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EXSOLUTION IN FRANKLINITE[1]

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ABSTRACT

Metallographic, *x*-ray diffraction and electron micro-probe observations have been made on exsolution growths of hetaerolite, gahnite and hematite in analyzed specimens of franklinite from Franklin and Sterling Hill, New Jersey. The hetaerolite exsolution when referred to the equilibrium diagram of Mason (1947) for the system Fe_3O_4-Mn_3O_4-$ZnFe_2O_4$ indicates a minimum temperature of formation of 650°–700° C for the initial homogeneous phase.

INTRODUCTION

Our observations are based on a collection of 20 franklinite specimens from Franklin and Sterling Hill, N.J., that had been analyzed chemically for their total content of Fe, Mn and Zn (Table 1). The specimens were selected to represent both the observed extremes in magnetic susceptibility and in characteristic mineral associations at these localities. No information is available as to the precise location of the specimens in the mines. The average composition of the finer-grained franklinite mill concentrates over a ten year period for the Franklin and Sterling mines, from well-distributed working places, is given in Table 2. These two analyses include small amounts of other minerals that were admixed, doubtlessly including calcite and willemite, and the calculated atomic ratio of Fe, Mn and Zn represents the franklinite only approximately.

The analytical data are plotted in Fig. 1. To this figure has been added the composition of 16 franklinites for which analyses have been reported in the literature, as summarized by Palache (1935). In the spinel structure-type, AB_2O_4, Zn has a marked preference for the tetrahedrally coordinated A position. In none of the analyses is Zn present in sufficient amount to fill this position. If the balance needed to fill the A position is taken as Mn^{2+} rather than Fe^{2+}, on the basis of the redox potentials in solution, then in many instances Mn^{3+} must be present together with Fe^{3+} in the octahedrally coordinated B position. The valences of the Mn and Fe in certain spinels, however, do not follow the redox potentials (Miller, 1960; O'Keeffe, 1961). The complete range of composition as shown in Fig. 1 extends from a slightly manganoan and zincian variety of magnetite through franklinite to material with Zn as the dominant A cation and with total Mn$\sim$total Fe.

All of the 20 newly analyzed samples were examined for exsolution growths in polished section under the reflecting microscope and by *x*-ray

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TABLE 1. CHEMICAL ANALYSES OF FRANKLINITE

Locality	Atoms per 100 cations in AB_2O_4			Exsolution	Immediate association
	Fe	Mn	Zn		
1 Franklin	38.59	40.06	21.36	Hetaerolite	Manganosite, zincite
2 Franklin	40.8	45.9	13.3	Hetaerolite	Manganosite, zincite
3 Franklin	40.56	35.93	23.51	Hetaerolite	Willemite, rhodochrosite
4 Franklin	41.03	38.81	20.16	Hetaerolite	Zincite, willemite
5 Franklin	43.76	31.26	24.65	Hetaerolite	Tephroite, zincite (Mason, 1946)
6 Not known	77.00	5.49	17.50	Hematite	Calcite, willemite
7 Franklin	86.85	4.57	8.58	Hematite	Andradite
8 Franklin	61.48	11.48	27.04	Gahnite	Calcite
9 Sterling	65.35	8.62	26.03	Gahnite	Calcite
10 Sterling	75.34	8.79	15.87	Gahnite	Gahnite
11 Sterling	75.46	7.09	17.45	Gahnite	Willemite
12 Not known	89.35	4.84	5.80	Gahnite	
13 Sterling	53.68	26.20	20.12	None	
14 Sterling	59.00	20.62	20.38	None	Willemite, andradite
15 Franklin	59.60	16.51	23.89	None	Calcite, willemite
16 Franklin	65.30	9.38	25.32	None	
17 Franklin	75.95	13.65	10.40	None	Hematite
18 Franklin	78.74	10.28	10.98	None	Andradite
19 Franklin	80.49	9.23	11.07	None	Hematite
20 Sterling	81.05	7.14	11.85	None	

Analyses by Dr. Jun Ito, 1964.

diffraction patterns taken on film and on charts in Fe radiation. Three types of exsolution were recognized, involving the precipitation of hetaerolite, gahnite and hematite. Representative examples of each type were then analyzed by the electron micro-probe technique.

TABLE 2. AVERAGE COMPOSITION OF FRANKLINITE MILL CONCENTRATES

	Weight per cent				
	Fe	Mn	Zn	CaO	SiO_2
Franklin	36.04	13.52	17.30	1.57	3.01
Sterling	41.40	6.53	17.09	2.72	2.42
		Atoms per 100 (Fe, Mn, Zn)			
Franklin	56	21	23		
Sterling	66	11	23		

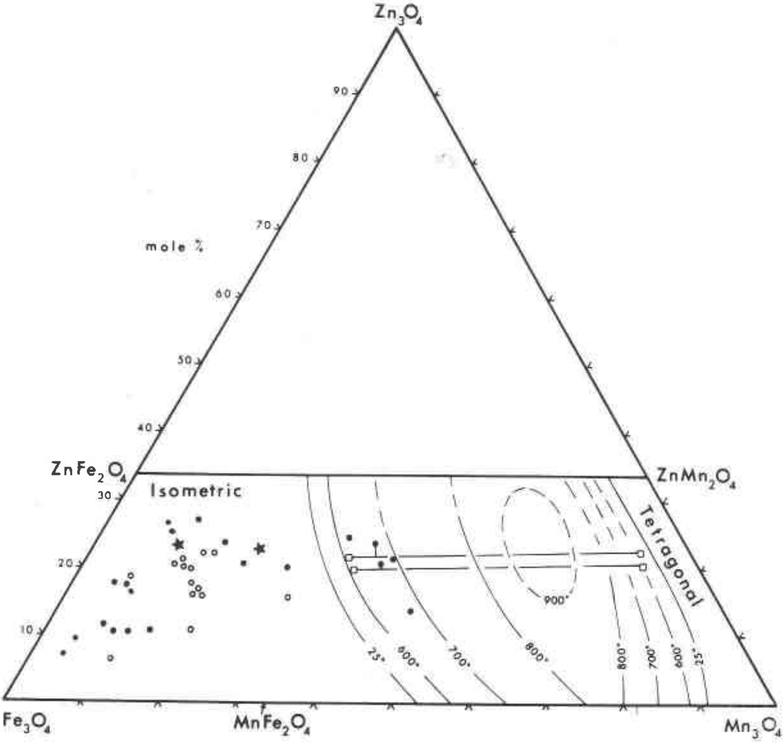

FIG. 1. Equilibrium diagram for Zn-Mn-Fe spinels (Mason, 1947), and composition of franklinite. Solid circles: new analyses; open circles: analyses from literature; squares: electron probe analyses of exsolved hetaerolite and host franklinite; stars: average composition of Franklin and Sterling Hill franklinite mill concentrates.

HETAEROLITE

The occurrence of hetaerolite as a lamellar exsolution growth in franklinite from Franklin has been described by Mason (1946). We have found four additional occurrences (Table 1 and Fig. 1). The specimens are characterized by an immediate association with minerals high in Mn, including manganosite and tephroite (Table 1). The manganosite contains coarse exsolved plates of zincite (Frondel, 1940).

In reflected light the hetaerolite is strongly anisotropic with distinct dichroism. It forms a lamellar network that is stated to be parallel to (111) in franklinite (Ramdohr, 1960, p. 863; see Figs. 2, 3 and also Mason, 1946, Fig. 1). The lamellae usually are 2 to 10 microns thick, with some up to 50 microns. Irregular blebs of hetaerolite are also present in some specimens. Bulk samples give fairly strong hetaerolite *x*-ray patterns on film. From these the unit cell dimensions were obtained (Table 3) with the unit cell refinement program of Burnham (1962). Indexed *x*-ray powder data for hetaerolite are given in Table 4.

The subsolidus in the system Fe_3O_4-Mn_3O_4-$ZnMn_2O_4$-$ZnFe_2O_4$ has been described by Mason (1947). A complete solid solution exists in the spinel structure-type above a temperature between 900° and 1000°. At lower temperatures the two-phase region between isometric spinel-type and tetragonal hausmannite-type solid solutions widens out. The isothermal boundaries have been experimentally determined down to 600°, as indicated in Fig. 1. The extrapolation of the solvus to room temperature was based by Mason on the evidence of natural specimens. The room temperature limits on the Fe-Mn join, at 54 and 91 atomic per cent Mn_3O_4, agree with those obtained by Van Hook and Keith (1958) by extrapolation down from 400° of the solvus in the system Fe_3O_4-Mn_3O_4.

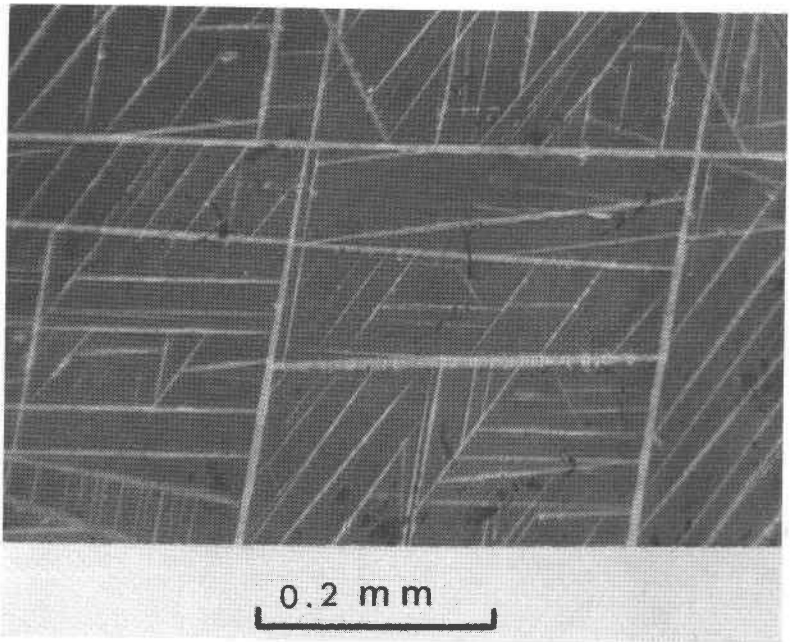

FIG. 2. Hetaerolite exsolution in franklinite, lamellar type. Polarized reflected light. Specimen no. 4.

In bulk composition all five specimens that contain exsolved hetaerolite fall within the experimentally determined part of the solvus, between the 600° and 700° isotherms (Fig. 1). This is at best only a rough indication of the minimum temperature of formation of the material. Aside from the precision of the data employed, and the probable existence of a small correction for pressure, the matter also is influenced by crystallochemical factors, not here evaluated, such as omissions in the cation positions and the presence of small amounts of Mg, Al or other cations. There is also the basic assumption that both the natural material and the experimental system to which it is referred represent equilibrium conditions. The exsolution presumably is influenced primarily by the distorting influence of Mn^{3+} ions in the B positions, as indicated by the role of this ion in determining the isometric-tetragonal transition (Goodenough and Loeb, 1955; Finch *et al.*, 1957). The valence and distribution between the A and B positions of the Fe and Mn and their resorting as a function of the cooling history thus may be critical. In the present system, which is very sluggish below about 600°, Fe_3O_4 has an essentially inverse and Mn_3O_4 an essentially normal structure.

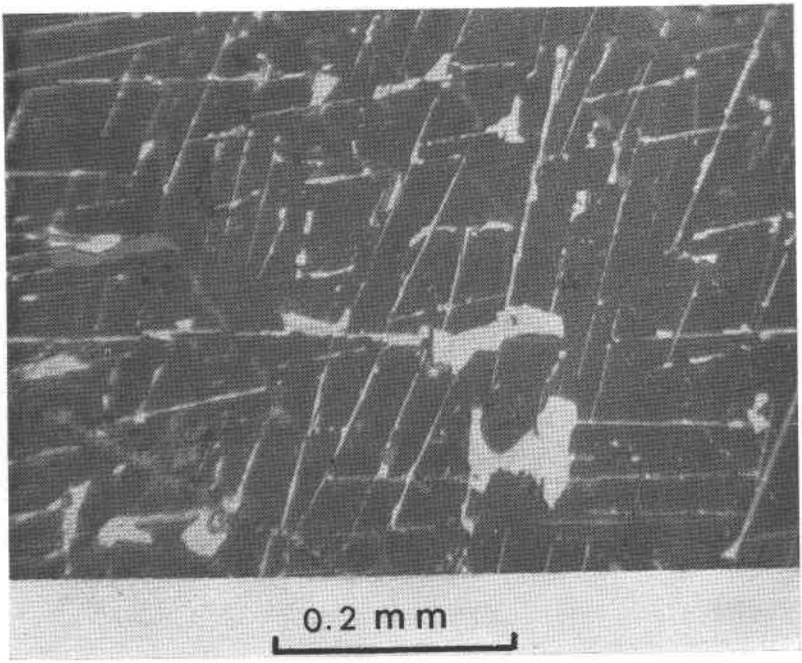

FIG. 3. Hetaerolite exsolution in franklinite, blebby type. Polarized reflected light. Specimen no. 3.

Separate analyses have been made by the electron micro-probe of the exsolved hetaerolite and of the host franklinite in two of our specimens

(Table 3). These compositions correspond to temperatures well above the reported room temperature boundary of the solvus (Fig. 1). This may indicate that equilibrium has not been reached or that, as Mason

Table 3. Analyses and Cell Dimensions of Exsolved Hetaerolite and Host Franklinite

Specimen no. 3

	Hetaerolite			Franklinite			Bulk analysis
	Weight %	Atoms per 100 cations	Atoms per 4 oxygen	Weight %	Atoms per 100 cations	Atoms per 4 oxygen	Atoms per 100 cations
Fe	4.9	6.8	.71	32.0	45.3	1.34	40.56
Mn	50.6	71.1	2.28	23.3	33.6	.99	35.93
Zn	18.7	22.1	.71	17.4	21.1	.62	23.51
a	5.754±.002 Å			8.456±.002 Å			
c	9.219±.005 Å						
Vol.	305.2±.2 Å^3			604.7±.4 Å^3			

Specimen no. 4

	Hetaerolite			Franklinite			Bulk Analysis
	Weight %	Atoms per 100 cations	Atoms per 4 oxygen	Weight %	Atoms per 100 cations	Atoms per 4 oxygen	Atoms per 100 cations
Fe	5.1	7.1	.22	32.0	44.8	1.38	41.03
Mn	51.5	72.2	2.32	24.9	35.5	1.09	38.81
Zn	17.6	20.7	.67	16.5	19.7	.61	20.16
a	5.750±.005 Å			8.465±.002 Å			
c	9.231±.009 Å						
Vol.	305.2±.3 Å^3			606.7±.4 Å^3			

Electron probe analyses were performed at 30 KV and 0.1 microamperes using a homogeneous analyzed franklinite as a standard. Background corrections and absorption corrections (Philibert, 1962) were applied. Mass absorption coefficients were taken from Birks (1963). The same analyses also were performed using pure Fe, pure MnO_2 and pure ZnS as standards and applying the above corrections as well as the atomic number corrections after Poole and Thomas (1962). The analyses obtained by these two methods differed by only a few tenths of a per cent; the data obtained from the franklinite standard are cited here.

Table 4. Indexed X-ray Powder Data for Hetaerolite. Iron Radiation ($FeK\bar{\alpha}$ = 1.93728 Å), Mn Filter, Camera Diameter 114.58 mm. Calculated Spacings for a 5.721 Å ± .001 Å and c 9.229 ± .005 Å, Obtained by Least Squares Refinement. Space Group I4/amd. Data on Analyzed Material of Palache (1928)

I	hkl	d obs.	d calc.	d (obs.-calc.)
80	1 1 2	3.040	3.042	−.002
50	2 0 0	2.855	2.860	−.005
90	1 0 3	2.707	2.709	−.002
100	1 2 1	2.462	2.465	−.003
30	0 0 4	2.307	2.307	0
40	2 2 0	2.019	2.023	−.004
30	2 0 4	1.794	1.796	−.002
40	1 0 5	1.756	1.756	0
35	3 1 2	1.683	1.684	−.001
20	3 0 3	1.620	1.621	−.001
50	3 2 1	1.5634	1.5637	−.0003
70	2 2 4	1.5209	1.5209	0
40	4 0 0	1.4300	1.4302	−.0002
10	3 0 5	1.3259	1.3263	−.0004
vf	3 3 2	1.2942	1.2943	−.0001
30	4 1 3	1.2642	1.2648	−.0006
40	2 1 7	1.1726	1.1719	−.0007
10	0 0 8	1.1546	1.1536	−.0010
10	4 2 4	1.1196	1.1188	+.0008
15 α_1	4 1 5	1.1094	1.1091	+.0003
vf α_1	5 1 2	1.0902	1.0902	0
20 α_1	5 0 3	1.0722	1.0724	−.0002
	4 3 3		1.0724	
vf α_1	5 2 1	1.0554	1.0554	0
20 α_1	3 2 7	1.0149	1.0141	+.0007
	3 3 6			

vf = very faint.

(1947) notes, the position of the room temperature boundary in the high Zn region may be in error.

GAHNITE

Gahnite was identified by optical study, electron micro-probe analyses and x-ray diffraction patterns in five specimens (Table 1). As a group, these specimens are distinguished by a high ratio of Fe to Mn. The Zn content varies widely, from the minimum to the maximum observed. Al_2O_3 has been reported in four analyses of franklinite (Palache, 1935; Mason, 1947), in three instances below 1 weight per cent and with

3.2 per cent in another. An analysis of one of our specimens (no. 16) gave 4.3 weight per cent Al_2O_3, with *a* 8.4289 ± .0005 Å. This specimen is translucent, with a deep red color in thin splinters and crushed grains. It is free of exsolution growths of any kind. The 4.3 weight per cent Al_2O_3 in this homogeneous specimen may be close to the maximum amount of Al_2O_3 that can be housed in franklinite at a temperature of 650-700° C. The franklinites that show gahnite exsolution have a maximum ratio of exsolved gahnite to matrix of about 1:12. Pure gahnite ($ZnAl_2O_4$) contains 55.7 weight per cent Al_2O_3. Assuming all the Al_2O_3 to be housed in the exsolved gahnite and none in the franklinite, bulk analyses of the samples that show gahnite exsolution would contain approximately 4.5 weight per cent Al_2O_3.

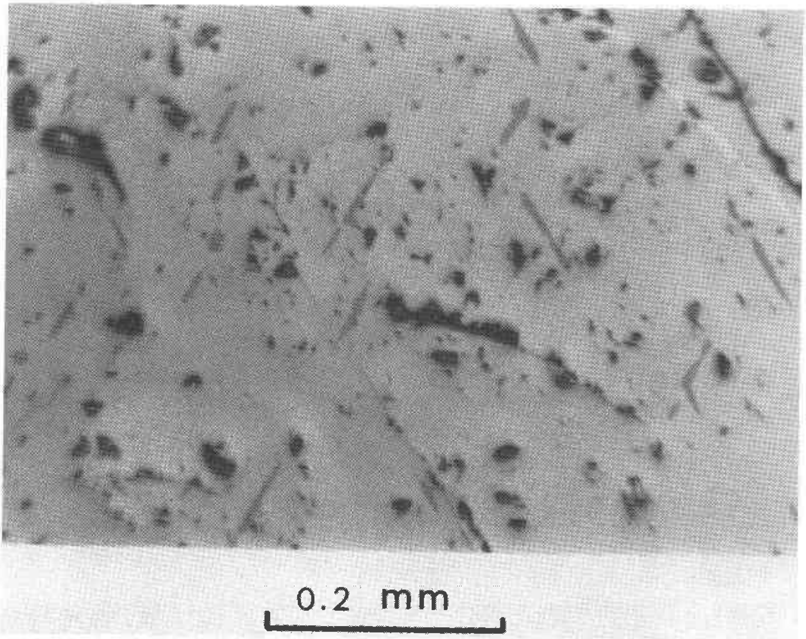

FIG. 4. Gahnite exsolution in franklinite, lamellar type. Reflected light. Specimen no. 12.

Two types of gahnite exsolution were observed. In one type, the gahnite formed isolated laminae or plates about 6 microns in thickness that were distributed in one or two positions of orientation (Fig. 4). In the other type, the gahnite formed rounded crystals up to 30 microns in size with a tendency for arrangement in rows (Fig. 5). The rows are discontinuous and may be curved or irregular. Micro-probe analyses of both types showed Zn and Al as the major constituents with a small amount of Fe. Ramdohr (1960) has observed a spinel, probably gahnite, as exsolved discs parallel to (100) in franklinite.

One specimen examined by us showed dodecahedral crystals of franklinite with dark green, parallelly oriented octahedral crystals of gahnite, up to 1 mm in size, projecting from their surface. Inclusions of the same type were present throughout the crystals. This intergrowth may be the result of the simultaneous crystallization of the two spinels. It may be noted that gahnite occurs as isolated crystals up to 4 or 5 inches in size both in the ore bodies, where it is associated with franklinite, and in the adjacent Franklin marble. Analyses of this gahnite (Palache, 1935) show 8–10 per cent Fe_2O_3 and 1 per cent of MnO.

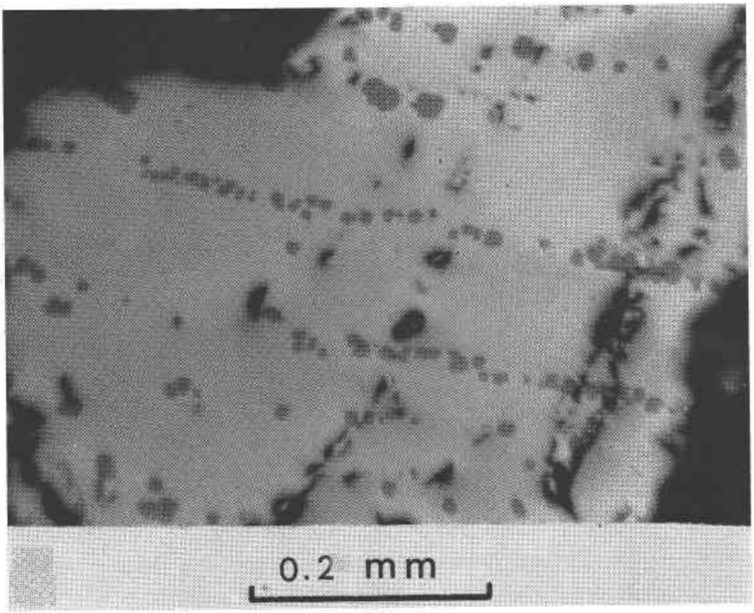

FIG. 5. Gahnite exsolution in franklinite, euhedral type. Reflected light. Specimen no. 11.

The phase relations in the system $ZnFe_2O_4$-$ZnAl_2O_4$ are not known experimentally. It may be presumed that at high temperatures there is an extensive or complete solid solution with a large solubility gap appearing at lower temperatures. There is a complete solid solution in the related system $FeFe_2O_4$-$FeAl_2O_4$ at 1000° (Atlas and Sumida, 1958; Pickart and Turnock, 1959). At low temperatures the mutual solubility here is apparently quite small. Exsolution growths of hercynite in magnetite and of magnetite in hercynite are well known (Ramdohr, 1960; Rimskaya-Korsakova, 1950).

HEMATITE

Two specimens were observed to contain exsolved hematite. The x-ray patterns showed hematite lines, and electron micro-probe analyses of the exsolved laminae showed them to be high in Fe with about 2 per cent Mn_2O_3 and no Zn. Titanium was not present. In one specimen, no. 6, initially a franklinite, the hematite formed an octahedral pattern of laminae very similar to the exsolution growths of hematite in magnetite. The other specimen, no. 7, initially a manganoan and zincian magnetite, was quite different. Here the hematite formed an undulating and anastomosing set of lamellae in only one position of orientation (Fig. 6), and the hematite and magnetite were about equal in volume. Several other specimens rather similar in bulk composition to these specimens contained gahnite exsolution, but not hematite, or lacked exsolution growths altogether.

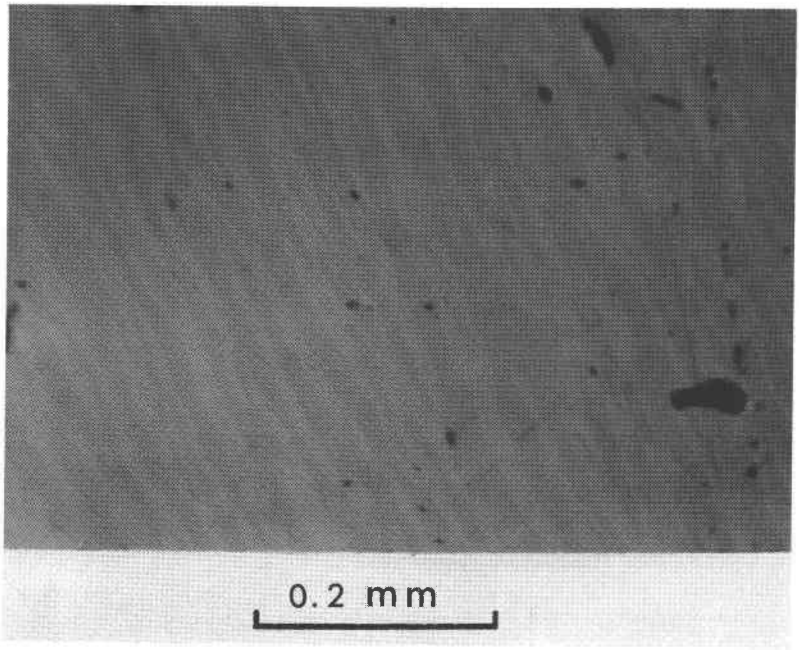

FIG. 6. Hematite exsolution in manganoan and zincian magnetite, abnormal type. Reflected light. Specimen no. 7.

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