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MICROTEXTURES OF Fe-Ti OXIDE MINERALS IN THE SOUTH-ROGALAND ANORTHOSITIC COMPLEX (NORWAY)

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ABSTRACT

Ilmenite and magnetite in anorthositic and related rocks (South-Rogaland igneous complex - S.W. Norway) are investigated from the point of view of their micro-textures.

The microtextures of the ilmenite result from simple exsolution of ilmenite-hematite solid solutions. Hematite lenses appear when the hematite content is higher than 7 to 9 mole percent Hem. Magnetite contains intergrowths of ilmenite according to two extreme types of microtexture : the cloth microtexture and the trellis microtexture (including its sandwich variant). Both types may coexist in the same grain. This ilménite is formed by oxidation of ulvöspinel, initially contained in the magnetite, at temperatures above or below the solvus magnetite-ulvöspinel. Arguments leading to rejection of the γ-$FeTiO_3$-Fe_3O_4 solid solution hypothesis are given.

Primary ilménite adjacent to a magnetite grain shows a zonal variation of hematite content. A rim of spinelliferous secondary ilmenite, in optical continuity with the neighbouring primary ilmenite grain, is also observed at the contact. It is shown that this secondary ilmenite is also produced by oxidation of ulvöspinel initially contained in the magnetite. Rim and zoning at the contact between ilmenite and magnetite indicate that a subsolidus reaction has brought about a deuteric readjustment of the initial orthomagmatic compositions. This phenomenon has to be taken into account when applying the geothermometer and oxygen fugacity barometer of Buddington and Lindsley.

RÉSUMÉ

Les microstructures de l'ilménite et de la magnétite sont étudiées dans les roches du complexe anorthositique du Rogaland méridional {Norvège méridionale}.

Les microstructures de l'ilménite résultent d'un simple processus de démixtion de la solution solide ilménite-hématite. Les lentilles d'hématite apparaissent seulement pour des teneurs en hématite supérieures à 7-9 % mol Hém. La magnetite contient des intercroissances d'ilménite disposées selon deux types extrêmes de microstructure : la microstructure en tissu et la microstructure en treiilis (et sa variante en sandwich}. Les deux types peuvent coexister dans un même grain. Cette ilménite est formée par oxydation d'ulvöspinelle initialement en solution solide dans la magnetite, cette oxydation commençant à des températures supérieures ou inférieures à celles du solvus magnétite-ulvöspinelle. L'hypothèse de l'existence d'une solution solide γ-$FeTiO_3$-Fe_3O_4 est discutée et rejetée.

L'ilménite primaire, lorsqu'elle est en contact avec un grain de magnétite, montre à proximité du contact un zonage de son contenu en hématite. Un cordon d'ilménite spinellifère, en continuité optique avec l'ilménite primaire voisine, est également présent au contact. Cette ilménite secondaire est produite par oxydation d'ulvöspinelle présent dans la magnétite. Cordon et zonage indiquent qu'une réaction subsolidus intervient quand les deux oxydes sont en contact et provoque une réadaptation deutérique de leur composition orthomagmatique. Ce phénomène doit être pris en considération dans l'utilisation des valeurs de la température et de la fugacité de l'oxygène déduites des travaux de Buddington et Lindsley.

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INTRODUCTION

Ilmenite and magnetite are widespread minerals in rocks. However, their study was often neglected by petrologists and remained for a long time in the sphere of applied geologists and ore microscopists.

VINCENT & PHILLIPS (1954) and BUDDINGTON & co-workers (1955) were among the first to investigate the Fe-Ti oxides while considering them as normal constituents of the rocks, just like the transparent minerals. More recently BUDDINGTON & LINDSLEY (1964) have put forward the use of coexisting ilmenite and magnetite as a geothermometer and oxygen barometer. Their work showed the importance of oxides minerals in petrogenetic studies.

The present author has studied the Fe-Ti oxides in the South-Rogaland anorthositic complex (S.W. Norway), particularly in the Bjerkrem-Sogndal layered lopolith (DUCHESNE, 1969). A recent review of the geology and petrology of the complex is to be found in MICHOT & MICHOT (1970) and MICHOT (1970). The present paper endeavours to present a synthetic description of the different types of micro-textures observed in the oxides and to discuss their mode of formation. The observations mainly refer to the Bjerkrem-Sogndal massif and to the most typical ore-bodies occurring in the neighbouring anorthositic massifs (HUBAUX, 1960). Some data concerning the La Blache Lake deposit (Quebec) and the Iron Mountain ore body (Wyoming) are also given.

MICROTEXTURES OF ILMENITE

Under the microscope primary ilmenite frequently contains thin hematite lenses arranged in the {0001} planes of the host mineral (Pl. 1, fig. a & b).

These hematite lenses arise through exsolution, as demonstrated experimentally by RAMDOHR (1926). Ilmenite and hematite form an extensive solid solution at high temperature. The solvus was recently reinvestigated by CARMICHAEL (1961).

Chemically, the ilmenites studied here can be expressed essentially as ilmenite (RTO_3) -f hematite (R_2O_3), with the latter ranging from 1 to 20 mole per cent (Table 1 & fig. 1). Exsolution of hematite appears only when the hematite content exceeds 7 to. 9 mole percent. In accordance with the terminology of BASLEY & BUDDINGTON (1958} they are called hemo-ilmenite. As already stressed by these authors, the abundance and size of the hematite lenses vary with the hematite content. It is therefore possible to carry out an approximate determination of the Hem content by means of the microscope (see Appendix I). Below 7 mol % Hem, exsolution is not visible. In this case, the ilmenite is called homogeneous. This limit is very near the value put forward by RAMDOHR (1960). Above 18 mol % Hem two generations of hematite lenses are clearly visible and inside the coarser lenses fine scale exsolution of ilmenite can be observed. Occasional minute lenses of AI-spinel can be observed in the {0001} planes of the host ilmenite or host hematite.

Taking into account the maximum Hem content of the ilmenite found in the samples here investigated (about 20 mole percent Hem — Table 1, anal. 1) and the experimental solvus determined by Carmichael *(op. cit.),* the exsolution phenomenon appears to have taken place at temperatures lower than 450° C.

MICROTEXTURES OF MAGNETITE

One of the essential characteristics of the magnetites considered here lies in their chemical composition which can be expressed in terms of magnetite (R_3O_4) and ilmenite (RTO_3) (Table 2 & fig. 1). An extensive chemical study has moreover shown that this appears to be the rule in the igneous province, irrespective of the massif or the kind of rock (DUCHESNE, 1969).

Under the microscope, magnetite contains intergrowths of ilmenite ; all variations occur between two extremes : i) the cloth microtexture, ii) the trellis microtexture and its sandwich variant.

In the *cloth microtexture (*Pl. 1, fig. c to f), ilmenite shows up in submicroscopic lamellae set out in the {111} planes of the magnetite but exclusively situated inside coarser lamellae (fig. 2B), which are themselves arranged in the {100} planes of the host-magnetite (fig. 2A). It is the coarse {100} lamellae pattern which gives the grain the appearance of a cloth (cloth-structure of RAMDOHR, 1953). The same cloth intergrowth is also characteristic of the ulvöspinel exsolutions in the magnetite as shown by RAMDOHR (1953), GIRAULT (1953), NICKEL (1958), VINCENT (1960), BASTA (1960) and ANDERSON (1968) among others.

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***TABLE 1 :** Chemical analyses of ilmenites*

	1	2	3	4	5	6	7
FeO	32.75	36.07	36.7	39.11	42.17	39.9	44.00
MnO	.24	.35	.28	.39	.46	.50	.71
MgO	1.97	.78	1.97	1.36	.74	3.25	.72
CaO	.04	.11	.10	.10	.10	.03	.12
Fe_2O_3	20.3	16.75	13.2	9.48	6.18	3.7	2.51
$A1_2O_3$	.15	.33	.30	.46	.34	.05	.20
V_2O_3	.37	.28	.23	.17	.09	.05	.01
Cr_2O_3	.04	.10	.04	—	—	—	—
TiO_a	44.0	43.80	46.1	47.65	49.11	52.3	50.88
SiO_2	.1	.63	.5	.78	.55	.35	.46
S	—	.15	.20	.30	.20	—	.17
O ≡ S	99.96	99.35	99.62	99.80	99.94	100.13	99.78
	—	.07	.10	.15	.10	—	.08
Total	99.96	99.28	99.52	99.65	99.84	100.13	99.70
RO	510	528	566	585	613	645	642
R_2O_3	131	111	88	65	43	24	18
TO_2	552	558	585	608	623	660	644
RO (mol, %)	42.7	44.1	45.7	46.4	48.0	48.5	49.3
R_2O_3 (id.)	11.0	9.3	7.0	5.2	3.3	1.8	1.4
TO_2 (id.)	46.3	46.6	47.3	48.4	48.7	49.7	49.4
Hem (mol. %)	20.5	17.4	13.4	10.0	6.5	3.6	2.6

Fe_{total} Ti by X-ray fluorescence spectrometry (borate fusion);
Fe2+ by titration with $K_aCr_aO_7$;
Mn, Ca, Ai, Si, S by X-ray fluorescence spectrometry (pressed powder);
Mcr, V, Cr by optical emission spectrography.

1. Hemo-ilmenite — Kydlandsvatn ore (6496).
2. id. — Bjerkrem-Sogndal massif (average of 10 samples).
3. id. — Storgangen ore (64146).
4. id. — Bjerkrem-Sogndal massif (average of 9 samples).
5. Homogeneous ilmenite — ibid, (average of 6 samples).
6. id. — Iron Mountain (Wy.) ore (IMW).
7. id. — Bjerkrem-Sogndal massif (average of 20 samples).

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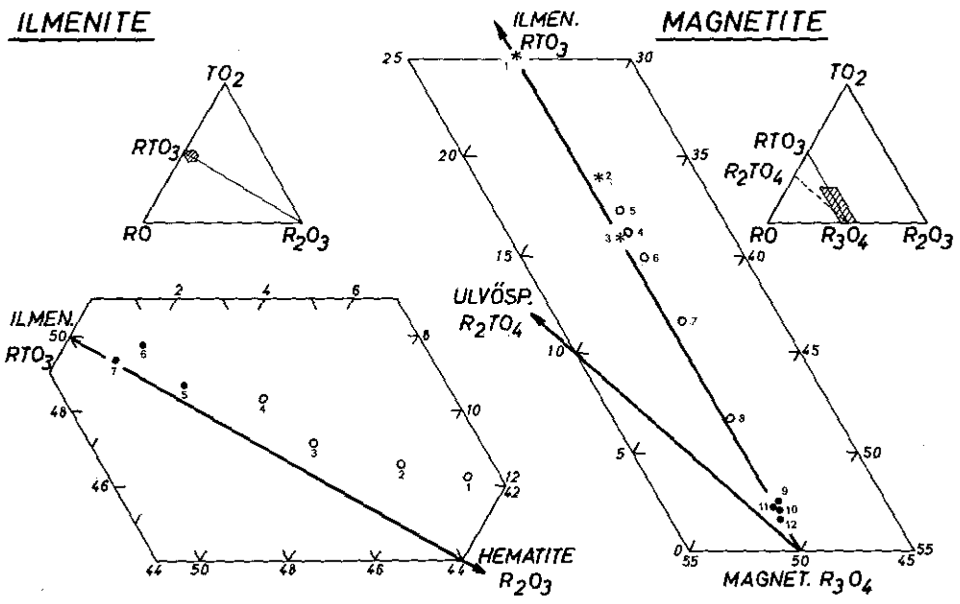
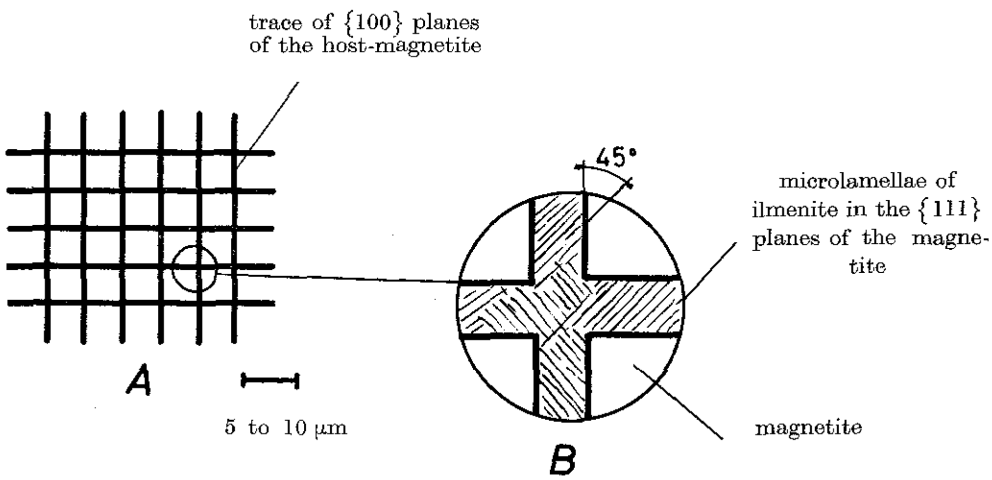
Fig. 1. Chemical analyses given in Tables 1 and 2 plotted in terms of RO, R_2O_3, TO_2 (mole percent).



For the ilmenite : o : hemo-ilmenite
• : homogeneous ilmenite
For the magnetite : * : cloth microtexture ;
o : trellis, sandwich and intermediates between cloth and trellis;
• : homogeneous magnetite.

Fig. 2. Cloth microtexture (section // to {100}).



A. Reticulation parallel to the {100} planes of the magnetite. In white, the host-magnetite; in black, lamellae of oxidized ulvöspinel.
B. Internal structure of dark lamellae at higher magnification : microlamellae of ilmenite in the {III} planes of the host.

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Ulvöspinel {Fe_2TiO_4 or R_2TiO_4) was synthesized by BARTH & POSNJAK (1932) and discovered in nature by MOGENSEN (1946) as intergrowths in the magnetite of the Södra Ulvön ore. It has the inverse spinel structure like magnetite and forms with magnetite a complete solid solution at temperature higher than 600° C, as was experimentally recognized by several workers (CHEVALLIER et al., 1955; VINCENT et al., 1957; BASTA, 1960; LINDSLEY, 1962). On cooling ulvöspinel forms exsolution lamellae in {100} planes of the magnetite. Pure ulvöspinel is only stable under very low oxygen fugacities, as was calculated by VERHOOGEN (1962). It has never been found on the earth[1] as an independent mineral but only as an exsolution product.

In the South-Rogaland occurrences, ulvöspinel has never been demonstrated either by chemical analysis or by X-ray diffraction. The following mechanism may explain the absence of ulvöspinel in the cloth microtexture of the magnetites studied. The {100} lamellae of the cloth were generated by exsolution of ulvöspinel and then, at a temperature below the magnetite-ulvöspinel solvus, ulvöspinel was completely transformed into microlamellar ilmenite through in situ oxidation. The reaction is

$$6\ Fe_2TiO_4 + O_2 \rightarrow 6\ FeTIO_3 + 2\ Fe_3O_4 \qquad (1)$$

It implies a simple addition of oxygen to the magnetite without sensible change in volume. It can then be concluded that in the cloth magnetite the only Ti compound soluble in magnetite at high temperature is the ulvöspinel.

The cloth microtexture can easily be detected by means of a brief HC1 etching. The ilmenite microlamellae are difficult to discern except when the reticulation is particularly coarse. However, between crossed nicols, one can frequently observe an extinction at 45° of the coarse {100} lamellae.

Rocks in which all grains of magnetite are cloth-microtextured occurred in the Bjerkrem-Sogndal massif (Bakka-Örsland, Table 2 anal. 1 & 3) and in the Eigeroÿ ore (Table 2, anal. 2). These are always rich in Ti but not all Ti-rich magnetites necessarily show this microtexture.

In the *trellis microtexture,* the {111} ilmenite lamellae are distinctly thicker and form a network with regular meshes suggesting a trellis (Pl. 1, fig. g). If one set of {111} planes is privileged, the grain of magnetite takes on the aspect of a sandwich (HUBAUX, 1956; BUDDINGTON & BASLEY, 1961) (Pl. 1, fig. h). When aluminous spinel is present in the magnetite, these ilmenite lamellae are dotted with, spinel micro-crystals.

When magnetite is surrounded by a network of ilmenite lamellae the network may appear either on a background of homogeneous magnetite, or on cloth-microtextured magnetite. This last point shows that both types of microtexture (namely a trellis and a cloth) can coexist inside the same grain.

From one rock to another, and even in some cases to be examined further on in different grains in the same rock, the proportion of trellis and cloth may vary considerably. In fact a continuous series of intermediates is found between cloth magnetites exempt from large ilmenite lamellae and magnetite with a trelhs of ilmenite lamellae on a homogeneous background from which cloth intergrowth is totally absent. In between these two extremes there exists, alongside the ilmenite lamellae of the trellis, a zone where the cloth gives place to a homogeneous Ti-poor magnetite (PL II, fig. a & b). This zone is less quickly etched by HC1 than the adjacent cloth and therefore appears clearer. In certain cases the transition between cloth and trellis lamellae is expressed by a zoning which is clearly demonstrated through HC1 etching (Pl. II, fig. c & d). Clear zone and zoning show the existence of a gradient of concentration (mainly of Ti; see Appendix 2) in the vicinity of the trellis lamellae.

The sandwich microtexture is a variant of the trellis microtexture. It is not due to simultaneous crystallization of magnetite and primary ilmenite as was put forward by HUBAUX (1956, 1960).

As a result of the decrease in Ti content the density of the network decreases, and eventually the magnetite tends to become homogeneous and only exceptionally contains one or two very thin ilmenite lamellae. Its chemical Composition approaches the R_3O_4 pole (Table 2, anal. 9 to 12) and falls near the ilmenite-magnetite join[2].

[1] In the Mare Tranquillitatis moon samples, ulvöspinel is mentionned as a common accessory mineral (Bailey et al.; Brown et al.; Cameron; Keil et al.; Ramdohr et al.; Simpson et al., in «Apollo 11 lunar science conference», *Science,* 167, n° 3918) thus indicating lower oxygen fugacities than on the earth.

[2] FOSLIE (1928) has published an analysis of the magnetite coming from the Storgangen ore which shows a great excess of FeO after recalculation in terms of Fe_2TiO_4-Fe_3O_4. Our analyses of the Storgangen magnetite (Table 2, anal. 10) and of other occurrences of almost homogeneous magnetite (Table 2, anal. 9 to 12) do not show this particularity.

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Exsolution of aluminous spinel is frequent in the {100} planes of the magnetite. Electron-probe microanalysis of exsolved lamellae in two magnetites of the Bjerkrem-Sogndal massif gives the following compositions $Mg_{.52}Fe_{.47}Zn_{.01}Al_2O_4$ and $Mg_{.32}Fe_{.58}Zn_{.10}Al_2O_4$. The Zn content should be noted, particularly in the second specimen (5.1 % ZnO).

When the magnetite comes more than 2 % Al_2O_3 two generations of lens-shaped exsolution are visible. In the cloth-magnetite the lenses of the first generation are usually surrounded by box-like structures (P1. I, fig. c & e), defined by RAMDOHR (1953). The occurrence of spinel microcrystals in the ilmenite lamellae of the trellis has already been mentioned. Such an ilmenite + spinel association is also found in the rims observed at the contact between grains of primary ilmenite and magnetite (Pl. II, fig. e to h) (see below). Electron-probe microanalysis shows no significant difference of composition between the spinel microcrystals of the rim and the {100} spinel lamellae. A decreasing frequency of fine spinel lenses of the second generation is perceptible in the zone contiguous with the ilmenite lamellae and with the ilmenite + spinel rims. Finally occasional ropes of spinel granules can be observed between two grains of magnetite.

TABLE 2 *Chemical analyses of magnetites*

	1	2	3	4	5	6	7	8	9	10	11	12
FeO	36.7	33.8	33.7	32.3	34.2	33.70	32.41	31.95	30.94	31.1	31.3	31.2
MnO	.57	.33	.22	.27	.41	.26	.14	.06	.01	.006	.01	.01
MgO	.63	.70	.90	1.4	.04	.12	.65	.53	.46	.50	.50	.53
CaO	.16	.07	.16	.03	.24	.18	.15	.11	.04	.02	.01	.06
ZnO	.21	.21	.21	.05	.22	.18	.17	.13	.06	.04	.04	.03
Fe_2O_3	39.2	47.6	49.7	49.2	51.4	53.5	54.44	59.26	64.12	63.5	63.5	64.0
$A1_2O_3$	1.4	1.8	2.1	2.1	.8	1.05	2.83	2.35	1.55	.87	.98	1.35
V_aO_3	.04	.38	.21	1.35	.06	—	.41	.87	1.10	.91	1.01	1.20
Cr_2O_3	—	.30	—	.20	—.	—	—	—	—	1.20	.64	.10
TiO_a	19.2	14.2	10.9	12.0	10.9	9.13	7.26	3.77	.71	.55	1.00	.45
SiO_a	1.5	.6	1.2	.6	2.0	1.7	1.17	.86	.79	.65	.40	.45
S	.38	—	.23	.08	.10	.10	.16	.20	.10	.25	.15	.18
O ≡ S	99.99	99.99	99.53	99.58	100.09	99.98	99.79	100.09	99.88	99.60	99.54	99.56
	.19	—	.12	.04	.05	0.5	.08	.10	.05	.12	.07	.09
Total	99.80	99.99	99.41	99.54	100.09	99.93	99.71	99.99	99.83	99.48	99.47	99.47
KO	527	497	491	486	485	477	469	456	440	438	444	442
R_2O_3	259	321	333	339	330	346	371	401	423	420	418	423
TO_2	265	188	156	160	169	143	110	61	22	18	19	13
RO	50.1	49.5	50.1	49.5	49.3	49.5	49.4	49.7	49.7	50.0	50.3	50.3
R_2O_3	24.6	31.9	34.0	34.3	33.5	35.7	39.0	43.6	47.8	48.0	47.5	48.2
TO_2	25.2	18.7	15.9	16.2	17.2	14.8	11.6	6.7	2.5	2.0	2.2	1.5

Fe_{total} Ti by X-ray fluorescence spectrometry (borate fusion);
Fe+2 by titration with $K_aCr_aO_7$;
Mn, Ca, Zn, Al, Si, S by X-ray fluorescence spectrometry (pressed powder);
Mg, V, Cr by optical spectrography.
The mole number of RO is calculated after subatraetion of a normativ pyrrhotite.

1. Cloth microtextured magnetite — Bjerkrem-Sogndal massif (Bakka-Orsland) (66216).
2. id. — Eigeroy ore (6604).
3. id. — Bjerkrem-Sogndal massif (Bakka-Orsland) (8482).
4. Trellis microtextured magnetite — Iron Mountain (Wy.) ore (IMW).
5. Sandwich microtextured magnetite — Bjerkrem-Sogndal massif (66261).
6. Trellis, sandwich and cloth microtextured magnetite — ibid, (average of 2 samples).
7. Trellis and cloth microtextured magnetite — ibid. (aver. of 5 samples).
8. id. — ibid. (average of 5 samples).
9. Homogeneous magnetite — ibid. (average of 5 samples).
10. id. — Storgangon ore (64146).
11. id. — Kydlandsvatn ore (64 96).
12. id. — Rodemÿr ore (6616).

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ORIGIN AND MODE OF FORMATION OF THE TRELLIS INTERGROWTH

As already explained microlamellar ilmenite present in the cloth microtexture is formed by oxidation of ulvospinel. CHEVALLIER *et al.* (1955), followed by several workers, have suggested that ilmenite may be soluble in magnetite at high temperature in form of γ-$FeTiO_3$ (see discussion in BUDDINGTON & LINDSLEY, 1964). So, the possibility that the trellis and sandwich intergrowths were formed by direct exsolution rather than by oxidation is to be considered.

This alternative seems unlikely since the two extreme types of microtexture — trellis on homogeneous background and cloth — are found in magnetite of the same bulk composition (see fig. 1) and hence the type of microtexture does not depend upon the initial Ti content of the magnetite. Moreover, since there exists a whole series of intermediates between cloth and trellis, the one disappearing to make place for the other, a genetic relationship between the two forms of ilmenite may be legitimately assumed.

Thus, the only Ti compound soluble in magnetite at high temperature appears to have been ulvöspinel, and the initial magnetite was a magnetite (R_3O_4)-ulvöspinel (R_2TO_4) solid solution.

Different modes of oxidation of ulvöspinel may account for the diversity of the microtextures observed. It can be assumed (1) that oxidation of ulvöspinel occurs over a wide range of temperatures; (2) that the temperature at which the process begins may be-above or below the magnetite-ulvöspinel solvus.

If oxidation begins at a relatively low subsolvus temperature, ilmenite is formed in difficult conditions of diffusion and shows up where the ulvöspinel has previously exsolved. As a result microlamellar ilmenite occurs inside the {100} lamellae of the cloth intergrowth (case n° 1, fig. 3). It may also be presumed that if oxidation occurs at a higher subsolvus temperature, Fe and Ti liberated by the oxidation of ulvöspinel can migrate towards the {111} planes to form trellis lamellae of ilmenite (case n° 2, fig. 3). A zoning appears when this subsolvus diffusion becomes more difficult with the decrease of temperature.

If, on the contrary, oxidation begins at a supersolvus temperature, the ulvöspinel dissolved in the magnetite is oxidized and (supersolvus) ilmenite is formed in the {111} planes to produce trellis lamellae. Supersolvus oxidation may be related to the total amount of ulvöspinel contained in the magnetite ; a trellis on a homogeneous background is then obtained (case n° 6, fig. 3). If the supersolvus oxidation is only partial it can be considered either that a quick diffusion maintains a uniform concentration of Fe and Ti in the non-oxidized part of the magnetite, and this down to the solvus; or that a concentration gradient appears before the solvus is reached. Below the solvus, the non-oxidized residue of ulvöspinel is exsolved in {100} planes and one is led either to case n° 4, fig. 3, or to case n° 3, fig. 3, according to whether or not one accepts that a subsolidus diffusion is possible in connection with the oxidation of the ulvöspinel. In case n° 4, some subsolvus ilmenite continues to feed the pre-existing lamellae of the trellis, a diffusion which determines the zoning (as in case n° 2, above) ; in case n° 3, the zoning is entirely produced at supersolvus temperatures, and the ilmenite of the trellis is not re-formed at subsolvus temperatures. The processes responsible for cases n° 2, 3 and 4 lead eventually at low temperature to the same type of microtexture, an ilmenite trellis on a background of zoned cloth.

Case n° 5, fig. 3 has not been observed in the South-Rogaland rocks but it occurs in a sample of La Blache Lake ore (Quebec) which shows a trellis of {111} ilmenite lamellae on a cloth microtextured background of non-oxidized ulvöspinel and magnetite. This association can be explained as a variant of case n° 4, in which no subsolvus oxidation would have taken place. It must be emphasized that in this microtexture the ulvöspinel-magnetite cloth is directly in contact with the lamellae of the trellis, without any zoning. This shows that the zoning may be due to subsolvus oxidation.

The occurrence of a trellis or a sandwich intergrowth indicates that the oxidation has started at a higher temperature than in the case of a cloth micro-textured grain of the same bulk composition, where oxidation takes place entirely subsolvus. In the same way the coarseness of the ilmenite lamellae in the sandwich intergrowth relative to that in the trellis is presumably due to a higher temperature of oxidation.

Difference in the mobility of the elements involved in the oxidation-exsolution process is to be emphasized. Oxygen has a greater mobility than Fe and Ti. Indeed in the case of a cloth magnetite, it can easily penetrate the magnetite at subsolvus temperature whereas there is extremely little diffusion of Fe and Ti to form micro-lamellar ilmenite. Zoning appears to be due to a difficult migration of Fe and Ti rather than to a difficulty of penetration by oxygen.

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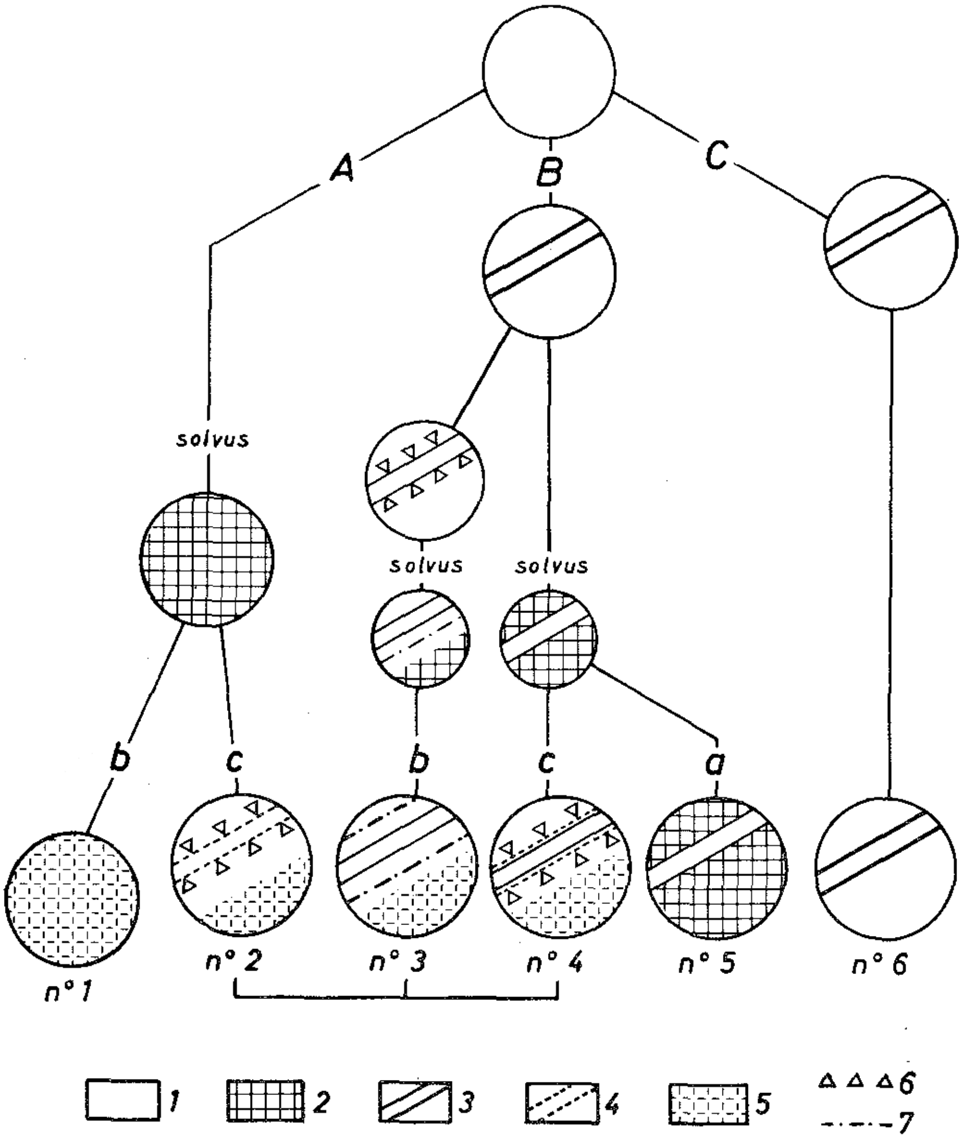
Fig. 3. — Schematic synthesis of the different modes of oxidation of a Ti-rich magnetite leading by decreasing temperature to the different types of microtextures observed.



Above, magnetite at high temperature (homogeneous ulvöspinel-rich solid solution). Below, the different types of observed microtextures (n° 1 to n° 6).

A : no supersolvus oxidation.
B : partial supersolvus oxidation.
C : total oxidation.
a : no subsolvus oxidation.
b : subsolvus oxidation without diffusion.
c : subsolvus oxidation with diffusion.

1. homogeneous magnetite; 2. cloth intergrowth of ulvöspinel and magnetite; 3. trellis lamellae of ilmenite formed supersolvus; 4. trellis lamellae of ilmenite formed subsolvus; 5. cloth intergrowth of ilmenite and magnetite; 6. concentration gradient; 7. zoning and/or clear zone.

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PHENOMENA AT THE CONTACT BETWEEN OXIDES

Magnetite and primary ilmenite frequently coexist in the same rock. At the contact between these two minerals, one may observe a rim of spinelliferous ilmenite and in the primary ilmenite a zone of progressive improverishment in the hematite content, which is called zoning.

The rim, of spinelliferous ilmenite (Pl. II, fig. e to h).

The rim is constituted by ilmenite dotted with spinel microcrystals. This ilmenite is in optical continuity with the neighbouring grain of primary ilmenite. The rim, of the order of 50 µm wide, can present indentations and swellings which always point to the interior of the magnetite grain. Locally it can be connected with the ilmenite lamellae of the trellis intergrowth. In the magnetites with trellis on cloth background the rim is lined by a zone where the cloth gives place to a homogeneous magnetite. Since the same ilmenite + spinel association and the same clear zones are observed in and alongside the ilmenite lamellae of the trellis, as well as in and alongside the rims, the latter can be considered to be produced similarly by oxidation of ulvöspinel contained in the magnetite. However, instead of arranging itself in {111} planes of the magnetite, this secondary ilmenite localises itself at the contact of the neighbouring grain of primary ilmenite. The size of the rim favours the interpretation that it was formed at relatively high temperature. However the existence of a clear zone at its periphery could signify equally that the rim was also partially formed subsolvus.

The spinel microcrystals can be arranged in one or several regular fringes inside the rim. However their size and distribution can often be very irregular.

The zoning of primary ilmenite.

Zoning of primary ilmenite exists in the zone adjacent to magnetite grains. It is due to a progressive decrease of the hematite content towards the contact.

In hemo-ilmenites zoning is observed under the microscope (Pl. II, fig. h). In a zone 20 to 80 µm from the contact, the number and size of the hematite lenses both decrease and eventually disappear. Inhomogeneous ilmenites, the hematite content (< 7 mol % Hem) is too low for the exsolution to be visible. Zoning can, however, be demonstrated with the electron-probe analyser.

Quantitative electron-probe microanalyses (following the method of SWEATMAN & LONG, 1969) were carried out on ilmenites of two different rocks : a norite and a mangerite of the Bjerkrem-Sogndal massif. The results of Table 3 are averages of several measurements in core and rim in several ilmenite grains. Differences observed[3] are significant from the chemical point of view.

FeO is calculated by the following formula

$$TiO_2/(MnO + FeO + 1.8\ MgO) = (TiO_2/FeO)_{in\ ilm} = 1.11$$

Fe_2O_3 is calculated by difference. The increase of MnO with the FeO content is to be noted. A similar relationship has been recognized in ilmenites separated from a large number of rocks (DUCHESNE, 1969).

This zoning never occurs at the contact with silicates or between two ilmenite grains. It reflects migrations in the ilmenite at supersolvus temperature. In the Kydlandsvatn ore (Table 1, anal. 1) hemo-ilmenite has the highest Hem content (about 20 mole %) found in the whole magnetite province and zoning appears at the contact with homogeneous magnetite. It can then be inferred that the migration inside the hemo-ilmenite took place at temperatures above 450° C.

[3] The secondary fluorescence excitation (LONG, 1967) due to the proximity of magnetite (which is richer in Fe and poorer in Ti than the ilmenite) is not taken into account. The observed difference for Ti and Fe between core and rim could therefore be smaller than the real one (J. V. P. LONG, personal communication). This could only confirm our conclusions.

TABLE 3

	Norite		Mangerite	
	CORE	RIM	CORE	RIM
FE_{total} (as FeO)	47.4	45.7	47.2	46.4
MnO	.50	.58	.78	.94
MgO	1.15	1.23	tr	tr
Al_2O_3	.15	.15	tr	tr
TiO_2	50.4	52.2	51.3	51.9
SiO_2	ND	ND	.15	.16
	99.60	99.86	99.43	99.55
FeO	42.9	44.3	45.5	45.8
Fe_2O_3	5.0	1.6	1.9	.7

tr : traces ND : not determined.

Contact phenomena commonly occur in all rocks and ores investigated in South-Rogaland. They were noticed by FOSLIE (1928) and EVEAKD (1944) who mentionned zoned hemo-ilmenite in the Storgangen and in the Haaland ore-bodies. In other provinces similar zoning is reported by ANDERSON (1966) in the Labrieville anorthosite and by KRETSCHMAR & MCNUTT (1969) in the order facies of the Whitestone anorthosite. Rims of ilmenite were described by SINGEWALD (1923} in the Iron Dam (N.Y.) ore and by WRIGHT (1961) in the La Blache Lake deposit. The present author has observed spinelliferous ilmenite rims in the Iron Mountain (Wy.) ore also[4]. More generally, BUDDINGTON & LINDSLEY (1964) pointed to granules of ilmenite on the external border of the magnetite which they attributed to an external granule « exsolution » process. However they did not refer to zoning in the ilmenite.

Rim and zoning indicate that a reaction took place between the oxides at the subsolidus stage of the history of the rock. Owing to intergranular diffusion, primary ilmenite can act as an oxidant with respect to the neighbouring magnetite grain, according to the reaction

$$Fe_2TiO_4 + Fe_2O_3 \rightarrow FeTiO_3 + Fe_3O_4 \qquad (2)$$

in which Fe_2TiO_4 and Fe_2O_3 are contained in the magnetite and ilmenite respectively. Equations (1) (p. 53) and (2) define the system Ilmenite-Magnetite-Oxygen in which the solid phases are solid solutions of $FeTiO_3$ + Fe_3O_2 and Fe_2TiO_4 + Fe_3O_4 respectively (LINDSLEY, 1962 & 1963). In the presence of a fluid phase the-chemical composition of each solid phase is controlled by temperature and oxygen fugacity only (the influence of total pressure being negligible). Thus, if in the subsolidus stage a magmatic fluid remains entrapped in the interstices between the minerals, equilibrium between oxides and fluid may be maintained and, as a consequence of the temperature decrease, chemical compositions will change. Contact phenomena are evidence of this deuteric readjustment of orthomagmatic chemical compositions.

CONCLUSIONS

During slow cooling at the subsolidus stage of the history of the rock oxide minerals do not remain homogeneous. Ilmenite and magnetite undergo processes of exsolution and oxidation-exsolution respectively. The variety of microtextures found in magnetite can be explained by oxidation starting at different temperatures relative to the temperatures of the ulvöspinel-magnetite solvus. The trellis and sandwich intergrowths are formed by oxidation starting at supersolvus temperatures ; the cloth is entirely oxidized subsolvus. The γ-$FeTiO_3$-Fe_3O_4 solid solution hypothesis is rejected in favour of a Fe_2TiO_4-Fe_3O_4 solid solution.

Rims and zoning show that, when both oxides are in contact, neither ilmenite nor magnetite remain close systems subsolidus. They react together and thus undergo a change of chemical composition called deuteric readjustment. The quantitative importance of the deuteric readjustment is usually difficult to assess, but its sense is clearly defined : ilmenite is losing Hem, and magnetite is impoverished in Ti (and Al) in the form of (spinelliferous) ilmenite. It follows that the geothermo-meter and oxygen barometer of BUDDINGTON &

[4] In the Skaergaard VINCENT (1960, p. 1007 & fig. 6) has described " a narrow border of magnetite completely free from exsolution bodies (of ulvöspinel) ... present between magnetite-ulvöspinel and ilmenite grains » that the present author would interpret as a clear zone. Deuteric readjustment of a lesser amplitude than in the Rogaland is thus likely to have taken place in the Skaergaard.

LINDSLEY (1964), which give the last equilibrium conditions between the coexisting ilmenite and magnetite, will lead to necessarily lower values than the orthomagmatic temperature and oxygen fugacity.

Moreover changes in the initial Fe^{2+}/Fe^{3+} ratio of the rock is obvious, and redistribution of trace elements among oxides is to be suspected.

Anorthosites and related rocks are particularly suited for the study of oxide minerals. Indeed these minerals are normal constituents of many rock types of the anorthosite-mangerite suite and in addition they form large ore-bodies. Moreover because these rocks originate in deep-seated conditions slow cooling gives rise to well developed subsolidus phenomena and in particular provides evidence of deuteric readjustment.

This latter process is likely to occur also in less deep but « wetter » environments

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APPENDIX 1

Microscopical evaluation of chemical compositions of some ilmenite and magnetite microtextures

A. *Ilmenite.*

Size of hematite lenses and their density of distribution vary with the bulk chemical composition of hemo-ilmenite. Hence the microscope can be used to determine approximately the Hem content of the hemo-ilmenite. The evaluation of density is carried out by using the limits of resolution of a series of objectives (Leitz) : dry objective : x 16 (N.A. .40}; oil-immersion objectives : x 25 (N.A. .65), x 80 (N.A. 1.30) and x 105 (N.A. 1.32).

The following microscopical characters are worth mentioning :

Hemo-ilmenite.

> 18 mol % Hem : Two generations of hematite lenses distinctly visible. Hematite lenses of the first generation about 5µm thick.

18 to 15 mol % Hem : Lenses from 1 to 2 µm thick. The second generation is only locally visible. This microtexture is easily observed with objective X 16.

15 to 12 mol % Hem : One generation. Easily visible with x 25 imm, ; with difficulty with x 16.

12 to 9 mol % Hem : Lenses are only visible with objectives higher than X 25. *Ilmenite.*

9 to 7 mol % Hem : Lens-shaped exsolution is not visible with the most powerful objectives (X 80 & x 105 imm.}, but on sections // to {0001} white globular patches can locally be observed.

7 to 0 mol % Hem : Totally homogeneous at the highest magnification (X 105 imm.).

B. *Magnetite.*

When magnetite presents a sandwich intergrowth on a homogeneous background, the determination of the volume content of ilmenite in the grain can be carried out by measuring the areal proportions of the ilmenite lamellae in suitably oriented sections (// to {100} or {111}). This is best accomplished by cutting out a photographic enlargement of the grain and weighing the relative areas of ilmenite and host-magnetite. Several grains are averaged.

APPENDIX 2

The etching technique

Etching of magnetite by means of HC1, controlled under the microscope, has proved very useful in revealing the microtextures. A cloth intergrowth of magnetite + ulvöspinel or microlamellar ilmenite is etched in a few seconds, the magnetite component being tarnished the more slowly. On the other hand, homogeneous magnetite, which is always poor in Ti in the rocks here investigated, are tarnished uniformly and above all very slowly. Since the cloth without any trellis lamellae is present in Ti-rich magnetites, a direct relationship between Ti content and relative speed of etching can thus be inferred. In a magnetite grain with a trellis on a cloth microtextured background the zone alongside the trellis lamellae is always etched very slowly and consequently appears clear. The magnetite inside the zone is therefore poor in Ti.

Electron-probe microanalysis confirms this observation. The magnetite grain of Pl. II, fig. a is taken as an example. Microanalysis at point 1 (clear magnetite between two 2 µm-thick ilmenite lamellae 20 µm apart) and at point 2 (using a defocused beam to average the Ti content of the cloth) are given in Table 4.

It can be seen that the clear magnetite is less rich in Ti. In fact, at point 1, the proximity of trellis lamellae of ilmenite (10 µm from 1) leads to overestimation of the Ti content (secondary fluorescence excitation — LONG, 1967). This influence is smaller or absent at point 2 which is at a larger distance (30 µm) from the nearest ilmenite lamella. The measured difference is therefore smaller than the real one.T'he secondary fluorescence excitation prevents any direct evaluation of the gradient of concentration in zoning (as for instance in PI. II, fig.

d) because the Ti-content variation is masked in a zone of at least 20 µjn from the ilmenite lamellae. The etching technique, although qualitative, proves in such cases more useful.

TABLE 4

	Point 1	Point 2
^{Fe}total (as FeO)	89.9	85.8
MnO	.05	.07
ZnO	.06	.09
Al_2O_3	.7	.7
TiO_2	2.3	6.6
$SiO_Ξ$	.2	.2
	93.2	93.5
O(*)	6.5	6.1
Total	99.7	99.7

(*) Oxygen calculated on the basis of a Fe_3O_4 + $FeTiO_3$ composition.

APPENDIX 3

Polishing specimens

An easy and rapid technique for polishing specimens which has proved very satisfactory in the study of oxides in reflected light and with the Geoscan electron-probe analyser is described here.

Λ slice of about 30 x 40 mm and about 5 mm thick, with edges bevelled, is ground with silicon carbide abrasive down to grit 1000. It is then polished by hand on a 8-in diameter bronze wheel rotating at 246 RPM in the following sequence :

1. 2 to 4 runs of about 2 min with 1 µm Cr_2O_3 (BUEHLER AB metpolish n° 1, n° 406481) on a billiard cloth;

2. 1 or 2 runs of 1 min with 3 µm diamond paste (BUEHLER type X-17) on a STRUERS DP-cloth (type Dur).

The specimen is cleaned and inspected between each run. After the Cr_2O_3-runs silicates are perfectly polished and oxides are slightly in relief. This relief is removed by the cutting action of the subsequent diamond polishing. Very few scratches are observed though the size of the diamonds is rather coarse (3 µm).

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PLATE 1

Fig. a. Hemo-ilmenite. Lens-shaped exsolution of hematite in {000l} planes of the host-ilmenite (x 220).

Fig. b. Same microtexture at higher magnification. Note the two generations of hematite lenses and fine lenses of ilmenite inside the coarse hematite lenses. Exsolution of spinel occasionally occurs in {0001} planes (X 700).

Fig. c. Cloth microtoxtured aluminous spinel-rich magnetite. The reticulation (revealed by HC1 etching) is parallel to {100}. Spinel lamellae are enclosed in box-like structures (X 200).

Fig. d. Cloth microtexture (without aluminous spinel exsolution) (x 220).

Fig. e *&* f. Details of the cloth with and without spinel exsolution. HC1 etching does not tarnish the magnetite component which therefore appears as small bright squares, lined up in {100} planes (X 650 *&* *x* 700).

Fig. g. Trellis on a background of homogeneous magnetite (section // to {100}). The {111} ilmenite lamellae are dotted with spinel microcrystals. {100} spinel lamellae in N-S & E-W directions (X 200).

Fig. h. Sandwich grain of magnetite. Thick ilmenite lamellae stand out against a background of cloth-microtexture magnetite. A zone of homogeneous magnetite appears alongside the ilmenite lamellae (clear zone) (X 190).

PLATE II

Fig. a. Coexistence of cloth and trellis in a magnetite grain. The cloth (NNW-SSE direction) disappears in zones adjacent to the ilmenite lamellae of the trellis (NNE-SSW direction). Electron-probe microanalysis at points 1 & 2 are given in Table 4, appendix 2 (x 190).

Fig. b. Another example of coexistence of cloth and trellis (x 220).

Fig. c. Trellis microtexture on a background of zoned magnetite revealed by HC1 etching (X 220).

Fig. d. Another example of zoning showing the transition between cloth and trellis (X 195).

Fig. e. Contact between a primary ilmenite grain (ILM) and magnetite (MA). A rim of secondary ilmenite and spinel microcrystals (S) develops in optical continuity with the neighbouring primary ilmenite grain (X 220).

Fig. f. Contact between the two oxide minerals. A rim of spinelliferous ilmenite deeply penetrates into the magnetite. Note the irregular size and distribution of spinel microcrystals (X 220).

Fig. g. Contact between primary ilmenite (above) and a cloth-microtexture magnetite (with Al-spinel lamellae) (below). A zone of homogeneous Ti-poor magnetite distinctly appears alongside the rim (x 220).

Fig. h, Contact between hemo-ilmenite and magnetite. Zoning of the hamo-iimenite demonstrated by a progressive decrease in size and number of hematite lenses towards the contact with a homogeneous magnetite. At the contact, a rim of spinelliferous ilmenite develops (x 200).

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PLATE I

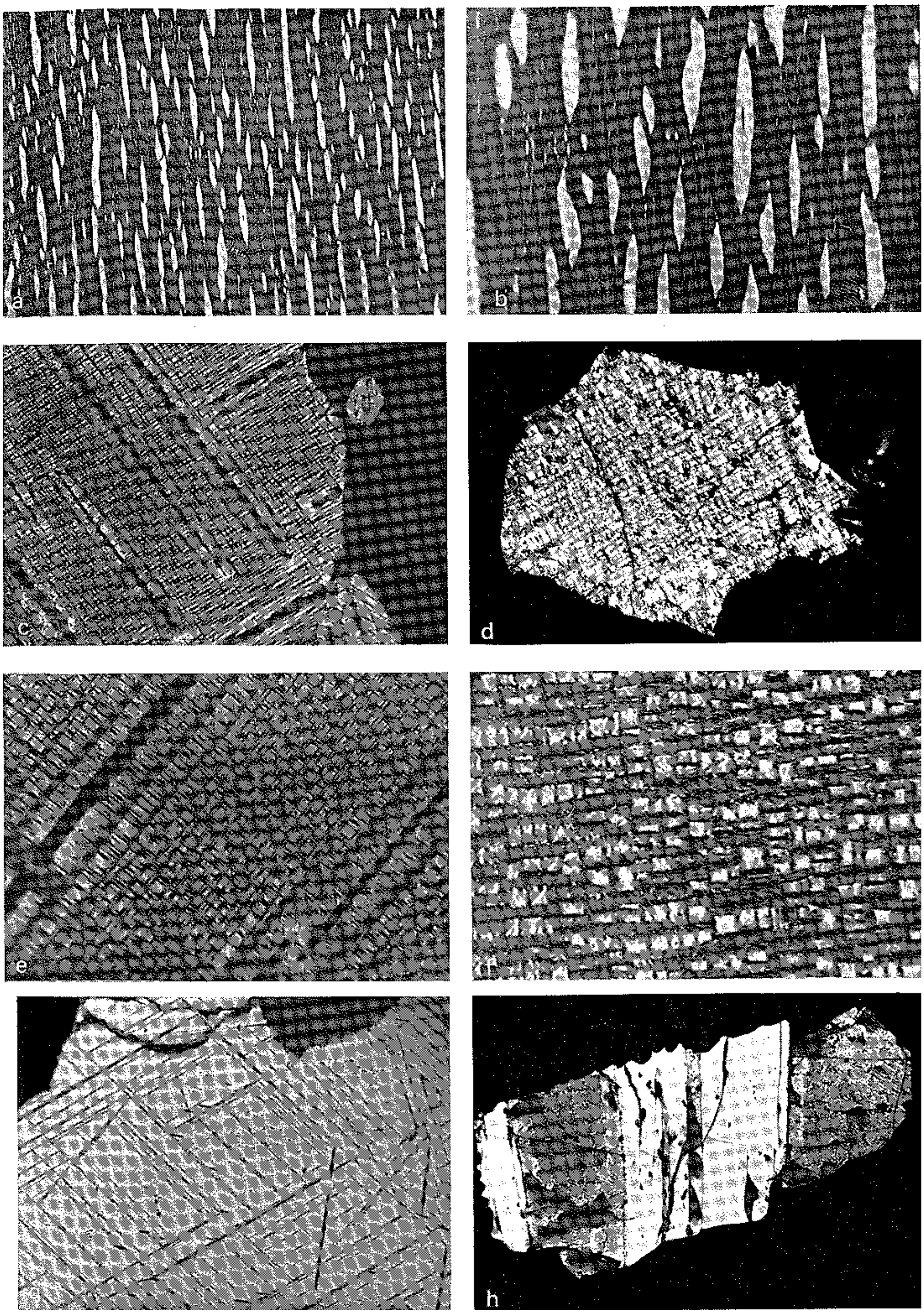

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PLATE II