Solid-solution relationships in some titaniferous iron oxide ores of basic igneous rocks.

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Summary. Calculations are presented, based on modal and chemical analyses of titaniferous iron ore minerals from two localities (Skaergaard and Schmoo Lake). They show that Fe:Ti ratios are constant for granular aggregates of ilmenite and titaniferous magnetite formed at any one stage in the cooling history of the containing rock body. From this and other evidence it is concluded that the aggregates are the result of exsolution from original high-temperature cubic solid solutions. For the Skaergaard rocks, the problem of separately crystallized ilmenite, distinct from the granular aggregates, is also discussed.

TITANIFEROUS iron ores in basic igneous rocks generally consist of ilmenite grains in close association with titaniferous magnetite containing exsolved lamellae of ilmenite or ulvöspinel or both (together with small amounts of aluminous spinels, with which this study is not concerned). The ulvöspinel intergrowth in titaniferous magnetite is always very fine, while ilmenite is exsolved as masses of widely varying size, from large lamellae and irregular blebs down to intergrowths as fine as those of ulvöspinel. The ilmenite grains in the assemblages are often idiomorphic towards the titaniferous magnetite (fig. 1), and can occasionally be seen passing into the larger blebs and lamellae of ilmenite in the latter (fig. 3*a*). The granular aggregates of ilmenite and titaniferous magnetite as a whole, however, are nearly always interstitial to the surrounding silicates.

The origin of the granular aggregates has been attributed by previous workers either to exsolution (Edwards, 1938; Evrard, 1949; Vincent and Phillips, 1954) or to contemporaneous crystallization (Buddington *et al.*, 1955; Heier, 1956). Quantitative data presented here, derived from modal and chemical analysis, suggest that an origin by exsolution processes is perhaps the more likely.

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The materials used in this investigation were eleven representative samples from the Skaergaard layered intrusion, east Greenland, and six random samples from the Schmoo Lake titaniferous iron ore, Quebec.

The Skaergaard samples.

Vincent (1960) has described in detail the titaniferous iron oxide ores and their intergrowths in rocks of the Skaergaard intrusion. The ores first appear in significant amount as a primary precipitate phase, rather high in the Lower Olivine Gabbros. At and above this level they are always much more concentrated in melanocratic than in average bands, sometimes forming over half the rock by volume.

The samples used were from adjacent average and melanocratic bands and from transgressive ore-rich veins in the layered Skaergaard intrusion, east Greenland (heights, in metres, refer to level in the layered intrusion):

E.G. 5052	830 m.	Average band	Lower Olivine Gabbros
E.G. 5051		Melanocratic band	
E.G. 2307	850 m.	Average band	
E.G. 2308		Melanocratic band	
E.G. 4353	1 150 m.	Less melanocratic band	Middle Gabbros
E.G. 4359		More melanocratic band	
E.G. 2574	1 730 m.	Average band	Hortonolite Ferrogabbros
E.G. 2580		Average band	
E.G. 2569		Melanocratic band	
E.G. 4458A	805 m.	Transgressive ore-rich veins	Lower Olivine Gabbros
E.G. 4355	1 150 m.		Middle Gabbros

Distinct from the granular aggregates of titaniferous magnetite and ilmenite, these Skaergaard rocks also contain separate ilmenite crystals, usually entirely surrounded by silicates. Such ilmenite typically occurs as elongate subhedral crystals—often in short chain-like aggregates—contrasting with the irregular but usually roughly equant form of the ilmenite grains associated with titaniferous magnetite; and it is largely confined to average bands in which the ores are not a major constituent (table I). Phillips (Vincent and Phillips, 1954) also distinguished this ilmenite and regarded it as a separately crystallized component of the ores—a conclusion supported by the present study.

Textural features typical of Skaergaard titaniferous iron oxides are illustrated in fig. 1.

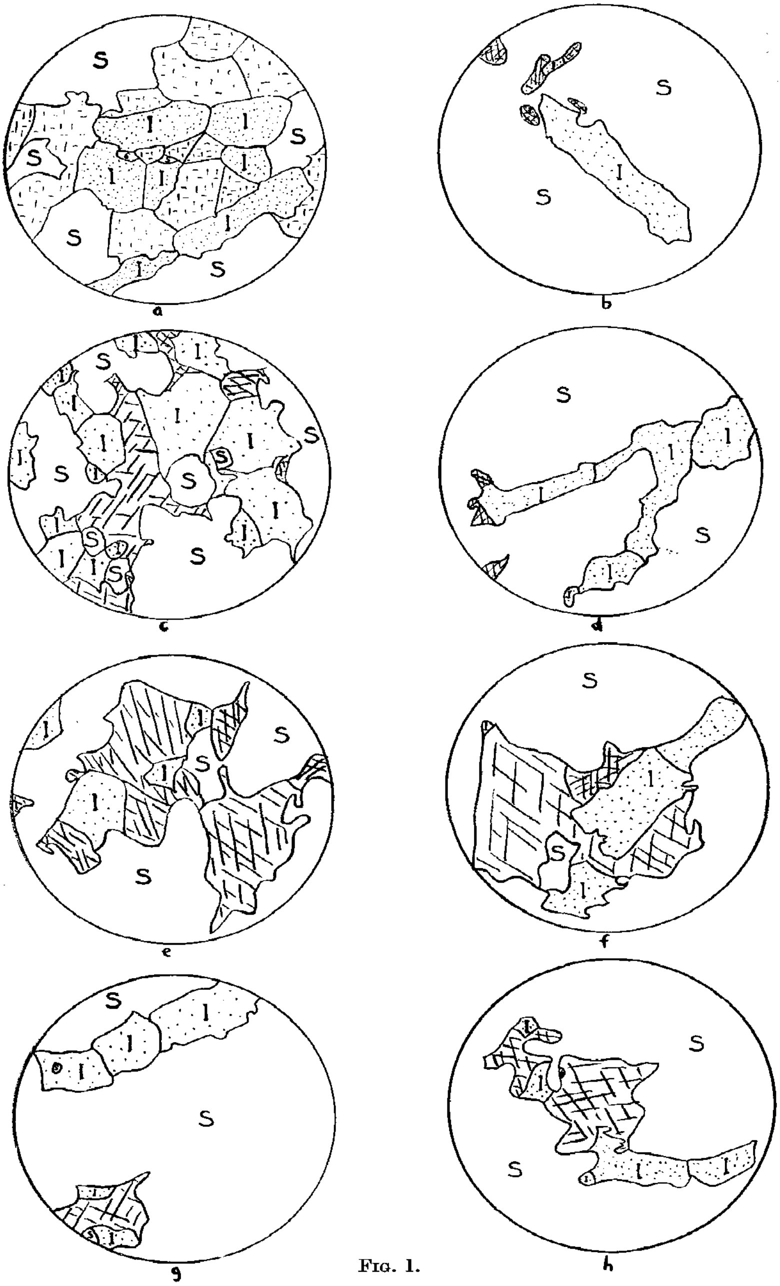

Fig. 1.

Modal analysis. Modal measurements were made in reflected light on polished sections, using a Swift automatic point counter; the three ore components counted were: titaniferous magnetite; ilmenite associated with titaniferous magnetite as grains, and exsolved from it as blebs and lamellae sufficiently large to be removed after crushing to 200 mesh size (cf. fig. 3*b*) during separation for chemical analysis; and separately crystallized ilmenite, in elongate crystals, typically surrounded by silicates, but sometimes connected to the granular aggregates of titaniferous magnetite and ilmenite (fig. 1*b*, *f*, *h*).

The modal determinations consisted of two mutually perpendicular traverses across a polished section, each usually of 1 400 or more counts. In table I the figures for each specimen are the averages of at least two such determinations.

From the figures in tables I and II it may be concluded that in general the ore minerals of average bands contain relatively more granular ilmenite in association with titaniferous magnetite than those of melanocratic bands (table I). Furthermore, the titaniferous magnetites of ores in the average bands are generally more oxidized than those in melanocratic bands (table II), and the titanium in them is usually exsolved as ilmenite; whereas ulvöspinel is commoner in the more reduced melanocratic bands (cf. Vincent and Phillips, 1954; Vincent, 1960). This relationship does not always hold, for in the Middle Gabbro

FIG. 1. (*a*) E.G. 2308. Granular association of ilmenite and ulvöspinel-rich magnetite; both minerals are better-formed than at higher levels in the intrusion, but the association as a whole is interstitial to the surrounding silicates.

(*b*) E.G. 2307. Elongate discrete ilmenite crystal in optical continuity with the ilmenite of the small interstitial ilmenite–titaniferous-magnetite association at its upper end.

(*c*) E.G. 4359. Association of ilmenite and ilmenite-rich magnetite; ilmenite is idiomorphic towards magnetite, but the whole is markedly interstitial towards the silicates.

(*d*) E.G. 4353. Aggregate of elongate discrete ilmenite grains, associated at extreme left with a little titaniferous magnetite.

(*e*) E.G. 2569. Interstitial association of ilmenite and titaniferous magnetite, the ilmenite showing a rather irregular habit towards the magnetite.

(*f*) E.G. 2574. An elongate ilmenite crystal forms part of an interstitial titaniferous-magnetite–ilmenite association. The outer portion would be modally counted as discrete ilmenite.

(*g*) E.G. 2574. Another aggregate of discrete ilmenite crystals, quite well-formed.

(*h*) E.G. 2580. Another example of discrete ilmenite attached to an interstitial association of titaniferous magnetite and ilmenite.

Magnification throughout approx. × 17. S, silicates; I, ilmenite (stippled); ornamented, titaniferous magnetite with lamellae of ulvöspinel and/or ilmenite.

TABLE I. Volume % iron ore minerals (balance is silicates).

Sample.	Titaniferous magnetite.	Ilmenite with titanif. mag.	Separately crystallized ilmenite.
E.G. 5052	5·0	5·9	3·6
5051	27·3	24·2	0·7
2307	7·1	3·7	3·7
2308	32·4	11·2	0·8
4353	5·2	8·0	9·8
4359	13·3	19·9	4·1
2574	3·8	2·6	4·3
2580	3·2	2·5	3·2
2569	20·8	6·0	0·2
4458A	79·2	13·3	—
4355	67·4	16·8	—

TABLE II. Partial analyses of titaniferous magnetites and ilmenites from the Skaergaard intrusion (weight %). Figures in parentheses are estimated from analyses of Skaergaard ilmenites (published by Vincent and Phillips, 1954) at levels in the intrusion similar to those from which the samples under discussion were taken, bearing in mind that the ilmenite in average bands is likely to be slightly more oxidized than that in melanocratic bands.

	Titaniferous magnetite.			Ilmenite.		
	FeO	Fe_2O_3	TiO_2	FeO	Fe_2O_3	TiO_2
E.G. 5052	39·6	41·2	13·2	(40·0)	(4·5)	(51·0)
5051	42·2	34·4	17·4	(40·5)	(4·0)	(51·0)
2307	40·4*	38·8*	15·4*	(40·0)	(4·5)	(51·0)
2308	46·3‡	28·6‡	19·3‡	40·3*	3·9*	51·2*
4353	39·8†	36·8†	15·6†	(40·5)	(5·5)	(50·0)
4359	34·1†	40·7†	18·6†	(40·0)	(6·0)	(50·0)
2574	33·9*	44·7*	17·2*	(41·5)	(4·0)	(51·5)
2580	32·1	46·3	12·8	(41·5)	(4·0)	(51·5)
2569	41·8‡	31·4‡	22·5‡	42·7*	2·6*	52·0*
4458A	42·8	33·2	18·3	(40·0)	(5·0)	(51·0)
4355	40·1†	36·9†	16·6†	(40·0)	(5·0)	(51·0)

* From Vincent and Phillips, 1954, slightly amended values.
† From Vincent *et al.*, 1957.
‡ Mean of two analyses.

pair, E.G. 4353 and 4359 (probably slightly unusual layered-series rocks), not only are the relative modal amounts of titaniferous magnetite and associated granular ilmenite nearly the same (table I), but E.G. 4353, with less ore, carries a more reduced titaniferous magnetite than E.G. 4359, which is richer in ore (table II).

Using the data listed in tables I and II and specific gravity values of 5·0 as a roughly calculated average for titaniferous magnetite, and 4·7 for ilmenite, weight ratios of Fe:Ti have been calculated for the following three ore components: titaniferous magnetites alone; granular aggregates of titaniferous magnetite and ilmenite; and total titaniferous iron oxides, comprising the granular aggregates together with the separately crystallized ilmenite.

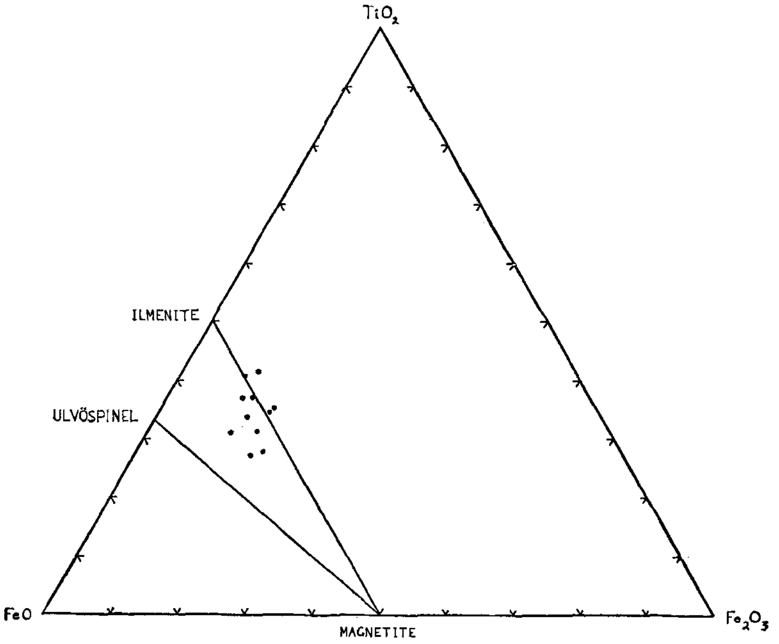

Fig. 2. Calculated molecular compositions of the granular ilmenite–titaniferous-magnetite associations, to illustrate their approximate position within the $FeO–Fe_2O_3–TiO_2$ system.

The ratios are listed in table III and in fig. 2 are shown the calculated mol. % compositions of the granular aggregates in the $FeO–Fe_2O_3–TiO_2$ ternary system.

From table III it is clear that, at a given level in the normal layered series rocks, the weight ratios of Fe:Ti in the titaniferous iron ores of adjacent average and melanocratic bands are much closer for the granular aggregates of titaniferous magnetite and ilmenite than for titaniferous magnetites alone, or for the total ores. Figures in table III

TABLE III. Weight ratios Fe:Ti for titaniferous iron ores in the Skaergaard rocks.

	Titaniferous magnetite.		Granular aggregates of titanif. magn. and ilmenite.		Total titaniferous ores (includes separately crystallized ilmenite).	
Sample.	Fe:Ti	Diff.	Fe:Ti	Diff.	Fe:Ti	Diff.
E.G. 5052 Average band	7·54	2·07	2·34	*0·04*	1·94	0·40
5051 Melanocratic band	5·47		2·38		2·34	
2307 Average band	6·37	1·54	3·12	*0·01*	2·34	0·70
2308 Melanocratic band	4·83		3·11		3·04	
4353 Less melanocratic band	6·04	1·13	2·04	*0·08*	1·61	0·24
4359 More melanocratic band	4·91		1·96		1·85	
2574 Average band	5·60	3·42	2·62	*0·29*	1·87	1·01
2580 Average band	7·45		2·71		1·95	
2569 Melanocratic band	4·03		2·91		2·88	
4458A Transgressive veins	5·14	0·56	3·95	*0·10*	No separately crystallized ilmenite	
4355 Transgressive veins	5·70		3·85			

show that the total titaniferous iron oxides of average bands have the lowest Fe:Ti ratios of all; this is due to the relatively large amounts of separately crystallized ilmenite in them (table I).

It has already been observed that in average bands the titaniferous magnetite is usually more oxidized than in the melanocratic bands. Vincent (Vincent and Phillips, 1954) considered this to be mainly due to differing amounts of interprecipitate liquid relative to ores, in adjacent average and melanocratic bands. The partial dissociation of water at high temperatures in such liquids is generally considered to govern the oxidation-reduction equilibria in crystallizing magmas. There may be other factors involved to account for such anomalous relationships as are observed in E.G. 4353 and 4359, mentioned above; but they need not be considered here.

Assuming that they crystallized as separate entities from the magma, titaniferous magnetites occurring in adjacent bands at a given level of the intrusion would have crystallized from the magma at the same time and therefore under the same conditions. They might therefore be expected to have the same Fe:Ti ratios, irrespective of differing oxidation states resulting from subsequent influence of the interprecipitate liquid. But, as was noted by Vincent and Phillips (1954), the composition of titaniferous magnetites from adjacent bands is very variable, and this is reflected in their greatly differing Fe:Ti ratios (table III). In fact, it is the granular aggregates of titaniferous magnetite and ilmenite that have closely similar Fe:Ti ratios in adjacent bands. It is therefore concluded that *granular aggregates of titaniferous magnetite and ilmenite are the product of exsolution from high temperature solid solutions, which originally separated from the magma as a single crystalline phase.*

The proposed solid solutions may most simply be regarded as members of the cubic binary magnetite–ulvöspinel series (Vincent *et al.*, 1957), in which oxidation of ulvöspinel would result in formation and exsolution of rhombohedral ilmenite. In support of this view may be cited some heating experiments, which have shown that magnetite–ilmenite intergrowths can only be homogenized by reducing the ilmenite to ulvöspinel (Wright, 1959). Other heating experiments, however (Vincent *et al.*, 1957), have indicated that a cubic polymorph of ilmenite, γ-$FeTiO_3$, may well form part of the high-temperature solid solutions, together with magnetite and ulvöspinel. In this case, exsolution of ilmenite would result from simple symmetry inversion as well as by oxidation of ulvöspinel. On this hypothesis, the exsolution processes are rather more complex than those involving merely oxidation of ulvöspinel, but, as they have already been adequately discussed by Nicholls (1955) and Vincent *et al.* (1957), they do not require further comment here. Vincent (1960) has, however, made some pertinent comments on the relative merits of the two hypotheses.

Exsolution from the solid solutions is considered to have commenced with separation of the relatively large idiomorphic ilmenite grains in the aggregates. As the temperature fell, and diffusion processes became more sluggish, ilmenite would cease to exsolve as grains, remaining in the titaniferous magnetite as blebs and ultimately lamellae. Exsolution of ulvöspinel would not commence until about 600° C. or lower, according to present knowledge of the solvus form in the Fe_3O_4–Fe_2TiO_4 binary system (Vincent *et al.*, 1957). Clearly, more ilmenite would have been exsolved in those bands (usually more melanocratic) where interprecipitate liquids were more abundant relative to ore minerals and could oxidize more of the ulvöspinel component in the solid solutions.

The textures illustrated in fig. 1, showing the frequently idiomorphic habit of ilmenite grains towards titaniferous magnetite, are consistent with an origin by exsolution. The interstitial habit of the aggregates as a whole towards silicate minerals, however, indicates that there was some subsequent addition of material from the interprecipitate liquid.

The separately crystallized ilmenite is thought to have separated from the magma after the granular aggregates, because it is mainly confined to the average bands (table I). If it had crystallized before the aggregates, it would chiefly be found in the melanocratic bands, and the Fe:Ti ratios would then have been abnormally low for the total ores of those bands. If, on the other hand, it had crystallized at the same time as the granular aggregates, it would be distributed between adjacent bands in much the same proportions, and the Fe:Ti ratios for the total ore assemblages of those bands would not differ as strikingly as they do (table III, third column).

It has been suggested that the ilmenite accumulated in average bands because it is less dense than magnetite; but ilmenite can be only slightly less dense than magnetite containing as much TiO_2 as these solid solutions presumably did when they first crystallized. Furthermore, both minerals are much denser than the olivine and pyroxene, which mainly accumulate in melanocratic bands; so that contemporaneous crystallization of magnetite-rich solid solutions and separate ilmenite would result in the latter being also mainly confined to the melanocratic bands.

Below about 800 m. in the Skaergaard intrusion, titaniferous iron oxide ores constitute only around 1% of the rocks. Therefore, during early separation of magnesian olivines and pyroxenes, which form most of the lower part of the layered pile, the magma must have become enriched in both Fe and Ti. Titaniferous iron ores would only start to separate in quantity when, broadly speaking, the amount of iron and titanium in the magma had increased sufficiently (cf. Vincent, 1960). But if the magmatic Fe:Ti ratio were not low enough at this stage, conditions in the magmatic environment might well tend to favour formation of cubic magnetite-rich solid solutions, with Fe:Ti ratios of between about 2 and 3 to 1, rather than ilmenite, in which Fe:Ti is only about 1·2 to 1. When these solid solutions crystallized, the entry of relatively larger amounts of iron than titanium into them might well lower the magmatic Fe:Ti ratio sufficiently to permit separation of ilmenite. In this way, a crop of magnetite-rich crystals would separate and accumulate in a melanocratic band, to be followed by ilmenite, which would perforce settle in the overlying adjacent average band. Hence the apparent anomaly of much lower overall Fe:Ti ratios in the total titaniferous ore mineral assemblages of average bands (table III, third column). The main drawback to this simple picture lies in its implication that crystallization of iron oxide ores was periodic rather than continuous, although closely related to the rhythmic pattern of convective circulation in the Skaergaard magma, which was responsible for the layered structure of the intrusion (Wager and Deer, 1939).

The transgressive ore-rich veins. The similarity of Fe:Ti ratios in the two samples from these veins (E.G. 4458A and 4355), both for the titaniferous magnetite components and the overall ore assemblages, is very striking (table III). It may be complete coincidence that two narrow veins 300 m. apart in the layered series should be in almost the same state of oxidation; but they are both transgressive and devoid of separately crystallized ilmenite, and are considered to be somewhat late-stage segregations in the intrusion (L. R. Wager, personal communication), so that these points of resemblance may have genetic significance.

The Schmoo Lake samples.

The six random samples from the Schmoo Lake ore body[1] were also modally analysed, but the modes must be regarded as approximate only; the ore textures are very much coarser than those in the Skaergaard rocks, and representative sections could not be obtained with the size of polished mounts available. There is no separately crystallized ilmenite in these rocks, for which the modes are:

	C.S.L. nos.					
	1	2	3	4	5	6
Titaniferous magnetite . . .	85·5	96·0	82·0	80·5	56·4	82·2
Ilmenite with titaniferous magnetite .	11·9	2·0	11·9	9·8	22·0	13·5

The relative amounts of titaniferous magnetite and ilmenite within the ore body are very variable, as is the composition of titaniferous magnetite. However, overall ore analyses of the samples are available, the relevant parts of which are reproduced in table IV, and show a remarkably constant Fe:Ti ratio for the six samples, although it is rather higher than those for the Skaergaard ores.

Textural features of two Schmoo Lake samples are shown in fig. 3, and these, together with the figures in table IV, indicate that the ilmenite and titaniferous magnetite in the ore body are probably genetically related, by exsolution from original solid solutions, in the same way as the components of similar aggregates in the Skaergaard rocks. As there is no discrete ilmenite, all the titanium in the Schmoo Lake ores was used in the formation of the solid solutions, which table IV shows to have Fe:Ti ratios higher than any in the Skaergaard.

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[1] A titaniferous iron ore segregate in Precambrian anorthosites at Lac la Blache, Saguenay County, Quebec. The samples, C.S.L. nos. 1 to 6, were kindly provided by Dr. J. P. Girault.

TABLE IV. Chemical analyses of Schmoo Lake titaniferous magnetite and overall ore analyses, with Fe: Ti ratios.

C.S.L.	Titaniferous magnetite.				Overall ore analysis.		
no.	FeO	Fe_2O_3	TiO_2	Fe:Ti	Fe	TiO_2	Fe:Ti
1 . .	34·7	37·4	20·5	4·32	48·43	21·86	3·69
2 . .	45·0*	25·8*	21·9*	4·06	48·36	21·35	3·78
3 . .	43·4*	29·3*	21·3*	4·24	48·25	21·78	3·69
4 . .	34·6	40·7	17·7	5·22	48·12	21·44	3·74
5 . .	33·8*	51·7*	9·4*	11·17	46·93	20·12	3·89
6 . .	42·7	31·4	19·1	4·80	48·19	20·70	3·88
Max. diff. in Fe:Ti ratio			7·11				0·20

* From Vincent *et al.*, 1957, table I.

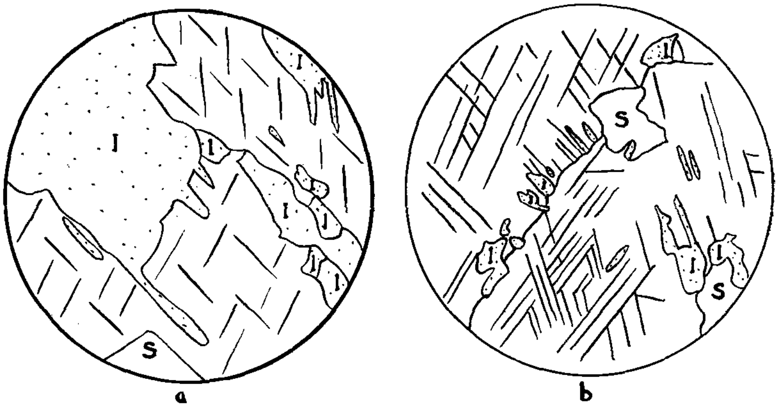

FIG. 3. (*a*) C.S.L. no. 5. Lamellae project into titaniferous magnetite from ilmenite grains, which are idiomorphic towards it.

(*b*) C.S.L. no. 4. Ilmenite blebs pass into long lamellae in titaniferous magnetite. The blebs and broader lamellae are large enough to be removed during separation for analysis (p. 781).

Magnification approx. ×20. S, silicate; I, ilmenite (stippled); ornamented, titaniferous magnetite with lamellae of ilmenite.

Conclusions.

Features of titaniferous iron oxide ores described and discussed here point to an origin by exsolution for granular aggregates of titaniferous magnetite and ilmenite, rather than by simultaneous crystallization. On the latter hypothesis it would be necessary to postulate two generations of ilmenite crystallized direct from the Skaergaard magma, the first preceding the titaniferous magnetite with which it is associated (because of its frequently idiomorphic habit towards the latter), the second forming the separately crystallized ilmenite. But it is more difficult to explain how separate crystallization, even if simultaneous, followed by clustering of titaniferous magnetite and ilmenite grains into aggregates, can account for consistently similar Fe:Ti ratios in the aggregates of adjacent bands—one would expect them to be as variable as those of the other ore components.

In rocks lacking separately crystallized ilmenite it is possible that granular aggregates of ilmenite and titaniferous magnetite would always have Fe:Ti ratios greater than 3—as in the transgressive veins of the Skaergaard, and the Schmoo Lake ores. Values of around 3 or less for this ratio would then be the expression of sufficient titanium in the original magma to permit separate primary crystallization of ilmenite—as in the normal layered Skaergaard rocks. These figures are further supported by calculations based on approximate data for titaniferous ores separated from two Cuillin gabbros. There is no separate ilmenite, and Fe:Ti is around 4·3:1 for the granular aggregates of titaniferous magnetite and ilmenite.

Further work with titaniferous ores of other basic rocks is necessary before the conclusions arrived at above can be confirmed. In ores where there is no separate ilmenite component, as in the Schmoo Lake samples, overall analyses of separated ore minerals can be made, obviating the errors inherent in calculations based on chemical and modal analyses. Such calculations become necessary, however, once a separate ilmenite phase is present, although they need not take the form of those used here.

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