magnetite-haematite solid solutions:

The results of Greig and co-workers (1935) indicate that the solubility of Fe_3O_4 in α-Fe_2O_3 is very small at all temperatures up to 1450°C. (1 wt.% or less), whereas the solubility of α-Fe_2O_3 in Fe_3O_4 is small but noticeable at low temperatures and increases rapidly at high temperatures, reaching 30 wt.% at about 1450°C. as shown in Table 9.

By heating a specimen of partially martitised magnetite (containing about 5% haematite) - from Edison, New Jersey - in evacuated silica glass tubes at 1050°C for 48 hours, complete homogeneisation resulted. X-ray powder photograph (Plate 3, Fig. 2) of the quenched charge, showed only magnetite lines; no change in the size of the unit cell occurred.

The systematic investigations of the system Fe_3O_4 - α-Fe_2O_3 have all been carried out at high temperatures, 1100°C. and above. By extrapolation of Greig's curve (p. 268), the solubility of Fe_2O_3 in Fe_3O_4, at ordinary temperatures, is almost negligible. However, such an extrapolation from 1100°C. down to ordinary temperatures is unreliable. Mason (1943, pp. 124-5), using data given by Hägg in his work on γ-Fe_2O_3 (1935, p. 98), tried to draw the solubility curve at low temperatures. Hägg, by heating homogeneous samples of composition between Fe_3O_4 and γ-Fe_2O_3, in sealed tubes at 675° and 490°C., had decomposed them into α-Fe_2O_3 and a magnetite solid solution poorer in oxygen than the original homogeneous phase. The cell-edge of the magnetite phase thus formed was 8.377 A. From Hägg's curve (p. 97) showing the relation between the composition of Fe_3O_4 - γ-Fe_2O_3 solid solutions and the cell-edge, the magnetite corresponded to the formula $FeO_{1.344}$. Mason (1943) thought that as this would correspond to Fe_3O_4 with 7 wt.% Fe_2O_3 in solid solution, then, by extrapolation, magnetite can contain up to about 7 wt.% haematite at ordinary temperatures. However, his interpretation is erroneous, as the magnetite obtained by Hägg actually contained γ-Fe_2O_3, not α-Fe_2O_3, and consequently Mason's extrapolation curve (p. 122) cannot be accepted.

From the above remarks it is evident that at ordinary temperatures the extent of solid solution of haematite in magnetite is very limited (definitely less than 8% Fe_2O_3), whereas haematite must correspond almost exactly to the formula Fe_2O_3. Most interesting in this connection is Fig. 393 in Ramdohr's book (1950), which shows an inclusion from a basalt of well-defined haematite and magnetite occurring in a typically recrystallised state, but without any sign of solid solution.

Table 9.

Effect of temperature on the extent of solid solution of α-Fe_2O_3 in Fe_3O_4 (data taken from Greig & Co-workers, 1935).

Temperature °C.	Composition of maximum solid solution.	
	Fe_3O_4	α-Fe_2O_3
1075	92	8
1200	87	13
1388	75.5	24.5
1452	70	30

The presence of excess Fe_2O_3 in the analyses of some magnetites is in most cases due to maghemite, and not haematite in solid solution (e.g. samples 1, 2, 3; Table 5). This can be distinguished by the considerable decrease in the size of the unit cell of magnetite with the increase of γ-Fe_2O_3 in solid solution (See Fig. 3). Greig and co-workers (1935, pp. 296-7), have found that in artificial preparations of Fe_3O_4 with 15% α-Fe_2O_3 in solid solution, the displacement of the lines was barely perceptible, and in those containing 22% α-Fe_2O_3 the decrease in the edge of the unit cell was not more than 0.01 A.

Since temperatures of 1100°-1200°C. and higher are necessary to increase the solubility of α-Fe_2O_3 in Fe_3O_4, so as to allow unmixing to take place on cooling, there is little possibility of finding oriented intergrowths of haematite in naturally formed magnetite. As far as the author is aware, only four examples of such an occurrence have been observed. Newhouse (1936, p. 19), while describing the opaque minerals in 265 different igneous rocks, recorded what he considered to be ex-solved haematite in magnetite from a basalt from Mt. Etna. Edwards (1949) described in a small pebble from Cairns, Queensland, Australia, and in grains from beach sands at Viti Levn, Fiji, octahedral intergrowths of haematite in magnetite with 30 and 15% haematite respectively. Another occurrence was recently noted by Baker (1952) in amphibolite from Matapau, New Guinea. The proportion of host magnetite to unmixed haematite lamellae in the intergrowth, measured micrometrically, is 88:12. Both Edwards and Baker have noticed that, according to Greig's data (Table 9), the ratio of the haematite intergrowths to the magnetite would indicate temperatures of about 1200°-1300°C., which are unduly high for igneous rocks. They predicted some additional unknown factor as causing the formation of solid solution in nature at temperatures lower than those found in the laboratory by Greig and his associates. However, an X-ray examination of 2 samples of Fiji beach sands - sent to me by Professor Edwards - did not reveal more than 7% haematite, a result which agrees with Greig's data. Besides, from a study of the polished section of Baker's amphibolite from Matapau (Plate 8, Fig. 1), the author could not reject the possibility that some of the haematite measured by him is actually martite. It should be pointed out here that the ex-solution texture is practically identical with the texture resulting from the replacement of magnetite by haematite (martitisation), which results from either hypogene or supergene oxidation of magnetite. The only distinction is that with the ex-solution intergrowths, the haematite lamellae are evenly distributed through the magnetite, whereas with oxidation, the alteration to haematite is most pronounced at the margins of the magnetite crystals or along cracks. The haematite lamellae produced by replacement also vary considerably in width in different parts, whereas ex-solution lamellae are typically of uniform width (Plate 8, Figs. 1,8).

d. The System Fe_2O_3 - TiO_2.

As has been stated before (Section **VI**, c), Fe_2O_3 has two main forms: γ-Fe_2O_3 (maghemite), and α-Fe_2O_3 (haematite). It is therefore convenient to treat the present system in two sections: 1) γ-Fe_2O_3 - TiO_2, 2) α-Fe_2O_3 - TiO_2.

1) γ-Fe_2O_3 - TiO_2:

Many analyses of maghemite, especially of specimens from Bushveld occurrences, show a considerable amount of TiO_2 (Table 10). Different assumptions have been made to account for the form in which the TiO_2 is present. Walker (1930, p. 18), suggested that in lodestone from Bon Accord, Transvaal (also in the Bushveld complex), the titanium is probably present as Ti_2O_3, in solid solution in Fe_2O_3 (Table 10, Col. 3). He was apparently supported in this belief by Professor Thomson's examination of a polished section of his material, which revealed "that 95% of the opaque material, apart from limonite, was made up of a single, definitely anisotropic mineral."

Table 10

Chemical Analyses of Titanomaghemites.

	1	2	3	4	Ore (1)		Mineral component (1)		
					%	Mol	Mol		%
TiO_2	19.45	13.00	15.50	15.20	21.27	266	33	$FeTiO_3$	5
Fe_2O_3	64.92	73.78	63.76	73.75	66.49	415	17.5	FeV_2O_4	3.9
Al_2O_3	<0.01	3.41	1.42	1.40			13	$CaFe_2O_4$	2.8
V_2O_3	2.40	1.30	-	-	2.62	17.5	74	$FeFe_2O_4$	17.2
Cr_2O_3	<0.01	0.33	-	0.35			328	Fe_2O_3	52.5
Fe O	7.87	2.59	16.43	5.00	8.60	120	233	TiO_2	18.6
Mn O	0.24	0.15	0.37	0.45	0.26	4			100.00
Ca O	0.70	0.39	-	0.40	0.76	13			
Mg O	1.05	0.78	1.12	Trace					
Si O_2	1.60	2.02	0.50	0.70			Impurities: 5% ilmenite, 3% limonite, and 1% chlorite.		
H_2O	-	2.12	1.34	1.05					
Rem.	-	0.07	-	2.10					
Total	98.23	99.94	100.44	100.40	100.00				

1. Titanomaghemite, with few ilmenite lamellae. Bon Accord, North of Pretoria, Transvaal, S. Africa. Analyst, H. B. Milner (new analysis). S 542.

2. Titanomaghemite, Bushveld Complex, S. Africa. Analyst, Liebenberg and Haumann. (Schwellnus and Willemse, 1943, p. 30).

3. Titanomaghemite, with ilmenite lamellae. Bon Accord, Transvaal, S. Africa. Analyst, M. C. Haller. (Walker, 1930, p. 17).

4. Titanomaghemite. Western part of Onerstepoort, Bushveld Complex. Analyst, H. G. Weall. (Wagner, 1928, p. 31).

However, Mason (1943, p. 112) examined polished sections of specimens from the same locality, and found that the mass of the specimen consisted of an isotropic mineral - maghemite - in which irregular grains and minute oriented lamellae of ilmenite occurred, so small that they might have been easily overlooked by Professor Thomson. He thought that the amount of ilmenite in the polished sections could have accounted for the TiO_2 in Walker's analysis.

A sample from Walker's specimen (Royal Ontario Museum, No. 17382) was kindly sent to me by Professor W. H. Newhouse of Chicago University, having previously been supplied to him by Walker himself. An X-ray powder photograph of this specimen was taken (Plate 2, Fig. 6), which showed maghemite with a cell-edge of 8.342 ± 0.001 A, together with weak, but definite, ilmenite reflections. By comparison with X-ray photographs of standard mixtures, the amount of admixed ilmenite was found to be about 4%. Newhouse and Glass (1936, p. 703), who had an X-ray analysis made by N. W. Buerger on the same specimen, could not observe ilmenite lines on their films, and gave 8.319 A for the unit cell. This low figure is probably due to the inaccurate technique in measurements; it was obtained by averaging all values calculated from the different lines.

Two other specimens (S 542, 536), also from Bon Accord, Transvaal, were examined by X-ray photographs and were found to give almost exactly the same pattern, with about 5 and 6% ilmenite, respectively. The X-ray measurements of the maghemite (S 542) are given in Table 6, Col. 5; the cell edge is 8.3475 ± 0.001 A.

Polished sections of the above three specimens were made, and all showed isotropic maghemite as the main constituent, with few small irregular grains of ilmenite, and some limonite along the cracks and crystal margins (Plate 8, Fig. 2).

Chemical analysis of specimen 542 (Table 10, Col. 1), showed a much higher percentage of TiO_2 than was necessary to saturate the amount of ilmenite actually present. Previous analyses of many maghemites have shown more TiO_2 than is necessary to combine with the insufficient FeO to form ilmenite (Table 10, Cols. 1, 2, 4). As this excess TiO_2 is only normative and no rutile, anatase, brookite or other titanium minerals were detected either in the polished sections or in the X-ray powder photographs, it must be present in the maghemite molecule. It is quite probable that the excess titanium is trivalent, and that Ti_2O_3 may exist in a cubic γ-form, isomorphous with

γ-Fe_2O_3. According to Jakob (1937), one may regard titanium as trivalent, instead of tetravalent, in calculating the ilmenite molecule, and then add equal molecular amounts of ferric oxides; the net result would be the same. He further pointed out that the existence of trivalent titanium in minerals might be much more widespread than has hitherto been assumed. It is easy to understand why the analysis does not allow the actual valency of titanium to be determined. On treating the mineral with HCl, the Ti^{3+} passes into Ti^{4+}, while the Fe^{3+} is transformed to Fe^{2+}.

It can thus be concluded that while part of the titanium in maghemite may be present as TiO_2 in admixed ilmenite, part of it at least occurs as Ti_2O_3 in solid solution. As has been stated before (Section VI, c) the author suggests naming the maghemite which contains Ti_2O_3 in solid solution "titanomaghemite", with the formula γ-$(Fe,Ti)_2O_3$, to distinguish it from maghemite, which should be restricted to natural γ-Fe_2O_3. The ionic radii of the two atoms involved in this substitution - Fe^{3+} 0.67 A, Ti^{3+} 0.69 A - are sufficiently close to cause little distortion of the lattice, but the unit cell may increase slightly. It is possible that titanomaghemite is formed by the oxidation of titanomagnetite, as in the case of the Bushveld occurrences.

The V_2O_3 content in the titanomaghemite from Bon Accord, Transvaal, (Table 10, Col. 1) is relatively high (2.4%), and should justify the classification of the mineral as "coulsonite". It should be pointed out that the name coulsonite - if it has to be used - should be restricted to vanadomaghemites with the formula $(Fe,V)_2O_3$, and not the vanadomagnetites as given in the 7th edition of Dana's System of Mineralogy (1944, p. 702). The description given by Dunn and Dey (1937, p. 132) for the original mineral from Singhbhum, India, can be applied fairly well to maghemite. Supporting this view is the fact shown by Frankel and Grainger (1941, p. 105) that in the Bushveld titaniferous iron ore, a test for vanadium on the maghemite was strongly positive, whereas the surrounding magnetite gave negative results.

2) α-Fe_2O_3 - TiO_2:

Pouillard (1949, p. 28), on heating a mixture of $2Fe_2O_3 + TiO_2$ at 950°C. for 3 hours, obtained a solid solution with α-Fe_2O_3 as a base. This was rhombohedral with a cell-edge identical with that of pure α-Fe_2O_3. The Curie point decreased from 675° (for pure α-Fe_2O_3) to 661° (for the solid solution limit). These weak variations in the physical constants of α-Fe_2O_3 show that the content of TiO_2 in the solid solution limit must be very low.

To determine the miscibility limit of TiO_2 in α-Fe_2O_3, and to check the results of Pouillard, a number of experiments were carried out. Two preparations were made by heating Fe_2O_3 with 5, 10 wt.% TiO_2 at 1050°C. for 20 hours in evacuated silica glass tubes. X-ray powder photographs of the quenched charges showed, in both cases, haematite together with weak lines of pseudobrookite ($Fe_2O_3.TiO_2$). On heating similar mixtures at 950°C. for 3 hours, faint rutile lines appeared in addition to the haematite and pseudobrookite patterns.

However, when a mixture of Fe_2O_3 with 10 wt.% TiO_2 was heated at an even lower temperature (800°C.) for 26 hours, and then quenched, no pseudobrookite was formed. The X-ray pattern (Plate 3, Fig. 6) was that of haematite together with about 5% rutile; no change in the size of the unit cell of Fe_2O_3 was observed.

The results of these experiments show that there is a very limited miscibility between TiO_2 and α-Fe_2O_3, not more than 5% TiO_2 in Fe_2O_3 at 800°C. At higher temperatures however, pseudobrookite is formed which is completely immiscibile in Fe_2O_3.

The presence of a considerable excess of TiO_2 in the chemical analyses of some haematites - after allowing for ilmenite - is usually due to admixed rutile. An example is the so-called "ilmenite" from Snarum, Norway, the chemical analyses of which show about 5-10% TiO_2 (Appendix, Table B, Cols. 36, 39). Warren (1918, p. 421) wrongly considered the Snarum specimens - on a morphological basis - as homogeneous ilmenite with up to 93% Fe_2O_3 in solid solution. Ramdohr (1926, p. 356) classified them as haematite, containing a few ex-solution lamellae of ilmenite. However, in an X-ray powder photograph of a specimen from the same locality, rutile lines appeared together with the haematite pattern (Plate 3, Fig. 4). A polished section of the same specimen showed haematite with a few stout lamellae of rutile (Plate 8, Fig. 3). Intensive decomposition has taken place leaving behind either hollow spaces, which make the preparation of polished section very difficult, or spaces filled with yellowish white, earthy material - leucoxene.

The presence of approximately equal parts of haematite and rutile, as in a specimen described by Ramdohr (1939, p. 11) from Costa Rica, is usually due to extensive oxidation of an original ilmenite. Polished sections of "ilmenite" from Kragerö, Norway, show partial oxidation to haematite and rutile. On heating a finely powdered sample of $FeTiO_3$ in air at 720°C. for four days, the X-ray powder photograph of the product showed haematite and rutile together with faint lines of brookite (Neg. 876).

Edwards (1947, p. 62) described the eutectic relationship of rutile and haematite in occasional specimens from Western Australia, rutile being in excess, and crystallising first as coarse, granular crystals.

In addition to the end-members of this system, two other compounds are known: an orthorhombic form, $Fe_2O_3.TiO_2$, found in nature as the mineral pseudobrookite, and the artificially prepared $2Fe_2O_3.3TiO_2$, which is tetragonal. The latter was prepared by Pouillard (1949) by heating a mixture of $2Fe_2O_3 + 3TiO_2$ at 950°C. for 3 hours; its lattice parameters were: $a = 9.30$ A, $c = 9.50$ A, $c/a = 1.02$ Å.

A third compound, $Fe_2O_3.3TiO_2$ - "arizonite" - was first described by Palmer (1909), from a granite-pegmatite vein at Hackberry, Arizona, and has since been frequently reported as a constituent of black ilmenite sands (Wadia, 1943; Miller, 1945). Ernst (1943), however, from an X-ray powder photograph of the same material, found it to be a mixture of haematite, rutile, and probably anatase. Overholt, Vaux, and Rodda (1950) took another X-ray photograph of "arizonite" which showed haematite, ilmenite, anatase, and rutile. By checking their spacing and intensity measurements, and from my measurements on an X-ray powder photograph which Dr. Ernst kindly sent to me - no sample from the original locality being available - I found that the material was formed mainly of anatase and haematite, together with a little rutile; ilmenite lines were completely absent (Table 11). This conclusion agrees well with the result of the chemical analysis made by Palmer, which showed only 0.7% FeO.

Miller (1945) found that the so-called ilmenite from the beach and dune sands of Florida has the chemical composition of "arizonite"; it contains about 53% TiO_2, and its iron is nearly all in the ferric state. However,

Table 11.

X-ray powder data of "Arizonite", Ilmenite sand, and their comparison with haematite, anatase, rutile and ilmenite.

"Arizonite" Hackberry, Arizona.		Anatase*		Haematite*		Rutile*		Ilmenite*		Ilmenite Sand Travancore, India.	
I	d	I	d	I	d	I	d	I	d	I	d
								40	3.72	40	3.730
40	3.67			70	3.67						
100	3.50	100	3.51								
30	3.23					90	3.24				
								100	2.74	100	2.745
90	2.66			100	2.69						
								80	2.54	80	2.544
80	2.51			90	2.51					10	2.515**
5	2.48					60	2.49				
10	2.37	30	2.37								
20	2.197			60	2.199						
10	1.885	80	1.885								
								70	1.860	40	1.866
20	1.833			70	1.833						
								90	1.72	90	1.724
70	1.687	60	1.695	80	1.69	100	1.69			15	1.702**
30	1.660	50	1.660								
5	1.624					50	1.62				
								60	1.50	50	1.504
30	1.478			60	1.479						
								60	1.467	50	1.468
20	1.449			50	1.45	30	1.45				
10	1.358			25	1.35	60	1.36				
10	1.335	10	1.335			50	1.34	30	1.337	40	1.340
20	1.260	50	1.260	40	1.26						

* Data from the A.S.T.M. card index.

** Titanhaematite lines.

X-ray photographs showed it to be essentially amorphous, with only weak lines corresponding to ilmenite. Similarly, an X-ray examination of material concentrated from Australian sands indicated ilmenite. Wadia (1943, p. 10) from chemical analysis alone considered it possible that some of Ceylon and Travancore "ilmenite" was arizonite.

The author took a number of X-ray powder photographs of samples of black "ilmenite" sand from the following localities: Travancore, India; Taranaki, New Zealand; Auckland, New Zealand; Seacombe, Liverpool; Nigeria. They all showed a mixture of titanhaematite and ilmenite (containing Fe_2O_3 in solid solution); in certain cases, together with magnetite (Plate 4, Figs. 1, 2). No lines due to anatase, rutile or brookite were detected in my photographs as also in the photographs taken by Miller. It is, therefore, possible that the increase in TiO_2 and Fe_2O_3 content observed in the chemical analyses of many of the black "ilmenite" sands, and which has frequently been attributed to "arizonite", may in some cases be due to an ex-solution intergrowth of titanhaematite and ilmenite, possibly with a little TiO_2 in solid solution (Section VI, f). It is usually difficult to distinguish the two main constituents in the X-ray photographs, owing to the slight difference in the spacings of titanhaematite and ilmenite which results in the superposition of the lines at the low angle θ; it is very possible that the titanhaematite lines have been overlooked by Miller. This conclusion is supported by a chemical analysis given by Hutton (1950, p. 673) of ilmenite sand from Mudtown, Stewart Island, New Zealand (Appendix, Table C, Col. 42). A recalculation of the analysis, on the assumption that the haematite is titanhaematite containing in solid solution 10% TiO_2, and the ilmenite is saturated at 6% Fe_2O_3, gives a mode of approximately 46% of titanhaematite and 54% of ilmenite, with no excess oxides. The polished section showed ilmenite-haematite ex-solution intergrowths.

As to the origin of "arizonite", it is certain that it is not due to ex-solution of an original solid solution. Ernst (1943, p. 405) failed to homogeneize the material, and similarly attempts to synthesize "arizonite" from oxide mixtures in the ratio of $Fe_2O_3 : 3TiO_2$ were unsuccessful, and only mixtures of pseudobrookite and rutile were obtained. Ernst suggested that it is due to the replacement of Fe_2O_3 by TiO_2. Overholt, Vaux, and Rodda (1950, p. 117) however, considered "arizonite" as being weathered ilmenite.

My experiments on the effect of heat on ilmenite supported this last view; the end products depend upon the temperature. On heating a pure sample of finely powdered $FeTiO_3$ in air at 520°C. for 38 hours, it was partly transformed to haematite and brookite. Another sample was heated at 730°C. for 4 days; ilmenite was completely oxidized, and the X-ray powder photograph (Plate 4, Fig. 3) showed haematite and rutile together with faint lines of brookite. A third sample when heated at 900°C. for 24 hours gave the X-ray patterns of pseudobrookite and rutile ~~was obtained~~ (Plate 4, Fig. 4). The reaction can be represented by the following equation:

$$FeO.TiO_2 + O_2 \longrightarrow Fe_2O_3 + TiO_2 \xrightarrow{900^\circ} Fe_2O_3.TiO_2 + TiO_2.$$

The form of TiO_2 differs according to the temperature. Above 700°C. rutile is the stable form, while at lower temperatures brookite and anatase are to be expected. The occurrence of "arizonite" in tropical beach sands which are exposed to strongly oxidizing conditions is in accordance with the hypothesis that it is formed by the alteration of ilmenite on oxidation.

In any case, as shown from the work on both natural occurrences and synthetic preparations, arizonite should be considered invalid as an independent mineral.

e. $FeTiO_3$ - TiO_2.

Little is known concerning the relationships of ilmenite and rutile. Schaller (1912) prepared a series of analyses which seemed to show that from the purest rutile with 100% TiO_2 to "nigrine" with 18-31% $FeTiO_3$, a continuous series of mixed crystals exist, and perhaps even further to the "iserite" (ferriferous rutile) of Iserwiese with 64% $FeTiO_3$. Warren (1918, p. 435) made four chemical analyses of the so-called "iserine" from the same locality, which vary considerably. The first three contain an excess of 3-24% TiO_2, over the ilmenite molecule; while in the fourth one there is a deficiency of TiO_2.

The marked difference in the results of the chemical analyses is mainly due to the lack of homogeneity of the material, as was indicated by Ramdohr (1926, p. 358), who also found no evidence of ex-solution texture. A number of specimens in my collection supports this finding:

1) "Nigrine" from Limoges, France. Crystals large and prismatic. X-ray powder photograph (Plate 4, Fig. 5) showed rutile together with moderately strong lines of ilmenite.

2) "Iserine" sand from Bohemia. Crystals small, rounded or octahedral. X-ray powder photograph for some crystals showed titanhaematite, while for the others, ordinary haematite pattern appeared (martite).

3) "Iserine" sand from Seacombe, Liverpool. The material for the powder photographs was separated by a magnet; the magnetic fraction showed magnetite together with ilmenite lines, while the less magnetic fraction showed haematite with faint magnetite lines.

4) "Iserine" from Riesengebirge, Germany. Large rounded, probably octahedral crystals (polished pea-sized balls). X-ray powder photograph (Plate 5, Fig. 3) showed ilmenite pattern with a = 5.0661 A, c = 13.952 A, c/a = 2.754; no haematite or rutile lines appeared.

Chemical analysis of this "iserine" from Riesengebirge (Table 13, Col. 4) shows about 18% Fe_2O_3, in solid solution. It corresponds reasonably well to Warren's analyses (all contained a considerable amount of Fe_2O_3), and shows that even if some of his material was homogeneous, the excess TiO_2 was not in solid solution in the ilmenite proper but in the ilmenite-haematite solid solution or ex-solution texture (see Section VI, f).

From the above it is clear that "iserine" is usually heterogeneous; the grains of the same sample differ in composition; most of them are haematite-ilmenite solid solutions or ex-solutions which may contain a little excess TiO_2, others are of martite, while others still are of magnetite with ilmenite intergrowths. As to the so-called "nigrine" and "iserite", it is almost certain that Schaller's analyses (1912, pp. 23-25) were of mixtures of rutile and ilmenite, and not of homogeneous rutile. These are due to the replacement of rutile by ilmenite by hydrothermal action. Posnjak and Barth (1934) have failed, after repeated grinding and heating, to produce a homogeneous solid solution intermediate between ilmenite and rutile. It can thus be safely concluded that the terms nigrine and iserite should be dropped; while the term "iserine" - if it has to be used at all- should be restricted to indicate the morphological character of ilmenite with polished pea-sized balls, and definitely not an independent mineral species.

Coarse-grained aggregates of rutile and ilmenite are common, and very occasionally the two form graphic intergrowths. Edwards (1938, p. 53) described such graphic intergrowths in a specimen from Kingaroy, Queensland, Australia, and considered them to indicate the development of eutectoid relationships between rutile and ilmenite.

The only mention of an ex-solution intergrowth of rutile in ilmenite proper (not in ilmenite-haematite solid solution) is in a recent paper by Baker (1952). In a specimen of gabbro from Babiang, New Guinea, he observed rare ex-solved rutile lamellae in the ilmenite lamellae (of ex-solution origin) in magnetite. Dr. Baker kindly lent me a polished section of this specimen which showed a few, small rutile lamellae lying obliquely across the length of the ilmenite bodies in a regular pattern corresponding to the rhombohedral directions of the ilmenite. These minute rutile lamellae could only be detected in two places under high-power oil immersion lenses.

To determine the extent of solid solution of rutile in ilmenite, two preparations were made by heating $FeTiO_3$ together with 5 and 10 wt.% TiO_2, at 1040°C. for 24 hours in evacuated silica glass tubes, and then quenching. X-ray powder photographs of the mixtures were taken before and after heating. The powder photograph of the first charge ($FeTiO_3$ + 5% TiO_2) showed ilmenite with no change in unit cell dimensions; the rutile lines which were previously present have completely disappeared. The powder photograph of the second charge ($FeTiO_3$ + 10% TiO_2) showed ilmenite together with faint rutile lines (Plate 4, Fig. 6); comparison with photographs of standard mixtures indicated less than 5% of admixed rutile. From these experiments the limit of solid solution can be fixed at 6 wt.% of TiO_2 in $FeTiO_3$, at 1040°C.

Another preparation was made by heating TiO_2 together with 10 wt.% $FeTiO_3$ at 1050°C. for 28 hours in evacuated silica glass tubes. X-ray powder photograph of the quenched charge showed rutile together with faint lines of ilmenite; comparisons with photographs of standard mixtures indicated less than 4% of admixed ilmenite. The limit of solid solution may, therefore, be fixed at 7 wt.% $FeTiO_3$ in TiO_2, at 1050°C. Ramdohr (1939, p. 6) described - in a rutile specimen from Siebenbürgen, Bohemia - fine ilmenite bodies elongated parallel to the c-axis of the rutile, and which he considered to be of ex-solution origin.

From the above, it can be summarised that besides the already known eutectic relationship between ilmenite and rutile, there is a very limited miscibility between the two minerals.

f. The System Fe_2O_3 - $FeTiO_3$.

The haematite-ilmenite system is generally considered as the most completely understood instance of substitutional solid solution among the opaque oxides, in which unmixing occurs. However, there are some points which require further investigation.

1) The limit of solid solution at high temperature.

Ramdohr (1926), and Posnjak and Barth (1934) have demonstrated experimentally that ilmenite and haematite form a solid solution series at temperatures above 700 - 800°C. Ramdohr heated two specimens showing ex-solved haematite lamellae in ilmenite, partly in air and partly in nitrogen, to various temperatures for periods of 24 hours, and finally obtained a homogeneous product. This has been confirmed by the author's experiment on a specimen of ilmenite-haematite intergrowth from Hamata, Eastern Desert, Egypt. The heating was carried out in evacuated silica glass tubes at 1000°C for 20 hours, and also resulted in homogeneisation. Posnjak and Barth were able to produce a solid solution between ilmenite and haematite by heating appropriate mixtures of Fe_2O_3 and TiO_2 in vacuum at 1200°C.

However, Pouillard (1949, p. 34) on heating mixtures of Fe_2O_3 and $FeTiO_3$ at 950°C. for 2 hours in evacuated silica glass tubes, could not obtain a single phase of the composition $Fe_2O_3.FeTiO_3$. He concluded that complete solid solution of haematite and ilmenite does not exist, but established the presence of two limited solid solutions: one with base Fe_2O_3, limited at $2Fe_2O_3.FeTiO_3$, and the other with base $FeTiO_3$, limited at $2FeTiO_3.Fe_2O_3$.

To check the results reached by Pouillard, three mixtures: $FeTiO_3 + 2Fe_2O_3$, $FeTiO_3 + Fe_2O_3$ and $2FeTiO_3 + Fe_2O_3$ (in molecular proportions), were heated in evacuated silica glass tubes at 1050°C for 24 hours, and then quenched. In the X-ray powder photographs of each of the three charges, only one homogeneous phase was observed (Plate 5, Fig. 5). The results of these experiments prove conclusively the existence of a continuous solid solution between ilmenite and haematite, at 1050°C. Pouillard's failure to obtain a single solid solution of the composition $Fe_2O_3.FeTiO_3$ was possibly due to the extremely short heating period in his investigation. The fact that complete miscibility between α-Fe_2O_3 and $FeTiO_3$ does exist, is supported by the presence in nature of ex-solution intergrowths of the two minerals in almost equal proportions e.g. ilmenite from Madagascar (Lacroix, 1920), and the so-called "washingtonite" from Litchfield, Connecticut (Warren, 1918). Ernst (1943, p. 395), by heating a specimen of "washingtonite" at 1200°C. for 10 days in vacuum was able to transform it into practically homogeneous ilmenite.

The capacity of ilmenite and haematite to form such extensive solid solution is readily understood from a comparison of their atomic structures. Both minerals have a rhombohedral unit cell containing two molecules, and both belong to the corundum type of structure. Table 12, and Fig. 4 show the continuous decrease in the unit cell dimensions of $FeTiO_3$ with the increase of α-Fe_2O_3 in solid solution.

Table 12.

The unit cell dimensions of haematite-ilmenite solid solutions.

No.	Mineral	a (in A)	c (in A)	c/a
1	α-Fe_2O_3.	5.029	13.73	2.730
2	Titanhaematite. Mt. Monger, W. Australia.	5.045	13.790	2.734
3	$2Fe_2O_3.FeTiO_3$.	5.0481	13.829	2.7395
4	$Fe_2O_3.FeTiO_3$.	5.0636	13.895	2.744
5	$2FeTiO_3.Fe_2O_3$.	5.0657	13.928	2.749
6	Ferriilmenite. Riesengebirge, Germany.	5.0661	13.952	2.754
7	$FeTiO_3$.	5.083	14.04	2.762

The mechanism of substitution can be interpreted by considering that two Fe^{+3} ions are replaced by one ion Fe^{+2} and one ion Ti^{+4}:

$$Ti^{+4}\ Fe^{+2} \rightleftharpoons 2Fe^{+3}$$

However, Edwards (1947, pp. 60-61) considered the substitution as $Ti^{+3} \rightleftharpoons Fe^{+3}$, an interpretation which implies the presence of trivalent titanium in ilmenite. Hámos and Stacherbina (1933), who measured the X-ray absorption edge of Ti in ilmenite, and compared it with that in titanium compounds of known valency, have proved that in ilmenite the iron was divalent and titanium quadrivalent. Thus Edwards' interpretation for the substitution of haematite cannot be accepted.

2) Unmixing.

If rapidly cooled, the Fe_2O_3 - $FeTiO_3$ solid solution is preserved in a metastable state, but with moderately slow cooling unmixing takes place into two solid solutions - a ferriferous ilmenite, and a titaniferous haematite - a process which continues on further cooling. A typical micro-texture results; the ex-solution bodies are all elongated with their long axes parallel to the (0001) plane of the ilmenite and haematite. Several of the specimens in the present collection, notably those from Kragerø,

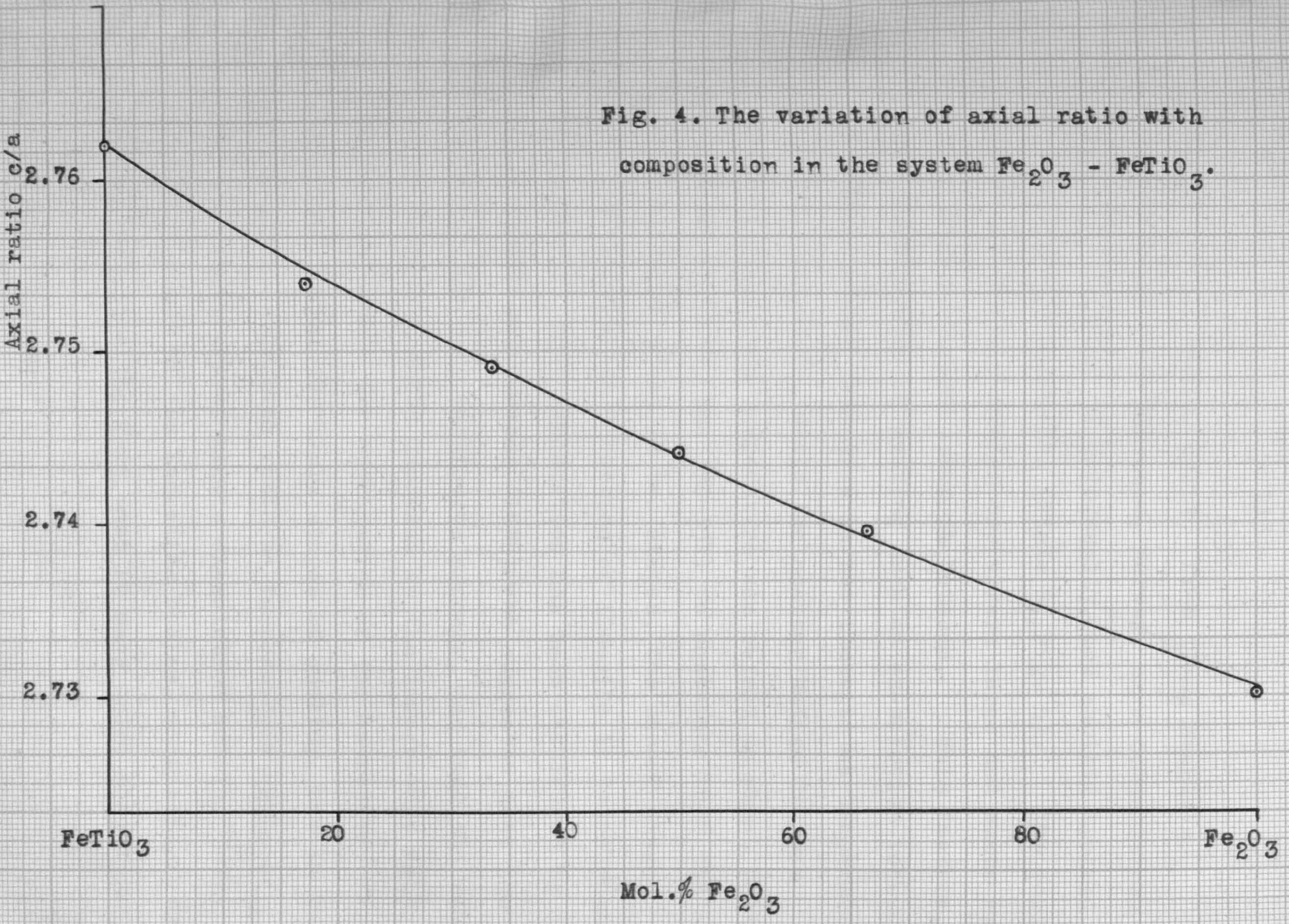

Fig. 4. The variation of axial ratio with composition in the system Fe_2O_3 - $FeTiO_3$.

Norway; from Hamata, Egypt; from Ilmen Mountains, U.S.S.R.; and from Ekersund, Norway, have compositions between the limits of homogeneity, and exhibit typical ex-solution intergrowths (Plate 8, Fig. 4). The earlier formed ex-solution bodies are always large and occur in rows, smaller bodies lying in between. This feature, and the fact that on heating such an ex-solution intergrowth the finer bodies dissolved in the ilmenite at temperatures between 500-600°C., while the coarser bodies did not dissolve until the temperature was raised to about 700°C., led Ramdohr (1926, pp. 350-351) to postulate that the ex-solution takes place in two stages, the second stage coinciding with the inversion of ilmenite to tetartohedral symmetry. This explanation has been challenged by both Greig (1932) and Edwards (1938) who suggested that the unmixing may be a continuous process, and that the rate of solid diffusion would decrease as the temperature fell. This would permit the segregation of the haematite, which separated during the early stages of cooling, but in the later stages diffusion would be increasingly restricted, with the formation of minute ex-solution bodies. The irregular shape of the haematite bodies, particularly the larger ones, and the fact that in many cases they appear to have coalesced (Plate 8, Fig. 4), indicate that they have grown by absorbing ex-solving haematite from the adjacent ilmenite solid solution. The ilmenite adjacent to the large haematite bodies is frequently free from even the minutest particles of haematite.

There can be little doubt of the validity of the interpretation given by Edwards that the intergrowth texture represents the progressive, continuous unmixing of two solid solutions derived from a single solid solution. During the unmixing process, the decreasing rate of solid diffusion that accompanies falling temperatures, and the decreasing concentration of the solute are the main facters which result in the formation of smaller ex-solution bodies. The size of the ex-solution bodies in any specimen depends on: 1) the rate of cooling, 2) the original composition of the solid solution, and 3) the presence or absence of foreign oxides e.g. MgO, MnO, Al_2O_3.

3) Haematite-rich solid solutions.

Both Ramdohr (1926) and Edwards (1938) have reached the conclusion that haematite can contain up to 10% TiO_2 in solid solution at ordinary temperatures. This TiO_2 is actually present as ilmenite in solid solution, and has led Edwards to suggest the name "titanhaematite" to indicate its difference from pure haematite. The streak and powder of the mineral are not red but dark brown to black, and in reflected light it is more grey-white than haematite, and has a somewhat lower reflective power. In Table 13, the only three published chemical analyses of titanhaematite are given. However, the homogeneity of these specimens was only determined in polished sections, no X-ray examination was made.

An X-ray powder photograph of a titanhaematite specimen from Mount Monger, Western Australia, showed a homogeneous haematite pattern, with no ilmenite lines. X-ray measurements (Table 14, Col. 1) gave slightly higher unit cell dimensions than those of pure haematite, possibly due to ilmenite in solid solution.

4) Ilmenite-rich solid solutions.

Ramdohr (1926) and Edwards (1938) considered 6% Fe_2O_3 to be the upper limit of what $FeTiO_3$ can contain in solid solution at normal temperatures. There is here a considerable lack of reliable data; Ramdohr based his figure on a previous analysis of a specimen from Binnental, which he did not examine himself, while the material analysed by Edwards contained ex-solution bodies of haematite.

Table 13.

Chemical analyses of Fe_2O_3 - $FeTiO_3$ solid solutions.

	1	2	3	4	5	6
TiO_2	5.98	9.60	10.02	45.76	46.50	48.50
Fe_2O_3	88.94	83.10	77.17	17.78	10.65	10.31
Al_2O_3	-	-	1.48	0.40	1.27	0.12
V_2O_3	-	-	-	-	0.21	0.04
Cr_2O_3	-	-	-	-	0.01	-
FeO	5.38	5.80	8.52	27.72	37.82	36.37
MnO	-	-	-	0.48	0.18	3.26
MgO	-	1.50	1.33	7.56	3.09	0.30
SiO_2	-	-	-	0.24	0.33	1.11
Total	100.30	100.00	98.58	99.94	100.06	100.01

1. Titanhaematite, homogeneous. Boolmacoota, S. Australia. Analyst, A. B. Edwards. (Edwards, 1938, p. 41).
2. Titanhaematite, homogeneous. New Plymouth, New Zealand. Analyst, F. T. Seelye. (Hutton, 1945, p. 298).
3. Titanhaematite, homogeneous. Snarum, Norway. Analyst, C. H. Warren. (Warren, 1918, p. 421).
4. Ferriilmenite, homogeneous. Riesengebirge, Bohemia, Germany. Analyst, W. H. Herdsman. (New analysis). S 502.
5. Ferriilmenite, with minute ex-solution lamellae of haematite. Storgangen, Ekersund, Norway. Analyst, E. Kluver. (Foslie, 1928, p. 8).
6. Ferriilmenite, with few minute ex-solution bodies of titanhaematite. Ilmen Mt., Miask, Urals, U.S.S.R. Analyst, H. B. Milner (New analysis). S 326.

A number of ilmenite specimens were therefore examined by X-ray analysis and occasionally in polished sections, two new chemical analyses being made. X-ray measurements (Table 14, Col. 3) on a powder photograph of an ilmenite specimen (the so-called iserine) from Riesengebirge, Germany, showed much lower unit cell dimensions than those of pure ilmenite; a = 5.0661 A, c = 13.952 A, c/a = 2.754 (for pure $FeTiO_3$ a = 5.083 A, c = 14.04 A, c/a = 2.76). Chemical analysis (Table 15, Col. 4) showed 17.78% Fe_2O_3, and as the X-ray photograph (Plate 5, Fig. 3) did not show any haematite lines, this Fe_2O_3 must be in solid solution in the ilmenite; a conclusion which agrees well with the decrease in the size of the unit cell.

There is thus no doubt that the Riesengebirge specimen represents a case of extensive solid solution of haematite in ilmenite which has been preserved under normal conditions. This result differs from the conclusion reached by Ramdohr (1926) and Edwards (1938), who suggested that if the Fe_2O_3 content of ilmenite exceeds about 6%, small bodies of titanhaematite appear as ex-solution intergrowths. It is possible that the high content of MgO (7.56%) has played an important role in preserving the solid solution. The author suggests the name "ferriilmenite" for those minerals which are formed of solid solution of haematite in ilmenite.

Table 14.

Haematite - ilmenite solid solutions. X-ray powder data. Co. target, Fe filter.

1		2		3		4		hkl
I	d(meas.)	I	d(meas.)	I	d(meas.)	I	d(meas.)	
50	3.686	60	3.705	50	3.714	60	3.725	(102)
100	2.703	100	2.721	100	2.732	100	2.747	(104)
80	2.522	80	2.529	80	2.530	80	2.544	(110)
60	2.210	50	2.218	60	2.222	40	2.236	(113)
70	1.845	50	1.852	60	1.855	60	1.868	(204)
90	1.698	90	1.706	90	1.711	90	1.725	(116)
20	1.602	30	1.612	25	1.619	20	1.634	(108)
50	1.488	50	1.493	50	1.497	50	1.505	(214)
60	1.455	50	1.459	50	1.461	60	1.468	(300)
30	1.313	30	1.320	30	1.330	40	1.341	(0010)
15	1.260	15	1.265	15	1.265	20	1.271	(220)
25	1.192	20	1.198	20	1.199	20	1.210	(312)
20	1.165	20	1.172	20	1.177	15	1.186	(2010)
30	1.142	20	1.146	20	1.149	30	1.155	(314)
30	1.105	30	1.109	30	1.112	30	1.118	(226)
40	1.058	40	1.063	50	1.067	40	1.075	(2110)
15	0.9904	25	0.9959	30	0.9970	15	1.003	(318)
30	0.9614 α_1	30	0.9658 α_1	30	0.9674 α_1	30	0.9721	(2013),
20	0.9618 α_2	20	0.9660 α_2					(324)
25	0.9530 α_1	25	0.9570 α_1	30	0.9574 α_1	25	0.9614 α_1	(410)
10	0.9534 α_2	20	0.9570 α_2	20	0.9574 α_2	15	0.9616 α_2	
30	0.9095 α_1	30	0.9139 α_1	30	0.9179 α_1	30	0.9236 α_1	(3110)
10	0.9101 α_2	20	0.9139 α_2	20	0.9177 α_2	20	0.9238 α_2	

1. Titanhaematite. Mt. Monger, W. Australia. a = 5.045A, c = 13.790A, c/a = 2.734.

2. $Fe_2O_3.FeTiO_3$. Artificially prepared. a = 5.0636, c = 13.895A, c/a = 2.744.

3. Ferriilmenite. Riesengebirge, Germany. a = 5.0661 A, c = 13.952 A, c/a = 2.754.

4. Ilmenite. Miask, Ilmen Mts., Urals. a = 5.0887 A, c = 14.049 A, c/a = 2.7608.

Such solid solution results in a decrease in the size of the ilmenite unit cell.

It was noticed that some grains of the ferriilmenite from Riesengebirge were strongly ferromagnetic, while others were paramagnetic. However, both fractions gave exactly the same X-ray pattern, which shows that the difference in the magnetic properties is not due to any change in structure. The same phenomenon was observed in the artificially prepared ilmenite-haematite solid solutions, which also showed ferromagnetic characters. It is difficult to determine whether the ferromagnetism in the ferriilmenite depends on the presence of Fe_2O_3 acting as an acid, as it is probably the case in magnetite and many ferrites (Hilpert and Wille, 1932), or whether it is due to the heating and cooling treatment of the solid solution.

Magnetic separation was made for an "ilmenite" from Ekersund, Norway, and an X-ray powder photograph was taken of the ilmenite fraction (Plate 5, Fig. 4); no haematite lines were observed. X-ray measurements showed a much smaller unit cell than that of pure ilmenite, which led the author to suggest that the specimen is possibly a ferri-ilmenite, containing Fe_2O_3 in solid solution.* A Chemical analysis of the Ekersund ilmenite published by Foslie (1928) showed 10.65% Fe_2O_3 (Table 13, Col. 5). Foslie described

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* Most substitutions in ilmenite (other than Fe_2O_3) - e.g. by $MgTiO_3$ (geikielite) or by $MnTiO_3$ (pyrophanite) - result in an increase in the size of the unit cell.

extremely small haematite lamellae in polished sections of this ilmenite, and suggested that about 8% Fe_2O_3 occurred in solid solution in the ilmenite molecule.

Edwards (1938, p. 40) described two homogeneous ilmenites from Australia, the chemical analyses of which showed 4.4 and 2.53 % Fe_2O_3 in solid solution. This type which he called "brown ilmenite" commonly occurs in thin tabular crystals elongated parallel to (0001). In polished sections, it is distinctly pleochroic in brownish tints, and is strongly anisotropic. Ramdohr (1950, p. 304), stated that ilmenites with high Fe_2O_3 content in solid solution, although rare, have been observed in the rapidly cooled volcanic rocks. Their properties correspond completely to those of the products obtained through the homogeneisation experiments (of ilmenite-haematite intergrowths), particularly as regards the increase in the reflective power with the increase of the Fe_2O_3 content.

5) Ilmenite-haematite-rutile solid solutions.

Edwards (1938, p. 54) described in specimens from S. Australia fine lamellae of rutile arranged along the rhombohedral planes of ilmenite-haematite ex-solution intergrowths. Later, Ramdohr (1939, p. 4) described an almost identical structure in a Norwegian specimen, and determined more than three directions (up to six) for the arrangement of the rutile lamellae. The regular arrangement of these rutile lamellae suggests that they are a product of ex-solution.

Examination of a polished section of an ilmenite from Miask, Ilmen Mountains, Urals revealed few minute ex-solution lamellae of titanhaematite. Chemical analysis of this specimen (Table 13, Col. 6) showed 10.31% Fe_2O_3, and after calculation of the mineral components (Table 15, 6), an excess of about 4% TiO_2 was found. The X-ray powder photograph (Plate 5, Fig. 2) showed an ilmenite pattern together with faint lines of haematite (titanhaematite); comparison with photographs of standard mixtures indicated that the admixed haematite was not more than 4%, the rest (about 6% Fe_2O_3) occurring in the ilmenite lattice. As no rutile was determined either in the polished section or from the X-ray photograph, the excess TiO_2 - which appeared in the chemical analysis - must be present in solid solution in the partly unmixed ferriilmenite. Warren (1918, p. 421) gave an analysis of Miask ilmenite which corresponds well to the present analysis; it also showed, after calculation, an excess of TiO_2 occurring in solid solution.

The above investigation on the Miask ilmenite proves without doubt, the solubility of rutile in ilmenite-haematite solid solutions. It also shows that the unmixing of the ilmenite-haematite solid solutions may start before the separation of the dissolved rutile. This result differs from the conclusion reached by Edwards (1938, pp. 54-55), who considered the rutile lamellae to be of an earlier generation than the ilmenite-haematite ex-solution bodies. Ramdohr (1939, p. 4), however, has pointed out the possibility that the rutile lamellae although older than the "second generation" of the ex-solution bodies, are probably younger than the "first generation".

Table 15.

Calculation of the chemical analyses of ferriilmenites

		% High grade concentrate	Ore		Mineral Component.		
			%	Mol	Mol		%
4.*	TiO_2	45.76	46.28	578	395	$FeTiO_3$	60.00
	Fe_2O_3	17.78	17.96	112	184	$MgTiO_3$	22.08
	Al_2O_3	0.40					
					112	Fe_2O_3	17.92
	FeO	27.72	28.48	395			100.00
	MnO	0.48					
	MgO	7.56	7.34	184			
	SiO_2	0.24					
	Total	99.94	100.00				
6.	TiO_2	48.50	51.72	646	542	$FeTiO_3$	82.4
	Fe_2O_3	10.31	5.38	34	49	$MnTiO_3$	7.4
	Al_2O_3	0.12			8	$MgTiO_3$	1.0
	Cr_2O_3	-					
	V_2O_3	0.04			34	Fe_2O_3	5.4
					47	TiO_2	3.8
	FeO	36.37	39.03	542			100.0
	MnO	3.26	3.57	49			
	MgO	0.30	0.30	8	Impurities: 5% haematite substracted in the calculation of the ore.		
	SiO_2	1.11					
	Total	100.01	100.00				

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* Numbers 4, 6 correspond to the same numbers in Table 13.

g. The System Fe_3O_4 - $FeTiO_3$.

Ilmenite-magnetite intergrowths in which ilmenite occurs as elongated lamellae oriented along the octahedral planes of magnetite, are very common. However, there is much disagreement as to the origin of such intergrowths. It is often stated that ilmenite and magnetite form extensive solid solution at high temperature, which may remain homogeneous if cooled rapidly, as is the case in volcanic rocks (Lindley, 1925; Ramdohr, 1926; Odman, 1932; Newhouse, 1936). With slow cooling, rapid unmixing is supposed to take place, giving rise to the well-known ilmenite-magnetite intergrowths. However, such ilmenite-magnetite solid solution, the so-called titanomagnetite, has never been isolated, nor has its composition been determined with certainty.

Singewald (1913), and Warren (1918), owing to an apparently constant Fe : Ti ratio in their ores, suggested that the ilmenite-magnetite intergrowths may be due to a eutectic crystallisation. However, the nature of these intergrowths, and the widely varying proportions of ilmenite to magnetite in other ores, contradict such a view.

Ramdohr (1926) studied microscopically a large number of specimens from different localities, and formed the opinion that at the temperature of separation of the ore, there is very extensive mutual solubility of magnetite and ilmenite. According to him, in two equally composed meltings, either a cubic titanomagnetite or a hexagonal "magnetoilmenite" may be formed. However, the "magnetoilmenite" is not so frequent as the titanomagnetite, and he was able to describe only three cases. Ramdohr considered the pinkish-brown colour of many microscopically homogeneous magnetites, to be due to ilmenite in solid solution. To confirm his suppositions, he made a number of experiments on specimens (from Taberg, Sweden) showing ilmenite-magnetite intergrowths, by heating them partly in air and partly in nitrogen for different periods. On heating above 800°C., he was able to obtain a microscopically homogeneous material, which he claimed to be the original magnetite-ilmenite solid solution.

However there is a number of objections to these experiments:

1) The first stages of heating were carried out in air, and consequently the magnetite was oxidized to haematite with subsequent complication of the process. Oxidation of ilmenite to pseudobrookite, at high temperatures, must

also have taken place, but was not noticed by Ramdohr.

2) Identification of the different phases and the determination of the homogeneity of the material were established by microscopic examination alone.

3) No attempt was made to separate the titanomagnetite, in order to determine its chemical composition.

Kamiyama (1929) described some heating experiments on titaniferous magnetite from Korea; his results differed from those of Ramdohr. He recognised two varieties of titaniferous magnetite. In one variety, the magnetite-ilmenite intergrowths became more pronounced up to 1150°C., but then diminished to 1390°C., at which point melting commenced and homogeneisation took place. In the second variety, the intergrowths were absent but appeared on heating. He concluded that at ordinary temperature titaniferous magnetite is in a metastable state; on heating there is an easier molecular diffusion to attain the stable state, and a more complete separation of magnetite and ilmenite takes place.

To reach a better understanding of the ilmenite-magnetite relationships, a number of experiments were carried out in vacuum, on natural ex-solution intergrowths, and on artificial preparations.

1) Experiments on natural ex-solution intergrowths.

A specimen of magnetite from Coruisk, Skye was used. A polished section of this specimen (Plate 8, Fig. 5) showed fine ex-solution intergrowths of ilmenite lamellae arranged along the octahedral planes of magnetite; X-ray powder photographs showed about 6% ilmenite. A finely powdered sample was heated in evacuated silica glass tubes at 1000°C. for 24 hours, and then quenched. X-ray photographs showed ordinary magnetite (no change in the size of the unit cell occurred), together with faint lines of ilmenite; comparison with photographs of standard mixtures showed that the undissolved ilmenite was about 3%. On heating another sample at 1100°C. for 48 hours in the same manner, it was still not possible to reach complete homogeneisation of the material.

2) Experiments on artificial preparations:

To confirm the above results, heating experiments were carried out on artificially prepared ilmenite-magnetite mixtures of definite composition. Three finely powdered mixtures of Fe_3O_4 with 5, 10 and 15% $FeTiO_3$ were heated in evacuated silica glass tubes at 1050°C. for periods of 24-48 hours. The quenched charges were examined by X-ray powder photographs; in the three samples studied complete homogeneisation was not obtained (Plate 6, Figs. 2, 3) and the dissolved ilmenite was not more than 4%.

However, there was a noticeable decrease in the unit cell dimensions of the ilmenite accompanied by an increase in the cell-edge of the magnetite; a change which became more pronounced with the increase of the ilmenite's percentage in the original mixture. Measurements of the unit cell dimensions of the ilmenite showed that it corresponds to the formula $2FeTiO_3.Fe_2O_3$ (see Section VI,f). Concerning the change in magnetite, Pouillard (1949) has proved that there is a continuous increase in the cell-edge of magnetite with the increasing amount of the spinel $2FeO.TiO_2$ in solid solution (this will be fully discussed in Section VI, h). It is therefore possible that besides the very limited solubility of ilmenite in magnetite, the following reactions may also have taken place:

1) Ilmenite takes Fe_2O_3 from the magnetite to form ferriilmenite, a process which results in the enrichment of magnetite in FeO.

$$2Fe_3O_4 \quad + \quad 2FeTiO_3 \longrightarrow 2FeTiO_3.Fe_2O_3 \quad + Fe_3O_4.FeO$$

2) Part of the ilmenite combines with the excess FeO in magnetite to form $2FeO.TiO_2$, which enters in solid solution.

$$Fe_3O_4.FeO + FeO.TiO_2 \longrightarrow Fe_3O_4 . (2FeO.TiO_2)$$

Another experiment was carried out by heating a mixture of $FeTiO_3$ with 10% Fe_3O_4 in evacuated silica glass tubes at 1050°C. for 48 hours. Complete homogeneisation was not obtained, and X-ray powder photograph of the quenched charge showed about 6% undissolved magnetite.

The results of the above experiments show conclusively that at the temperatures of formation of igneous rocks, there is a very limited miscibility between magnetite and ilmenite, the limit of solid solution is less than 5%, at 1050°C. This conclusion supports the views of Goldschmidt (1926) and Foslie (1928). Goldschmidt emphasised that extensive formation of mixed crystals between rhombohedral $FeTiO_3$ and isometric Fe_3O_4 is improbable on crystallographic grounds. Foslie suggested that it is the cubic orthotitanate Fe_2TiO_4, and not ilmenite, which is isomorphous with magnetite at high temperatures.

Jouravsky (1936) found that homogeneous titanomagnetite from basalts of Madagascar possessed a reflective power which was notably much lower than both magnetite and ilmenite, and which had an abnormal dispersion. He also described some grains of titanomagnetite in which the nucleus was homogeneous while the border showed microperthitic structures. These properties cannot be explained by Ramdohr's view of a homogeneous solid solution between magnetite and ilmenite, the unmixing of which depends on the rate of cooling.

Many of the microscopically homogeneous titanomagnetites which were described by Lindley (1925) and Ramdohr (1926), as having properties intermediate between magnetite and ilmenite, are probably extremely fine intergrowths. Examples of these very fine, submicroscopic ilmenite-magnetite intergrowths were found in the present study, e.g. the magnetite from Magnet Heights, Transvaal, and the magnetite from Skaergaard Intrusion, East Greenland. Polished sections of these specimens were completely homogeneous under the highest magnification, but the X-ray powder photographs showed definite ilmenite lines. In addition, in some of the volcanic rocks examined, ilmenite was found to be in a metamict state in the magnetite or titanomagnetite. X-ray powder photographs of the separated minerals showed pure homogeneous titanomagnetite, but on heating the finely powdered samples in evacuated silica glass tubes at 1000°C. for 2-3 days, the X-ray photographs of the quenched charges showed definite ilmenite lines. This admixed ilmenite was also noticed on calculation of the chemical analyses of such samples (Table 20). X-ray measurements and chemical analyses of the homogeneous titanomagnetite separated from a number of volcanic rocks showed that it is mostly formed of Fe_3O_4 - Fe_2TiO_4 solid solution and not - as Ramdohr thought - of magnetite-ilmenite solid solution (see Section VI, h).

The results of a chemical analysis of magnetite-ilmenite intergrowths separated from an essexite from Tofetholine, Oslo Fjord, Norway are given in Table 16. Calculation of the analysis, after substraction of the silicate impurities, showed about 21% ilmenite; the rest was formed of magnetite and Fe_2MgO_4 with no excess oxides.

The nature of the original titanomagnetite from which the ilmenite-magnetite intergrowths are separated will be thoroughly discussed in Section VII. As to the so-called "magnetoilmenites", it is possible that the magnetite in them is due to the reduction of original haematite lamellae (Ramdohr, 1939).

Table 16.

Chemical analysis of magnetite-ilmenite intergrowths.*

	% High grade concentrate	Ore		Mineral component.		
		%	Mol	Mol		%
TiO_2	9.58	10.97	137	137	$FeTiO_3$	20.8
Fe_2O_3	47.27	54.13	338	7	Fe_2MgO_4	1.4
Al_2O_3	1.28	0.30	3	335	Fe_3O_4	77.8
V_2O_3	0.22	0.25	2			100.0
Cr_2O_3	0.09	0.10				
FeO	29.79	33.62	467			
MnO	0.32	0.36	5			
CaO	1.30					
MgO	2.74	0.27			Impurities: 6% augite and 2% labradorite	
SiO_2	6.22					
Total	98.81	100.00				

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* Magnetite-ilmenite ex-solution intergrowths, separated from essexite. Tofetholine, Oslo Fjord, Norway. Analyst, H.B. Milner (new analysis). S 461.

h. The System Fe_3O_4 - Fe_2TiO_4.

As has been mentioned before (Section VI, g), both Goldschmidt (1926) and Foslie (1928) have supposed the existence of a spinel Fe_2TiO_4 which may enter into solid solution in magnetite.

Artificial Fe_2TiO_4 was first prepared by Barth and Posnjak (1932, p. 333) who heated together, in vacuum, TiO_2, Fe_2O_3 and metallic iron, in proper molecular proportions, at 1150°C. They determined its structure as a spinel with variate atom equipoints, having the character of a double oxide $2FeO.TiO_2$; the cell-edge was 8.5 ± 0.01 A.

Ernst (1943) prepared $2FeO.TiO_2$ by fusion of TiO_2 and FeO, and found it to be optically isotropic, nonmagnetic, and with a cell-edge of 8.49 ± 0.010 A. Pouillard and Michel (1949) also obtained $2FeO.TiO_2$ by direct combination of the oxides at 950°C, and showed that the compound is cubic, with face-centered lattice. Their measurement of the cell-edge gave a = 8.534 A.

Natural Fe_2TiO_4 was found only once before, by Mogensen (1946) in a highly ferriferous dolerite from Södra Ulvön, Sweden; he named the mineral "ferro-ortho-titanate". Chemical analysis of the concentrated ore

(Table 17, Col. 2) disclosed a surplus of FeO lying 15-20% above the value which would have been obtained had the concentrate been composed of magnetite and ilmenite alone. X-ray powder photographs showed two spinels with the cell-edges 8.47, 8.40 A, which compare fairly well with those of Fe_2TiO_4 and Fe_3O_4, respectively. A number of specimens of this ore, showing all transitions to delerite, were sent to me by the Höganäs-Billesholms Co., the owner of the Ulvö mines in Sweden. In polished section the mineral grains are slightly idiomorphic, and are exceptionally brown in colour. When highly magnified (over 500 times), the ore shows a very fine net work of two minerals of nearly equal proportions; one is brownish, probably the spinel Fe_2TiO_4, while the other, the true magnetite, is grey. Ilmenite also occurs, either in the form of very rare stout lamellae or as irregular homogeneous grains enclosed in the magnetite. My X-ray powder photographs of the magnetically separated ore showed faint ilmenite lines, together with the patterns of the two spinels.

New occurrences of natural Fe_2TiO_4 (ulvöspinel).

Two other specimens of natural Fe_2TiO_4 - besides the original, and only previously described, occurrence of Södra Ulvön - have been found in the present investigation one from Norra Ulvön, Sweden, and the other from the Skaergaard intrusion, East Greenland.

The first specimen occurred in a diabase from Norra Ulvön, Sweden. Polished sections of this specimen showed that the ore is very similar to that of Södra Ulvön except that the intergrowth of the two spinels is so exceptionally fine-grained that it has been very difficult to identify them. The rare ilmenite lamellae are somewhat coarser (Plate 8, Fig. 6) than in the Södra Ulvön ore, and are arranged along the octahedral planes of the magnetite-Fe_2TiO_4 grains. This led Ramdohr to describe the ore - in a letter to Mogensen (Mogensen, 1946, p. 588) - as magnetite-ilmenite ex-solution intergrowths; he stated that he "could hardly imagine that the material at Södra Ulvön should still not be ex-solved, in contrast to that at Norra Ulvön, which he has thoroughly examined". However, X-ray powder photographs (Plate 6, Fig. 5) of the highly concentrated ferromagnetic fraction separated from the Norra Ulvön ore showed clearly the patterns of Fe_2TiO_4 and magnetite, and were very similar to those of the Södra Ulvön ore. It is therefore evident that Ramdohr's statement is erroneous, and that the Norra Ulvön and Södra Ulvön ores are of the same type; both being due to the unmixing of an original Fe_3O_4-Fe_2TiO_4 solid solution, partial splitting up of Fe_2TiO_4 into ilmenite having just started (see Section VII). This result also shows the necessity of using X-ray analysis for the identification of Fe_2TiO_4.

The second specimen occurred in a hypersthene-olivine gabbro from the base of Skaergaard intrusion, East Greenland. Extensive magnetic and heavy - liquid separations were carried out on this specimen, and a chemical analysis of the ferro-magnetic fraction was made by Dr. E. A. Vincent (Table 17, Col. 1). There is a striking agreement between the results of this analysis and those of the ore from Södra Ulvön (Table 17, Col. 2), especially in the contents of FeO and TiO_2. Recalculation of the analysis showed 44.29% Fe_2TiO_4, together with a number of other spinels, magnetite being the second most frequent (34.41%); an appreciable amount of $FeTiO_3$ was also found (6.53%). The analysis showed an exceptionally high percentage of V_2O_3 (1.74%) as well as MgO, and, as in the analysis of the Södra Ulvön ore, a surprising content of CaO; it was not possible to determine whether the corresponding spinels existed in the Fe_3O_4 or in the Fe_2TiO_4 lattice. The X-ray powder photograph of the analysed material (Plate 6, Fig. 6)

Table 17.

Chemical analyses of ulvöspinel - magnetite ores.

	High grade concentrate		Mineral components.		
	1	2		1	2
TiO_2	19.28	18.2	Fe_2TiO_4	44.29	51.8
Fe_2O_3	32.27	26.7	$MgAl_2O_4$	1.08	3.3
Al_2O_3	0.78	2.70	$MnFe_2O_4$	1.06	1.4
V_2O_3	1.74	0.88	$MgFe_2O_4$	8.30	7.6
Cr_2O_3	0.13	0.9	$CaFe_2O_4$	1.62	2.8
			FeV_2O_4	2.58	1.4
FeO	43.07	44.9	$FeCr_2O_4$	0.18	1.4
MnO	0.33	0.41	$FeFe_2O_4$	34.41	27.6
CaO	0.42	0.95			
MgO	1.98	3.00	$FeTiO_3$	6.53	-
SiO_2	0.24	1.61	FeO	-	2.7
H_2O	0.06	-			
Rem.	-	0.31		100.05	100.0
Total	100.30	100.58			

1) Ulvöspinel-magnetite ore from hyperthene-olivine gabbro. Skaergaard intrusion, East Greenland. Analyst, E.A. Vincent (new analysis), S 680.

2) Ulvöspinel-magnetite ore from olivine dolerite. Södra Ulvön, Sweden. Analyst, B. Rennholm, and others (Mogensen, 1946, p. 586).

was almost identical with that of the Södra Ulvön ore; it showed two spinels of the magnetite pattern together with faint lines of ilmenite. X-ray measurements (Table 18, Col. 3) showed that the two spinels have cell-edges of 8.475 A and 8.396 A, which correspond fairly well with those of Fe_2TiO_4 and Fe_3O_4 respectively.

The results of the above investigations confirm the work of Mogensen, and prove conclusively the existence of natural Fe_2TiO_4. As to the nomenclature of the mineral Fe_2TiO_4, Mogensen, in an early paper (1943), used the terms "ulvöspinel" and "titanspinel", but, in his second publication (1946), without giving any reason, discarded these two terms and refered to Fe_2TiO_4 as "ferro-ortho-titanate". This long term "ferro-ortho-titanate" is unsuitable on the grounds that it has been shown by Barth and Posnjak (1932) that the mineral is structurally not a titanate but an inversed spinel. I should like to re-establish the use of the name "ulvöspinel,", after the original locality in Ulvön, Sweden, for natural Fe_2TiO_4.

Ulvöspinel is cubic, with a face-centred lattice and a cell-edge of about 8.475 A; this value is slightly lower than the corresponding value for artificial Fe_2TiO_4

(a = 8.51 A), probably due to a little Fe_3O_4, or other spinels, in solid solution. It has a 2-4 inverse spinel structure (2 and 4 refer to the valencies of the iron and titanium respectively), and its formula can thus be written as $Fe^{2+}(Ti^{4+}Fe^{2+})O_4$. Ulvöspinel forms an extremely fine net work with magnetite (distinguished only under high power oil-immersion lenses) and is probably arranged parallel to (100). It is similar in colour and reflective power to ilmenite, being slightly darker and browner than ordinary magnetite. Minute ilmenite intergrowths can easily be mistaken for ulvöspinel if the microscopic study is not supported by X-ray analysis, as, in such fine structure, the anisotropy of ilmenite can be seen only with difficulty. Ramdohr, in his recent book on ore minerals (1950, p. 663), made such a mistake in identifying a specimen from Magnet Heights, Bushveld, Transvaal, which he described and photographed (Fig. 376) as relatively coarse Fe_2TiO_4. However, an X-ray powder photograph of the same specimen, which he kindly sent to me, has shown that it is definitely formed of magnetite and ilmenite; no lines of ulvöspinel appeared (Plate 6, Fig. 1). A photomicrograph of a polished section of this specimen is given in Plate 8, Fig. 7.

It is possible that ulvöspinel may be more common than has hitherto been thought, and that its apparent rarity may be due to the difficulty in its identification under the microscope, while in X-ray photographs the slight doubling of the lines, due to the small difference in the size of the unit cell of Fe_3O_4 and Fe_2TiO_4, may be easily overlooked, especially if small-diameter X-ray cameras are used.

Artificial Fe_3O_4 - Fe_2TiO_4 solid solutions.

The analogy in structure of the two cubic spinels Fe_3O_4 and Fe_2TiO_4 suggests the possibility of solid solution between the two minerals. Pouillard (1949) was able to prepare these solid solutions by two methods: 1) by direct action on TiO_2 on Fe_3O_4 at high temperature (900°C.) in the absence of air, 2) by reduction of Fe_2O_3 with hydrogen in the presence of TiO_2. In both methods of preparation the composition of these Fe_3O_4-Fe_2TiO_4 solid solutions was not determined directly by chemical analysis (other phases being present), but their constitution was deduced from their X-ray and thermomagnetic data. The following table, modified from Pouillard (1949, p. 36), shows the relation between the lattice parameters and the composition of the Fe_3O_4-Fe_2TiO_4 solid solutions.

Parameter a	8.396	8.420	8.428	8.430	8.44	8.46	8.534
% mol. Fe_2TiO_4	0	8	10	18	25	42	100

There is a considerable replacement of the Fe^{3+} ions of magnetite by groups of $(Ti^{4+}Fe^{2+})$ ions; the mechanism of substitution can be represented as follows:

$$2Fe^{3+} \rightleftharpoons Ti^{4+}Fe^{2+}$$

The formula of the solid solutions formed can be written as $(Fe^{3+}_{2-2x} . Ti^{4+}_{x} . Fe^{2+}_{1+x})O_4$. The composition prepared by Pouillard, which was ~~most~~ richest in Fe_2TiO_4, had $x = 0.42$, but, from the similarity of structure and the proximity of unit cell dimensions, it is very possible that continuous solid solution between Fe_3O_4 and Fe_2TiO_4 does exist, i.e. the value of x may vary from 0 to 1. As can be seen from the above Table, there is a continuous rise of the cell-edge of magnetite with the increase of Fe_2TiO_4 in solid solution.

The author was able to prepare two such solid solutions by a method similar to that used by Pouillard; two mixtures of Fe_3O_4 and TiO_2, in the molecular ratios of 4:3 and 1:1 respectively, were heated in evacuated silica glass tubes for 36 hours, and then quenched. X-ray powder photographs showed the presence of three phases: a cubic phase of Fe_3O_4-Fe_2TiO_4 solid solution, a rhombohedral phase of ferriilmenite ($2FeTiO_3.Fe_2O_3$), and an orthorhombic phase of pseudobrookite ($Fe_2O_3.TiO_2$)! Pouillard (1949, p.41) was not able to distinguish pseudobrookite in his X-ray photographs, but, from his thermomagnetic analysis, suspected the presence of excess TiO_2. The unit cell dimensions of the Fe_3O_4-Fe_2TiO_4 solid solutions prepared from the two mixtures $4Fe_3O_4 + 3TiO_2$ and $Fe_3O_4 + TiO_2$ are a = 8.442 A and a = 8.451 A respectively, which agree fairly well with the results of Pouillard. These solid solutions are usually ferromagnetic, even when the amount of magnetite present is small. Fig. 5 in Plate 7 shows an X-ray powder photograph of the ferromagnetic fraction in the prepared charges, after the separation of pseudobrookite.

Natural Fe_3O_4 - Fe_2TiO_4 solid solutions (titanomagnetites).

Natural magnetite-Fe_2TiO_4 solid solutions were supposed to be present by Goldschmidt (1926) and Foslie (1928), who considered them to be the origin of the magnetite-ilmenite intergrowths. However, such supposition, although sound on crystallographic grounds, has not been confirmed; the Fe_3O_4-Fe_2TiO_4 solid solutions, as far as the author is aware, have never been separated, and their composition has not been determined with certainty. This is probably due to the difficulty in separating these solid solutions from the fine-grained volcanic rocks where they are supposed to exist (in these rocks, owing to rapid cooling, no unmixing of the original solid solutions has taken place).

To approach such a problem, a large number of igneous rocks, especially dolerites and basalts, was studied, small specimens being ground to a very fine powder, less than 0.1 mm. grain diameter, and magnetic separation applied. X-ray powder photographs were taken of the minute amounts of ferromagnetic fractions separated. In these cases where a marked change in the size of the unit cell of the homogeneous magnetite was noticed, and where no ilmenite lines appeared, a sample was examined, semiquantitatively by spectrochemical or microchemical analysis, for titanium. From those samples which showed an appreciable amount of titanium, some - if further separation was possible - were chosen for quantitative chemical analysis.

In the case of plutonic rocks, the phases present in the X-ray powder photographs of the ferromagnetic fractions, were usually magnetite and ilmenite (probably as ex-solution intergrowths), and there was no change in the size of the unit cell of the magnetite, except when partial oxidation to maghemite occurred (see Appendix, Table A). On the other hand, the X-ray photographs of the ferromagnetic fractions of the volcanic rocks usually showed homogeneous magnetite pattern, (with the exception of a few cases, ilmenite lines did not appear); X-ray measurements often disclosed a definite increase in the unit cell dimensions of the magnetite ~~than~~ compared with those of pure Fe_3O_4 (Plate 7, Figs. 1-4).

Table 18.

X-ray powder data of titanomagnetites and ulvöspinel.
Co. target, Fe filter.

1		2		3		4	hkl
I	d(meas.)	I	d(meas.)	I	d(meas.)	d(calc.)	
30	4.870	30	4.892				(111)
70	2.982	70	2.994			3.02	(220)
100	2.542	100	2.550	100	2.552	2.57	(311)
10	2.435	10	2.443			2.46	(222)
60	2.107	60	2.115	50	2.117	2.13	(400)
30	1.721	40	1.728	30	1.730	1.742	(422)
80	1.622	80	1.629	80	1.631	1.642	(511) (333)
90	1.490	90	1.496	90	1.498	1.508	(440)
10	1.331	10	1.341	10	1.341	1.349	(620)
30	1.287	20	1.290	30	1.292	1.302	(533)
20	1.218	10	1.220	15	1.224	1.232	(444)
15	1.127	10	1.131	10	1.133	1.140	(642)
30	1.0978α_1	30	1.1018	40	1.1028	1.111	(731)
20	1.0546	15	1.0583	20	1.0592	1.067	(800)
10	0.9956	10	0.9977			1.006	(822)
35	0.9750α_1	30	0.9777α_1	35	0.9784		(751)
20	0.9750α_2	15	0.9777α_2				(555)
20	0.9441α_1	20	0.9486α_1				(840)
15	0.9441α_2	10	0.9484α_2				

1. Titanomagnetite (1-x)Fe_3O_4.xFe_2TiO_4, separated from basalt. Blagolkot, Deccan, India. a = 8.4480 ± 0.001 A.
2. Titanomagnetite (1-x)Fe_3O_4.xFe_2TiO_4, separated from basalt. Giant's Causeway, Ireland. a = 8.4697 ± 0.0005 A.
3. Ulvöspinel Fe_2TiO_4, separated from gabbro. Skaergaard Intrusion, East Greenland. a = 8.475 ± 0.002 A.
4. Artificial Fe_2TiO_4, prepared by Pouillard (1949, p. 33). a = 8.534 A.

The following four rocks were subjected to extensive magnetic and heavy-liquid separations, to obtain pure ferromagnetic fractions sufficient for chemical analysis: 1) basalt from Giant's Causeway, Ireland, 2) basalt from Blagolkot, Deccan, India, 3) augitite from Ngong, Nairobi, Kenya, and 4) basalt from Dunglas Hill, near Strathblane, Scotland. Owing to their being very fine-grained, and the fact that some of them (e.g. specimen 4) contained iron-rich silicates which may be strongly magnetic, the separation was rendered very difficult. However, by very fine grinding, to less than 0.1 mm. diameter, and by applying the procedure described in Section IV, it was possible to obtain from the first three specimens relatively pure material which appeared to be practically homogeneous in X-ray powder photographs. Chemical analyses of the high grade concentrates from these three specimens are given in Table 19, Cols. 1, 2, 3; all of them show a considerable amount of TiO_2. The analyses were calculated after the substraction of the small amount of silicate present (mainly augite or titan-augite), the composition and amount of which were determined microscopically and from X-ray powder photographs. Determination of the mineral components in the ore (Table 20), showed the presence of 32.5, 25.1 and 27% Fe_2TiO_4, in the three analysed specimens, together with the magnetite.

Table 19.

Chemical analyses of Fe_3O_4-Fe_2TiO_4 solid solutions (Titanomagnetites).

	1	2	3	4	5	6
TiO_2	24.86	27.77	16.20	6.98	12.18	10.83
Fe_2O_3	26.88	25.86	28.96	57.11	47.00	41.97
Al_2O_3	0.40	0.60	6.64	3.62	3.75	6.50
V_2O_3	-	-	0.22	0.10	-	trace
Cr_2O_3	-	-	0.01	0.01	-	0.42
FeO	42.33	39.74	36.21	21.83	34.94	33.30
MnO	0.72	0.58	0.74	1.82	0.10	0.39
CaO	-	-	1.56	0.94	-	0.74
MgO	2.07	2.54	3.25	7.18	2.35	5.54
SiO_2	2.64	2.83	4.38	0.38	-	0.64
Total	99.90	99.92	98.17	99.97	100.32	100.33

1. Titanomagnetite with some ilmenite ~~(metamict)~~, separated from basalt. Giant's Causeway, Ireland. Analyst, W. H. Herdsman (new analysis). S 729.
2. Titanomagnetite with some admixed ilmenite, separated from olivine basalt. Blagolkot, Deccan, India. Analyst, W. H. Herdsman (new analysis). S 571.
3. Titanomagnetite with little ilmenite ~~(metamict)~~, separated from augitite. South of Ngong, Nairobi, Kenya. Analyst, H. B. Milner (new analysis). S 595.
4. Titanomagnetite, separated from ore. Magnet Cove, Arkansas. Analyst, H. B. Milner (new analysis). S 411.
5. Titanomagnetite, from basaltic sands. Ardèche, France. Analyst, G. Jouravsky (Jouravsky, 1936, p. 1691).
6. Titanomagnetite, separated from sand, Monti Rossi, Etna. Analyst, S. F. Starrabba (Starrabba, 1939, p. 5).

An appreciable amount of $FeTiO_3$ also appeared in the analyses. On heating samples of these three specimens in evacuated silica glass tubes at about 1000°C. for two days, moderately strong ilmenite lines appeared in the X-ray powder photographs of the quenched charges. This proves that most of the $FeTiO_3$ that was disclosed on calculation of the analyses is present as admixed ilmenite, possibly in an amorphous state. On the other hand, the absence of any ulvöspinel lines in the X-ray powder photographs, both before and after the heating of the material, shows conclusively that the Fe_2TiO_4 which appeared in the analyses must be present in solid solution in the magnetite molecule. This fact explains the considerable increase in the size of the unit cell of the "magnetite" as compared to that of pure Fe_3O_4. Table 18, Cols. 1, 2, show the results of X-ray measurements for the two specimens from Blagolkot and Giant's Causeway, the lattice parameters being $a = 8.4480 \pm 0.001$ A, $a = 8.4697 \pm 0.0005$ A, respectively (for pure magnetite $a = 8.3963 \pm 0.0005$ A). These figures agree fairly well with the values given by Pouillard (1949) for his artificial Fe_3O_4-Fe_2TiO_4 solid solutions, and, from the Table of lattice parameters (p. 140, this thesis), correspond to about 25, 42% Fe_2TiO_4 respectively, The above investigation proves conclusively that extensive solid solution of ulvöspinel in magnetite exists in nature, and, owing to rapid cooling, can be preserved in volcanic rocks. This is the first time, as far as the author is aware, that such Fe_2TiO_4-Fe_3O_4 solid solutions have been separated from volcanic rocks, and their structure and composition determined with certainty. These minerals are ferromagnetic, and are similar to the artificial solid solutions prepared by Pouillard and in the present work; the size of the cubic unit cell increases with the increase of the amount of Fe_2TiO_4 in the magnetite molecule. They have the formula $(Fe^{3+}_{2-2x}.\ Ti^{4+}_{x}.\ Fe^{2+}_{1+x})O_4$, and are the true titanomagnetites (see Section VII).

Chemical analysis (Table 19, Col. 4) of a homogeneous titanomagnetite separated from an ore specimen from Magnet Cove, Arkansas was also carried out. Calculation of the analysis (Table 20-4) showed, besides 10% Fe_2TiO_4, a considerable amount of magnesioferrite (Fe_2MgO_4), together with spinel proper (Al_2MgO_4) and jacobsite (Fe_2MnO_4). X-ray powder photographs of this specimen showed ordinary magnetite pattern, with no change in the unit cell dimensions. It is possible that the presence of Fe_2MgO_4 and Al_2MgO_4, which have unit cells smaller than that of magnetite (a = 8.366 A, 8.086 A, respectively), has counteracted the rise which would occur in the size of the unit cell of the magnetite due to the presence of Fe_2TiO_4 (a = 8.51 A) and Fe_2MnO_4 (a = 8.457 A) in solid solution.

Few reliable chemical analyses of pure magnetite have been published (all of magnetite separated from ores or from plutonic rocks) which, after calculation, showed an excess of FeO over the magnetite and ilmenite molecules (Table 19, Cols. 5, 6). As solid solution of FeO in magnetite is very limited, less than 2% (see Section VI, b), this surplus FeO is very probably combined with the TiO_2 of the analyses to form Fe_2TiO_4, which enters into solid solution in the magnetite. Foslie (1928), Starrabba (1939), Evrard (1944) and Vaasjoki (1947) observed an excess of FeO on calculation of their chemical analyses of magnetite. The molecular percentage of this FeO was about double the molecular percentage of the TiO_2 present, a fact which strongly supports the supposition of an Fe_2TiO_4 molecule. However, their materials were not examined by X-ray analysis.

Table 20.

Calculation of the chemical analyses of titanomagnetites.

		% High grade concentrate	Ore		Mineral component.		
			%	Mol	Mol		%
1.*	TiO_2	24.86	26.03	325	10	$MnFe_2O_4$	2.31
	Fe_2O_3	26.88	28.21	176	23	$MgFe_2O_4$	4.60
	Al_2O_3	0.40			143	$FeFe_2O_4$	33.18
					145	Fe_2TiO_4	32.48
	FeO	42.33	44.10	613			
	MnO	0.72	0.75	10	180	$FeTiO_3$	27.36
	MgO	2.07	0.91	23			
	SiO_2	2.64			Impurities: 4% titan-augite, and ilmenite.		
		99.90	100.00				
2.	TiO_2	27.77	22.86	286	6	$MgAl_2O_4$	0.85
	Fe_2O_3	25.86	33.40	209	28	$MgFe_2O_4$	5.61
	Al_2O_3	0.60	0.64	6	9	$MnFe_2O_4$	2.08
					172	$FeFe_2O_4$	39.91
	FeO	39.74	41.06	570	112	Fe_2TiO_4	25.10
	MnO	0.58	0.67	9			
	MgO	2.54	1.37	34	174	$FeTiO_3$	26.45
							100.00
	SiO_2	2.83			Impurities: 4% titan-augite, and ilmenite (10% $FeTiO_3$ was substracted).		
	Total	99.92	100.00				

Table 20 (contin.)

		% High grade concentrate	Ore		Mineral component.		
			%	Mol	Mol		%
3	TiO_2	16.20	18.04	225	57	$MgAl_2O_4$	8.1
	Fe_2O_3	28.96	32.24	201	214	Fe_3O_4	49.6
	Al_2O_3	6.64	7.07	69	120	Fe_2TiO_4	26.9
	V_2O_3	0.22	0.24	1			
	Cr_2O_3	0.01			105	$FeTiO_3$	15.4
	FeO	36.21	39.31	546			100.0
	MnO	0.74	0.82	12		Impurities: about 7% augite, and ilmenite.	
	CaO	1.56					
	MgO	3.25	2.28	57			
	SiO_2	4.38					
		98.16	100.00				
4	TiO_2	6.98	7.01	87	36	$MgAl_2O_4$	5.1
	Fe_2O_3	57.11	57.35	359	144	$MgFe_2O_4$	28.8
	Al_2O_3	3.62	3.64	36	26	$MnFe_2O_4$	6.0
	V_2O_3	0.10			17	$CaFe_2O_4$	3.7
	Cr_2O_3	0.01			172	Fe_3O_4	39.9
	FeO	21.83	21.92	304	46	Fe_2TiO_4	10.3
	MnO	1.82	1.83	26	41	$FeTiO_3$	6.2
	CaO	0.94	0.94	18			100.0
	MgO	7.18	7.21	180		Impurities: about 5% ilmenite, not substracted.	
	SiO_2	0.38					
		99.96	100.00				

* Numbers 1, 2, 3, 4 correspond to the same numbers in Table 19.

VII. Interpretation of the Constitution of Titanomagnetites and the Origin of the Magnetite-Ilmenite Intergrowths.

It is evident, from what has been mentioned before (Section VI, g, h), that there is much disagreement between the different investigators regarding the composition of the original solid solution, which on cooling has given rise to the magnetite-ilmenite intergrowths. The two main theories are those put forward by Ramdohr (1926, 1939), and by Foslie (1928).

1) Ramdohr's theory.

Ramdohr (1926) suggested that at high temperatures, above 800°C, magnetite and ilmenite can form very extensive solid solutions (the titanomagnetites and the "magnetoilmenites"). On slow cooling, as in plutonic rocks, unmixing of these supposed solid solutions takes place giving rise to the well-known magnetite-ilmenite intergrowths. On rapid cooling, however, as in volcanic rocks, the homogeneous titanomagnetite can be preserved.

This theory is the one more generally accepted (Lindley, 1925, Odman, 1932; Newhouse, 1936; Edwards, 1938), as it provides the simplest way of interpreting the magnetite-ilmenite ex-solution intergrowths. However, it fails to explain the mechanism of substitution and the way in which the rhombohedral ilmenite can be arranged in the cubic magnetite lattice. As has been mentioned before (Section VI, c), Greig and his co-workers (1935) have proved, beyond doubt, that the solubility of α-Fe_2O_3 in magnetite is not more than 8% at 1075°C; it is therefore difficult to accept the that ilmenite, which has the same crystal structure as α-Fe_2O_3, can form extensive solid solutions in magnetite (up to 50% or more, according to Ramdohr). Many titaniferous magnetite deposits, e.g. those of Ekersund, Norway, show granular magnetite and ilmenite which form independent grains without any sign of intergrowth between them. It is not conceivable that the supposed magnetite-ilmenite intergrowths will give rise, on cooling, to exsolution intergrowths in one case and to individual grains in the other.

In Section VI, g, I have shown the important defects in Ramdohr's experiments - on which he based his theory- and from my own heating experiments, in vacuum, I was able to prove the very limited miscibility between magnetite and ilmenite (less than 5% at 1050°C).

2) Foslie's theory.

Foslie (1928) suggested that the orthotitanate Fe_2TiO_4 is isomorphous with magnetite at high temperatures, and can form very varied mixed crystals. He found that when intergrowth lamellae of haematite occurred in ilmenite, the magnetite was poor in TiO_2. According to Foslie (p. 13), the following rules govern the factors which determined the magnetite-ilmenite intergrowths:

a. If Fe_2O_3 occurs in excess over TiO_2 and FeO, Fe_2TiO_4 cannot be formed. The small solubility of $FeTiO_3$ will be decisive, and the magnetite will be poor in Ti.

$$Fe_2TiO_4 + Fe_2O_3 \longrightarrow FeTiO_3 + Fe_3O_4$$

b. If, on the other hand, there is no or insufficient Fe_2O_3, Fe_2TiO_4 can be formed, and will dissolve extensively in the magnetite. On cooling, it splits up with accompanying formation of $FeTiO_3$, and, if the cooling is slow enough, ex-solution intergrowth suddenly appears.

$$Fe_2TiO_4 \longrightarrow FeTiO_3 + FeO$$

FeO is then contained in the magnetite as a solid solution.

The results of my investigations (Section VI, h) have proved conclusively that Foslie's supposition as to the presence of extensive solid solution of Fe_2TiO_4 in Fe_3O_4 is correct. It has also been confirmed (Mogensen, 1946, and the present work) that Fe_2TiO_4 can exist as a mineral, ulvöspinel.

However, Foslie could not explain why in his analysed magnetite from Storgangen, Norway, which should confirm to rule "a" in his theory (Fe_2O_3 in excess), there was an excess of 3.16% FeO, even if all the Ti was to be reckoned as Fe_2TiO_4. A corresponding FeO surplus was also found on calculating the analyses of similar specimens, given by Evrard (1944), Vaasjoki (1947) - (see points 24, 26, 30 in the ternary diagram, Fig. 5). It is possible that in these titanium-poor magnetites containing excess FeO, there is a reaction similar to that which took place on heating my artificial preparations of magnetite-ilmenite mixtures (Section VI, g, p. 128), i.e. the ilmenite takes Fe_2O_3 from the magnetite to form ferriilmenite (which unmixes on cooling to ilmenite-haematite ex-solution intergrowths), with the consequent enrichment of the magnetite in FeO.

$$2(FeO.Fe_2O_3) + 2FeTiO_3 \longrightarrow Fe_3O_4.FeO + 2FeTiO_3.Fe_2O_3$$

This reaction is strongly supported by Evrard's description (1944) of a titaniferous iron ore from Håland, Ekersund, Norway. The magnetite and ilmenite occur in independent grains, the ilmenite containing ex-solution lamellae of haematite, but, at the contact of an ilmenite grain with a magnetite one, there is a small area where the haematite disappears. Chemical analysis of the magnetite (Appendix, Table B, Col. 29) shows a deficiency in Fe_2O_3 molecule (i.e. excess FeO), while that of ilmenite shows excess Fe_2O_3.

He suggests that the inequilebrium is caused by the migration phenomenon; the capacity of solubility of the titanomagnetite permitting the departure of Fe_2O_3 which segregates in the ilmenite.

Another point which requires further consideration is Foslie's statement that, on cooling the original titanomagnetite, the FeO formed by the decomposition of Fe_2TiO_4 ($Fe_2TiO_4 \longrightarrow FeTiO_3 + FeO$), enters into solid solution with the magnetite. However, calculation of the chemical analysis of magnetite-ilmenite intergrowths from Tofetholine, Oslo Fjord, Norway (Table 16) does not show any excess FeO. Dunn and Dey (1937, p. 159) who also questioned this point in Foslie's theory, have even found a deficiency of FeO in their analysed ores from Sighbhum-Mayurbhanj, India. I suggest that the FeO, formed from the splitting up of Fe_2TiO_4, becomes incorporated in the silicate minerals.

One can distinguish two types of titaniferous magnetite deposits:

1) In the first type, magnetite and ilmenite occur in independent grains, the ilmenite usually containing ex-solution bodies of haematite, e.g. ores from Soggendal and Håland in Norway, and from Otanmäki in Finland (Foslie, 1928; Evrard, 1944; Vaasjoki, 1947). It is suggested that in these ores

there was insufficient FeO to form Fe_2TiO_4; ilmenite is formed instead, and dissolves very slightly in magnetite (less than 5%). In addition, Fe_2O_3 is partly drained from the magnetite into the ilmenite where it forms ilmenite-haematite solid solutions or ex-solution intergrowths. The magnetite formed is thus poor in TiO_2, but contains excess FeO.

2) In the second type, which is very common, the magnetite shows ilmenite ex-solution intergrowths which may reach up to 50% of the ore. It is suggested that in this case there was enough FeO to form the ulvöspinel Fe_2TiO_4 which dissolves extensively in the magnetite to form the true titanomagnetite. On rapid cooling, as in volcanic rocks, this titanomagnetite can be preserved as solid solution. On slow cooling, however, it unmixes into magnetite and ulvöspinel; the latter also decomposes on further cooling, to give $FeTiO_3$, which forms the well-known magnetite-ilmenite intergrowths, and FeO. The reactions can be represented as follows:

a. $Fe_3O_4 + xFe_2TiO_4 \longrightarrow (1-x)Fe_3O_4 \cdot xFe_2TiO_4$

b. $(1-x)Fe_3O_4 \cdot xFe_2TiO_4 \longrightarrow Fe_3O_4 + Fe_2TiO_4$

c. $Fe_3O_4 + Fe_2TiO_4 \longrightarrow (Fe_3O_4 + FeTiO_3) + FeO$

The FeO becomes incorporated in the silicate minerals.

There are, however, a few cases where, in spite of slow cooling, complete unmixing of the original titanomagnetite did not take place, or where the unmixing has stopped at stage "b" i.e. with the formation of magnetite and ulvöspinel. Examples of these cases are the ores from Södra Ulvön, Norra Ulvön, and Skaergaard, occurring in dolerite, diabase, and olivine gabbro, respectively, and all of which are formed of magnetite and ulvöspinel, with very little ilmenite. Calculation of my chemical analysis of the magnetite ore from Magnet Cove, Arkansas has shown 10.3% Fe_2TiO_4 in solid solution (see Section VI, h). Starrabba (1939) has also noticed a considerable amount of Fe_2TiO_4 (40.3%) on calculating the chemical analysis of homogeneous magnetite octahedra, 1.5 mm. diameter, separated from sand, Monte Rossi, Etna. Another example of homogeneous titanomagnetite which has not ex-solved by slow cooling is that separated from sand from Ardèche, France (Jouravsky, 1936). On examining these analyses (Table 19, Cols. 4-6), as well as the ulvöspinel-magnetite ores (Table 17, Cols. 1, 2), one can notice a character common to all, that is the presence of a high percentage of MgO and Al_2O_3. It is possible, as has been previously supposed by Jouravsky (1936), that this high content of

Al_2O_3 and MgO plays an important part in preserving the original titanomagnetite solid solution. Mogensen (1946, p. 588) suggested that "if FeO has in no way been removed, the formation of FeO will counteract the decomposition of Fe_2TiO_4, so that a surplus of FeO may always be anticipated in primary Fe_2TiO_4 ores". Such supposition, although possible in principle, should not, in fact, lead to an excess of FeO in the Fe_2TiO_4 ores. No such FeO surplus (over the Fe_2TiO_4 molecule) has been found in the present analysis of the ore from the Skaergaard intrusion (Table 17, Col. 1).

During the present investigation, it was noticed that, if ilmenite occurred in the magnetite-ulvöspinel ores, it was usually free from any Fe_2O_3. X-ray powder photographs of ilmenite separated from the Skaergaard ore showed typical ilmenite pattern (no change in the size of the unit cell); no haematite lines were observed. Polished sections of the Södra Ulvön and Norra Ulvön ores showed exceptionally pure ilmenite free from haematite ex-solution intergrowths.

In a recent work, Chevallier and Girard (1950) suggested the presence of two types of titanomagnetites:

titanomagnetite "I" with the formula $xFe_3O_4,(1-x)Fe_2TiO_4$, and titanomagnetite "II" to which they gave the formula $yFe_3O_4,(1-y)FeTiO_3$. They suggested that natural titanomagnetite is probably formed of titanomagnetite "I" with some titanomagnetite "II" in solid solution. Chevallier and Girard claimed to have prepared titanomagnetite "II" by heating mixtures of Fe_2O_3 and TiO_2 with borax at 1000°C., first in nitrogen, then in a determined amount of hydrogen, and finally cooling slowly in nitrogen. The resulting mixture of titanomagnetite, ilmenite, haematite, pseudobrookite, and rutile was separated magnetically. Separation of the titanomagnetite from the ferromagnetic ilmenite (possibly ferriilmenite) was carried out, in air, at 250°C. the temperature at which the ilmenite loses all its ferromagnetism. Chemical analysis of six samples of the titanomagnetite confirmed the formula $yFe_3O_4.(1-y)FeTiO_3$. X-ray powder photographs showed it to be homogeneous, and to have a pattern which was almost that of magnetite.

However, there are strong objections to these results; 1) It is difficult to understand how unmixing of the magnetite-ilmenite solid solutions did not take place during the very slow cooling of the preparations in nitrogen (not less than 5 hours were needed to reach a temperature of 100°C from an initial temperature of 1000°C).

2) During the magnetic separation of the titanomagnetite and the ferromagnetic ilmenite, which was carried out in air at 250°C., partial oxidation of the titanomagnetite to γ-Fe_2O_3 must have occurred.*

3) Chevallier and Girard did not measure the unit cell dimensions of this titanomagnetite, and could not explain how as much as 37 mol. % of $FeTiO_3$, which is rhombohedral, can be placed in the magnetite cubic lattice.

4) Some admixed ilmenite was possibly present in their analysed materials. They stated (p. 577) that when one of the two constituents (titanomagnetite and ferromagnetic ilmenite) was of a poor amount in the mixture obtained, the magnetic separation was not satisfactory; from their curve (Fig. 1), showing the respective proportions of titanomagnetite and ferromagnetic ilmenite, it is clear that, in some of their preparations (No. 2, 5, 6), this was the case.

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* Magnetite is oxidized in air to γ-Fe_2O_3 at 220°C. (Van der Marel, 1951).

It is possible that the original titanomagnetite prepared by Chevallier and Girard was actually formed mainly of $(1-x)Fe_3O_4 \cdot xFe_2TiO_4$ which was partially oxidized to maghemite or titanomaghemite during the magnetic separation. The γ-Fe_2O_3 thus formed can enter in solid solution in the titanomagnetite cubic lattice and will account for the result of the chemical analyses, as can be seen from the following equations:

$$Fe_3O_4 \cdot Fe_2TiO_4 + O \longrightarrow \gamma\text{-}Fe_2O_3 \cdot Fe_2TiO_4$$

$$\gamma\text{-}Fe_2O_3 \cdot (2FeO \cdot TiO_2) = Fe_3O_4 \cdot FeTiO_3$$

The X-ray data given by Chevallier and Girard (p. 579) for their synthetic titanomagnetite show an appreciable decrease in the lattice spacings from those of pure magnetite. The question then arises: are these low values due to the limited accuracy in measurements (as admitted by them), or are they the result of γ-Fe_2O_3 in solid solution (see Section VI, c)? On examining the results of their chemical analyses a slight excess of FeO over the amount required for the magnetite and ilmenite molecules was observed in most cases. I suggest that the formula of the titanomagnetite prepared by Chevallier and Girard can be written as $(1-x)\ (Fe_3O_4 \cdot Fe_2O_3) \cdot xFe_2TiO_4$, probably with a little ilmenite in solid solution.

In conclusion, it can safely be stated that there is only one main type of titanomagnetite, the structure and composition of which have been established with certainty: this can be represented by the formula $(1-x)Fe_3O_4 \cdot xFe_2TiO_4$ (x ranging from 0 to 1), and is the source of the magnetite-ilmenite intergrowths. It is ferromagnetic, cubic, and the cell-edge varies from 8.40 A for pure magnetite to about 8.51 A for pure ulvöspinel. It is possible, however, as can be seen from the ternary diagram Fig. 5 (see Section VIII), that a slight amount of $FeTiO_3$ may also enter in solid solution in the natural titanomagnetites. Partial oxidation of titanomagnetite may take place to titanomaghemite which may also enter in the titanomagnetite lattice.

Ramdohr (1950, p. 660), in his book on ore minerals, although still keeping to his view of extensive solubility of ilmenite in magnetite at high temperatures, accepts the fact that Fe_2TiO_4 and Fe_3O_4 form a complete series of solid solutions and that, on cooling, the ex-solved Fe_2TiO_4 may change afterwards into ilmenite intergrowths; perhaps the net unmixing of ilmenite in magnetite may be interpreted altogether in this way.

VIII. The Ternary Diagram of the System $FeO-Fe_2O_3-TiO_2$.

Knowing now the definite compounds which can be formed between FeO, TiO_2, and Fe_2O_3, and the possible extent of solid solutions between them, it would be useful to find a practical means of representing them. Their being formed of three basic oxides, FeO, Fe_2O_3 and TiO_2, imposes the idea of a representation in a ternary diagram, with the three oxides at the peaks of an equilateral triangle (Fig. 5). The compositions are plotted in percentage molecular proportions.

Tabulation of the data used in the ternary diagram.

In Table B (in the Appendix), the results of 21 new chemical analyses, as well as 24 analyses chosen from the literature and found to be reasonably reliable, are arranged. A tabulation of the essential data relating to these analyses has been assembled in Table C and Table D (Appendix). With two exceptions, the original paper has been examined to ascertain the basis on which the author's identification of the material depends, and to check the analysis. Although most of the headings in Table D are self-explanatory some call for special comment.

Column (4) comprises comments by the analyst, or original author, concerning crystal form, or mode of aggregation of the analysed material, and the method by which the homogeneity has been established (polished sections, X-ray methods, or both).

To render the data comparable, the obvious impurities, such as silicates and insoluble residues, are eliminated; MnO is added to FeO, V_2O_3 and Cr_2O_3 are added to Fe_2O_3, and the analyses are recalculated to 100 percent. The molecular proportions are then determined, those of FeO (after addition of the molecular proportion of MgO), Fe_2O_3 (after addition of the molecular proportion of Al_2O_3), and TiO_2 being recalculated to 100 molecules of the three oxides. This $FeO:Fe_2O_3:TiO_2$ percentage molecular ratio for every analysed specimen is given in column (5).

In column (7) a revised interpretation of the nomenclature given by the original author is given. This is based on the original description of the analysed material, in many cases supported by microscopic and X-ray data obtained in the course of the present study on material from the locality in question.

In Table C, the ratio $FeO:Fe_2O_3:TiO_2$ was obtained in the same way described for Table D. In the few cases where ex-solved minerals were present, their amount and composition were approximately determined under the microscope and from X-ray powder photographs, and the analyses were recalculated after the substraction of their respective percentages, e.g. the ilmenite from Miask (No. 21), containing a little unmixed titanhaematite, and the three titanomagnetites separated from volcanic rocks (No. 9, 11, 13), containing unmixed ilmenite (metamict, appeared on heating).

Description and interpretation of the ternary diagram.

The percentage molecular ratios of all the 45 analyses in Table B, as well as some artificial preparations, are plotted in the ternary diagram (Fig. 5). The following are the compounds of definite composition which are first encountered:

A = TiO_2 = Rutile, anatase or brookite.

B = FeO = Wüstite.

C = α- or γ-Fe_2O_3 = Haematite or maghemite (only on the line CH is Fe_2O_3 in the γ-form).

D = $FeTiO_3$ = $FeO.TiO_2$ = Ilmenite.

E = Fe_2TiO_4 = $2FeO.TiO_2$ = Ulvöspinel.

F = Fe_2TiO_5 = $Fe_2O_3.TiO_2$ = Pseudobrookite.

G = $(TiO_4)_3Fe_4$ = $2Fe_2O_3.3TiO_2$.

H = Fe_3O_4 = $FeO.Fe_2O_3$ = Magnetite.

From the diagram it is clear that there are three main groups of solid solutions:

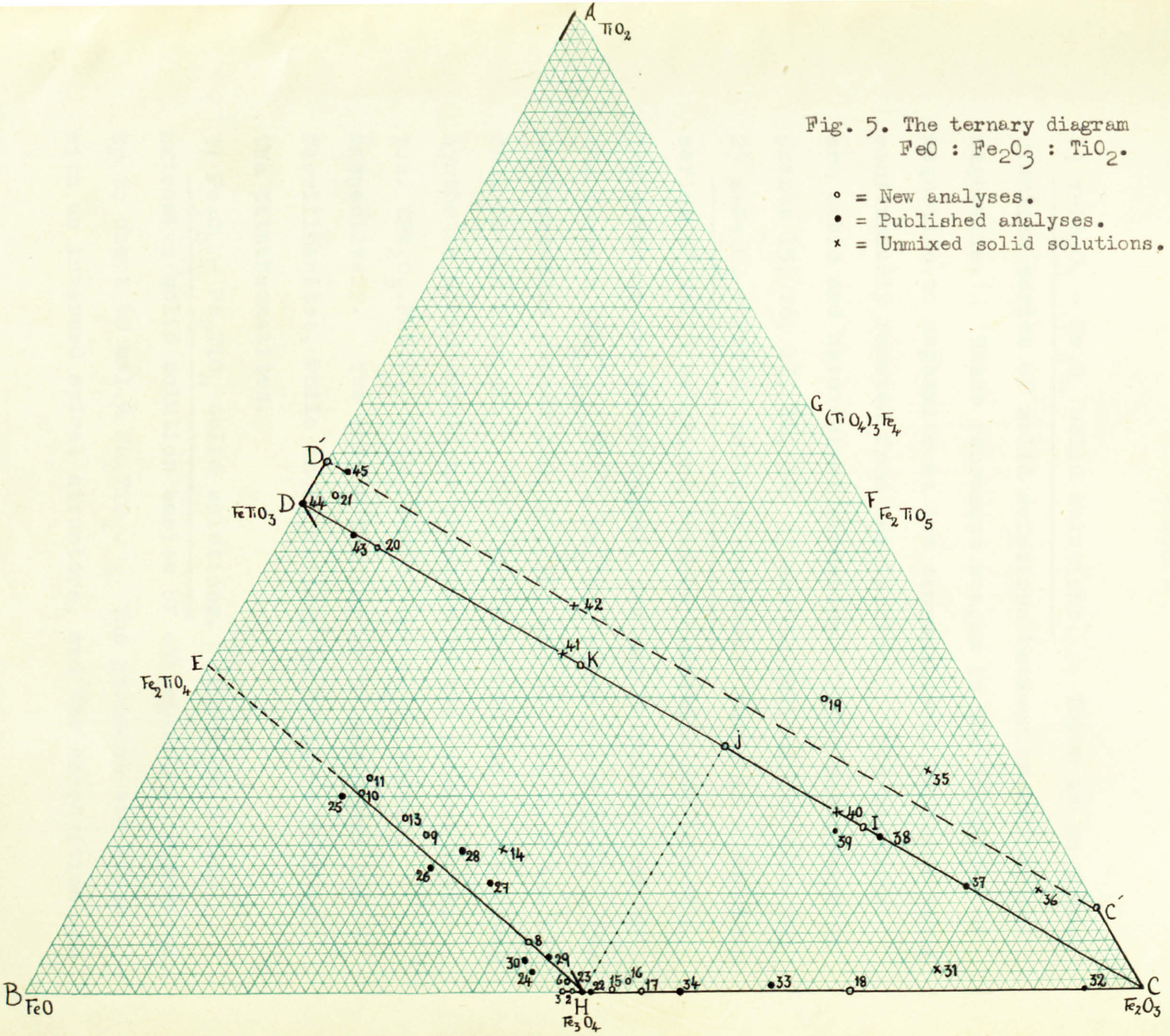


Fig. 5. The ternary diagram
FeO : Fe_2O_3 : TiO_2.

○ = New analyses.
● = Published analyses.
× = Unmixed solid solutions.

1) γ-Fe_2O_3 - Fe_3O_4 solid solutions. There is an almost complete series of solid solutions between magnetite and maghemite. These represent stages in the oxidation of magnetite to maghemite at low temperatures, Fe atoms being continuously removed from the lattice. The products are cubic and have spinel structure. The corresponding points 15, 16, 17, 18, 32, 33 and 34 fall on the line CH.

2) α-Fe_2O_3 - $FeTiO_3$ solid solutions. There is a complete series of solid solutions between haematite and ilmenite. The products are rhombohedral, and may be represented by the formula $(Fe^{3+}_{2-2x} \cdot Ti^{4+}_{x} \cdot Fe^{2+}_{x})O_3$ where $x = 0$ to 1. The corresponding points (20, 37, 38, 40, 41, 43, I, J and K) fall on the line CD. I, J and K correspond to the three synthetic solid solutions prepared in the present work, i.e. $2Fe_2O_3 \cdot FeTiO_3$, $Fe_2O_3 \cdot FeTiO_3$ and $Fe_2O_3 \cdot 2FeTiO_3$ respectively. The points falling on DJ represent the ferriilmenites, while those falling on CJ correspond to the titanhaematites.

3) Fe_3O_4 - Fe_2TiO_4 solid solutions. There is a very extensive solid solution series of ulvöspinel in magnetite, up to about 60 mol.% Fe_2TiO_4. The products are cubic with an inversed spinel structure, and the composition can

be represented by the formula $(Fe^{3+}_{2-2x} \cdot Ti^{4+}_{x} \cdot Fe^{2+}_{1+x})O_4$, where x may probably range from 0 to 1. The corresponding points 8, 10 and 29 fall on the line EH and represent the titanomagnetites.

In the diagram, it is possible to investigate four main zones: BEH, EDJH, HJC and ADC. Any point in each of these zones corresponds to a particular composition of $FeO.Fe_2O_3.TiO_2$, and represents an equilibrium between certain phases.

a. <u>The zone BEH.</u> Any point lying inside the triangle BEH, is composed of two phases: a titanomagnetite $(1-x)\ Fe_3O_4 \cdot xFe_2TiO_4$, and FeO. It is interesting to note that most of the analysed Ti-poor magnetites in this triangle fall very near to the line EH, due to their containing a little excess FeO in solid solution. Between FeO and pure Fe_3O_4 there is a very limited miscibility, not more than 3% FeO, and the corresponding points, 2 and 3 fall on the line BH.

b. <u>The zone EDJH.</u> Any point lying inside the quadrilateral EDJH, is composed of <u>two</u> phases: a titanomagnetite $(1-x)Fe_3O_4.xFe_2TiO_4$, and an ilmenite or ferriilmenite $(1-x)\ FeTiO_3.xFe_2O_3$. From the diagram it may be noticed that the natural titanomagnetites either lie on the line EH, or are arranged equally on either side of the line EH and very near to it. The deviation from the line EH (in the zone EDJH) may be due to unmixed ilmenite, from the incomplete separation of the analysed material, or to a little ferriilmenite in solid solution. Point 14, which is the only point on the line DH, represents the analysis of magnetite-ilmenite intergrowths.

c. The zone HJC. Points lying inside the triangle HJC, near to the line CH, are composed of two phases: a titanomaghemite γ-$(Fe,Ti)_2O_3$, and a magnetite, e.g. point 31. On the other hand point 39, near to the line JC, is composed of titanhaematite $(1-x)Fe_2O_3.xFeTiO_3$, and magnetite, probably as a mixture.

d. The zone ADC. Most of the points inside the triangle ADC fall very near the line DC, e.g. points 21, 36, 42 and 45. For the points 21 and 45 the phases in equilibrium are ferriilmenite and TiO_2; for point 36 they are titanhaematite and TiO_2. Point 42, however, is composed of three phases: ferriilmenite, titanhaematite, and TiO_2. A straight line passes through most of these points as well as through points C' and D' which represent the two synthetic solid solutions prepared in the present work, viz. Fe_2O_3 with about 9 mol.% TiO_2, and $FeTiO_3$ with about 10 mol.% TiO_2. This line C'D', which is very near, and almost parallel, to the line CD represents the haematite-ilmenite-rutile solid solutions, and shows that the slight solubility of rutile in ilmenite-haematite solid solutions extends over the range of composition from haematite to ilmenite. Points 19 and 35 represent titanomaghemite-maghetite solid solutions, the titanium being plotted as TiO_2, although it is most probably present as Ti_2O_3.

It is evident, from the diagram, that the two compounds $(TiO_4)_3Fe_4$ and Fe_2TiO_5 do not combine with either the other mixed oxides of iron and titanium, or with the iron compounds.

IX. Summary and Conclusions.

A study has been made of the system $FeO-Fe_2O_3-TiO_2$ by chemical, physical, and mineralogical methods, for the purpose of determining the phase relations, and to define the limits of the different mineral species. The work comprised examination of natural minerals, as well as high temperature experiments on artificial preparations. Mineral separations were made of a large number of specimens, partly igneous rocks and partly ores. The separated ore minerals were examined, by both X-ray powder analysis and in polished sections, and 21 new chemical analyses were made. The results are represented in the ternary diagram $FeO:Fe_2O_3:TiO_2$ (Fig. 5). The conclusions reached are the following:

1. Pure natural magnetite from Bisperg, S. Sweden, which corresponds almost exactly to the formula Fe_3O_4, has the lattice parameter $a_o = 8.3963 \pm 0.0005$ A, at 18°C. Variation in the values given for the unit cell dimensions of artificial preparations of Fe_3O_4 may be due to the presence of oxygen in excess of the stoichiometric formula requirements.

2. There is a very limited miscibility between magnetite and FeO (wüstite), not more than 3% FeO, at ordinary temperatures. There is also no evidence for the existence of FeO as a mineral, and the name "iozite" should be discarded.

Wüstite always contains more oxygen than required by the formula FeO, and is unstable below 575°C, tending to disintegrate into iron and Fe_3O_4.

3. In the system γ-Fe_2O_3-Fe_3O_4, all the stages in the oxidation of magnetite to maghemite may take place in nature, and may account for some of the contradictory statements on the appearance of magnetite in polished sections. The intermediate substances were found to be common, and were determined with certainty by X-ray and chemical analysis; the unit cell of magnetite decreased continuously with the progressive increase in its oxidation to maghemite. Titanium can enter into the maghemite lattice, possibly as Ti_2O_3, and the name "titano-maghemite" is suggested for such a solid solution with the formula γ-$(Fe,Ti)_2O_3$.

4. At the temperatures of formation of igneous rocks, there is a very limited miscibility of α-Fe_2O_3 in magnetite, about 8%, but this increases rapidly above 1100°C, reaching about 30% at 1450°C. Ex-solution intergrowths of haematite in magnetite are very rare, and it is difficult to distinguish their texture from that produced by the oxidation of magnetite to haematite (martitisation). The solubility of Fe_3O_4 in Fe_2O_3 is almost negligible at all temperatures.

5. The miscibility of TiO_2 in α-Fe_2O_3 is very limited, less than 5% at 800°C, but the two minerals may show a

eutectic relationship. In the system α-Fe_2O_3-TiO_2, four phases are present, viz. haematite, rutile, pseudobrookite $Fe_2O_3.TiO_2$, and $2Fe_2O_3.3TiO_2$. The last compound is tetragonal, and has not been found as a mineral. $Fe_2O_3.3TiO_2$, the so-called "arizonite", is actually a mixture of anatase, haematite and rutile, and is formed by the oxidation of ilmenite at low temperatures.

6. In the system $FeTiO_3$-TiO_2 the limit of solid solution is about 6% at 1050°C. The so-called "iserine", "iserite", and "nigrine" are formed of heterogeneous materials. Ilmenite and rutile may, however, crystallise as a eutectic.

7. Ilmenite and haematite form a continuous series of solid solutions above 900°C; a single phase of the composition $Fe_2O_3.FeTiO_3$ can be prepared. There is a continuous decrease in the unit cell dimensions of ilmenite with the increase of haematite in solid solution, On slow cooling, unmixing takes place into two solid solutions; the process is continuous and is accompanied by a decrease in the rate of solid diffusion. Owing to rapid cooling, or to the presence of foreign oxides e.g. MgO, the solid solution can be preserved at ordinary temperatures. Natural ilmenite may contain up to 18% Fe_2O_3 in solid solution, and the name "ferriilmenite" is suggested for such a mineral with the composition $(Fe^{2+}_{1-x}.Ti^{4+}_{1-x}.Fe^{3+}_x)O_3$. This mineral, together

with the artificial ferriilmenites, is partly ferromagnetic. Natural titanhaematite may contain up to 10% TiO_2 in solid solution. There is a slight solubility of rutile in ilmenite-haematite solid solutions at high temperatures, which extends over the whole range of composition from ilmenite to haematite.

8. In the system Fe_3O_4-$FeTiO_3$ there is a very limited miscibility between magnetite and ilmenite, the limit of solid solution being less than 5% at 1050°C. The supposed magnetite-ilmenite solid solutions are actually submicroscopic intergrowths of the two minerals. At high temperatures, however, a certain reaction takes place between magnetite and ilmenite; Fe_2O_3 is partly removed from the magnetite to form ilmenite-haematite solid solutions, leaving the magnetite with an excess of FeO, but poor in Ti.

9. Between Fe_3O_4 and Fe_2TiO_4, there is a complete series of solid solutions; the intermediate compounds are cubic, with inversed spinel structure, and are the true titano-magnetites $(Fe^{3+}_{2-2x} \cdot Ti^{4+}_{x} \cdot Fe^{2+}_{1+x})O_4$. On slow cooling, unmixing takes place into magnetite and Fe_2TiO_4, and, on further cooling, Fe_2TiO_4 decomposes into ilmenite and FeO; the ilmenite forms intergrowths with the magnetite, while the FeO becomes incorporated in the silicate minerals. Owing to rapid cooling, or to a high content of MgO or Al_2O_3, the original titano-magnetite can be preserved at ordinary temperatures. Analyses

of titanomagnetites separated from volcanic rocks show extensive solubility of Fe_2TiO_4 in Fe_3O_4, probably with a little ilmenite in solid solution. These natural titanomagnetites are similar in structure and composition to the artificial preparations; there is a continuous increase in the size of the unit cell with the increase in the amount of Fe_2TiO_4 in solid solution. Fe_2TiO_4 exists as a mineral, ulvöspinel, which is identified with certainty by means of X-ray analysis, and which may be more common than has hitherto been assumed.

In the two solid solution systems Fe_2O_3 - $FeTiO_3$, and Fe_3O_4 - Fe_2TiO_4, the substitution can be represented by the equation: $Ti^{4+}Fe^{2+} \rightleftharpoons 2Fe^{3+}$

This mechanism of substitution confers to the ion Ti^{4+} a metallic character in the compounds $FeTiO_3$ and Fe_2TiO_4, which should, therefore, be considered as mixed oxides of iron and titanium, and not as titanates.

The mineral species in the system FeO-Fe_2O_3-TiO_2, which have been found valid, are: magnetite, haematite, maghemite γ-Fe_2O_3, rutile, ilmenite, titanhaematite $(1-x)Fe_2O_3.xFeTiO_3$, ferriilmenite $(1-x)FeTiO_3.xFe_2O_3$, ulvöspinel Fe_2TiO_4, titanomagnetite $(1-x)Fe_3O_4.xFe_2TiO_4$, and pseudobrookite $Fe_2O_3.TiO_2$. The terms iozite, arizonite, iserite, nigrine, and magnetoilmenite should be removed from the list of valid mineral names.

X. Works to which reference is made.

Abrahams, S. C., & B. A. Calhoun. (1953): The low-temperature transition in magnetite, Acta Cryst. 6, 105-106.

Baker, G. (1952): Opaque oxides in some rocks of the basement complex, Torricelli Mountains, New Guinea. Amer. Min. 37, 567-577.

Barth, T. F. W., & E. Posnjak. (1932): Spinel structures with and without variate atom equipoints. Zeit. Krist. 82, 325-341.

Bénard, J. (1939): Décomposition du protoxyde de fer. Thèse, Paris.

__________ & G. Chaudron. (1937): Préparation de ferrites par substitution des ions ferreux dans la magnétite. Compt. Rend. Acad. Sci. Paris, 204, 766-768.

Bragg, W. H. (1915): The structure of the spinel group of crystals. Phil. Mag. 30, 305-315.

Bragg, W. L. (1947): The conversion factor for kX units to Ångström units. Journ. Sci. Instrum. 24, 27.

Broderick, T. M. (1919): Some of the relations of magnetite and haematite. Econ. Geol. 14, 353-366.

Broughton, H. J., L. C. Chadwick, & T. Deans. (1950): Iron and titanium ores from Bukusu Hill alkaline complex, Uganda. Colon. Geol. Min. Res. London, 1, 262-266.

Brun, A. (1924): L'evolution des oxydes du fer. Arch. Sci. Phys. nat. Genève, 6, 244-263.

Brunton, S. (1913): Some notes on titaniferous magnetites. Econ. Geol. 8. 670-680.

Bunn, C. W. (1945): Chemical Crystallography. Oxford.

Chevallier, R., & J. Girard. (1950): Synthèse de titanomagnétites. Bull. Soc. Chem. France. ser.5, 17, 576-581.

Clark, G. L., A. Ally, & A. E. Badger. (1931): The lattice dimensions of spinels. Amer. Journ. Sci. 22, 539-546.

Dana, J. D., & E. S. Dana. (1944): System of mineralogy. 1, ed. 7, by C. Palache, H. Berman & C. Frondel. New York.

Dunn, J. A., & A. K. Dey. (1937): Vanadium-bearing titaniferous iron ores in Singhbhum and Mayurbhanji, India. Trans. Min. Geol. Inst. India. 31, 117-184.

Edwards, A. B. (1938): Some ilmenite microstructures and their interpretation. Proc. Austr. Inst. Mining & Metall. 110, 39-58.

——— (1947): Textures of the ore minerals. Melbourne.

——— (1949): Natural ex-solution intergrowths of magnetite and haematite. Amer. Min. 34, 759-761.

Ernst, Th. (1943): Über Schmelzgleichgewichte im System Fe_2O_3 - FeO-TiO_2 und Bemerkungen über die Minerale Pseudobrookit und Arizonit. Zeit. angew. Min. 4, 394-409.

Evrard, P. (1944): Introduction à l'étude physico-chemique de la métallogénie des gites d'ilménites et de fers titanés. L'ilménite du gisement de Håsland, région d'Egersund (Norvège). Ann. Soc. Geol. Belgique. 66, 110-132.

Foslie, S. (1928): Gleichsgewichtsverhältnisse bei einigen Titaneisenerzen. Fennia, 50, no. 26, 1-16.

Frank-Kamenecky, V. A. (1939): The course of oriented displacement of magnetite by iron. Compt. Rend. Acad. Sci. U.S.S.R. 23, 561-564.

Frankel, J. J., & G. W. Grainger. (1941): Notes on Bushveld titaniferous iron ores. South African Journ. Sci. (South African Assoc. Adver. Sci.). 37, 101-110.

Gaglioti, V., & O. D'Agostino. (1936): Ricerche sugli areogeli. I. La struttura di ossidi metallici. Gaz. Chim. Ital. 66, 547-548.

Gilbert, G. (1925): Some magnetite-haematite relations. Econ. Geol. 20, 587-596.

Goldschmidt, V. M., T. Barth & G. Lunde. (1926): Geochemische Verteilungsgesetze der Elemente. Norske Vidensk. Akad. Skr. 7.

Greig, J. W. (1932): Temperature of formation of the ilmenite of the Engels Copper deposits. A discussion with appendix. Econ. Geol. 27, 25-38.

__________ E. Posnjak, H. E. Merwin & R. B. Sosman. (1935): Equilibrium relationship of Fe_3O_4, Fe_2O_3, and oxygen. Amer. Journ. Sci. ser. 5, 30, 239-316.

Grieve, J.,& J. White. (1939): The system $FeO-TiO_2$. Journ. Royal Tech. College Glasgow. 4, 441-448.

Gruner, J. W. (1922): Paragenesis of the martite ore bodies and magnetites of the Mesabi Range. Econ. Geol. 17, 1-14.

__________ (1929): Structural reasons for oriented intergrowths in some minerals. Amer. Min. 14, 227-237.

__________ (1934): Magnetite cementing certain ore conglomerates of the Mesabi Range. Econ. Geol. 29, 757-760.

Hägg, G. (1935): Die Kristallstruktur des magnetischen Ferrioxydes, γ-Fe_2O_3. Zeit. Physik. Chem. B29, 95-103.

Hámos, L. V.,& W. Stacherbina. (1933): Über die Röntgenabsorptionskante von Ti in Ti-Verbindungen und über die Konstitution des Ilmenits. Nachr. Ges. Wiss. Göttingen, Math.-Phys. Kl. 232-234.

Haul, P.,& Th. Schoon. (1939): Zur Struktur des Ferromagnetischen eisen (III) oxyds gamma Fe_2O_3. Zeit. Physik. Chem. 44, 216-226.

Henry, N. F. M., H. Lipson & W. A. Wooster. (1951): The interpretation of X-ray diffraction photographs. London.

Hilpert, S., & A. Wille. (1932): Zusammenhänge zwischen Ferromagnetismus und Aufbau der Ferrite. Zeit. Physik. Chem. B18, 291-315.

Holgersson, S. (1927): Röntgenographische Untersuchungen der Mineralien der Spinellgruppe und von synthetisch dargestellten Substanzen von Spinell-typus. Lunds Univer. Årsskr., N.F. Avd. (2) 23, 9. Kungl. Fysiogr. Sällsk. Handl. N.F. 38, 1-112.

Hutton, C. O. (1945): The ironsands of Fitzroy, New Plymouth. New Zealand Journ. Sci. Tech. sec. B, 26, 291-302.

____________ (1950): Studies of heavy detrital minerals. Bull. Geol. Soc. America. 61, 635-710.

Jakob, J. (1937): Zwei Analysen von Ilmenit. Schweiz. Min. Petr. Mitt. 17, 269-270.

Jette, E. R., & F. Foote. (1933): An X-ray study of the Wüstite (FeO) solid solutions. Journ. Chem. Phys. 1, 29-36.

Jouravsky, G. (1936): Sur la composition chimique des titanomagnétites. Compt. Rend. Acad. Sci. Paris. 202, 1689-1691.

Kamiyama, M. (1929): Journ. Geol. Soc. Tokyo. 36, 12-29. (Abstract: Report of a heating experiment with titaniferous magnetite from Korea. Japanese Journ. Geol. Geog. 7, 1, 1930).

Kordes, E. (1935): Kristallchemische Untersuchungen über Aluminiumverbindungen mit spinellartigem Gitterbau und über γ-Fe_2O_3. Zeit. Krist. 91, 193-228.

Lacroix, M. A. (1920): Sur les groupements réguliers de deux minéraux différents constituant certains fers titanés. Compt. Rend. Acad. Sci. Paris. 171, 481-485.

Lindley, H. W. (1925): Mikrographie der Eisenerzmineralien oberhessischer Basalte. Neues Jahrb. Min. B.B. 53A, 333-356.

Lipson, H., & A. J. C. Wilson. (1941): The derivation of lattice spacings from Debye-Scherrer photographs. Journ. Sci. Instrum. 18, 144-148.

Mason, B. (1943): Mineralogical aspects of the system FeO-Fe_2O_3-MnO-Mn_2O_3. Geol. Fören. Förhandl. 65, 95-180.

Miller, R. (1945): Heavy minerals of Florida beach and dune sands. Amer. Min. 30, 65-75.

Mogensen, F. (1943): Ett nytt Svenskt järumalmsmineral. Blad för Bergshandteringens Vänner, Stockholm. 26, 128-135.

____________ (1946): A ferro-ortho-titanate ore from Södra Ulvön. Geol. Fören. Förhandl. 68, 578-588.

Nelson, J. B., & D. P. Riley. (1945): An experimental investigation of extrapolation methods in the derivation of accurate unit cell dimensions of crystals. Proc. Phys. Soc. London. 57, 160-177.

Newhouse, W. H. (1936): Opaque oxides and sulphides in common igneous rocks. Bull. Geol. Soc. America. 47, 1-52.

____________ & J. P. Glass. (1936): Some physical properties of certain iron oxides. Econ. Geol. 31, 699-711.

NishiKawa, S. (1915): The structure of some crystals of the spinel group. Proc. Math. Phys. Soc. Tokyo. 8, 199.

Odman, O. H. (1932): Mineragraphic study of the opaque minerals in the lavas from Mt. Elgon, British East Africa. Geol. Fören. Förhandl. 54, 285-304.

Overholt, L. J., G. Vaux, & J. L. Rodda. (1950): The nature of arizonite. Amer. Min. 35, 117-119.

Palmer, C. (1909): Arizonite, a ferric metatitanate from a pegmatite near Hackberry, Arizona. Amer. Journ. Sci. ser. 4, 28, 353-356.

Palmunen, M. K. (1925): On the ilmenite-magnetite olivinite of Susimäki. Fennai. 45, no.9, 1-27.

Parrish, W., & E. Cisney. (1948): An improved X-ray diffraction camera. Philips Tech. Review. 10, 157-167.

Posnjak, E., & T. F. W. Barth. (1934): Notes on some structures of the ilmenite type. Zeit. Krist. 88, 271-280.

Pouillard, E. (1949): Sur le comportement de l'alumine et de l'oxyde de titane vis-a-vis des oxydes de fer. Thèse, Lille.

____________ & A. Michel. (1949): Études des composés définis et des solutions solides que peuvent former l'oxyde de titane TiO_2 et les oxydes de fer. Compt. Rend. Acad. Sci. Paris. 228, 1232-1233.

Ramdohr, P. (1926): Beobachtungen an Magnetit, Ilmenit, Eisenglanz und Überlegungen über das System FeO, Fe_2O_3, TiO_2. Neues Jahrb. Min. BB., 54A, 320-379.

__________ (1939): Wichtige neue Beobachtungen an Magnetit, Hämatit, Ilmenit, und Rutil. Abh. Preuss. Akad. Wiss., Math.-nat. Kl. Nr. 14.

__________ (1950): Die Erzmineralien und ihre Verwachsungen. Akademie-Verlag, Berlin.

Robinson, A. H. A. (1922): Titanium. Canada, Mines Branche, Ottawa. no. 579, 1-127.

Schaller, W. T. (1912): A study of the rutile group. U. S. Geol. Surv. Bull. 509, 8-39.

Schenck, R., & T. Dingmann. (1927): Gleichgewichtsuntersuchungen über die Reduktions-, Oxydations- und Kohlungsvorgange beim Eisen. III. Zeit. anorg. allgem. Chem. 166, 113-154.

Schlaepfer, M., & P. Niggli. (1914): Neue Beiträge zur hydrthermalen Silikatbildung. Zeit. anorg. Chem. 87, 52-80.

Schmahl, N. G. (1941): Die Beziehungen zwischen Sauerstoffdruck, Temperatur und Zusammensetzung im System Fe_2O_3-Fe_3O_4. Zeit. Elektrochem. 47, 821-835.

Schneiderhöhn, H., & P. Ramdohr. (1931): Lehrbuch der Erzmikroskopie, Band 2, Berlin.

Schwartz, G. M. (1930): The relations of the magnetite and ilmenite in the magnetite deposits of the Duluth gabbro. Amer. Min. 15, 243-252.

____________ (1942): Progress in the study of ex-solution in ore minerals. Econ. Geol. 37, 345-364.

Schwellnus, C. M., & J. Willemse. (1943): Titanium and vanadium in the magnetic iron ores of the Bushveld Complex. Trans. Geol. Soc. S. Africa. 46, 23-38.

Short, M. N. (1940): Microscopic determination of the ore minerals. U. S. Geol. Survey Bull. 914.

Singewald, J. T. (1913): The microstructure of titaniferous magnetites. Econ. Geol. 8, 207-214.

Sosman, R. B., & J. C. Hostetter. (1916): The oxides of iron. I. Solid solution in the system $Fe_2O_3 - Fe_3O_4$. Journ. Amer. Chem. Soc. 38, 807-833.

——————————— (1918): The ferrous iron content and magnetic susceptibility of some artificial and natural oxides of iron. Trans. Amer. Inst. Min. Eng. 58. 409-433.

——————— & E. Posnjak. (1925): Ferromagnetic ferric oxide, artificial and natural. Journ. Wash. Acad. Sci. 15, 329-342.

Starrabba, S. F. (1939): Magnetite dei Monti Rossi (Etna). La Composizione. Atti Accad. Gioenia Sci. Nat. Catania, ser. 6, 3, Mem. no. 7, 7 pp.

Tombs, N. C., & H. P. Rooksby. (1951): Structure transition and antiferromagnetism in magnetite. Acta Crystallographica. 4, 474-475.

Twenhofel, L. H. (1927): Changes in oxidation of iron in magnetite. Econ. Geol. 22, 180-188.

Vaasjoki, O. (1947): On the microstructure of titaniferous iron ore at Otanmäki. Bull. Comm. Géol. Finlande, no. 140, 107-114. (Compt. Rend. Soc. Géol. Finlande, 20, P. Eskola volume).

Van der Marel, H. W. (1951): Gamma ferric oxide in sediments. Journ. Sed. Petrol. 21, 12-21.

Verwey, E. J. W. (1935): The Crystal Structure of γ-Fe_2O_3 and γ-Al_2O_3. Zeit. Krist. 91, 65-69.

Verwey, E. J. W., & J. H. De Boer. (1936): Cation arrangement in a few oxides with crystal structures of the spinel type. Rec. Trav. Chim. Pays-Bas, 55, 531-540.

_______________ & E. L. Heilmann. (1947): Physical properties and cation arrangement of oxides with spinel structures. I. Cation arrangement in spinels. Journ. Chem. Phys. 15, 174-180.

Wadia, D. N. (1943): Rare earth minerals in Ceylon rocks. Rec. Dep. Min., Ceylon. Prof. Paper 1, 3-14.

Wagner, P. A. (1927): Changes in the oxidation of iron in magnetite. Econ. Geol. 22, 845-846.

_______________(1928): The iron ore deposits of the Union of South Africa. Mem. Geol. Survey S. Africa, 26, 29-34.

Walker, T. L. (1930): Lodestone from Bonn Accord, Transvaal. Toronto Univer. Studies, Geol. Ser. 29, 17-19.

Warren, C. H. (1918): On the microstructure of certain titanic iron ores. Econ. Geol. 13, 419-442.

Welo, L. A., & O. Baudisch. (1925): The two-stage transformation of magnetite into haematite. Phil. Mag. 50, 399-408.

White, C. H. (1938): Equilibrium at high temperatures in systems containing iron oxides. Iron Steel Inst. London, Carnegie School. Mem. 27, 1-75.

Winchell, A. N. (1931): Maghemite or Oxymagnite ? Amer. Min. 16, 270-271.

XI. Appendix.

Appendix

Table A.

No. of Sp.	Locality	Type of Occurrence.	Result of X-ray Investigation.
1	Green Canyon, Colorado, U.S.A.	Separation from pegmatite.	Neg.173. Normal magnetite.
2*	Barras Nose, Tintagel, Cornwall.	Separation from spilite.	Neg.714. Normal magnetite.
3*	S. of Ngong, Nairobi, Kenya.	Separation from augitite.	Neg.595. Titanomagnetite.
4*	Dunglas Hill, nr. Strathblane.	Separation from basalt.	Neg.815. Titanomagnetite. a = 8.4480 ± 0.001 A
5*	Giant's Causeway, Ireland.	Separation from basalt.	Neg.729. Titanomagnetite. a = 8.4697 ± 0.0005 A.
6*	Blagolkot, Deccan, India.	Separation from basalt.	Neg.571. Titanomagnetite, + ilmenite traces.
7	Palmas, Teneriffe, Canary Is.	Separation from basalt.	Neg.696. Titanomagnetite.
8*	Skaergaard, E. Greenland.	Separation from gabbro.	Neg.680. Magnetite + titanomagnetite + ilmenite traces.
9*	Södra Ulvön, Sweden.	Separation from dolerite (ore).	Neg.596. Magnetite + titanomagnetite + ilmenite traces.
10**	Norra Ulvön, Sweden.	Separation from dolerite (ore).	Neg.597. Titanomagnetite + magnetite (equal proportions).

Table A. (contin.)

No. of Sp.	Locality	Type of Occurrence.	Result of X-ray Investigation.
11	Arthur's Seat, Edinburgh.	Separation from basalt.	Neg.303. Normal magnetite.
12	Beaufort W., Cape Province.	Separation from dolerite.	Neg.547. Magnetite + ilmenite (ex-solution intergrowths).
13	Whin Sill, Brag Lough, Haltwhistle.	Separation from dolerite.	Neg.438. Magnetite + ilmenite (ex-solution intergrowths)
14	Smålands, Sweden.	Separation from gabbro.	Neg.616. Normal magnetite.
15	Duluth, Minnesota, U.S.A.	Separation from anorthosite.	Neg.424. Magnetite + ilmenite. (ex-solution intergrowths).
16	Donegal, Eire.	Separation from gabbro.	Neg.417. Magnetite + ilmenite.
17**	Aufa, S.E. of Aitope, New Guinea.	Separation from gabbro.	Neg.804. Normal magnetite.
18	St. Helena.	Separation from basalt.	Neg. 418. Normal magnetite.
19	Lugar, Ayrshire.	Separation from theralite.	Neg. 421. Magnetite + ilmenite.
20**	Magnet Heights, Bushveld, Transvaal.	Separation from norite.	Neg. 528. Magnetite + ilmenite. (ex-solution intergrowths).
21*	Tofetholine, Oslo Fjord, Norway.	Separation from essexite.	Neg. 461. Magnetite + ilmenite. (ex-solution intergrowths).

Table A. (contin.)

No. of Sp.	Locality	Type of Occurrence.	Result of X-ray Investigation.
22	Krang Hill, Kildare.	Separation from basalt.	Neg.488. Normal magnetite.
23	Horngraben, Manderscheid, Eifel.	Separation from basalt.	Neg. 617.Normal magnetite.
24	N. of Trail Creek, Oregon.	Separation from basalt	Neg.504. Normal magnetite.
25**	Babiang, New Guinea.	Separation from gabbro.	Neg.803. Magnetite + ilmenite + rutile (ex-solution inter-growths).
26	E. of Cload Bay, Coll.	Separation from dolerite.	Neg.702. Magnetite-maghemite.
27	Coverack,Lizard.	Separation from troctolite.	Neg.615. Magnetite-maghemite + haematite traces.
28	Chipley Quarry, Devon.	Separation from spilite.	Neg.614. Magnetite-maghemite + haematite traces.
29	Between Damascus and Kuneitra, Syria.	Separation from basalt.	Neg. 618. Magnetite-maghemite.
30	Disko Is., Greenland.	Separation from basalt.	Neg. 507. Magnetite-maghemite.
31	S. Head, Auckland, New Zealand.	Separation from basalt.	Neg. 552. Normal magnetite.
32	Eireannale,Skye.	Separation from basalt.	Neg. 550. Pyrrhotite + magnetite.

Table A (contin.)

No. of Sp.	Locality	Type of Occurrence.	Result of X-ray Investigation.
33	Marabaut, nr.Ain, Algeria.	Separation from limburgite.	Neg.508. Normal magnetite.
34	Nyeri, Kenya.	Separation from basalt.	Neg.551. Magnetite + ilmenite.
35	Skaergaard, E. Greenland.	Separation from gabbro.	Neg.679. Normal ilmenite.
36	Tofetholine,Oslo Fjord, Norway.	Separation from essexite.	Neg. 686.Ilmenite + magnetite.
37	Rhodesia.	Separation from minverite.	Neg.420.Pyrrhotite.
38**	Coruisk, Skye.	Separation from gabbro.	Neg.801. Magnetite + ilmenite (ex-solution inter-growths).
39*	Co. Antrim, Ireland.	Separation from basalt.	Neg.731. Magnetite-maghemite. a = 8.3690 ± 0.002 A.
40**	Matapau, New Guinea.	Separation from amphibolite.	Neg.802.Magnetite + haematite (ex-solution inter-growths).
41	Carrock Fell.	Separation from gabbro.	Neg.412. Normal ilmenite + magnetite traces.
42	Zillertal, Tyrol.	Separation from chlorite schist.	Neg. 184. Normal magnetite.
43	Ardnamurchan.	Massive ore.	Neg. 434.Magnetite + ilmenite.

Table A (contin.)

No. of Sp.	Locality	Type of Occurrence.	Result of X-ray Investigation.
44	Ardnamurchan.	Massive ore.	Neg.422. Spinel + magnetite + ilmenite.
45	Taranaki, New Zealand.	"Ilmenite" sand.	Neg.352.Magnetite + ferriilmenite.
46	Travancore, India.	Ilmenite sand.	Neg.179. Ilmenite + titanhaematite. (ex-solution intergrowhts).
47	Auckland, New Zealand.	Ilmenite sand.	Neg.565.Haematite. Neg.185.Ilmenite. Neg.186.Magnetite.
48**	Nigeria.	Ilmenite sand.	Neg.450.Magnetite + haematite. Neg.460. Ilmenite.
49**	Seacombe, Liverpool.	"Iserine" sand.	Neg.433.Magnetite + ilmenite (ex-solution inter-growths). Neg.437.Haematite (martite).
50*	Bisperg, Säter,Dalecarlia, S.Sweden.	Massive ore.	Neg.687.Normal magnetite. a = 8.3963 ± 0.0005 A.
51***	Bon Accord, Transvaal, S. Africa.	Massive ore. (lodestone).	Neg.542.Maghemite-magnetite + ilmenite traces. a = 8.3475 ± 0.001 A.
52**	Kragerö,Norway.	Massive ore.	Neg.164.Titan-haematite + rutile. Neg.246.Ilmenite + titanhaematite + magnetite + rutile.

Table A (contin.)

No. of Sp.	Locality	Type of Occurrence.	Result of X-ray Investigation.
53	Striberg, Nora Sweden.	Massive ore.	Neg.351. Normal magnetite.
54	Elandsfontein, Rustenburg, Transvaal.	Massive ore.	Neg.354. Chromite.
55*	Devon.	Massive ore.	Neg.534.Magnetite-maghemite a = 8.394 ± 0.001 A. + haematite traces.
56*	Forola, Sweden.	Massive ore.	Neg.715. Normal magnetite.
57*	Hall, Ottawa, Canada.	Massive ore.	Neg.728. Normal magnetite.
58	Kalstads, Kragerö, Norway.	Massive ore.	Neg.315.Haematite.
59	Berggiesshübel, Saxony.	Massive ore.	Neg.321.Magnetite-maghemite.
60	Magnet Cove, Arkansas,U.S.A.	Octahedral crystals.	Neg.322. Normal magnetite.
61	Messina Mine, N.Pietersburgh, Transvaal.	Massive ore.	Neg.176.Haematite.
62*	Kropferberg, Saxony.	Massive ore.	Neg.448. Magneso-magnetite.
63**	Snarum, Norway.	Rhombohedral crystal, so-called "ilmenite".	Neg.770.Haematite + rutile. Neg.769.Haematite + rutile + magnetite traces.
64	Schmiedeberg, Silesia.	Massive ore.	Neg.748.Magnetite-maghemite.

Table A (contin.)

No. of Sp.	Locality	Type of Occurrence.	Result of X-ray Investigation.
65	Bohemia, Czechoslovakia.	Small octahedral crystals.	Neg.743, Haematite (martite).
66	Sweden.	Massive ore.	Neg. 611.Magnetite-maghemite.
67*	Mourne, Co.Down, Ireland.	Massive ore.	Neg.407.Magnetite-maghemite. a = 8.3860 ± 0.001 A.
68	Mytor Iron Mine, Bovey Tracey, Devon.	Separation from ore.	Neg. 607.Magnetite-maghemite + ilmenite traces.
69*	Mt. Blagodot, Urals,U.S.S.R.	Separation from ore.	Neg.716. Magnetite-maghemite. a = 8.3905 ± 0.001 A.
70**	Bonn, Finkenberg, Germany.	Massive ore.	Neg.520.Magnetite-maghemite.
71**	Schischimskaja, C.Kussa,Urals.	Massive ore.	Neg.527.Magnetite-maghemite + ilmenite + haematite (ex-solution intergrowths).
72	Lake Shirwa, E. Africa.	Separation from ore.	Neg.459. Magnetite-maghemite + haematite.
73	Pretoria, Transvaal, S. Africa.	Massive ore.	Neg.536. Maghemite-magnetite + ilmenite traces.
74***	Bon Accord, Transvaal, S. Africa.	Massive ore.	Neg.767.Maghemite-magnetite + ilmenite traces.

Table A (contin.)

No. of Sp.	Locality	Type of Occurrence.	Result of X-ray Investigation.
75**	Miask, Ilmen Mts., Urals, U.S.S.R.	Massive ore.	Neg.543. Ferri-ilmenite + titan-haematite traces. a = 5.0887, c = 14.049 A.
76**	Ilmen Mts., Urals,U.S.S.R.	Massive ore.	Neg.535. Ferri-ilmenite + titanhaematite.
77	Twin Peaks, Millards Co. Utah, U.S.A.	Octahedral crystals.	Neg. 548.Haematite (martite).
78	Moriah Mine, Essex Co., N.Y.	Separation from ore.	Neg.441. Normal magnetite. Neg.442. Haematite.
79*	Binnenthal, Switzerland.	Separation from ore.	Neg.609. Normal magnetite.
80**	Ekersund,Norway.	Separation from ore.	Neg.452. Magnetite + ilmenite traces.
81	Ekersund,Norway.	Separation from ore.	Neg.768. Ferri-ilmenite + 3% haematite.
82*	Arendal,Norway.	Separation from ore.	Neg.458. Normal magnetite.
83**	Matto Grosso, Brazil.	Octahedral crystals.	Neg.430.Magnetite + haematite. Neg.457.Haematite + magnetite.
84**	Edison, New Jersey,U.S.A.	Massive ore.	Neg.432.Magnetite + haematite (martite).
85**	Smålands,Taberg, Sweden.	Massive ore.	Neg.529.Magnetite + ilmenite.

Table A. (contin.)

No. of Sp.	Locality	Type of Occurrence.	Result of X-ray Investigation.
86*	Riesengebirge, Bohemia, Germany.	Big rounded crystal (sub-octahedral ?).	Neg.502. Ferri-ilmenite. a = 5.0661, c = 13.952 A. Neg.746. Ferri-ilmenite + haematite traces.
87**	Unkel, Rheinland, Germany.	Massive ore.	Neg.521. Normal magnetite.
88**	Kilakänner, Gebirge, Urals.	Massive ore.	Neg.519. Magnetite + haematite.
89	Cumberland, England.	Massive ore.	Neg.168. Haematite.
90**	Hamata, Eastern Desert, Egypt.	Massive ore.	Neg.745. Ferri-ilmenite + 10% haematite.
91	Bouligny Quarry, Guernsey.	Massive ore.	Neg. 396. Normal magnetite.
92*	Magnet Cove, Arkansas, U.S.A.	Massive ore.	Neg. 574. Titan-magnesioferrite.
93**	Rieden, Laacher See, Germany.	Massive ore.	Neg.526. Normal magnetite.
94	Elba.	Massive ore.	Neg.170. Haematite.
95	N.E. Norway.	Massive ore.	Neg.516. Normal magnetite.
96**	Sanvikedal, Kragerö, Norway.	Separation from rhombohedral crystals.	Neg.772. Ilmenite + rutile + magnetite traces. Neg.454. Magnetite + rutile + ilmenite.

Table A. (contin.)

No. of Sp.	Locality	Type of Occurrence.	Result of X-ray Investigation.
97	Dunstan Mt., Cent. Otago, New Zealand	Separation from schist.	Neg.416. Normal magnetite + haematite traces.
98**	Achmatovsk, Urals, U.S.S.R.	Separation from chlorite schist.	Neg. 445. Normal magnetite.
99	Cornwall.	Massive ore.	Neg.443.Magnetite + boulangerite.
100	Sanvikedal, Krageró, Norway.	Acicular crystals on surface of ilmenite.	Neg.771. Rutile.
101**	Mt. Monger, W. Australia.	Rhombohedral crystal.	Neg.819. Titan-haematite.
102	Vunda River, Fiji Island.	Beach sand.	Neg.799.Magnetite + haematite (exsolution intergrowths).
103**	Olary, S.Australia.	Massive ore.	Neg.800. Titan-haematite.
104	Lautoka, Fiji Island.	Beach sand.	Neg.816.Magnetite + haematite (exsolution intergrowths).
105	Limoges, France.	Prismatic crystal.	Neg. 806. Rutile + ilmenite.
106	Great Work Mine, Breage, Helston, Cornwall.	Separation from tin ore.	Neg.851.Maghemite + cassiterite.

* Specimens which have been chemically analysed.

** Specimens which have been studied in polished sections.

Table B

No.	TiO_2	Fe_2O_3	Al_2O_3	V_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	SiO_2	H_2O	Rem.	Total
1	0.05	67.55	0.04	0.01	0.02	31.43	0.05	0.01	0.18	0.73	-	-	100.07
2	Traces	66.54	Traces	-	-	29.72	0.26	-	0.49	2.02	-	-	99.03
3	Traces	65.42	Traces	-	-	30.64	0.49	-	0.14	2.48	-	-	99.17
4	0.28	66.92	Traces	-	-	30.58	0.27	-	0.28	1.08	-	-	99.41
5	0.27	66.42	0.37	0.27	-	31.05	0.03	-	0.46	1.22	-	-	100.09
6	0.36	65.08	1.54	-	-	30.76	0.29	-	0.19	1.20	-	-	99.42
7	0.05	67.57	0.14	-	-	28.40	0.06	-	1.85	1.55	-	-	99.62
8	6.98	57.11	3.62	0.10	<0.01	21.83	1.82	0.94	7.18	0.38	-	-	99.96
9	16.20	28.96	6.64	0.22	<0.01	36.21	0.74	1.56	3.25	4.38	-	-	98.16
10	19.28	32.27	0.78	1.74	0.13	43.07	0.33	0.42	1.98	0.24	0.06	-	100.30
11	24.86	26.88	0.40	-	-	42.33	0.72	-	2.07	2.64	-	-	99.90
12	23.74	22.44	2.05	-	-	32.01	1.12	3.52	2.53	12.12	-	-	99.53
13	27.77	25.86	0.60	-	-	39.74	0.58	-	2.54	2.83	-	-	99.92
14	9.58	47.27	1.28	0.22	0.09	29.79	0.32	1.30	2.74	6.22	-	-	98.81
15	0.16	69.88	0.34	0.02	0.07	27.93	0.07	0.03	0.14	1.07	-	-	99.71
16	0.84	70.46	Traces	-	-	26.08	0.58	-	0.18	1.24	-	-	99.38
17	0.49	69.88	0.16	0.18	<0.01	22.90	0.10	1.00	1.88	2.20	-	-	98.79
18	2.54	80.63	0.30	0.12	<0.01	12.75	0.18	0.76	0.91	0.84	-	-	99.03
19	19.45	64.92	<0.01	2.40	<0.01	7.87	0.24	0.70	1.05	1.60	-	-	98.23
20	45.76	17.78	0.40	-	-	27.72	0.48	-	7.56	0.24	-	-	99.94
21	48.50	10.31	0.12	0.04	-	36.37	3.26	-	0.30	1.11	-	-	100.00

Table B (continued)

No.	TiO_2	Fe_2O_3	Al_2O_3	V_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	SiO_2	H_2O	Rem.	Total
22	Trace	68.85	0.21	-	-	30.78	-	-	Trace	0.27	-	Trace	100.11
23	-	69.05	-	-	-	30.94	Trace	-	-	-	-	-	99.99
24	1.45	60.33	2.39	0.54	0.09	33.78	0.02	-	0.81	0.62	-	-	100.03
25	18.2	26.7	2.70	0.88	0.9	44.9	0.41	0.95	3.00	1.61	-	0.31	100.58
26	10.83	41.97	6.50	Trace	0.42	33.30	0.39	0.74	5.54	0.64	-	-	100.33
27	8.57	49.74	2.49	0.39	0.03	29.46	0.71	0.17	2.81	2.95	0.38	2.53	100.23
28	12.18	47.00	3.75	-	-	34.94	0.10	-	2.35	-	-	-	100.32
29	2.77	61.73	3.72	-	-	31.75	-	-	1.25	-	-	-	101.22
30	2.50	62.09	-	0.68	0.20	33.14	0.03	-	1.08	-	-	-	99.72
31	1.37	89.15	0.04	-	-	8.67	-	Trace	Trace	1.15	-	1.19	100.38
32	-	85.3	-	-	-	2.4	-	-	-	-	3.1	4.3	95.1
33	0.35	73.75	2.96	0.31	-	15.3	1.43	0.43	0.30	2.35	3.01	-	100.19
34	Trace	75.26	Trace	-	-	24.48	-	Trace	0.10.	0.53	-	-	100.37
35	13.00	73.78	3.41	1.30	0.33	2.59	0.15	0.39	0.78	2.02	2.12	0.07	99.94
36	5.64	93.56	-	-	-	0.11	-	-	1.10	-	-	-	100.38
37	5.98	88.94	-	-	-	5.38	-	-	-	-	-	-	100.3
38	9.6	83.1	-	-	-	5.8	-	-	1.5	-	-	-	100.0
39	10.02	77.17	1.48	-	-	8,52	-	-	1.33	-	-	-	98.52
40	11.31	78.92	-	-	-	10.07	-	-	-	-	-	-	100.3
41	27.41	47.95	-	-	-	23.99	0.22	-	0.25	-	-	-	99.82
42	30.5	45.48	1.00	-	-	20.28	1.49	-	0.21	0.52	0.21	-	99.69
43	46.5	10.65	1.27	0.21	0.01	37.82	0.18	-	3.09	0.33	-	-	100.06
44	52.73	-	-	-	-	45.83	-	-	1.25	-	-	-	99.81
45	54.44	4.26	-	0.29	0.07	40.94	0.52	-	-	0.34	-	-	100.86

Table C

No.	Locality	Analyst	X-ray measurements and comment on homogeneity.	$FeO: Fe_2O_3: TiO_2$ % molecular ratio	Mineral name
1	Bisperg, Sater, Dalecarlia, S. Sweden	Milner & Calkin.	a = 8.3963 ± 0.0005 A. Separation from ore, Homogeneous.	51: 48.9: 0.1	Magnetite.
2	Binnental, Switzerland.	Herdsman	Separation from ore, homogeneous.	51: 49: 0	Magnetite- FeO solid solution.
3	Forola, Sweden.	Herdsman	Faint quartz lines. Separation from ore.	51.6: 48.4: 0	Magnetite $(1-x)Fe_3O_4.xFeO$
4	Barras Nose, Tintagel, Cornwall	Herdsman	Homogeneous. Separation from spilite.	50.8: 48.8: 0.4	Magnetite $(1-x)Fe_3O_4.xFeO$
5	Arendal, Norway.	Milner & Calkin.	Homogeneous. Separation from ore.	51.3: 48.2: 0.5	Titanomagnetite $(1-x)Fe_3O_4.xFe_2TiO_4$
6	Hall, Ottawa, Canada.	Herdsman	Homogeneous. Separation from ore.	51: 48.4: 0.6	Titanomagnetite $(1-x)Fe_3O_4.xFe_2TiO_4$
7	Kropferberg, Saxony, Germany.	Milner & Calkin.	Homogeneous. Separation from ore.	50.7: 49.3: 0	Magnesomagnetite $(1-x)Fe_3O_4.xFe_2MgO_4$
8	Magnet Cove, Arkansas, U.S.A.	Milner	Homogeneous. Separation from ore.	52.4 : 42.6: 5	Magnesotitanomagnetite. $(1-x)Fe_3O_4.xFe_2TiO_4$
9	South of Ngong, Nairobi, Kenya.	Milner	Amorphous ilmenite. Separation from augitite.	56 : 27.7: 16.3	Titanomagnetite + ilmenite.
10	Skaergaard intrusion, E. Greenland.	Vincent	a = 8.475 ± 0.002 A, Faint ilmenite lines. Separation from gabbro.	59.9: 19.7: 20.4	Ulvöspinel + magnetite.
11	Giant's Causeway, Antrim, Ireland.	Herdsman	a = 8.4697 ± 0.0005 A. ~~Metamict~~ ilmenite, amorphous. Separation from basalt.	58.2: 19.9: 21.9	Titanomagnetite $(1-x)Fe_3O_4.xFe_2TiO_4$ + ilmenite.

Table C (continued)

No.	Locality	Analyst	X-ray measurements and comment on homogeneity.	$FeO;Fe_2O_3: TiO_2$ % molecular ratio	Mineral name
12	Dunglas Hill, nr. Strathblane, Scotland.	Herdsman	a = 8.4470 ± 0.001 A. Faint plagioclase & augite lines. Separation from basalt, amorphous ~~metamict~~ ilmenite.		Titanomagnetite $(1-x)Fe_3O_4.xFe_2TiO_4$ + ilmenite.
13	Blagolkot, Deccan, India.	Herdsman	a = 8.4480 ± 0.001 A. Faint ilmenite lines. Separation from basalt.	56.7: 25.2: 18.1	Titanomagnetite + ilmenite.
14	Tofetholine, Oslo Fjord, Norway.	Milner	Ilmenite lines. Separation from essexite.	50 : 35.7: 14.3	Magnetite + ilmenite.
15	Devon.	Milner & Calkin.	a = 8.394 ± 0.001 A. Homogeneous. Separation from ore.	47.2: 52.5: 0.2	Magnetite-maghemite solid solution. $(1-x)Fe_3O_4.xFe_2O_3$
16	Mt. Blagodot, Urals, U.S.S.R.	Herdsman	a = 8.3905 ± 0.001 A. Homogeneous. Separation from ore.	45.5: 53.2: 1.3	Magnetite-maghemite solid solution.
17	Mourne, Co. Down, Ireland.	Milner.	a = 8.3860 ± 0.001 A. Homogeneous. Separation from ore.	45 : 55 : 0	Magnetite-maghemite solid solution.
18	Co. Antrim, Ireland.	Milner	a = 8.3690 ± 0.002 A. Faint ilmenite lines. Separation from basalt.	26.5 : 73.5 : 0	Maghemite-magnetite $(1-x)Fe_2O_3.xFe_3O_4$
19	Bon Accord, Transvaal.	Milner	a = 8.3475 ± 0.001 A. Faint ilmenite lines. Separation from ore.	13.4:56.5: 30.1	Titanomaghemite. $(FeTi)_2O_3$.
20	Riesengebirge, Germany.	Herdsman	a = 5.0661, c = 13.952 A. Homogeneous.	45.6 : 8.9: 45.5	Ferriilmenite $(1-x)FeTiO_3.xFe_2O_3$
21	Ilmen Mt., Miask, Urals, U.S.S.R.	Milner	a = 5.0887, c = 14.049 A. 5% haematite & 2% magnetite. Separation from ore.	46.8: 2.7 : 50.5	Ferriilmenite. $(1-x)FeTiO_3.xFe_2O_3$

No.	(1) Locality	(2) Analyst	(3) Source of data	(4) Original description with comment on homogeneity.	(5) $FeO:Fe_2O_3:TiO_2$ % molecular ratio.	Mineral Name.	
						(6) Assigned to material in original source.	(7) Assigned to material on basis of present study
22	Lover's Pit, Mineville, N.Y.	Keyes	Newhouse & Glass, (1936), p. 701.	No description. X-rays, a = 8.379.	49.88:50.12:0	Magnetite.	Magnetite.
23	Mesabi Range, Minnesota.	? Ell~~a~~estad	Gruner, (1934), p. 757.	Massive, octahedra or dodecahedra. Polished sections.	49.9: 50.1: 0	Magnetite.	Magnetite.
24	Storgangen, Ekersund, Norway.	Kluver	Foslie, (1928), p. 8.	Separation from ilmenite-norite. Polished sections, ex-solution lamellae of spinel.	53.5: 44.5: 2	Magnetite.	Titanomagnetite with FeO in solid solution.
25	Södra Ulvön, Sweden.	Rönnholm & other labs. Stockholm.	Mogensen, (1946), p. 586.	Polished sections, very fine intergrowths of brown & grey minerals. X-rays, a = 8.47, 8.40.	62: 18.1: 19.9	Ferro-orthotitanate (Fe_2TiO_4) + magnetite.	Titanomagnetite $(1-x)Fe_2TiO_4 \cdot xFe_3O_4$ partly ex-solved.
26	Monti Rossi, Etna.	Starrabba	Starrabba, (1939), p. 5.	1.5 mm. octahedra, separated from sand. Polished sections.	57.6:30: 12.4	Magnetite.	Magnesio-titanomagnetite.
27	Fitzroy, New Plymouth, New Zealand.	Seelye	Hutton, (1945), p. 298.	Separation from sand. Polished sections, grey with brown tint.	52.6:35.9:11.5	Titanomagnetite.	Titanomagnetite + ilmenite.
28	Ardèche, France.	Jouravsky	Jouravsky, (1936), p. 1691.	From basaltic sands. Polished sections.	53.3: 32: 14.7	Titanomagnetite.	Titanomagnetite + ilmenite.
29	Haaland, Egersund, Norway.	Evrard	Evrard, (1944), p. 116.	Separation from ore. Polished sections, X-rays, but no measurements.	51.1:45.1: 3.8.	Titanomagnetite $xFeTiO_3 \cdot yFe_3O_4$	Titanomagnetite $(1-x)Fe_3O_4 \cdot xFe_2TiO_4$
30	Otanmäki, Finland.	Vaasjoki.	Vaasjoki, (1947), p. 109.	Magnetic separation from ore Polished sections.	53.5:43.1:3.4	Magnetite.	Titanomagnetite $(1-x)Fe_3O_4 \cdot xFe_2TiO_4$
31	Alameda Co., California, U.S.A.	Keyes	Newhouse & Glass, (1936), p. 701.	Polished sections, white to grey-blue, isotropic. X-rays, a = 8.326. (both patterns observed).	17.4:80.1:2.5	Maghemite + 20-40% magnetite.	Titanomaghemite + magnetite.
32	Iron Mt., Shasta Co., Calif., U.S.A.	Hostetter	Sosman & Posnjak, (1925), p. 333.	Polished sections, grey, isotropic X-rays, a = 8.30.	5.9:94.1: 0	Ferromagnetic ferric oxide.	Maghemite + magnetite.
33	Bukusu Hill, Uganda.	Broughton	Broughton, Chadwick, & Deans, (1950), p. 263.	No description.	32.9:66.5:0.6	Magnetite.	Magnetite + maghemite or $(1-x)Fe_3O_4 \cdot xFe_2O_3$.

Table D (continued)

No.	(1) Locality	(2) Analyst	(3) Source of data	(4) Original description with comment on homogeneity.	(5) FeO:Fe_2O_3:TiO_2 % molecular ratio.	Mineral Name.	
						(6) Assigned to material in original source.	(7) Assigned to material on basis of present study
34	Windpass mine, British Golumbia.	Keyes	Newhouse & Glass, (1936), p. 701.	Polished sections, white to blue-grey. X-rays, a = 8.369 (no maghemite pattern).	42.1: 57.9: 0	Magnetite + maghemite.	Magnetite-maghemite solid solution $(1-x)Fe_3O_4.xFe_2O_3$
35	Bushveld Complex S. Africa.	Liebenberg & Haumann	Schwellnus & Willemse, (1943), p. 30.	Polished sections. No description.	8:69.2: 22.8	Magnetic iron ore ?	Titanomaghemite $(1-x)Fe_2O_3.xTi_2O_3$ + magnetite.
36	Snarum, Norway.		Warren, (1918), p. 421.	No description. Homogeneity doubtful.	4.1:85.8:10.1	Ilmenite	Titanhaematite + rutile.
37	Boolmacoota, S. Australia.	Edwards	Edwards, (1938), p. 41	Polished sections, white, anisotropic.	10.6:78.8:10.6	Titan-haematite.	Titanhaematite $(1-x)Fe_2O_3.xFeTiO_3$
38	New Plymouth, New Zealand.	Seelye	Hutton, (1945), p. 298.	Separation from sand. Polished sections.	15.6:68.6:15.8	Titan-haematite.	Titanhaematite $(1-x)Fe_2O_3.xFeTiO_3$
39	Snarum, Norway.		Warren, (1918), p. 421.	No description. Homogeneity doubtful.	19.5:64.3:16.2	Ilmenite	Titanhaematite
40	Myponga, South Australia.	Edwards	Edwards, (1938), p. 41.	Polished sections, grey-white, anisotropic, few ex-solution bodies of ilmenite.	18.1:63.5:18.4	Titan-haematite	Titanhaematite + ilmenite.
41	Madagascar.	Raoult.	Lacroix, (1920), p. 483.	Polished sections, ex-solution intergrowth.	34.5: 31:34.5	Ilmenite + haematite.	Ilmenite + haematite.
42	Mudtown, Stewart Isl., New Zealand.	Seelye	Hutton, (1950), p. 673.	Polished sections of grains from sand, intergrowth structure.	31.4:29.6: 39	Ilmenite-titan-haematite intergrowth.	Ferriilmenite + titanhaematite + rutile.
43	Storgangen, Ekersund, Norway.	Kluver	Foslie, (1928), p. 8.	Separation from ilmenite-norite. Polished sections.	47.7:6.1:46.2	Ilmenite with 8% Fe_2O_3 in solid solution.	Ferriilmenite $(1-x)FeTiO_3.xFe_2O_3$
44	Mt. Ruwenzori, Belgian Congo.	Colomba	Dana, (1944), p. 537.	No description.	50.3: 0:49.7	Ilmenite.	Ilmenite.
45	Nelson Co., Virginia, U.S.A.	Watson & Taber.	Robinson, (1922), p. 24.	No description. Homogeneity doubtful.	44.7:2.3 :53	Ilmenite.	Ilmenite + rutile + haematite.

PLATE 1.

Explanation of Plate 1.

X-ray powder photographs with CoK_{α} radiation. Camera diameter 114.6 mm. Full size reproduction of contact prints.

Fig. 1. High θ lines for Bisperg magnetite, before annealing.

Fig. 2. High θ lines for Bisperg magnetite, after annealing, showing the doubling of the lines.

Fig. 3. Pure magnetite, Bisperg, Dalecarlia, S. Sweden.

Fig. 4. Magnetite with 1.9% FeO in solid solution. Forola, Swëden.

Fig. 5. Magnesiomagnetite, Kropferberg, Saxony.

Fig. 6. FeO (wüstite), prepared artificially by decomposition of ferrous oxalate, in vacuum.

PLATE I

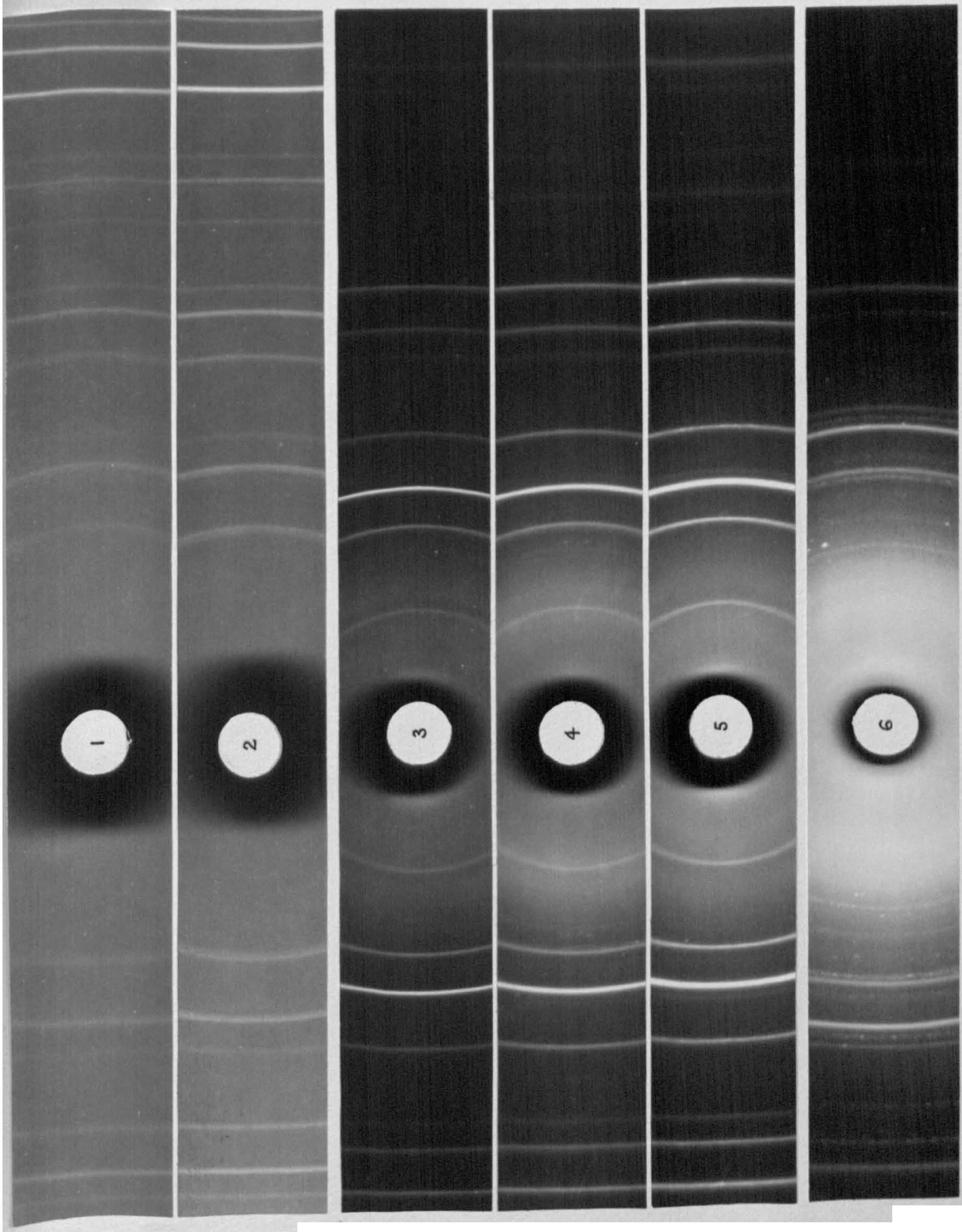


PLATE 2.

Explanation of Plate 2.

X-ray powder photographs of γ-Fe_2O_3 - Fe_3O_4 solid solutions, showing the decrease in the size of the unit cell of magnetite with the increase in the amount of maghemite in solid solution, i.e. from Fig. 1 to Fig. 6.

Fig. 1. Pure magnetite, from Bisperg, S. Sweden.

Fig. 2. Magnetite-maghemite, Devon. Faint haematite line appears.

Fig. 3. Magnetite-maghemite, Mourne, Co. Down, Ireland.

Fig. 4. Magnetite-maghemite, Mt. Blagodot, Urals.

Fig. 5. Maghemite-magnetite, Co. Antrim, Ireland. Faint lines of ilmenite appear.

Fig. 6. Titanomaghemite, Bon Accord, Transvaal. Faint lines of ilmenite appear.

PLATE 2

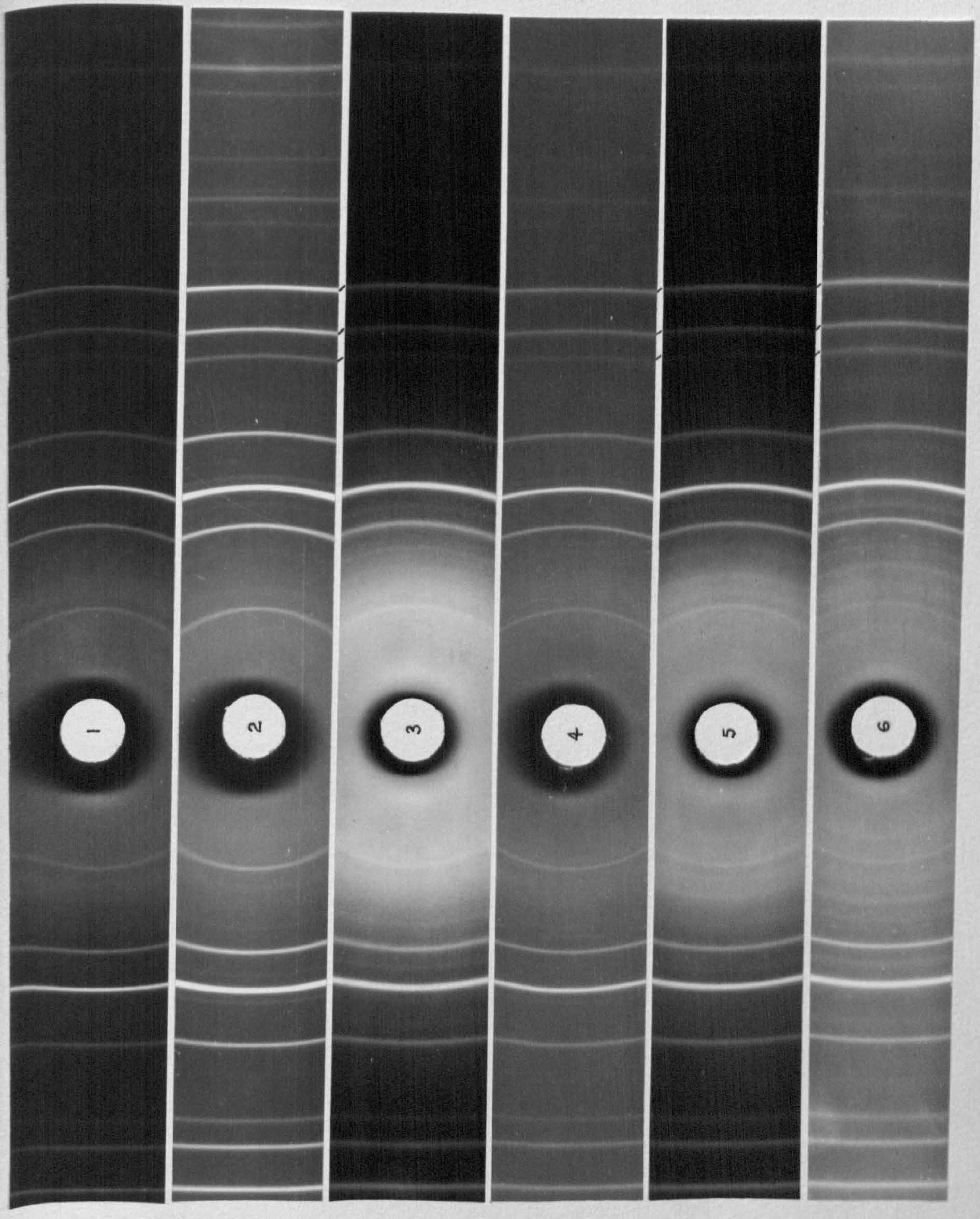


PLATE 3.

Explanation of Plate 3.

X-ray powder photographs with CoK$_\alpha$ radiation. Camera diameter 114.6 mm. Full size reproduction of contact prints.

Fig. 1. Magnetite + haematite (ex-solution intergrowths), Edison, New Jersey.

Fig. 2. The same specimen in Fig. 1, but after homogeneisation by heating at 1050°C. for 48 hours, in vacuum (charge 6).

Fig. 3. Haematite, from Elba.

Fig. 4. Haematite + rutile, formed by decomposition of ilmenite, Snarum, Norway.

Fig. 5. Rutile, British Titan Products Co., Ltd.,

Fig. 6. Fe_2O_3 + 10%TiO_2, after being heated in vacuum at 800°, for 26 hours (charge 29). A few faint rutile lines are still present.

PLATE 3

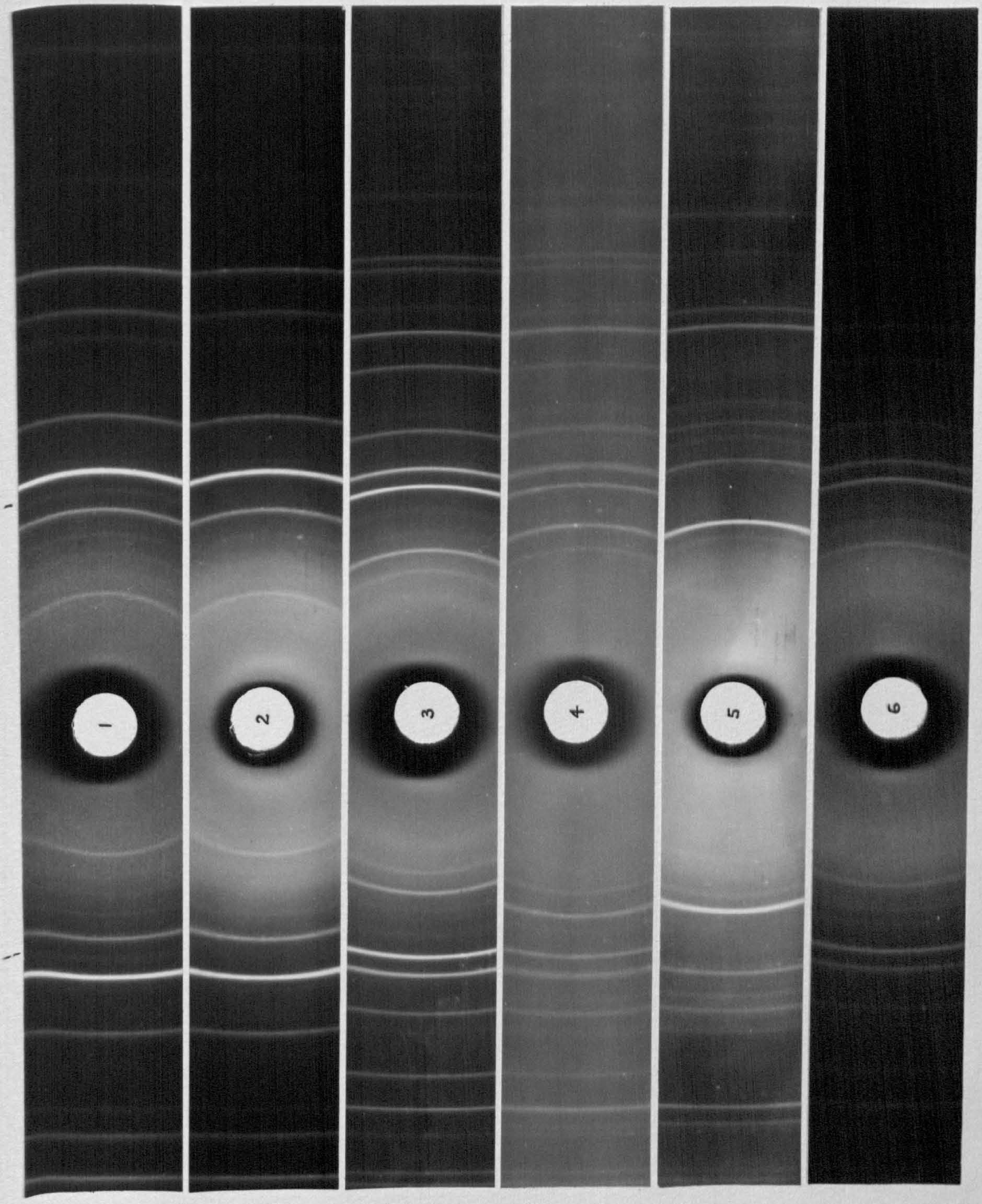


PLATE 4.

Explanation of Plate 4.

X-ray powder photographs. CoK_{α} radiation. Camera diameter 114.6 mm. Full size reproduction of contact prints.

Fig. 1. Ilmenite sand (the so-called arizonite), Travancore, India, showing ilmenite and faint titanhaematite lines.

Fig. 2. "Iserine" sand, Seacombe, Liverpool. The photograph shows ilmenite, haematite, and magnetite lines.

Fig. 3. Ilmenite after being heated in air at 730°C for 4 days (charge 23); the photograph shows haematite, rutile, and faint brookite lines, ilmenite lines are absent.

Fig. 4. Ilmenite after being heated in air at 900°C for 24 hours (charge 21); the photograph shows pseudobrookite and rutile.

Fig. 5. "Nigrine", Limoges, France; the photograph shows rutile and ilmenite lines.

Fig. 6. $FeTiO_3$ + 10% TiO_2, after being heated in vacuum at 1040°C for 24 hours (charge 10). Few faint rutile lines are still present.

PLATE 4

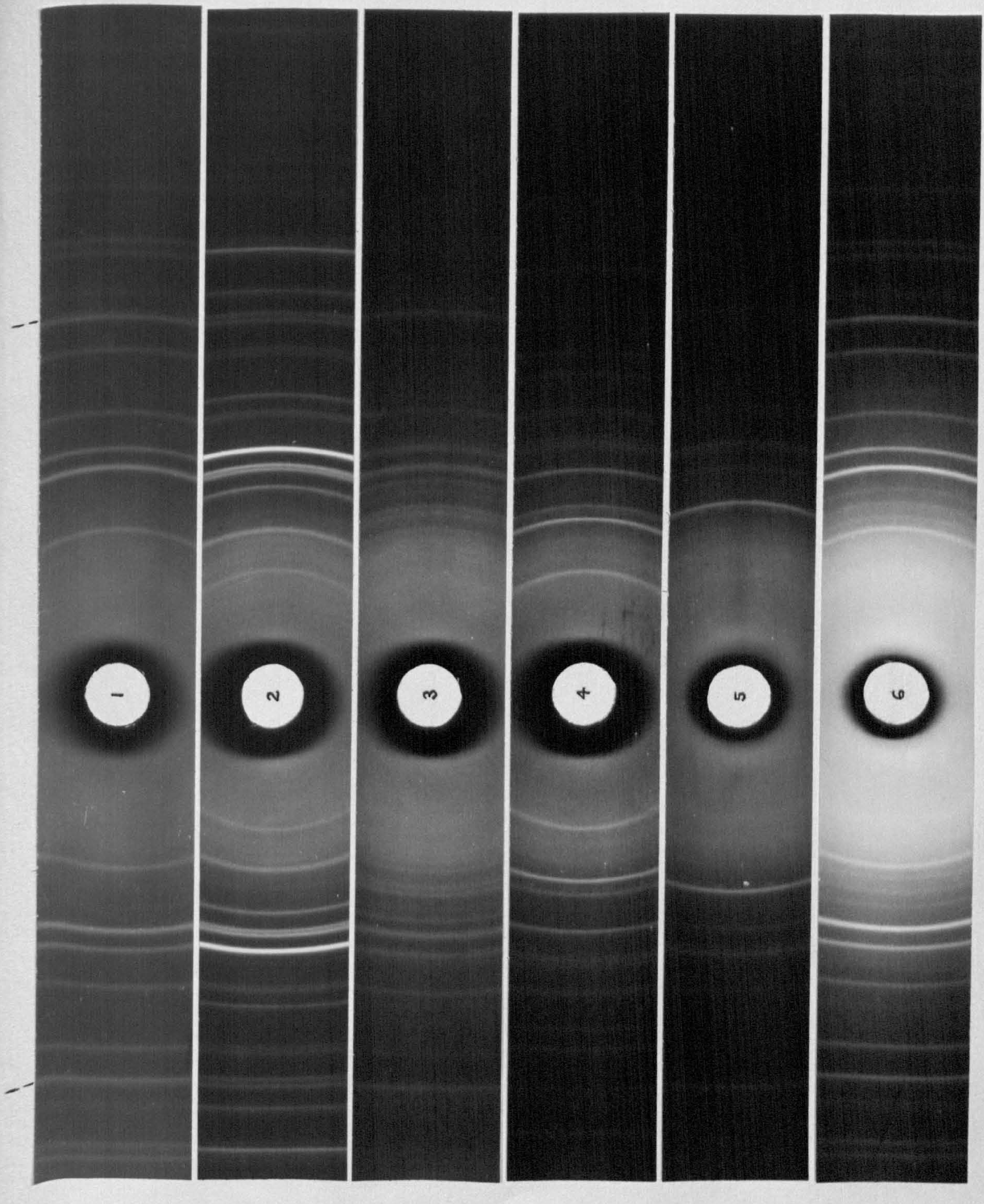


PLATE 5.

Explanation of Plate 5.

X-ray powder photographs of Fe_2O_3 - $FeTiO_3$ solid solutions, showing the decrease in the size of the unit cell of ilmenite with the increase in the amount of Fe_2O_3 in solid solution, i.e. from Fig. 2 to Fig. 6.

Fig. 1. Ferriilmenite + titanhaematite (ex-solution intergrowths), Hamata, Eastern Desert, Egypt.

Fig. 2. Ilmenite, Ilmen Mts., Urals. Faint haematite lines are not possible to detect in the print.

Fig. 3. Ferriilmenite (the so-called "iserine"), Riesengebirge, Germany.

Fig. 4. Ferriilmenite, Ekersund, Norway.

Fig. 5. Fe_2O_3. $FeTiO_3$, obtained by heating a mixture of Fe_2O_3, and $FeTiO_3$ in the molecular ratio 1:1, in vacuum at 1050°C for 24 hours (charge 26).

Fig. 6. Titanhaematite, Mt. Monger, S. Australia.

PLATE 5

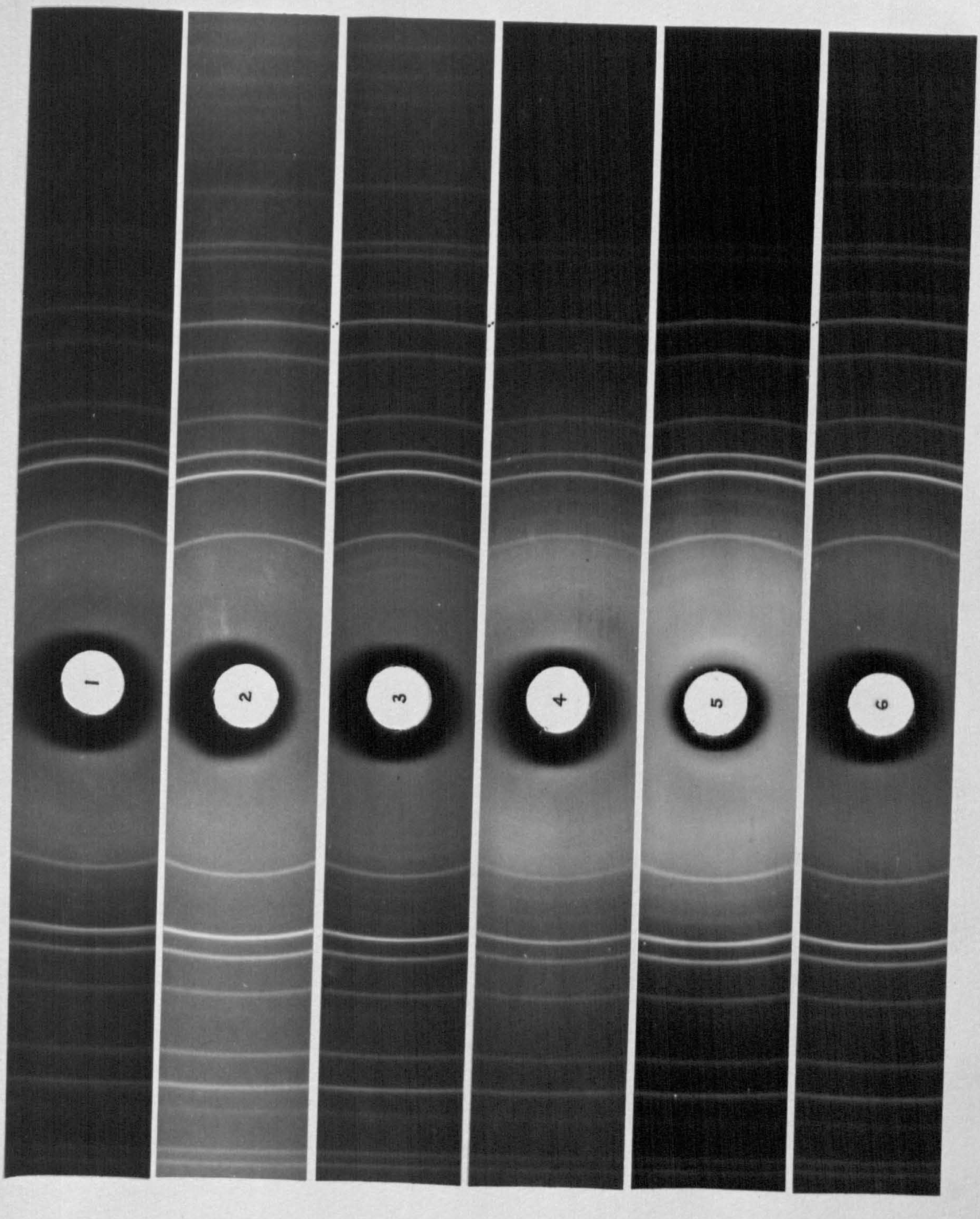


PLATE 6.

Explanation of Plate 6.

X-ray powder photographs with CoK_{α} radiation. Camera diameter 114.6 mm. Full size reproduction of contact prints.

Fig. 1. Magnetite + ilmenite (ex-solution intergrowths), Magnet Heights, Transvaal.

Fig. 2. Fe_3O_4 + 5% $FeTiO_3$, after being heated in vacuum at 1050°C, for 38 hours (charge 8). One faint ilmenite line can be traced.

Fig. 3. Fe_3O_4 + 15% $FeTiO_3$, after being heated in vacuum at 1030°C, for 48 hours (charge 22). Ferriilmenite lines appear.

Fig. 4. Magneso-titanomagnetite, Magnet Cove, Arkansas.

Fig. 5. Magnetite + ulvöspinel, Norra Ulvöh, Sweden.

Fig. 6. Magnetite + ulvöspinel, Skaergaard intrusion, East Greenland. Faint ilmenite lines appear.

PLATE 6

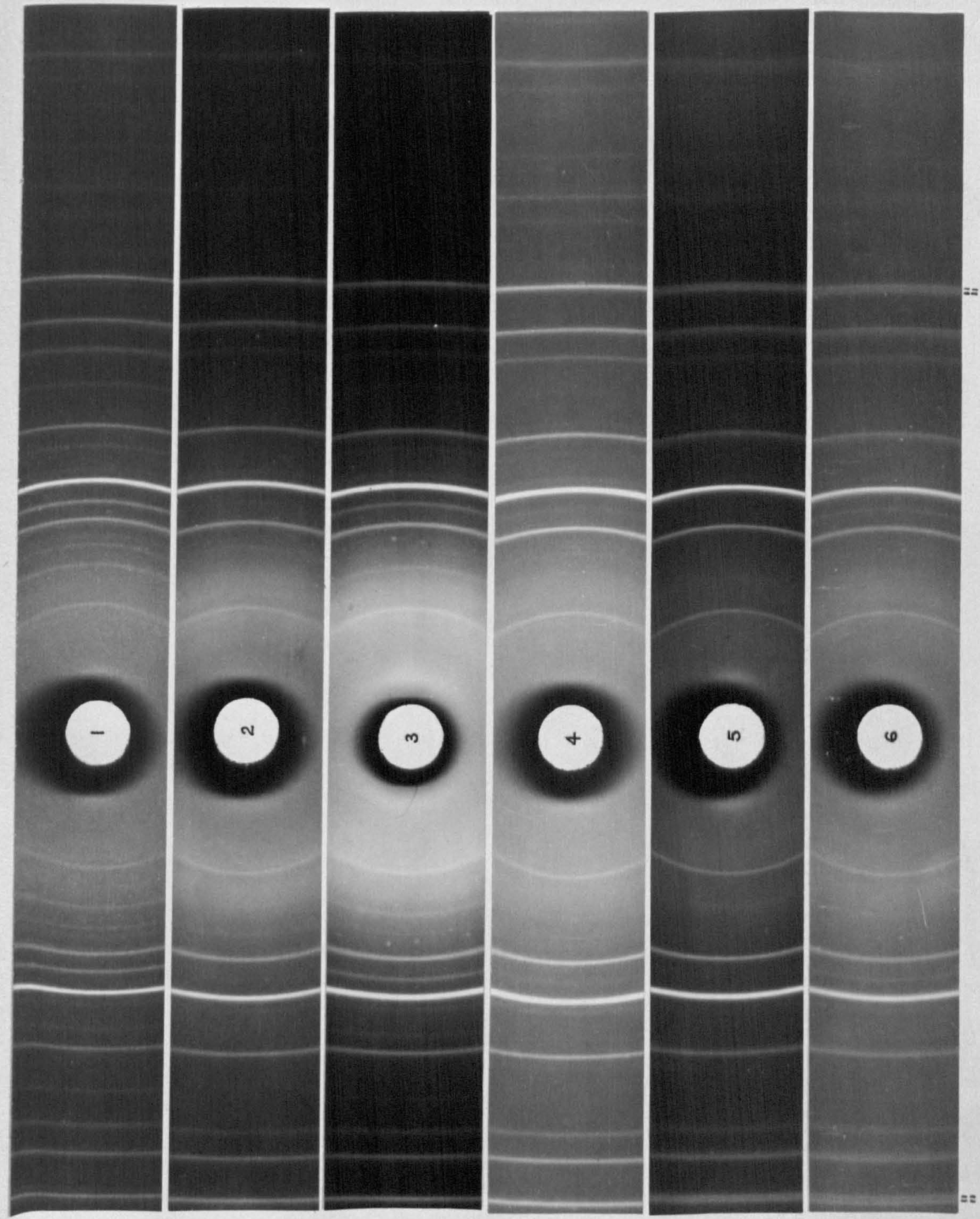


PLATE 7.

Explanation of Plate 7.

X-ray powder photographs of titanomagnetites, showing the increase in the size of the unit cell of magnetite with the increase in the amount of Fe_2TiO_4 in solid solution, i.e. from Fig. 1 to Fig. 4.

Fig. 1. Pure magnetite, Bisperg, S. Sweden.

Fig. 2. Titanomagnetite, Dunglas Hill, Strathblane, Scotland. Separated from basalt.

Fig. 3. Titanomagnetite, Blagolkot, Deccan, India. Separated from basalt. Faint ilmenite lines appear.

Fig. 4. Titanomagnetite, Giant's Causeway, Ireland. Separated from basalt.

Fig. 5. Artificial titanomagnetite $(1-x)Fe_3O_4 . xFe_2TiO_4$, prepared by heating Fe_3O_4, and TiO_2, in the molecular proportion 1:1, in vacuum, at 1050°C for 24 hours (charge 31). The photograph is of the ferromagnetic fraction; faint ferriilmenite lines appear

PLATE 7

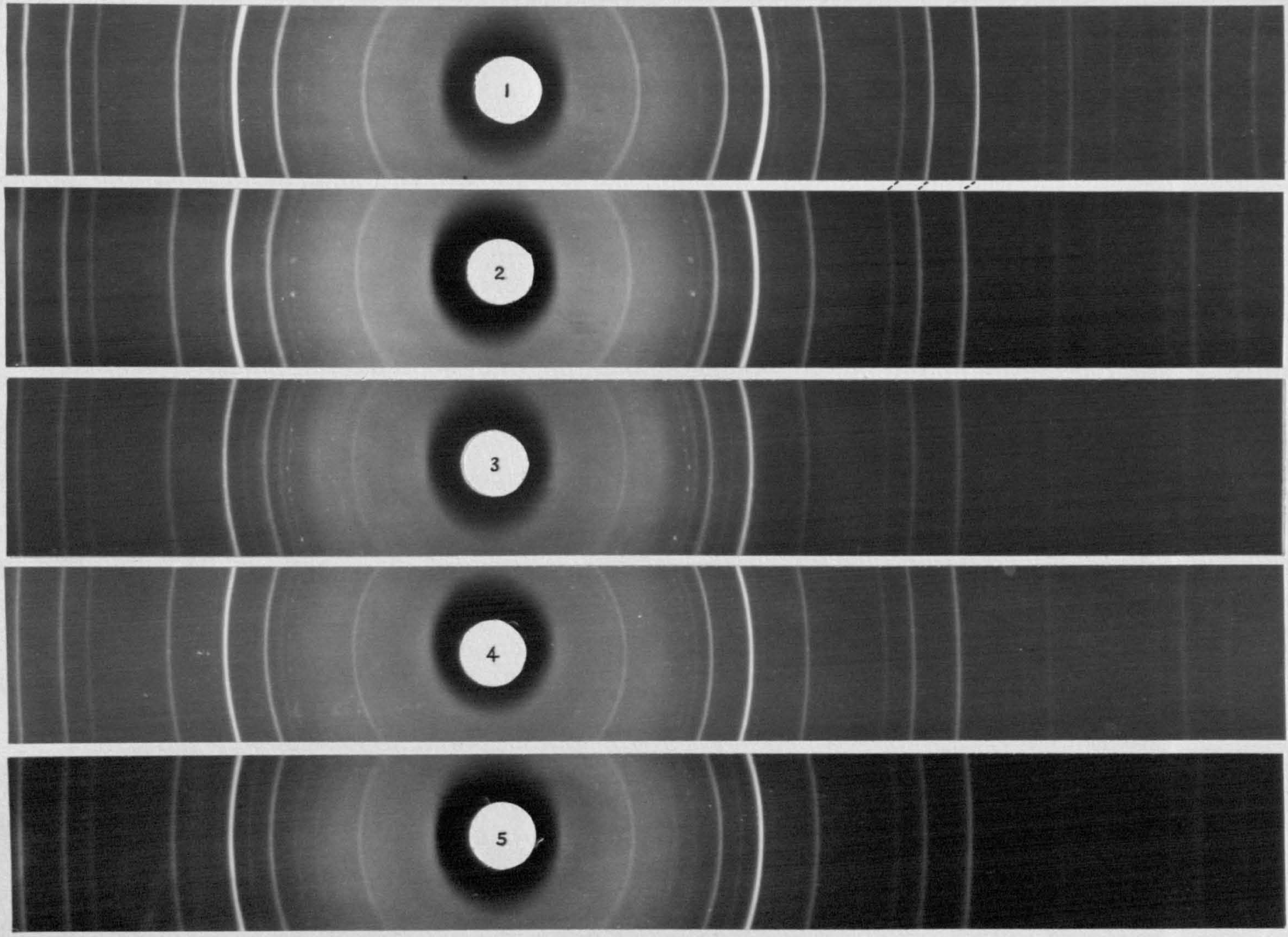


PLATE 8.

Explanation of Plate 8.

Photomicrographs of polished sections.

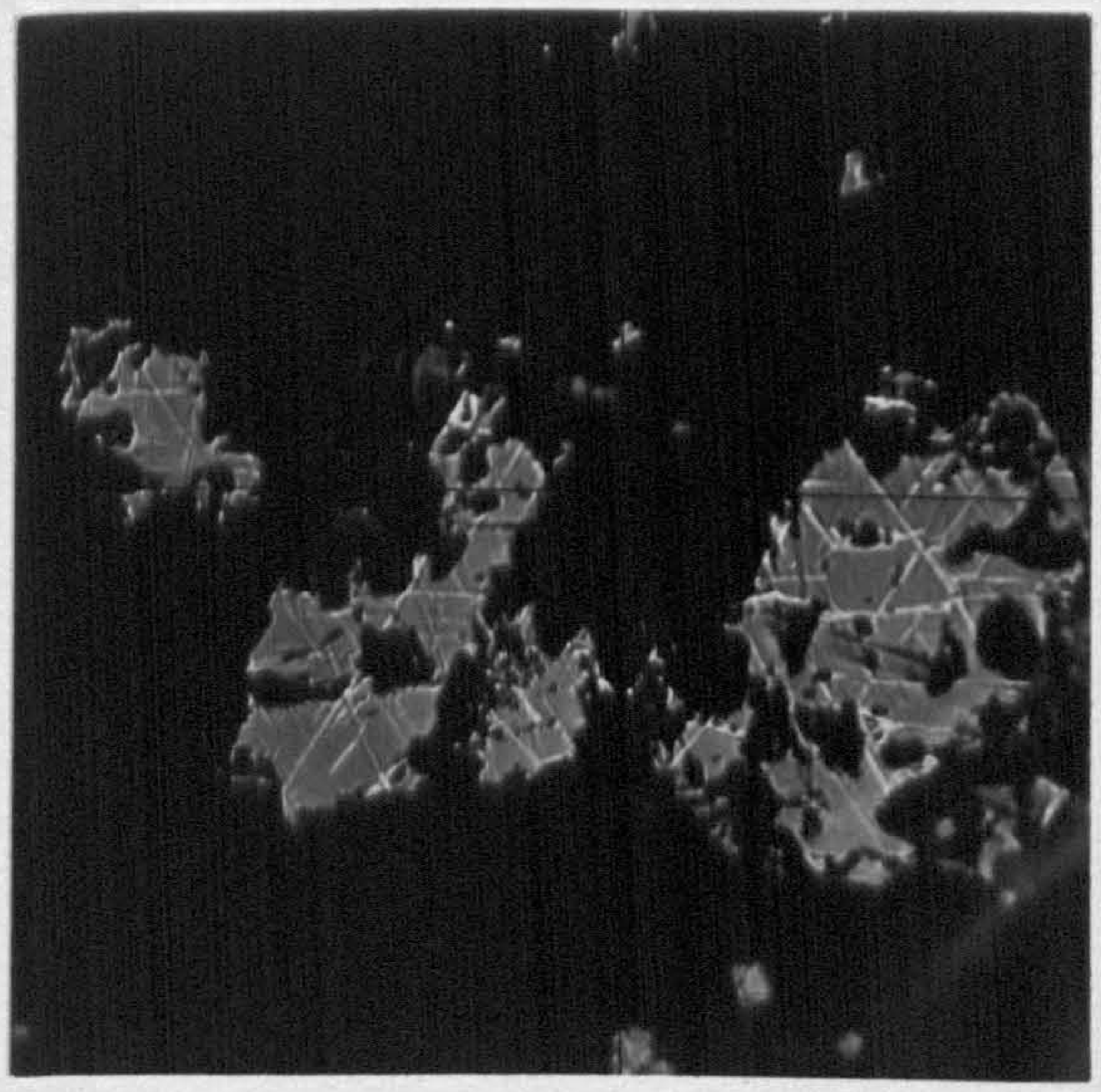
Fig. 1. Ex-solution intergrowth of haematite lamellae (white) in the (111) planes of magnetite (grey), in a specimen of amphibolite from Matapau, New Guinea. x 460.

Fig. 2. Intergranular ilmenite (dark grey) in titanomaghemite (light grey), with limonite (black) along the cracks. Bon Accord, Bushveld Complex, Transvaal. x 120. Nicols partially crossed.

Fig. 3. Stout lamellae of rutile (grey), and haematite (white), formed by extensive oxidation of original ilmenite; the black grains are cavities filled with leucoxene. Snarum, Norway. x 150.

Fig. 4. Ilmenite-haematite ex-solution intergrowth, showing the coalescence of the coarse haematite bodies (white) which are arranged in parallel rows in the ilmenite base (dark grey). Miask, Ilmen Mts., Urals. x 120.

PLATE 8



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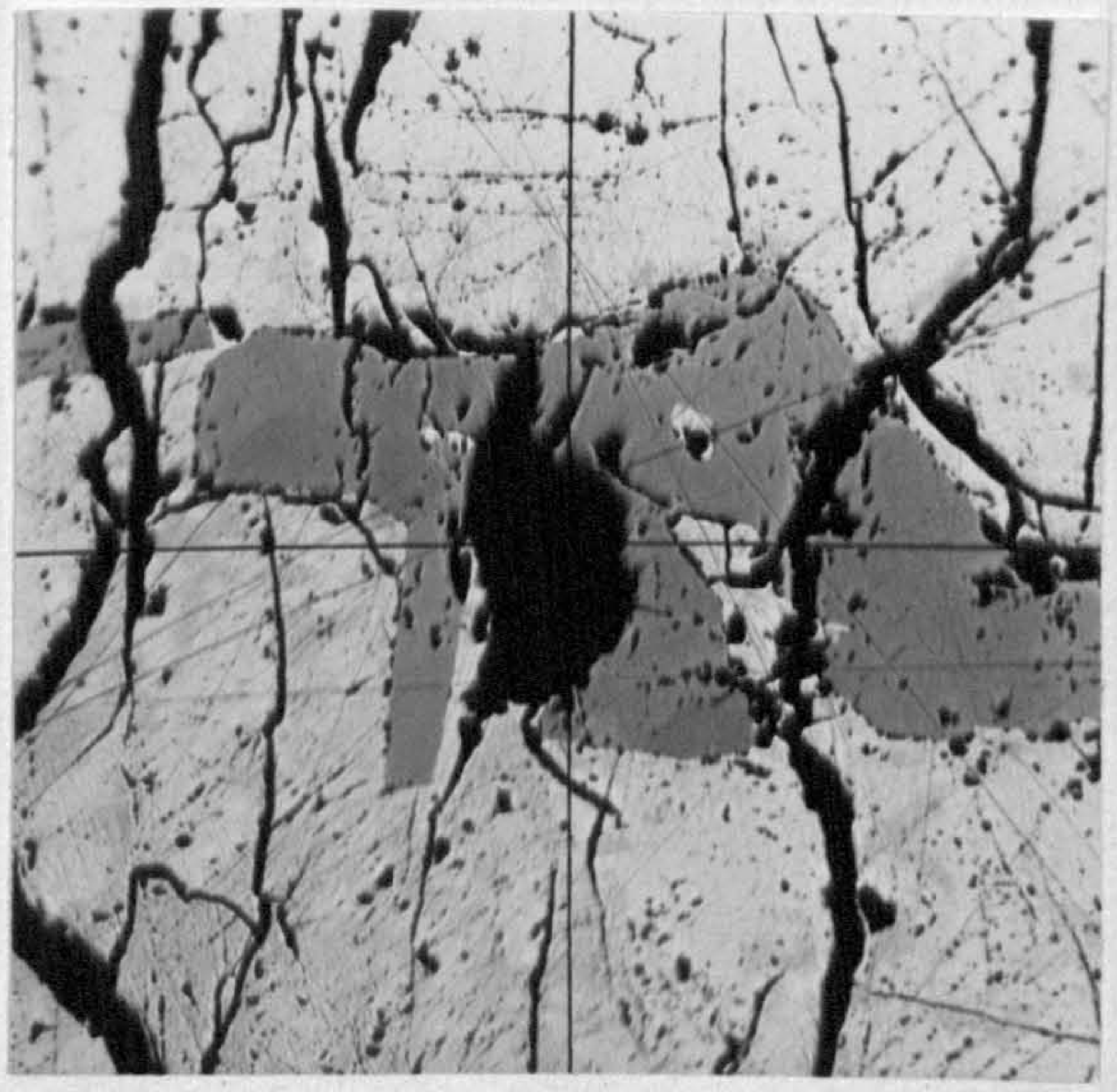

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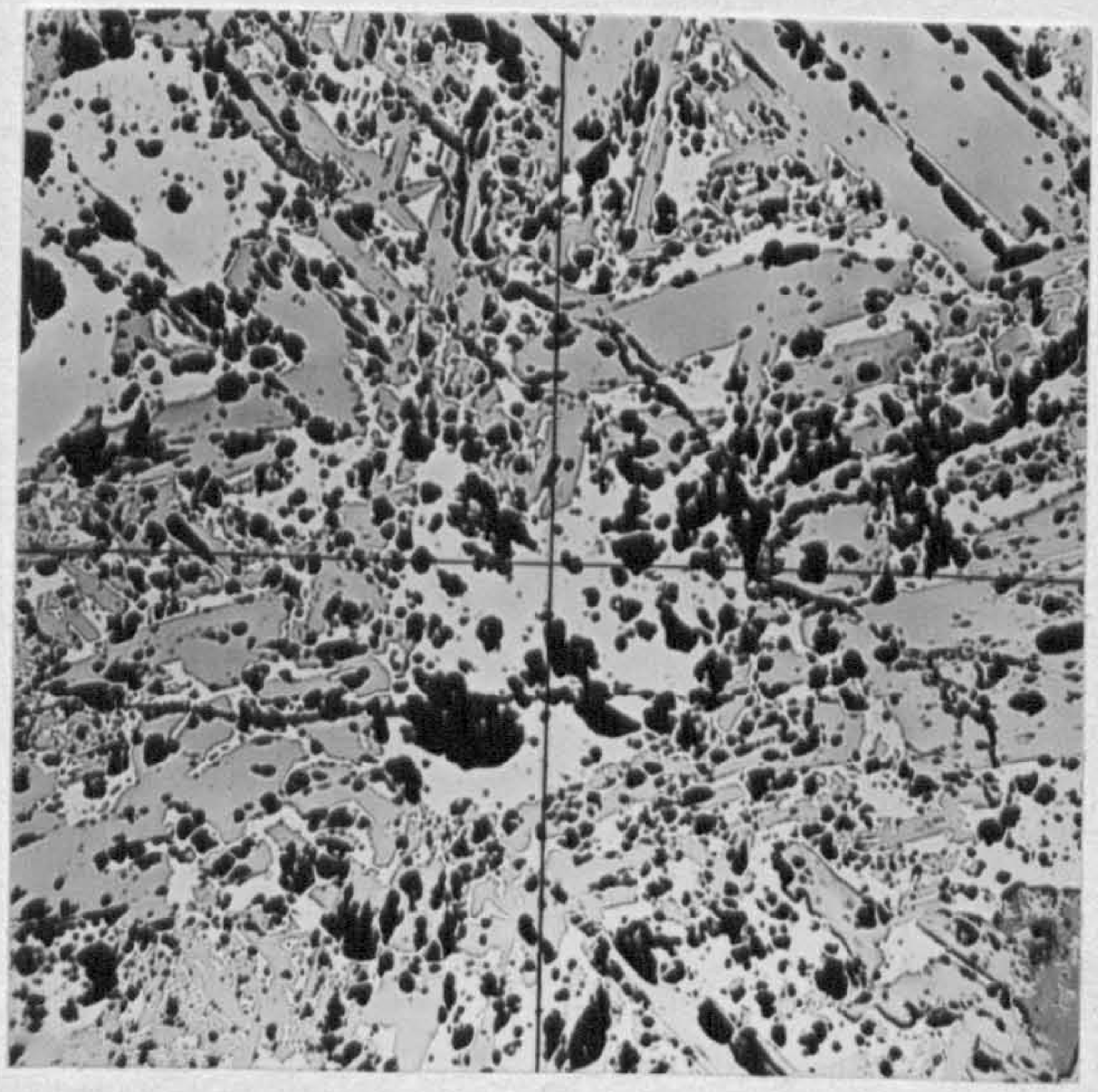

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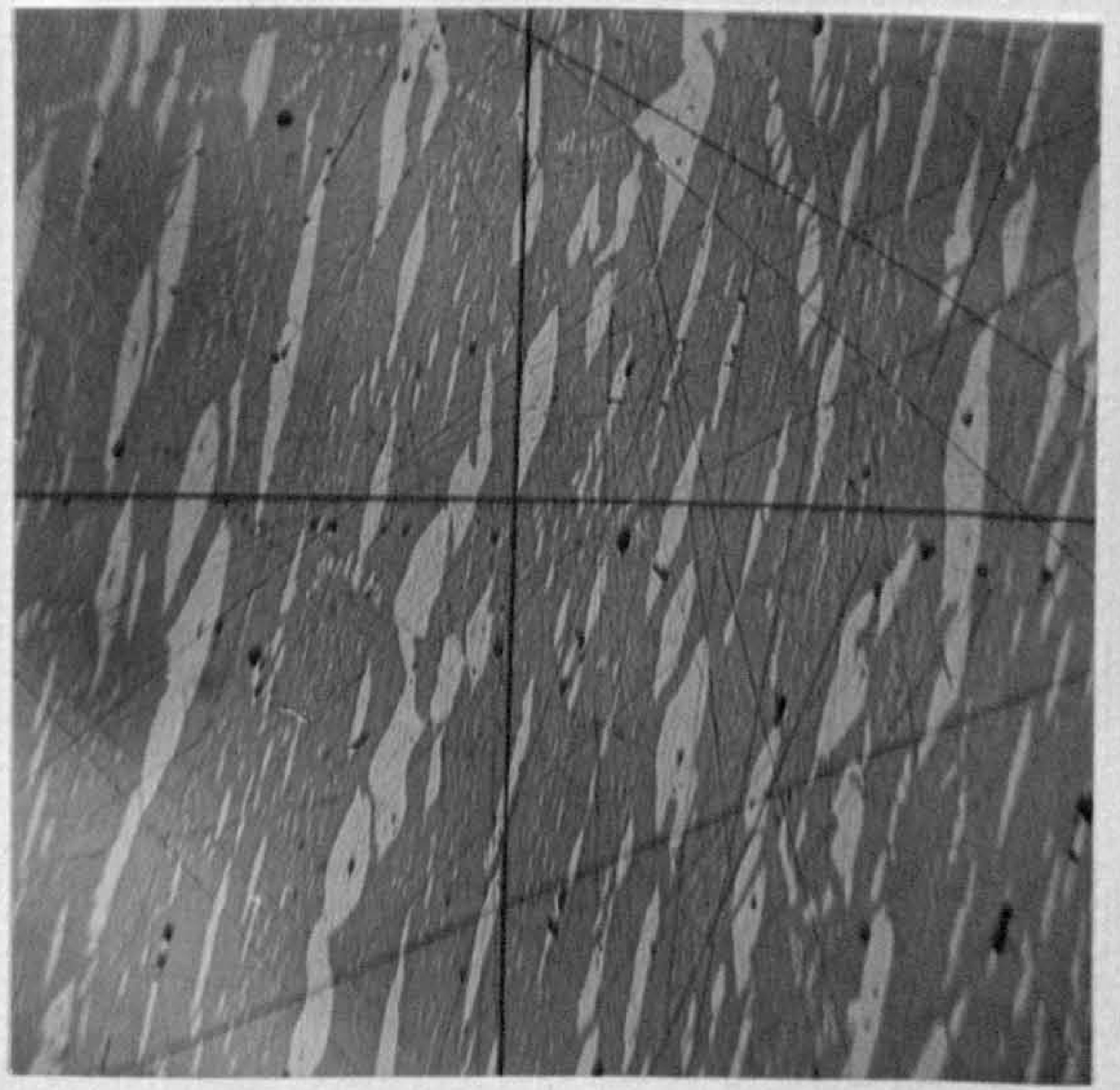

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PLATE 8 (contin.)

Explanation of Plate 8 (contin.).

Photomicrographs of polished sections.

Fig. 5. Ex-solution intergrowths of ilmenite lamellae (dark grey) in the (111) planes of magnetite (light grey), in a specimen of gabbro from Coruisk, Skye. x 120.

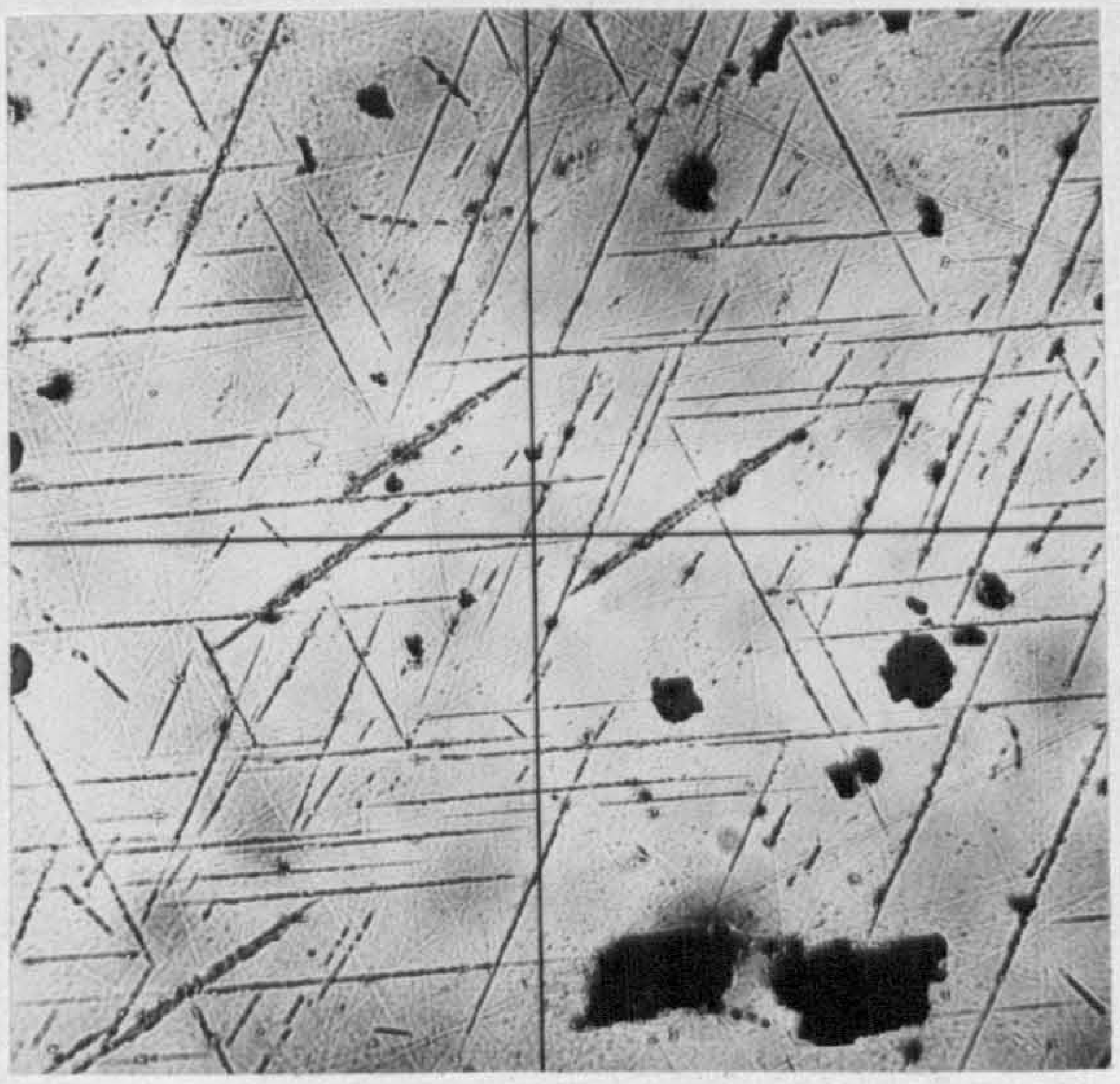
Fig. 6. Ulvöspinel ore, showing large ilmenite lamellae(I) which are comparatively rare. The mosaic structure of the magnetite-ulvöspinel is discernible. Norra Ulvön, Sweden. x 500.

Fig. 7. Extremely fine ex-solution intergrowth of ilmenite (dark grey) in the octahedral planes of magnetite (light grey). In a specimen of norite from Magnet Heights, Bushveld, Transvaal. x 560.

Fig. 8. Martitised magnetite; the magnetite (dark grey)is partly altered to haematite (white) at the margins and along the octahedral cracks. The haematite lamellae may vary considerably in width in different parts. Schischimskaja, C. Kussa, Urals. x 550.

PLATE 8

(CONTINUED)



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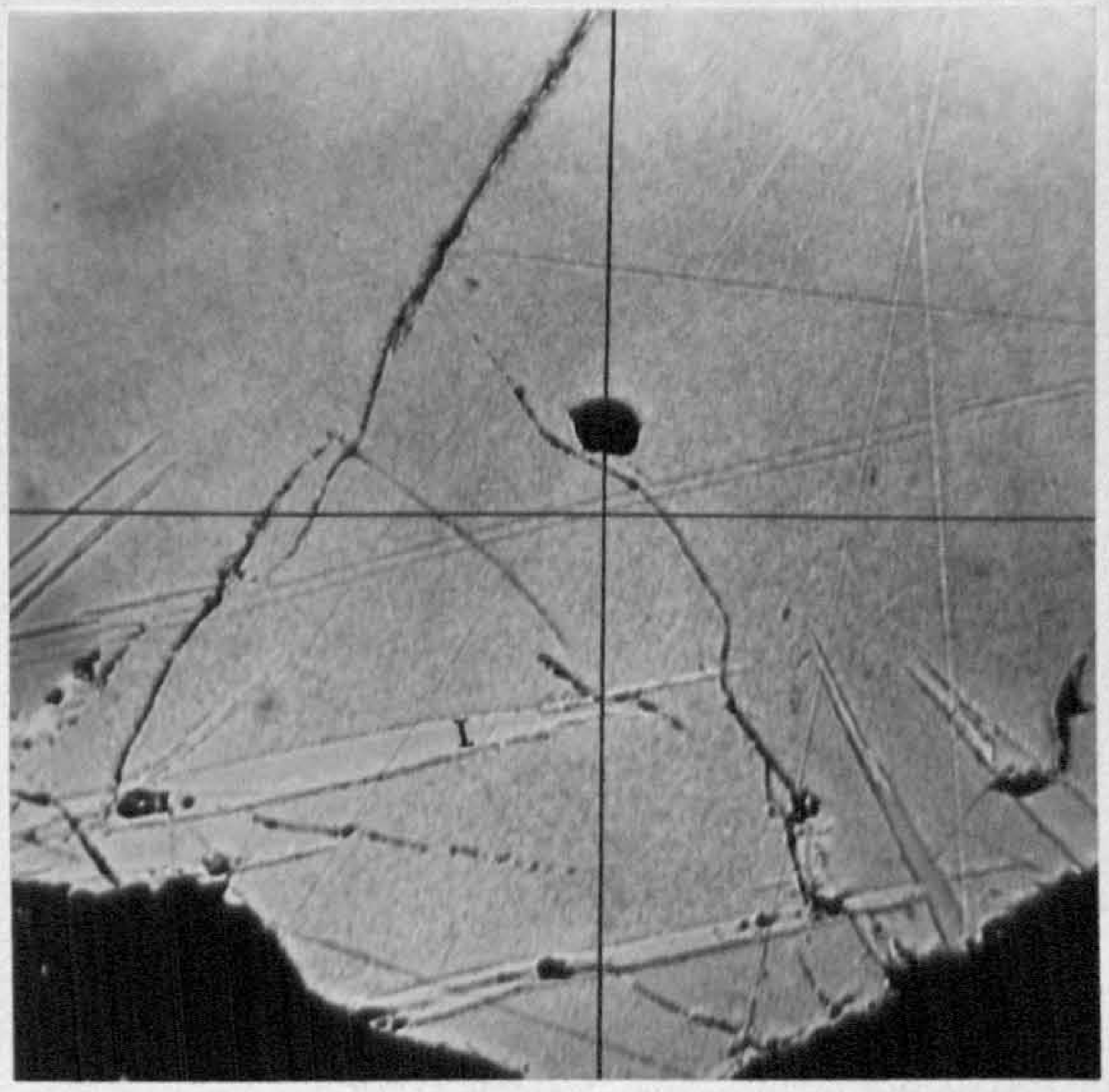

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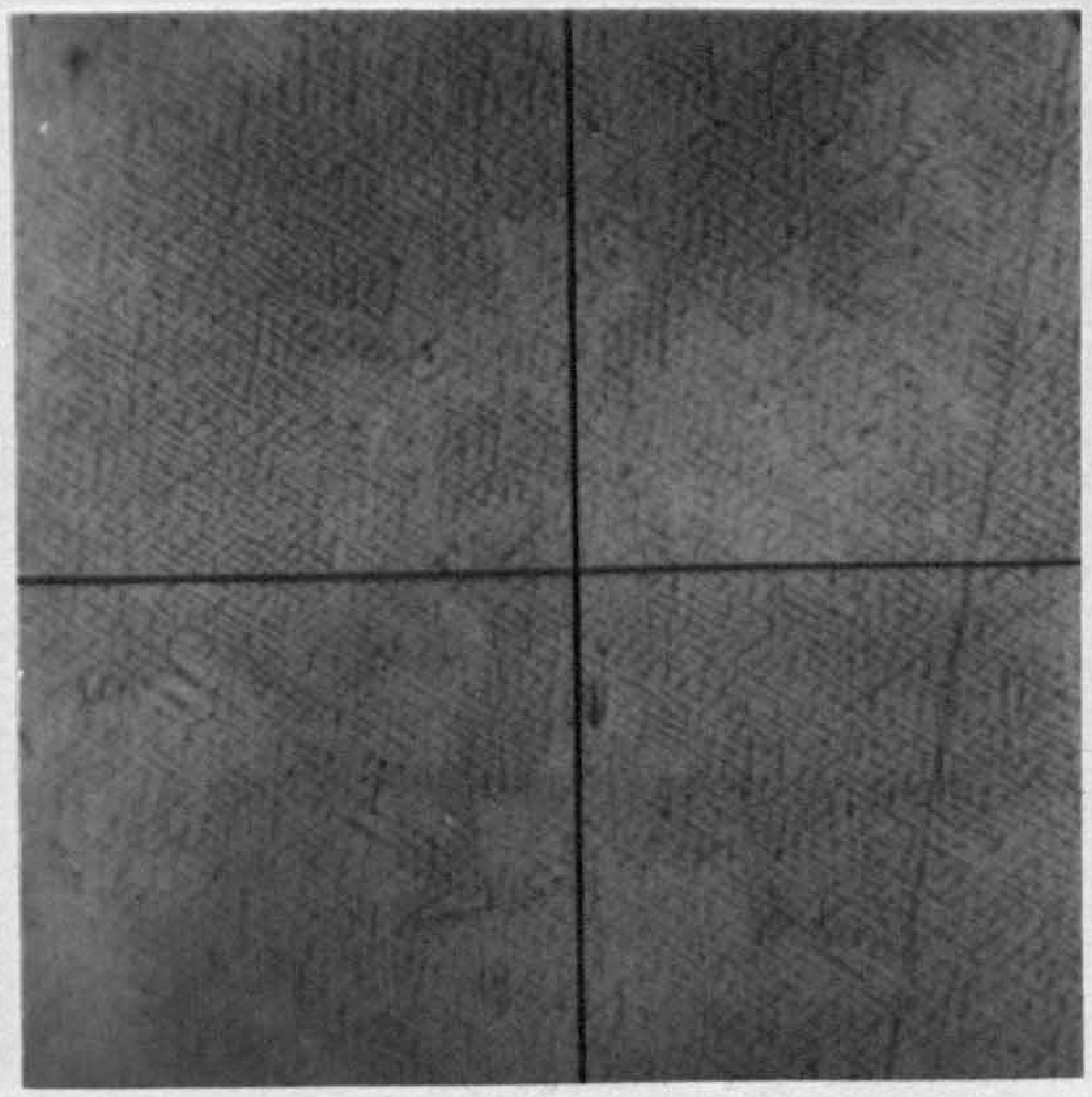

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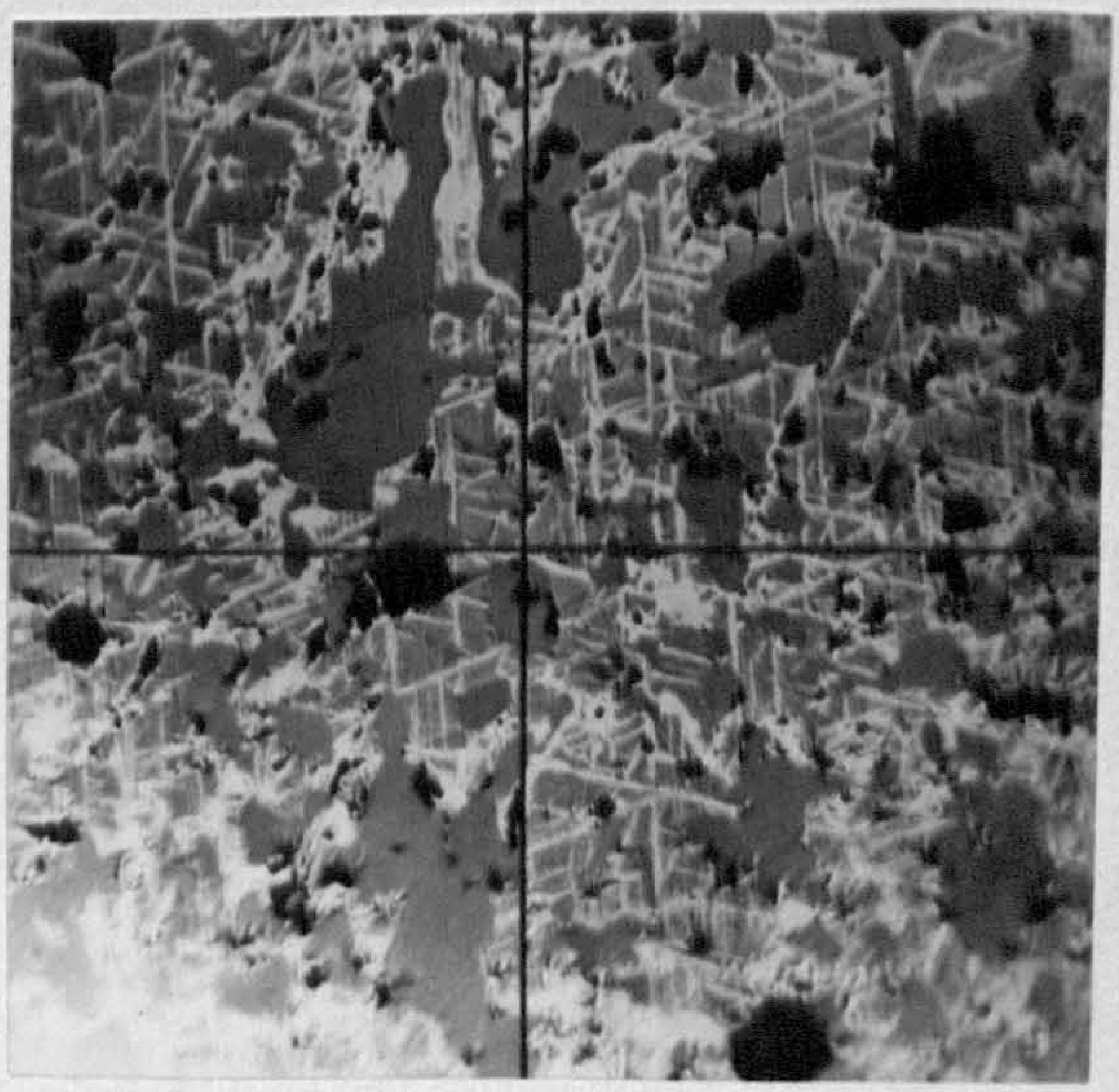

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