

*Titanomagnetites from a differentiated teschenite sill.*

By J. F. G. WILKINSON, M.Sc., Ph.D.

Department of Geology, University of New England, Armidale,  
New South Wales.

[Read 24 January 1957.]

*Summary.* Mineragraphic, chemical, and X-ray data are presented on the titanomagnetites<sup>1</sup> from a differentiated teschenite sill. The minerals are generally homogeneous. The earliest titanomagnetites are  $\text{Fe}_3\text{O}_4\cdot\text{Fe}_2\text{TiO}_4\cdot\text{FeTiO}_3$  solid solutions; the titanomagnetite crystallization trend is one of enrichment in  $\text{Fe}_3\text{O}_4$  and  $\text{FeTiO}_3$  at the expense of  $\text{Fe}_2\text{TiO}_4$ . The relations of the titanomagnetites to the parent rocks and associated minerals, and their role in basaltic magma iron enrichment are also discussed.

WHILE mineragraphic data are available on the opaque minerals of common igneous rocks (Newhouse, 1936) and certain volcanic suites (e.g. Odman, 1932; Cornwall, 1951), the recent detailed mineragraphic and chemical investigation of Vincent and Phillips (1954) on the iron-titanium oxide minerals of the tholeiitic Skaergaard intrusion constitutes one of the few studies on the opaque oxides from a genetically related intrusive series. The present study embraces certain aspects of the iron-titanium oxide minerals from a differentiated teschenite sill, Tertiary in age and approximately 500 feet thick, situated three miles south-west of Gunnedah, New South Wales.

Polished sections were prepared of specimens B1, B2, B3, B4, B7, B9, and H8, teschenites approximately 20, 20, 120, 270, 420, 500, and 500 feet above the lower intrusion contacts. Chemical analyses are available of the parent rocks. Modal and trace element data on the titanomagnetites will be discussed in more detail in a separate paper.

*Microscopic study of the opaque minerals.*

The monotony of the mineralogy and a general homogeneity within individual grains constitute the most important features of reflected-light studies. Titanomagnetite<sup>1</sup> predominates, while ilmenite is rare.

<sup>1</sup> The term 'titanomagnetite' is used to denote a single-phase solution of  $\text{TiO}_2$  compounds in magnetite (Ramdohr, 1926, p. 345; Buddington, Fahey, and Vlissidis, 1955, p. 498). Although both X-ray and chemical data on the titanomagnetites

All the sections carry droplets of sulphide. Hematite and rutile were not identified.

Except for rare exsolution lamellae enriched in  $\text{FeTiO}_3$  the titanomagnetite is homogeneous in all the polished sections. Although analyses of this mineral from specimens B1 and B4 (table I, analyses 1 and 2) indicate considerable amounts of  $\text{Fe}_2\text{TiO}_4$ , the titanomagnetite,

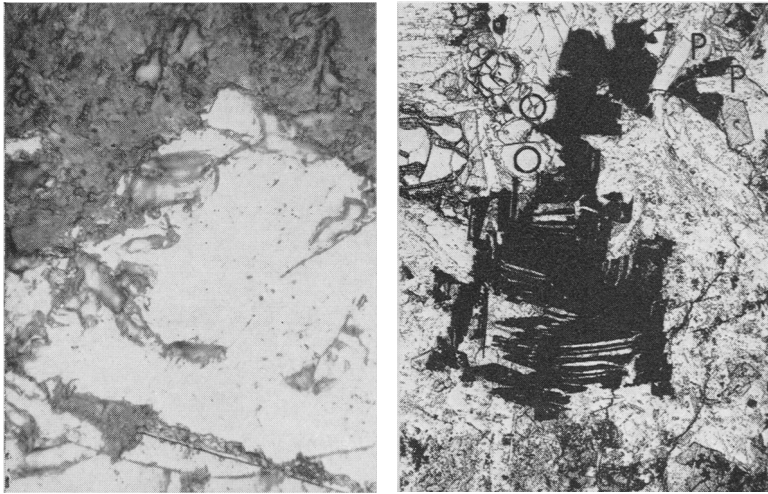


FIG. 1 (*left*). Portion of titanomagnetite crystal from specimen B1 (analysed), indicating the absence of any exsolution structures. The polished section has been etched with HF. (Reflected light  $\times 700$ .)

FIG. 2 (*right*). Skeletal titanomagnetite from teschenite E8, 410 feet above the lower contact. The titanomagnetite is moulded against olivine (O) and plagioclase (P). (Ordinary transmitted light  $\times 13$ .)

even after etching with HF and under high magnification, still retains its homogeneity (fig. 1) with no indication of the characteristic 'cloth texture' of exsolved ulvöspinel. Despite their relatively high  $\text{TiO}_2$  content, the titanomagnetites are also homogeneous with respect to exsolved ilmenite. In rare cases *faintly* anisotropic lamellae representing initial stages in the unmixing of  $\text{FeTiO}_3$  are observed. Occasional titanomagnetite phenocrysts also reveal a similar degree of anisotropism, resulting from  $\text{Fe}_3\text{O}_4$ - $\text{FeTiO}_3$  solid solutions (Edwards, 1954, p. 76).

indicates the presence in solid solution of the iron-titanium spinel  $\text{Fe}_2\text{TiO}_4$  (ulvöspinel), this mineral has not been detected as a separate phase, and hence is referred to in general by its chemical formula only (following Vincent and Phillips, 1954, p. 3).

The titanomagnetites are often altered internally to deuteric silicate, sometimes recognizable either as sphene or leucoxene. The leucoxene sometimes shows faint relic structures suggesting its derivation from previous exsolved lamellae. It would be anticipated that such exsolution products, enriched in  $\text{FeTiO}_3$ , would be more susceptible to leucogenization. This alteration to silicate is not considered responsible for the intricate skeletal outlines (cf. Odman, 1932, p. 288) in the titanomagnetite from the upper levels of the sill (fig. 2). In reflected light the adjacent silicate generally presents knife-edge contacts against the titanomagnetites and in the areas between the branching titanomagnetite 'arms'. The degree of idiomorphism of the magnetite tends to vary with its position in the crystallization sequence, the skeletal ores indicating a later crystallization. The titanomagnetites frequently curve around plagioclase and adjoining ferro-magnesian silicates. Newhouse (1936, p. 25) and Osborne (1928, p. 749) have summarized opinions dealing with the late crystallization of the opaque oxides in many basic rocks.

Homogeneous ilmenite was detected as scattered rare grains in B2 and H8. The degree of homogeneity of the titanomagnetite, and the absence of this mineral in the vicinity of the ilmenite grains, suggests that the ilmenite is a primary precipitation mineral and not an exsolution product of  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_2\text{TiO}_4$ - $\text{FeTiO}_3$  solid solutions (cf. Vincent and Phillips, 1954, p. 6).

The data on the opaque oxides from hypabyssal alkaline basic rocks appear to be meagre. In volcanic representatives Newhouse (1936, tables 11-12) recorded only magnetite in seventeen nepheline- and leucite-basalts. Ilmenite was absent. On the other hand, in sixty-five gabbros, diabases, and allied rocks studied by Newhouse, ilmenite and ilmenite-magnetite intergrowths were the most important opaque oxides. Homogeneous magnetite was found to be comparatively rare.

The minor amounts of sulphides appear to be more abundant in the teschenites from the upper levels of the sill. Chalcopyrite predominates over pyrite. As in the Duluth gabbro (Schwartz, 1930, p. 250), the sulphides generally occur as granules disseminated interstitially to the silicates. Chalcopyrite in analcime veinlets was noted in H8.

#### *Chemical and X-ray data on the titanomagnetites.*

The three analysed titanomagnetites (table I, analyses 1-3) have been recalculated into possible spinel molecules, ilmenite, and silicates, following the method applied by Mogensen (1946) and by Vincent and

Phillips (1954). The titanomagnetite chemistry reveals an excess of FeO when an attempt is made to interpret the analyses solely on a basis

TABLE I. Chemical analyses of titanomagnetites, with a recalculation into end-members following Mogensen (1946) and Vincent and Phillips (1954).

	1.	2.	3.	4.	5.	6.	7.	8.	9.
SiO <sub>2</sub>	0.33	0.54	2.85	0.24	0.23	—	1.81	—	—
TiO <sub>2</sub>	26.76	27.29	29.66	19.28	23.74	18.41	15.30	18.02	14.03
Al <sub>2</sub> O <sub>3</sub>	2.31	3.55	2.45	0.78	0.91	2.35	6.16	—	—
Fe <sub>2</sub> O <sub>3</sub>	21.10	23.18	30.21	32.27	31.26	27.93	32.39	36.03	40.62
FeO	45.22	41.86	29.32	43.07	41.69	45.82	36.67	43.89	44.12
MnO	0.61	0.69	1.17	0.33	0.45	0.42	0.43	0.93	0.74
MgO	1.93	2.33	0.79	1.98	1.21	2.48	4.37	—	—
CaO	0.59	0.27	2.63	0.42	tr.	0.73	0.16	—	—
V <sub>2</sub> O <sub>5</sub>	0.37*	0.44*	0.30*	1.74	0.40	0.92	0.86	1.13	0.49
Cr <sub>2</sub> O <sub>3</sub>	0.38*	0.10*	nil*	0.13	nil	0.94	n.d.	—	—
S	n.d.	n.d.	0.09	—	—	—	n.d.	—	—
&c.	—	—	—	0.09	0.11	—	1.36	—	0.004
Total	99.60	100.25	99.47	100.33	100.00	100.00	99.51	100.00	100.00

\* These constituents were determined spectrographically.

*Recalculated compositions (wt. %)*

CaO.SiO <sub>2</sub>	0.58	0.58	—	0.46	—	—	0.35	—	—
MgO.SiO <sub>2</sub>	—	—	0.10	—	0.38	—	2.70	—	—
FeO.SiO <sub>2</sub>	—	—	—	—	—	—	—	—	—
MgO.Al <sub>2</sub> O <sub>3</sub>	3.27	4.83	2.70	1.08	1.27	3.3	8.67	—	—
FeO.Al <sub>2</sub> O <sub>3</sub>	—	—	0.87	—	—	—	—	—	—
CaO.Fe <sub>2</sub> O <sub>3</sub>	1.30	—	—	0.75	—	2.8	—	—	—
MgO.Fe <sub>2</sub> O <sub>3</sub>	5.00	4.00	—	8.30	3.46	7.6	4.20	—	—
MnO.Fe <sub>2</sub> O <sub>3</sub>	2.08	2.31	3.70	1.06	1.45	1.4	1.39	3.00	2.31
FeO.V <sub>2</sub> O <sub>5</sub>	0.44	0.67	0.44	2.58	0.60	1.4	1.33	1.78	0.67
FeO.Cr <sub>2</sub> O <sub>3</sub>	0.45	0.22	—	0.18	—	1.4	—	—	—
FeO.Fe <sub>2</sub> O <sub>3</sub>	21.34	26.68	40.14	35.33	39.87	27.6	40.60	49.18	56.61
FeO.TiO <sub>2</sub>	20.67	33.44	34.51	7.14	28.48	—	8.21	9.12	—
2FeO.TiO <sub>2</sub>	44.35	27.10	—	43.39	24.40	51.8	30.69	36.96	39.20
FeO.	—	—	—	—	—	2.7	—	—	1.15
TiO <sub>2</sub>	—	—	7.68	—	—	—	—	—	—
CaO.TiO <sub>2</sub> .SiO <sub>2</sub>	—	—	9.21	—	—	—	—	—	—
&c.	—	—	—	—	—	—	1.36	—	0.004
Total	99.48	100.23	99.35	100.27	99.91	100.0	99.50	100.04	99.94

Analyses 1-3, titanomagnetites from the Black Jack sill. Anal. J. F. G. W.

1. Titanomagnetite from teschenite B1, 20 feet above lower contact.
2. Titanomagnetite from teschenite B4, 270 feet above lower contact.
3. Titanomagnetite from teschenite H8, approx. 500 feet above lower contact.
4. Magnetite from melanocratic band in hypersthene-olivine-gabbro (2308), Skaergaard intrusion, East Greenland. Anal. E. A. Vincent (Vincent and Phillips, 1954, table 2).
5. Magnetite from melanocratic band in hortonolite-ferrogabbro (2569), Skaergaard intrusion, East Greenland. Anal. E. A. Vincent (Vincent and Phillips, op. cit.).
6. Magnetite from dolerite, Södra Ulvön, Sweden (Mogensen, 1946, p. 586). Composition of magnetite calculated from analysis of a high grade concentrate containing 1.61 % SiO<sub>2</sub> (2.5 % other minerals).
7. Magnetite from magnetite-olivinite dyke, Taberg, Sweden. Anal. A. Aaremäe (Hjelmqvist, 1950, p. 28).
- 8 and 9. Magnetites from Japanese augite-olivine-basalts (recalculated to 100 %). Anal. T. Katura (Taneda, 1950, table 2).

of Fe<sub>3</sub>O<sub>4</sub>-FeTiO<sub>3</sub> solid solutions. In other titanomagnetites similar difficulties have been largely resolved by the microscopic and X-ray recognition of exsolved ulvöspinell (table I, analyses 5 and 6). The

recalculated analyses of titanomagnetites B1 and B4 suggest approximately 44 and 27 %  $\text{Fe}_2\text{TiO}_4$  in solid solution. In both cases the X-ray powder patterns show only one set of magnetite-spinel lines, with no indication of shadowing of the lines by another spinel of slightly different cell dimensions. Ilmenite lines are absent. The cell dimensions of both these magnetites are  $a$  8.48 Å. ( $\pm 0.01$  Å.). These values are higher than those usually given for naturally occurring and artificial magnetites, namely  $a$  8.36 to 8.42 Å. (Mason, 1943, p. 105). Tombs and Rooksby (1951, p. 474) and Abrahams and Calhoun (1953, p. 105) have determined the cell edge of artificial magnetite as  $a$  8.394 Å. It would be anticipated that titanomagnetite B4, containing less recalculated  $\text{Fe}_2\text{TiO}_4$  than B1, would have slightly smaller cell dimensions. However, conclusions of this type are not justified until we know more of the effects of constituents other than  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and Ti on the cell dimensions of the complex solid solutions.

The recalculated analysis of titanomagnetite H8 indicates the absence of  $\text{Fe}_2\text{TiO}_4$ ; only magnetite lines are present on the powder photograph, and  $a = 8.42$  Å. H8 is veined with sphene and is also slightly leucoxenized. The recalculated analysis indicates a predominantly  $\text{Fe}_3\text{O}_4$ - $\text{FeTiO}_3$  solid solution. In this case the CaO has been allotted for the formation of sphene.

All the Black Jack titanomagnetites are characterized by high  $\text{TiO}_2$ , and, in B1 and B4, high FeO contents. They show even greater amounts of  $\text{TiO}_2$  than some similar titanomagnetites in which exsolution of other phases has occurred (e.g. table I, analyses 5 and 6). The 'ilmenite-magnetite' from Susimäki, Finland (Palmunen, 1925, table 8), listed by Buddington *et al.* (1955, table 6) as a titaniferous magnetite, has FeO 42.81,  $\text{Fe}_2\text{O}_3$  28.39, and  $\text{TiO}_2$  26.12 %; the recalculated  $\text{Fe}_2\text{TiO}_4$  content is approximately 24 %. The Black Jack minerals are also similar chemically to homogeneous titanomagnetites from volcanic rocks (table I, analyses 8 and 9).<sup>1</sup> Akimoto (1951, table I) lists a magnetite from an olivine-basalt, Kwanto district, Japan, with FeO 43.89,  $\text{Fe}_2\text{O}_3$  36.03, and  $\text{TiO}_2$  18.02 %.

The alumina in all three analyses (see also table I, analyses 6 and 7) is probably present in spinel molecules, principally  $\text{MgAl}_2\text{O}_4$ , in solid solution. Approximately 2 % MgO is present in B1 and B4, decreasing

<sup>1</sup> Dr. E. Z. Basta (unpubl. thesis, University of Bristol; this vol., p. 431) has described homogeneous titanomagnetites from volcanic rocks whose chemistry, cell dimensions, and recalculated compositions are very similar to titanomagnetites B1 and B4.

in amount in H8 as less magnesia became available from the magma. Under conditions of slow cooling, the spinel may exsolve from the magnetite, along with ulvöspinel (Hjelmqvist, 1950, figs. 29 and 30; Girault, 1953, figs. 2 to 4; Vincent and Phillips, 1954, p. 4). In both the Black Jack and Skaergaard titanomagnetites there is an increasing proportion of MnO to FeO with magmatic evolution (cf. Goldschmidt, 1954, p. 631).

#### *General Discussion.*

*The concept of  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_2\text{TiO}_4$ - $\text{FeTiO}_3$  solid solutions.* Pouillard and Michel (1949) and Pouillard (1950) have prepared continuous solid solutions between  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{TiO}_4$ , whose members show an increase in cell dimensions compared with pure  $\text{Fe}_3\text{O}_4$ . In a synthetic titanomagnetite of this type prepared by Pouillard (op. cit., p. 199), and containing 42 molecular %  $\text{Fe}_2\text{TiO}_4$ , the cell dimensions were  $a$  8.46 Å., compare titanomagnetite B1. Chevallier and Girard (1950) have synthesized titanomagnetites possessing the magnetite structure with  $a$  8.300 to 8.412 Å.<sup>1</sup> whose compositions may be expressed by the general formula  $y\text{Fe}_3\text{O}_4 \cdot (1-y)\text{FeTiO}_3$ . These authors suggest that natural titanomagnetite is probably composed of the  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_2\text{TiO}_4$  series with some of the  $\text{Fe}_3\text{O}_4$ - $\text{FeTiO}_3$  series also in solid solution. This appears to be the case in titanomagnetites B1 and B4. The homogeneity of these minerals, comparable to that of volcanic titanomagnetites, resulted from the relatively rapid cooling attendant on a small volume of magma crystallizing under near-surface conditions. The homogeneity of the titanomagnetites in the upper teschenites was aided also by their relatively late position in the crystallization sequence. In the Black Jack sill the titanomagnetites are not the only solid solution series prone to unmixing that has failed to unmix. Anorthoclase ( $\text{Or}_{26}$ ) from a teschenite 450 feet above the lower contacts is homogeneous as revealed by the X-ray powder photograph; the spectrometer pattern reveals only slight submicroscopic unmixing.

It should be noted that in other naturally occurring titanomagnetites with excess FeO, the exsolved material with  $a$  8.47 to 8.48 Å. has been referred to as ulvöspinel (Mogensen, 1946, p. 586; Girault, 1953, p. 307; Vincent and Phillips, 1954, p. 11). These cell dimensions are less than those of synthetic  $\text{Fe}_2\text{TiO}_4$ , namely  $a$  8.50 Å. (Barth and Posnjak, 1932, p. 341) or  $a$  8.534 Å. (Pouillard, 1950, p. 199). It may well be that in the above examples complete unmixing of ulvöspinel had not yet

<sup>1</sup> The value 8.300 Å. seems improbably low; perhaps it is a misprint.

occurred, and that the unmixing of  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_2\text{TiO}_4$  solid solutions is of a progressive type whereby magnetite ( $a$  8.37 to 8.39 Å.) may separate as one end member, the other phase being predominantly an  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_2\text{TiO}_4$  solid solution that might yield ulvöspinel on extremely slow cooling. In certain cases it seems likely that the composition of the initial homogeneous solid lies slightly to the left of the eutectoid  $E$  in the phase diagram for  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_2\text{TiO}_4$  given by Phillips (in Vincent and Phillips, 1954, fig. 2). The problem warrants further attention;

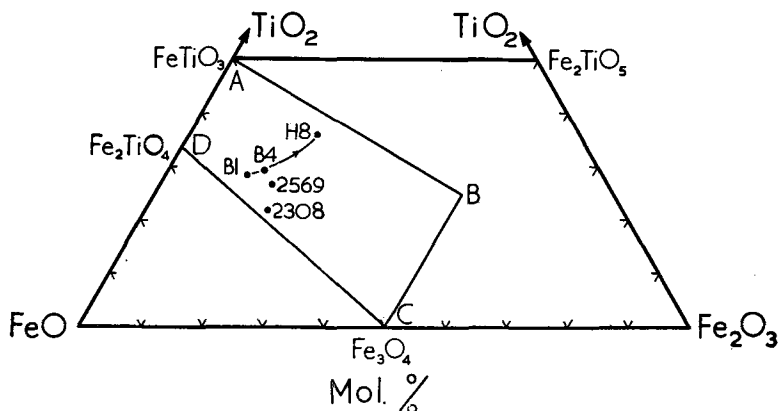


FIG. 3. The Black Jack titanomagnetites plotted on the system  $\text{FeO}.\text{Fe}_2\text{O}_3.\text{TiO}_2$ . The titanomagnetite crystallization trend is  $\text{B1} \rightarrow \text{H8}$ . 2308, 2569 are magnetites from the Skaergaard intrusion, E. Greenland (Vincent and Phillips, 1954, table 2.)

a full assessment of the unmixing process is probably complicated by oxidation-reduction reactions during exsolution, and the complex nature of the original solid solutions.

The initial decrease and final disappearance of  $\text{Fe}_2\text{TiO}_4$  in the Black Jack titanomagnetites substantiate the contention of Foslie (1928) that ulvöspinel does not form in the presence of excess  $\text{Fe}_2\text{O}_3$ . With progressive teschenite differentiation, ferric iron progressively increased in those liquids from which the upper titanomagnetites crystallized.

*Crystallization trend of the titanomagnetites and relations to the parent rocks and associated minerals.* In fig. 3 the titanomagnetites have been plotted on the system  $\text{FeO}.\text{Fe}_2\text{O}_3.\text{TiO}_2$ . All the Black Jack minerals fall in the field  $ABCD$ , comprising ores composed of two dominant phases, a titanomagnetite and an ilmenite. The titanomagnetite crystallization trend is towards the area of low melting in the as yet

incompletely determined  $\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$  thermal system (Ernst, 1943, fig. 1), and involves enrichment in  $\text{Fe}_3\text{O}_4$  and  $\text{FeTiO}_3$  at the expense of  $\text{Fe}_2\text{TiO}_4$ ; it is consistent with similar temperature trends indicated by the compositions of the associated olivines, clinopyroxenes, and plagioclase feldspars. The variation in the principal oxides with falling temperature is a decrease in  $\text{FeO}$  whilst  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  both increase (cf. Buddington *et al.*, 1955, pp. 516–517). Considering variation with respect to  $\text{FeO}$  in the principal ferriferous minerals of the teschenites, the titanomagnetite undergoes variation slightly less (45 to 29 %  $\text{FeO}$ ) than the olivines (20 to 48 %). The clinopyroxene (6.6 to 10 %  $\text{FeO}$ ) is the least susceptible to compositional change.

G. C. Kennedy (1948) has stressed the importance of the ferric-ferrous iron ratio in petrology, the concentration or pressure of water vapour playing an important role in the state of oxidation of the iron in the rock melt. With increasing height in the Black Jack sill, concomitant with progressive differentiation, the increasing activity of the late-stage solutions, in some instances iron-rich, becomes more pronounced, effecting a wide variety of mineralogical alteration, solution, and redeposition. The analcimization of the plagioclase and the deposition of analcime and a highly ferriferous carbonate in small vughs, the precipitation of an iron-charged mesostasis, the alteration of the olivine to bowlingite, and also to iddingsite (when the residual solutions had become enriched in ferric iron, compare Edwards, 1938, pp. 280–281), are all changes essentially deuteric in the original sense of Sederholm. The ferric-ferrous iron ratio of the teschenites increases during differentiation (table II), a relationship emphasized by Goldschmidt (1954, pp. 34 *et seq.*). Although the  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratios for both the parent rocks and the associated titanomagnetites are approximately the same in the early stages of consolidation, this ratio increases much more rapidly for the ores than for the rocks. The  $\text{Fe}_2\text{O}_3$  of the residual liquids was constantly built up during differentiation so that the titanomagnetites in the upper teschenites, dominantly late crystallization products, are enriched in this constituent.

Discussing the differentiation of titaniferous magmas, Evrard (1949, p. 213) points out that in general the ratio of titania to the total iron oxides increases with increased differentiation. The degree of differentiation of the teschenites is best expressed by the ratio  $(\text{FeO} + \text{Fe}_2\text{O}_3)/(\text{FeO} + \text{Fe}_2\text{O}_3 + \text{MgO})$ , which in table II is compared with the molecular ratios  $\text{TiO}_2/(\text{TiO}_2 + \text{FeO} + \text{Fe}_2\text{O}_3)$  (after Evrard, *op. cit.*). This latter ratio does reveal a general increase with differentiation. In the lavas



of the Keeweenaw Series in Michigan the ratio  $TiO_2/(TiO_2 + FeO + Fe_2O_3)$  also increases with differentiation (Cornwall, 1951a, p. 64).

*The relations of the opaque iron-titanium oxide minerals to iron enrichment in basic magma.* The debatable question of whether the residual liquids of basaltic magmas undergo enrichment in iron has attracted the attention of petrologists for many years (Fenner, 1929, 1931; Bowen, 1928; Edwards, 1942; Walker and Poldervaart, 1949). The

TABLE II. Differentiation ratios for the Black Jack teschenites and their associated titanomagnetites.

$$\left( t = \frac{TiO_2}{TiO_2 + FeO + Fe_2O_3} \times 100, \text{ mol. \%}; \quad f = \frac{FeO + Fe_2O_3}{FeO + Fe_2O_3 + MgO} \times 100, \text{ wt. \%} \right)$$

Specimen number.	Height in feet above lower contact.	FeO.	Fe <sub>2</sub> O <sub>3</sub> .	TiO <sub>2</sub>	t.	f.	Fe <sub>2</sub> O <sub>3</sub>
							FeO
<i>Rocks</i>							
B1	20	9.15	4.15	2.49	16.9	58.2	0.45
B2	20	9.51	2.93	2.58	18.0	60.6	0.31
B3	120	8.36	2.59	2.71	20.5	69.7	0.31
B4	270	9.28	3.12	2.62	18.2	62.4	0.34
B7	420	7.93	2.71	2.79	21.6	69.8	0.34
B9	500	9.43	3.83	4.07	24.8	72.6	0.41
H1	approx. 500	9.48	3.20	3.60	22.9	78.2	0.34
H8	approx. 500	9.57	4.15	3.53	21.5	82.2	0.43
H4	approx. 500	5.49	3.26	0.59	76.2	95.4	0.59
<i>Titanomagnetites</i>							
B1	—	45.22	21.10	26.76	30.5	—	0.47
B4	—	41.86	23.18	27.29	32.0	—	0.55
B8	—	29.32	30.21	29.66	38.3	—	1.03

B1-H8 teschenites. H4 is an analysis of a vein of microcrystalline mesostasis (analcime-syenite in composition) from the teschenite H4.

Black Jack teschenites, representatives of alkali olivine-basalt magma, reveal only slight absolute iron enrichment in the later stages of evolution, not on any scale comparable with the tholeiitic Skaergaard rocks. It has been argued that this latter type of differentiation, namely absolute enrichment in iron in basic magma for the greater part of its crystallization history, is abnormal in type. That this does not appear to be the case is illustrated by absolute iron enrichment trends in the New Amalfi, Breven, Hällefors, Beaver Bay, and Okonjeje rocks.

Presumably the reason why certain intrusions, dominantly tholeiitic, show absolute enrichment in iron is to be found in the changing chemistry and variable position in the crystallization sequence of the iron ores, a reflection of oxidation-reduction equilibria prevailing during crystallization. The state of oxidation of the iron is directly controlled by the

concentration or pressure of water in the melt, high  $[H_2O]$  resulting in a high  $Fe_2O_3/FeO$  ratio. Hence analcime-bearing alkali olivine-basalt hypabyssal rocks, reflecting in their mineralogy a 'wet' magmatic parentage, would not be expected to reveal absolute iron enrichment to any great extent.

If crystallization of basic magma takes place initially under reducing conditions, most of the iron is present as  $FeO$ . Goldschmidt (1954, p. 38) has drawn attention to the primitive reduced state of the Skaergaard chilled marginal facies. A specimen (J5) from one of the feeder dykes to the Black Jack sill, collected from colliery workings below the main intrusion, has the lowest  $Fe_2O_3/FeO$  ratio (0.24) of any of the teschenites, despite slight modification by residual solutions. This rock completed its crystallization before the magma entered the final magma chamber, after which oxidizing conditions became increasingly more effective.

In the early and middle stages of differentiation of basic magma the iron, principally in the ferrous state, enters the ferro-magnesian silicates, which, with falling temperature, become progressively enriched in iron relative to magnesia. If  $Fe_2O_3$  is low in the early stages, the amount of ore precipitated is very slight; the Skaergaard marginal facies contains 0.5 to 1.0 % ore. Under continued reducing conditions very little  $FeO$  is lost as ore in the early and middle stages of differentiation, for the ore consists predominantly of  $Fe_3O_4-Fe_2TiO_4$  solid solutions. The amount of titanomagnetite precipitated depends on the available  $Fe_2O_3$ . Whilst more data on the titanomagnetites from more primitive basic representatives is desirable, present information on such minerals would suggest that the quantity of  $Fe_2TiO_4$  entering into solid solution does not exceed 50 %. Indirectly, then, the amount of  $Fe_2O_3$  available at this stage for ore formation tends to control the quantity of  $FeO$  and  $TiO_2$  lost to magma as precipitated ore.

Under continued reducing conditions,  $FeO$  (and to a lesser extent  $TiO_2$ ) may be continually concentrated in successive magmatic fractions. The olivine may then attain compositions in the vicinity of  $Fa_{90-95}$ ; tholeiitic pyroxenes also show strong iron enrichment. If the Black Jack magma had not undergone progressive oxidation in the final magma chamber, it is probable that olivine compositions up to nearly pure fayalite<sup>1</sup> would have been encountered, while the composition of the most iron-rich analysed clinopyroxene ( $Ca_{47}Mg_{33}Fe_{20}$ ) would have moved farther towards hedenbergite.

<sup>1</sup> The most iron-rich olivine has a composition of  $Fa_{80}$ .

If oxidation processes are effective in the early and middle stages of differentiation, much of the excess iron over that necessary for the ferro-magnesian silicates is dissipated as ore, which may show an even distribution throughout the rock series, or, as is often the case, actually increase in amount in the middle and later stages of evolution. In the Black Jack sill the amount of modal iron ore decreases slightly at first in the lower teschenites. In the teschenites occurring at elevations greater than 250 to 300 feet above the lower contacts the amount of modal iron ore increases.

In hypabyssal basic rocks the stage of maximum iron enrichment following earlier conditions of slight oxidation is exemplified by the ore-enriched tholeiitic dolerite pegmatites, whose consolidation occurred when volatile (oxidizing) conditions became important (Walker, 1953). These rocks in certain instances contain up to 18 % total iron, a large proportion of which is in the ferric state.

*Acknowledgements.* This work was carried out in the Department of Mineralogy and Petrology, Cambridge, during the tenure of a Royal Dutch/Shell Commonwealth Postgraduate Scholarship. The writer is indebted to Prof. C. E. Tilley for many helpful discussions. Thanks are due also to Dr. S. R. Nockolds and Mr. R. S. Allen for spectrographic determinations, to Mr. J. H. Scoon for duplicate determinations of certain constituents, and to Mr. K. Rickson for taking the titanomagnetite powder photographs.

#### *References.*

- ABRAHAM (S. C.) and CALHOUN (B. A.), 1953. *Acta Cryst.*, vol. 6, p. 105. [M.A. 12-318.]
- AKIMOTO (S.), 1951. *Journ. Geomagnetism & Geo-electricity*, Tokyo Univ., vol. 3, p. 47.
- BARTH (T. F. W.) and POSNJAK (E.), 1932. *Zeits. Krist.*, vol. 82, p. 325. [M.A. 5-179.]
- BOWEN (N. L.), 1928. *Evolution of the igneous rocks*. Princeton Univ. Press. [M.A. 4-123.]
- BUDDINGTON (A. F.), FAHEY (J.), and VLISIDIS (A.), 1955. *Amer. Journ. Sci.*, vol. 253, p. 497.
- CHEVALLIER (R.) and GIRARD (J.), 1950. *Bull. Soc. Chim. France*, vol. 17, p. 576. [M.A. 11-368.]
- CORNWALL (H.), 1951. *Econ. Geol.*, vol. 46, p. 51.
- 1951a. *Bull. Geol. Soc. Amer.*, vol. 62, p. 159. [M.A. 11-340.]
- EDWARDS (A. B.), 1938. *Amer. Min.*, vol. 23, p. 277. [M.A. 7-184.]
- 1942. *Journ. Geol.*, Chicago, vol. 50, pp. 451, 579. [M.A. 9-161.]
- 1954. *Textures of the ore minerals and their significance*. Australian Inst. Min. Met., Melbourne. [M.A. 12-456.]
- ERNST (T.), 1943. *Zeits. angew. Min.*, vol. 4, p. 394.
- EVARD (P.), 1949. *Econ. Geol.*, vol. 44, p. 210.
- FENNER (C. N.), 1929. *Amer. Journ. Sci.*, ser. 5, vol. 18, p. 225. [M.A. 4-507.]
- 1931. *Min. Mag.*, vol. 22, p. 539.

- FOSLIE (S.), 1928. *Fennia*, vol. 50, p. 1.
- GIRAULT (J. P.), 1953. *Naturaliste Canadien*, vol. 80, p. 307. [M.A. 12-447.]
- GOLDSCHMIDT (V. M.), 1954. *Geochemistry*. Oxford. [M.A. 12-295.]
- HJELMQVIST (S.), 1950. The titaniferous iron-ore deposit of Taberg in the south of Sweden. *Sveriges Geol. Undersök. Avhandl. ser. C*, no. 512, p. 1. [Årsbok 43, no. 10.]
- KENNEDY (G. C.), 1948. *Amer. Journ. Sci.*, vol. 246, p. 529. [M.A. 10-424.]
- MASON (B.), 1943. *Geol. För. Förh.*, vol. 65, p. 97. [M.A. 9-32.]
- MOGENSEN (F.), 1946. *Ibid.*, vol. 68, p. 578. [M.A. 10-101.]
- NEWHOUSE (W. H.), 1936. *Bull. Geol. Soc. Amer.*, vol. 47, p. 1.
- ÖDMAN (O. H.), 1942. *Geol. För. Förh.*, vol. 54, p. 285. [M.A. 5-443.]
- OSBORNE (F. F.), 1928. *Econ. Geol.*, vol. 23, p. 724.
- PALMUNEN (M. K.), 1925. *Fennia*, vol. 45, no. 9.
- POUILLARD (E.), 1950. *Ann. de Chimie*, ser. 12, vol. 5, p. 164.
- and MICHEL (A.), 1949. *Compt. Rend. Acad. Sci. Paris*, vol. 228, p. 1232.
- SCHWARTZ (G. M.), 1930. *Amer. Min.*, vol. 15, p. 243. [M.A. 4-409.]
- TANEDA (S.), 1950. *Journ. Geol. Soc. Japan*, vol. 56, p. 415.
- TOMBS (N. C.) and ROOKSBY (H. P.), 1951. *Acta Cryst.*, vol. 4, p. 474.
- VINCENT (E. A.) and PHILLIPS (R.), 1954. *Geochimica Acta*, vol. 6, p. 1. [M.A. 12-293.]
- WALKER (F.), 1953. *Amer. Journ. Sci.*, vol. 251, p. 41. [M.A. 12-147.]
- and POLDERVAART (A.), 1949. *Bull. Geol. Soc. Amer.*, vol. 60, p. 591. [M.A. 11-32.]
-