Distinct cooling histories of troctolites from the Freetown layered gabbro

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SUMMARY. The iron-titanium oxide minerals of three troctolites from the Freetown layered gabbro have been analysed using an electron microprobe. Comparisons of the analyses of the iron–titanium minerals with the data of Buddington and Lindsley (1964) provide temperature and oxygen fugacity information relating to particular magnetite–ilmenite grains. Magnetite–ilmenite grains occurring in different silicate environments within any one single troctolite rock have equilibrated at differing times in the cooling history of that rock and this enables part of that history to be established. The partial cooling histories established for the three specimens can be clearly distinguished, and are strongly influenced by the appropriate buffer reactions.

THE crystallization history of three troctolite samples from the layered gabbro of Freetown, Sierra Leone, have been investigated by studying the magnetite–ilmenite grains. Electron-microprobe analyses of the iron–titanium oxide minerals allow an indication of the temperatures and oxygen fugacities of equilibration of the oxides to be obtained by applying the experimental results of Buddington and Lindsley (1964). Bowles (in press) provides two points in the temperature and oxygen fugacity history of a further specimen from Freetown as recorded by a single, complex magnetite–ilmenite grain. It is more common, however, to find iron–titanium oxides showing only one generation of ilmenite derived from magnetite and it is specimens of this type that are described here.

The samples were provided by M. K. Wells who has given a full description of the complex (Wells, 1962). The intrusion is divided into four sequential major zones each containing many cycles of rhythmic layering and within each rhythmic unit there is a smaller scale layering parallel to the major structure. The small-scale layering is formed by changes in the modal proportions of plagioclase and is accompanied by a fluxion structure with plagioclase laths arranged parallel to the layering. The rhythmic units vary from troctolite at the base to leucogabbro or anorthosite at the top, with olivine giving way to plagioclase and pyroxene upwards. The minerals are uniform in composition throughout the intrusion and no cryptic variation has been detected. Of the three troctolites described here BA 700 is from the base of a rhythmic unit at the foot of zone 2, BA 666 is from a similar position in the succeeding rhythmic unit, and BA 542 is from zone 3. BA 879 described previously (Bowles in press) is from an ore-rich segregation towards the top of zone 1.

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Petrography

Specimen BA 666 is a gabbro that shows strongly fluxioned plagioclase laths interspersed with pyroxenite or olivine-pyroxenite laminae, which are 2 or 3 grains in thickness. In the laminae the olivine is of similar size and shape to the pyroxene and it may be inferred that the two minerals crystallized over the same temperature interval. The pyroxene is an augite showing diallagic lamellae of orthopyroxene and large irregular magnetite–ilmenite grains are closely associated with the clinopyroxene. The part of the specimen that has been analysed is from a lamina and is shown in fig. 1a.

The opaque minerals occur as irregular grains more or less enclosed by pyroxene such as the grain labelled M_2-I_2 (fig. 1a). Other irregular grains (M_1-I_1 and M_3-I_3) are more closely associated with plagioclase and are often separated from the pyroxene by a thin zone of plagioclase. The magnetite shows occasional fine ceylonite lamellae, which are usually confined to a corner or edge of the magnetite remote from the ilmenite, whilst the ilmenite is homogeneous. In other sections the oxides occur as rounded grains within the olivine, as developments along the olivine fractures, as minute plates within the cleavage planes of the augite, or as extremely irregular grains intergrown with the late-stage orthopyroxene.

Specimen BA 700 is a troctolite containing some clinopyroxene. Lenticular aggregations of ferromagnesian minerals are contained within aligned plagioclase laths. The plagioclase crystals have a composition of about Ab_{35} and the lenticular aggregations are formed principally of olivine with some iron–titanium oxide minerals and a few clinopyroxene crystals. The boundaries between olivine crystals are straight and where three olivines are adjacent the boundaries meet at about 120° in a manner comparable with metamorphic triple-junction texture.

The larger opaque grains are contained between olivine crystals where they participate in the triple-junction texture of the olivine. Usually these oxides are a magnetite–ilmenite pair. The magnetite may contain minute ceylonite lamellae, which are confined to small but randomly located areas of the magnetite. The oxide–olivine boundary is usually curved, and is concave towards the oxide. It is interesting to note that this curvature is stronger on ilmenite–olivine boundaries than on magnetite–olivine boundaries (fig. 1b). Smaller grains in this situation often have straight boundaries especially if they are composed only of magnetite. The contact between oxides and the pyroxene grains is irregular and this may be connected with the tendency of the pyroxene to exsolve minute plates of oxide along the cleavage planes. The oxides also penetrate into the plagioclase around the lenticular masses, but in a less irregular way. In the example shown in fig. 1b the magnetite is separated from the plagioclase by a thin selvedge (S_{13}) of clinopyroxene. Rounded blebs of opaque minerals are found within the olivine (fig. 1c), and these are ilmenite–magnetite grains where the magnetite is free from exsolution lamellae. Here, the oxide–olivine boundary is convex towards the oxide. In rare instances these blebs of opaque minerals include digenite (grain D_{10} in fig. 1c).

Specimen BA 542 has the mafic minerals grouped together in irregular clots surrounded by plagioclase, which is not aligned. The olivine crystals in the clots show a
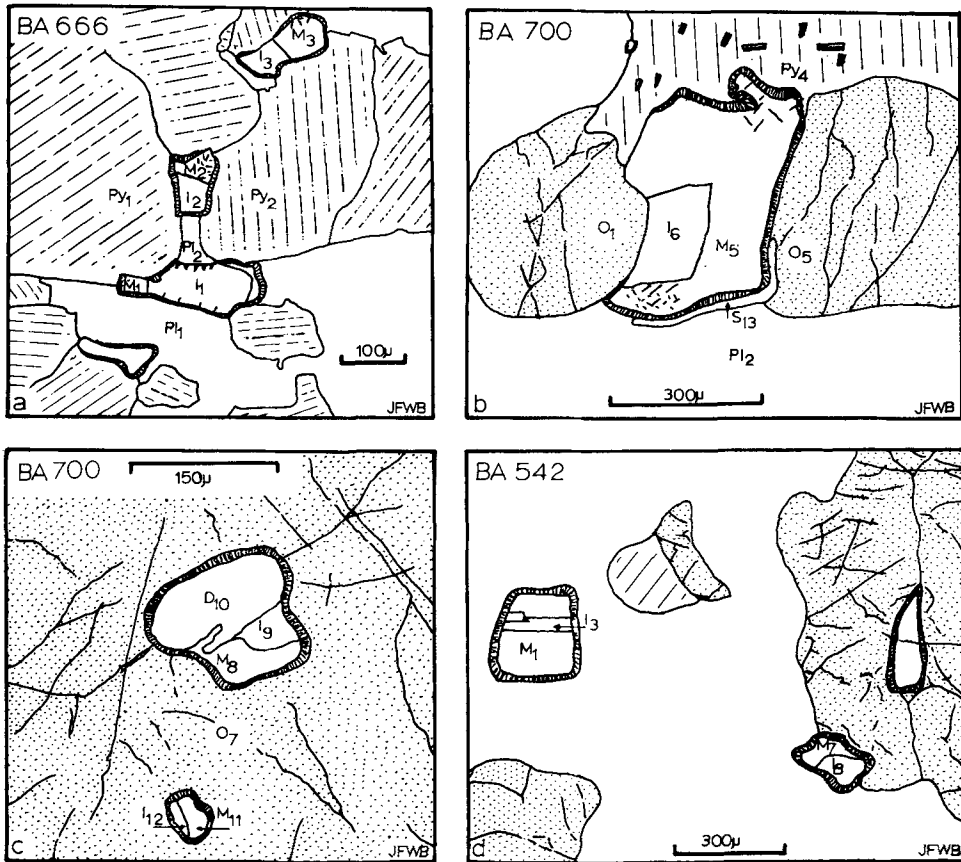
FIG. 1. Olivine is shown stippled whilst plagioclase remains blank. The augite is shaded and the shading represents the extent and direction of the diallage. The boundaries of the oxide grains have been emphasized to indicate the differences in size of these grains as they appear in transmitted and reflected light. Minerals analysed have been numbered and the position of the number indicates the point analysed. The same numbering is applied to the results of the analyses in Table I.

tendency to form triple-junction texture but the mutual boundaries are irregular. Associated with the olivines is a diallagic augite, which, in the larger grains, is twinned, producing herring-bone texture. The oxides are often attached to the surfaces of the mafic aggregates and project into the plagioclase. The composite magnetite–ilmenite grain illustrated in fig. 1d (M_7, I_8) is an example of this type and is characteristic in showing an irregular, rounded outline. Occasionally the iron–titanium minerals occur between the olivine grains or as rounded blebs within the olivine. The plagioclase contains important oxides, which are subhedral with rounded corners and contain ilmenite lamellae within the magnetite. A grain of this type contains a small grain of native copper (M_1, I_3 of fig. 1d). All the oxide grains are free from minor ceylonite lamellae.

Specimen BA879 is a magnetite–ilmenite segregation associated with a pegmatite that has been described by Wells (1962, pp. 102–4) and by Bowles (in press), who also provided analytical details.

Electron microprobe analyses

These analyses were obtained using a Cameca microprobe modernized by the author. Pure metal standards were used for elements of atomic number 22 and over whilst silicate standards, kindly provided by Dr. A. M. Clark, were used for the lighter elements. The computer program devised by Mason *et al.* (1969) provided the necessary correction procedure, and the data were prepared for this program using the technique described in Bowles (1975).

Table I presents the analyses of the magnetite–ilmenite pairs of grains described here. The total iron, measured by the microprobe, is allocated to Fe^{2+} or Fe^{3+} so as to produce stoichiometric, solid-solution series compositions, after the minor constituents have been taken into account. This follows the modification by Anderson (1968) of the method developed by Wones and described by Buddington and Lindsley (1964).

The low totals of the BA666 magnetites indicate that these magnetites are not stoichiometric due to late-stage oxidation. The results produced here are calculated to stoichiometric compositions on the basis of the $Ti/(Ti+Fe)$ ratio, effectively reducing the mineral to its composition before late-stage oxidation. The data can, therefore, be used to study earlier processes.

As reported by many other authors the aluminium, chromium, and vanadium have remained in the magnetite whilst magnesium and manganese have participated in the formation of ilmenite. This division is particularly marked in the specimens considered here, although vanadium does not always adhere to this rule.

The concentrations of Al, Cr, and V in the magnetites are particularly high, the Cr_2O_3 rising to 6–7 % in BA542 and the R_2O_3 constituents total between 7 and 13 wt. % of the magnetites. This is considerably higher than most magnetite analyses in the literature. A notable exception is provided by analyses of certain basal layers of the Sudbury Nickel Irruptive in which magnetites containing up to 13 % Cr_2O_3 have been described by Gasparrini and Naldrett (1972).

The higher concentration of manganese in the magnetites of BA666 reflects the higher concentration of Mn in the silicates of that specimen, described by Bowles (in preparation). The difference in MnO content between the grains (M_1, I_1 and M_3, I_3) associated with plagioclase and the grain M_2, I_2 which is associated with pyroxene reflects the higher MnO concentration in the pyroxene. The distribution of manganese between the coexisting phases closely resembles that due to fractional crystallization as observed by Wager and Mitchell (1951) in the gabbros of Skaergaard. The origin of the layered series of Freetown is shown by Wells (1962) to exhibit neither fractional crystallization nor continuous differentiation, and the manganese distribution observed here is ascribed to partitioning between concomitant minerals.

The magnetites of BA666, which contain ceylonite lamellae, show higher concentrations of MgO than those examples from BA700 and BA542, which do not contain these lamellae. All the analyses were conducted on areas of the magnetite free of

ceylonite lamellae, so that the results relate to the magnetite and are not affected by the presence of the lamellae. Thus the presence of these lamellae indicates an initial high magnesium composition related to the conditions of formation of the grain, and the absence of the lamellae does not necessarily indicate different secondary processes.

The magnetite of the pegmatitic specimen BA879 shows considerably less Cr_2O_3 and somewhat less V_2O_3 although both MgO and SiO_2 are more abundant. The ilmenites of BA879 contain more Al_2O_3 and SiO_2 but less V_2O_3.

The magnetites and ilmenites that are associated with copper minerals contain the greatest quantity of copper, and there appears to be an inverse relationship between MgO and CuO, which is particularly noticeable in the ilmenites of BA700.

Presentation of temperature and oxygen fugacity results

The magnetite–ilmenite results of Table I may be used in conjunction with the work of Buddington and Lindsley (1964) in order to obtain points in the temperature and oxygen-fugacity field corresponding to each of the magnetite–ilmenite pairs. The results of this technique are given in Table II.

The experimental work of Buddington and Lindsley is shown in their fig. 5 (p. 316) projected on the temperature and oxygen-fugacity axes, and this figure is frequently used. However, in an appendix, the authors provide data for redrawing their results on a larger scale, and this has been done here. Further, it was realized that the spacing between the curves does not represent a linear change in composition, and it is neces-sary to use non-linear techniques for interpolation between the curves. Using this method the results given in Table II are quoted to the nearest degree of temperature and to the first decimal place of $\log f_{O_2}$ in accordance with normal practice (e.g. Drake, 1975). However, all the comparisons made in this work cover tens of degrees of temperature and several orders of magnitude of oxygen fugacity.

Fig. 2 shows the present results plotted with those already obtained for BA879 on a base of curves corresponding to important buffer reactions. The data used for drawing the reaction curves have been taken from Verhoogen (1962). The lines drawn through the points plotted for each specimen have been drawn with a curvature similar to that of the reaction curves. Two important points emerge from fig. 2 and these will be described in turn:

The errors estimated for the experimental work of Buddington and Lindsley (1964) are given by these authors as ± 50 °C and $\pm 1\cdot0$ atm. $\log f_{O_2}$. This has prompted Anderson (1968) very properly to indicate the measure of uncertainty in the numerical value of his results by delineating an area, rather than a single point, in the tempera-ture and oxygen-fugacity field. Fig. 2 has not been treated in this way for greater clarity and it is therefore necessary to stress the difference between accuracy and pre-cision. The lower temperature grain of BA700 and the corresponding grain of BA666 differ by 3 % hematite content in the ilmenite and 6 % ulvöspinel content in the mag-netite. For the present purpose the titanium measurements can serve as an index of the accuracy of measurement. The titanium content in the associated ilmenite was measured as $26\cdot9\pm0\cdot2$ %. The errors of measurement are, therefore, sufficiently small compared with the differences between the cooling trends to show that these

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TABLE I. *Electron-probe analyses of ilmenite and magnetite; for allocation of the total Fe to* Fe^{2+} *and* Fe^{3+} *see text*

Ilmenite analyses

	BA879 L	BA879 G	BA666 I1	BA666 I2	BA666 I3	BA700 I6	BA700 I9	BA700 I12	BA542 I3	BA542 I8
FeO	38·47	39·57	37·88	37·85	35·83	37·75	39·29	39·42	35·58	35·30
Fe_2O_3	3·02	2·65	4·70	2·24	4·79	6·57	6·20	6·03	6·09	9·24
TiO_2	52·35	52·27	51·04	50·44	52·23	48·77	47·94	49·13	50·40	50·34
MgO	4·56	3·92	4·05	3·85	5·81	3·25	1·96	2·53	5·17	5·31
MnO	0·70	0·53	0·69	0·54	0·65	0·49	0·49	0·58	0·53	0·53
NiO	n.d.	0·13	0·11	0·10	0·10	0·06	0·07	0·05	n.d.	n.d.
CaO	n.d.	n.d.	0·00	0·02	0·00	0·00	0·00	0·01	0·00	0·00
CuO	n.d.	n.d.	0·00	0·00	0·00	0·09	0·47	0·07	0·00	0·00
Al_2O_3	0·62	0·49	0·11	0·00	0·25	0·20	0·07	0·00	0·16	0·16
Cr_2O_3	0·04	0·11	0·29	0·20	0·25	0·12	0·11	0·14	0·15	0·08
V_2O_3	0·35	0·29	1·34	1·45	1·58	2·31	1·97	2·06	0·42	0·42
SiO_2	0·21	0·08	0·00	0·03	0·02	0·18	0·20	0·35	0·02	0·02
Total	100·32	99·91	100·21	97·69	101·49	99·80	98·77	100·37	98·51	101·40

Molecular proportions of discarded components*

	BA879 L	BA879 G	BA666 I1	BA666 I2	BA666 I3	BA700 I6	BA700 I9	BA700 I12	BA542 I3	BA542 I8
R_2O_3	0·009	0·007	0·012	0·111	0·015	0·018	0·015	0·015	0·005	0·005
$RO.SiO_2$	0·004	0·001	0·0	0·001	0·0	0·003	0·003	0·006	0·0	0·0
$RO.TiO_2$	0·119	0·103	0·112	0·104	0·154	0·085	0·053	0·066	0·012	0·015

Molecular percentages of the principal components calculated to total 100 %

	BA879 L	BA879 G	BA666 I1	BA666 I2	BA666 I3	BA700 I6	BA700 I9	BA700 I12	BA542 I3	BA542 I8
Hematite	3·4	12·0	5·3	3·7	5·7	7·3	6·6	6·4	7·2	10·5
Ilmenite	96·6	88·0	94·7	96·3	94·3	92·7	93·4	93·6	92·8	89·5

Magnetite analyses

	BA879	BA666 M1	BA666 M2	BA666 M3	BA700 M5	BA700 M8	BA700 M11	BA542 M1	BA542 M7
FeO	34·32	35·89	34·17	35·74	35·86	35·88	38·02	38·88	39·42
Fe_2O_3	45·19	41·00	42·35	40·27	45·33	44·87	42·18	38·93	37·43
TiO_2	8·07	9·35	8·74	9·01	6·92	5·73	7·84	8·25	8·65
MgO	3·00	1·70	2·28	1·40	2·01	0·30	0·49	0·40	0·81
MnO	0·21	0·52	0·71	0·51	0·25	0·24	0·30	0·20	0·32
NiO	n.d.	0·27	0·11	0·24	0·20	0·00	0·20	n.d.	n.d.
CaO	n.d.	0·00	0·09	0·01	0·00	0·00	0·12	0·05	0·25
CuO	n.d.	0·00	0·00	0·00	0·07	0·20	0·00	0·02	0·00
Al_2O_3	5·05	3·69	3·52	3·98	5·75	4·59	5·17	5·17	5·09
Cr_2O_3	0·85	2·15	2·44	2·04	2·80	3·77	3·75	6·10	7·03
V_2O_3	1·09	1·72	1·61	1·67	1·61	1·79	1·52	1·45	1·46
SiO_2	0·24	0·00	0·00	0·04	0·37	0·10	0·07	0·12	0·64
Total	98·02	96·29	96·02	94·91	101·17	97·58	99·66	99·57	101·10

*Molecular proportions of discarded components**

	BA879	BA666 M1	BA666 M2	BA666 M3	BA700 M5	BA700 M8	BA700 M11	BA542 M1	BA542 M7
$2RO.SiO_2$	0·004	0·0	0·0	0·001	0·006	0·002	0·001	0·002	0·011
$FeO.R_2O_3$	0·0	0·0	0·0	0·001	0·023	0·072	0·062	0·087	0·095
$2RO.TiO_2$	0·013	0·005	0·013	0·0	0·0	0·0	0·0	0·0	0·0
$(RO_{0.7}FeO_{0.3}).R_2O_3$	0·062	0·062	0·061	0·063	0·062	0·010	0·024	0·014	0·011

Molecular percentages of the principal components calculated to total 100 %

	BA879	BA666 M1	BA666 M2	BA666 M3	BA700 M5	BA700 M8	BA700 M11	BA542 M1	BA542 M7
Ulvöspinel	23·7	30·4	26·6	30·9	23·4	20·3	27·1	29·8	31·6
Magnetite	76·3	69·6	73·4	69·1	76·6	79·7	72·9	70·2	68·4

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n.d. = not determined.
* RO = total of mol. proportions of $MgO + MnO + NiO + CaO + CuO$.
  R_2O_3 = total of mol. proportions of $Al_2O_3 + Cr_2O_3 + V_2O_3$.
  Following the method of Wones, described by Buddington and Lindsley (1964), the minor components of the ilmenite are reduced to R_2O_3, $RO.SiO_2$ and $RO.TiO_2$, which are discarded leaving a pure Fe–Ti–O system. A modification by Anderson (1968) of the method of Wones is used to form $2RO.SiO_2$, $(RO_{0.7}FeO_{0.3}).R_2O_3$, and $FeO.R_2O_3$ or $2RO.TiO_2$ from the minor components of the magnetite.

differences are real. However, the exact position of the entire set of results in the temperature and oxygen-fugacity field is subject to the limits of error laid down by Buddington and Lindsley (1964).
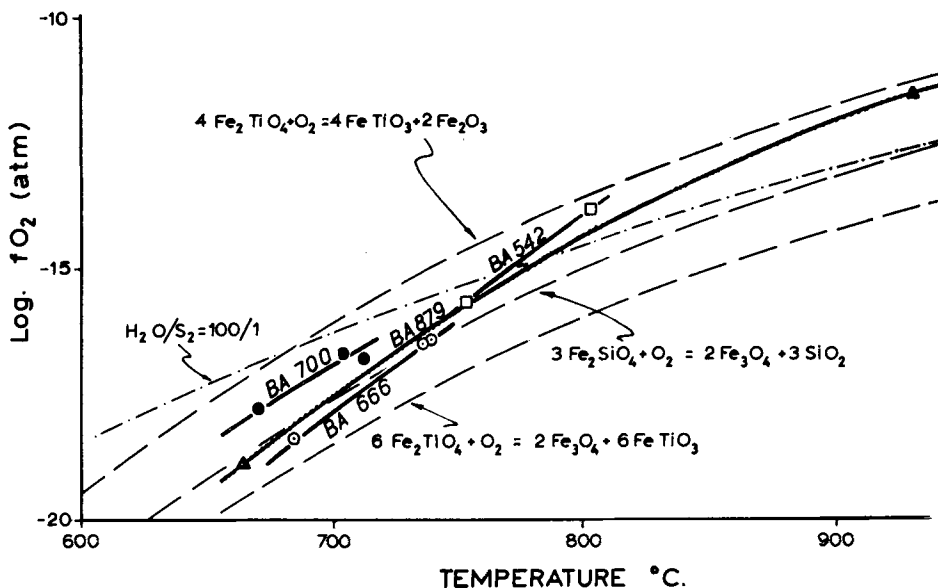

FIG. 2. Cooling trends in the temperature and oxygen-fugacity field compared with buffer reactions provided by Verhoogen (1962). Drawn by C. Stuart.

TABLE II. *Temperature and oxygen-fugacity results from magnetite–ilmenite grains*

Rock	BA 666			BA 700			BA 542		BA 879	
Grain	M_1, I_1	M_2, I_2	M_3, I_3	M_5, I_6	M_8, I_9	M_{11}, I_{12}	M_1, I_3	M_7, I_8	M, IL	M, IG
Temperature	737 °C	685	740	704	670	713	751	802	662	930
Log f_{O_2}	−16·5	−18·4	−16·4	−16·7	−17·8	−16·8	−15·9	−13·8	−19·0	−11·5

Discussion

Distinct equilibration conditions for separate oxide grains within a single specimen. Each of the specimens for which analyses have been presented in this paper shows a distinct distribution of points in the temperature and oxygen-fugacity field and this can be related to the association between the iron–titanium oxide minerals and the coexisting silicates. Specimen BA666 shows two points grouped close together, which relate to the two grains M_1, I_1 and M_3, I_3, which are enclosed principally by plagioclase. A lower temperature and oxygen fugacity are shown by the remaining grain (M_2, I_2), which is mainly enclosed by pyroxene. The temperatures and oxygen fugacities produced in this work correspond to the conditions at which equilibration between the two components of the individual grain ceased and this must reflect the conditions

in the immediate area of that grain. A normal cooling curve shows decreasing temperature and oxygen fugacity and the present results must therefore indicate that the iron-titanium oxide grains contained by pyroxene equilibrated later than those grains surrounded by plagioclase. A line drawn between the points in the temperature and oxygen-fugacity field corresponding to the grains of specimen BA666 must represent part of the cooling history of that specimen.

The grain (M_{11}, I_{12}) of specimen BA700, which is totally enclosed by olivine, equilibrated under conditions similar to the grain (M_5, I_6), enclosed by olivine and pyroxene; whilst the grain associated with the digenite and also enclosed by olivine equilibrated at a distinctly later, cooler stage. There is a similar distinction between the grain (M_1, I_3) of BA542, enclosed by plagioclase, and the higher temperature grain (M_7, I_8), attached to the olivine.

In the light of these results it is necessary to re-examine some of the previous work on this topic. Many of the previously published results have been based upon chemical analyses of the iron–titanium minerals after separation, and this is subject to the implicit assumption that all the grains have the same composition. If the grains have different compositions, then the chemical analysis provides a weighted average, which is dependent upon the compositions of the grains and the numbers and sizes of the grains of each of the different compositions. The result, in such a case, would not necessarily represent an instant in the temperature and oxygen-fugacity history of the rock although, because the cooling curves in the temperature and oxygen-fugacity field are only gentle curves, the result is probably not too far from some point on the actual cooling curve. The original results of Buddington and Lindsley (1964) and the more recent results of Duchesne (1972) must therefore be subject to this criticism.

It is apparent, then, that for a particular rock, magnetite–ilmenite grains in a similar silicate environment equilibrated at similar conditions, which are, in turn, quite different from the equilibration conditions of magnetite–ilmenite grains showing different silicate associations.

To obtain a complete picture would require many more results, which, like the present study, would be limited by the fact that each section is only seen in two dimensions, so that the complete association of any one grain with its neighbours is obscured. The importance of the present results is the illustration that differences of this type do exist and that, in general terms, when pyroxene is adjacent to an oxide grain, in an otherwise similar environment, the equilibration of the oxide grain occurs at a lower temperature. It is also apparent that when a copper mineral is present the equilibration of an associated magnetite–ilmenite grain is also delayed.

The concept that the same mineral can equilibrate at different times in the cooling history of one small rock section is at first somewhat surprising and requires further consideration. Evidently each oxide grain must be considered to be isolated from other grains of the same type and contained within a small, independent system. Presumably, during and immediately after crystallization of the main silicates, connected intergranular spaces existed, occupied by residual fluids or vapours that directly controlled the oxygen fugacity. As cooling proceeded, these intergranular spaces were increasingly blocked up until only isolated pockets remained. The isolation of independent

systems probably occurred at various times and may have been complicated by small scale cracks opening in the rock or in individual minerals due to thermal contraction or mechanical stresses induced in the cooling intrusion. In this respect, the pyroxenes show considerable development of cracks compared to the plagioclases and olivines due to the higher coefficients of thermal expansion of the pyroxenes.

The triple-junction features displayed by the olivines provide evidence that some processes of the type usually associated with metamorphism occurred during the cooling of the Freetown layered gabbro. Wells (private communication in preparation for publication) has shown that secondary pyroxene crystallization occurred in similar troctolites, considerably later than the main crystallization and controlled by mechanical stress systems produced in the developing intrusion. In the final equilibration of any magnetite–ilmenite grain the most significant events were probably the final isolation of the microsystem containing the grain and possible equilibrations with surrounding silicates. Clearly this could have happened over a wide range of conditions and the spread of results obtained here suggests that this is so.

In studying crystallizing systems it is usual to consider whether the system remained open or closed during crystallization and the same consideration applies, on the smaller scale, during continued cooling below crystallization temperature.

The present results have shown that the latest magnetite–ilmenite to crystallize is often associated with pyroxene but it is far from clear whether this is due to chemical control exerted by the pyroxene or whether it is because the pyroxene contains more cracks, developed during cooling, which kept the microsystem open until a later stage.

Distinct cooling histories of related rocks. The cooling histories of the four specimens, within the range of the data presented in fig. 2, are quite distinct. Specimen BA700 and, to a lesser extent, specimen BA542 show evidence of equilibration under conditions of higher oxygen fugacity for a given temperature, compared with BA879, whilst specimen BA666 equilibrated at a lower oxygen fugacity. The results for specimen BA542 indicate that the iron–titanium minerals investigated for that specimen equilibrated at a higher temperature and oxygen fugacity than those of BA700 or BA666. Thus the equilibration of the grains analysed for specimen BA542 occurred comparatively earlier in the cooling history than the grains analysed in the latter specimens. If the cooling trend of BA542 were extended it would occupy a position intermediate between BA700 and BA666.

The oxygen fugacity in a magmatic body is believed to be closely controlled by the availability of water, thus the higher oxygen fugacity, at a given temperature, shown by BA700 indicates that the conditions of equilibration of this specimen were more hydrous than those for specimen BA666. These conditions are reflected by the appearance of biotite in BA700. The petrographic study of these rocks by Wells (1962, p. 38) has suggested that water played a significant role in the crystallization of these rocks, and Elsdon (1971) has been impressed by the effects of water in the Kap Edvard Holm layered gabbro.

Carmichael (1967) separated magnetite, ilmenite grains, and silicate phenocrysts from a large number of lavas and showed that iron–titanium oxides from lavas containing biotite and amphibole phenocrysts equilibrated at higher oxygen fugacities for a given

temperature than iron–titanium oxides from lavas containing olivine or pyroxene phenocrysts. Although the phenomenon studied by Carmichael occurred at a temperature higher by between 100 and 200 °C, the difference in oxygen fugacity between specimens containing hydrous minerals and specimens without hydrous minerals is similar to that shown in the present work.

The close parallelism between the temperature and oxygen-fugacity histories shown in fig. 2 and the reactions illustrated in the same figure is informative. A number of authors (e.g. Anderson, 1968; Buddington, 1963; Czamanske and Mihálik, 1972; Dasgupta, 1970) have taken the view that cooling processes of natural rocks in the temperature and oxygen-fugacity field follow a path that a note on the subject by Czamanske and Mihálik (1972, p. 507) described as 'a fairly systematic, if not buffered path'. The results presented here, particularly those for BA700, show that for an individual gabbroic specimen the buffer reactions do, in fact, exert a strong influence. Despite this control it is apparent that the cooling trends of specimens such as BA666 are able to cross the line of a buffering reaction at a low angle. Results, for various suites of rocks, plotted on axes similar to those of fig. 2 by Anderson (1968), Dasgupta (1970), and Elsdon (1972) have tended to confirm that control is exerted by the buffer reactions, but because these diagrams have represented trends compiled from different specimens the confirmation has previously been only approximate. This type of argument is usually directed towards showing that the system has remained closed during cooling but it has been shown that the equilibration conditions recorded by a particular magnetite–ilmenite grain relate in part to the closing of the microsystem containing that grain. In these circumstances the buffer reaction will undoubtedly play an important role. At high temperatures it may be possible to argue that because the cooling curve follows the buffer reaction, then the system is closed. With continued cooling the system is closing and dividing into closed microsystems so that that argument becomes decreasingly valid.

Each rock in a sequence may follow different cooling paths in the temperature and oxygen-fugacity field and from the evidence presented here it is seen to be inappropriate to compare single temperature and oxygen-fugacity points from different specimens as previous authors have done. The correct approach to a sequence of rocks, such as those in a layered gabbro, would seem to be to establish the cooling trends of each specimen and, subsequently, to make comparisons between trends. There is insufficient evidence in the present paper to make a useful comparison of this type since the specimens are from widely different stratigraphical locations. However, the specimens BA700 and BA666 represent the lower portions of adjacent rhythms of layering and a comparison between them shows how rapidly the cooling conditions can vary.

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