Ilmenite-magnetite geothermometry in trondhjemites from the Scourian complex of NW Scotland

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SYNOPSIS

THE crystallization history of four trondhjemite samples from the Scourian complex, NW Scotland, has been investigated using composite ilmenite-magnetite grains. A variety of compositions are present both as large- and small-scale exsolution lamellae, which can be used to unravel the complex cooling history of these rocks. The samples were collected near Upper Badcall, Sutherland, where intrusive trondhjemite sheets 1-2 m thick cut banded gabbro. The trondhjemites have a complex history that includes four stages: magmatic intrusions, granulite facies metamorphism, hydration and retrogression to amphibolite facies, and slow cooling with uplift.

Ilmenite-magnetite grains in samples HR. 49, 53, 86 display a complex exsolution pattern (fig. 1A). An original titanomagnetite exsolved into large-scale (up to 50 μm wide) ilmenite-magnetite lamellae from which have subsequently exsolved small-scale lamellae (c.4 μm wide) parallel to the earlier lamellae. The ilmenite-magnetite pairs form subhedral grains in a granoblastic aggregate of plagioclase and quartz. A little biotite overgrows some oxide grains. Ilmenite-magnetite grains in sample HR. 56 are composed of broad-zoned lamellae (fig. 1B); small-scale exsolution lamellae are absent. Silicate-grain boundaries are irregular and lower-temperature minerals (chlorite and carbonate) are more common.

The experimental results of Buddington and Lindsley (1964) allow the equilibration temperature and oxygen fugacity of coexisting ilmenite and magnetite to be determined from their chemical composition. Subsequent workers have shown that it is possible to determine liquidus temperatures and oxygen fugacity for volcanic rocks (Carmichael, 1967; Anderson, 1968a). Slowly cooled igneous and metamorphic rocks, however, have continued to equilibrate below their solidus and show a range of temperatures and oxygen-fugacity conditions (Anderson, 1968b; Duchesne, 1972; Oliver, 1978; Bowles, 1976, 1977).

This paper presents 42 new pairs of analyses made by electron-probe microanalysis, from 13 composite ilmenite-magnetite grains (Table I). Mole % ulvöspinel and R_2O_3 values have been calculated using the method of Carmichael (1967) and used to determine temperature and oxygen fugacity at equilibration, from the experimental data of Buddington and Lindsley (1964).

By using a scanning electron beam it is possible to obtain the average composition of a broad lamella that contains smaller exsolution lamellae in order to estimate its composition prior to exsolution. A $-\log_{10} f_{O_2} . T$ °C plot of lamellae whose original composition has been determined in this way shows that they lie on a curve slightly above the Ni-NiO buffer between 1010 and 850 °C (fig. 2). Temperatures of the order of 1000 °C are probably magmatic temperatures since they are higher than is
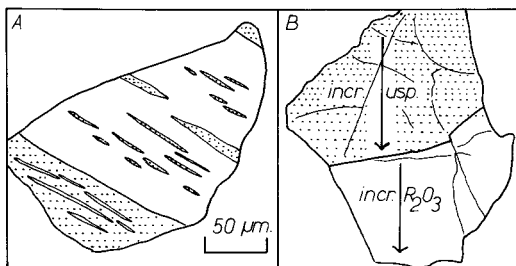

FIG. 1. (A) A complex ilmenite-magnetite grain with late exsolution lamellae; the magnetite is stippled. (B) a low-temperature ilmenite-magnetite grain showing the direction of zoning; the magnetite is stippled.

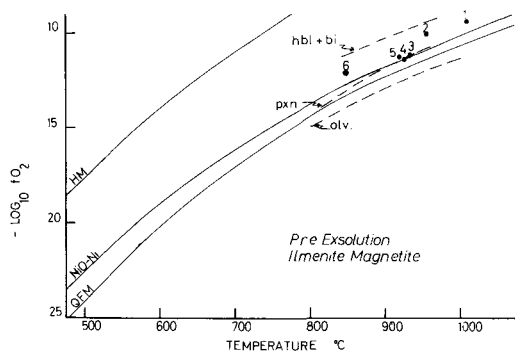[1] Present address: Dept. of Earth Sciences, The University, Leeds.

FIG. 2. Plots of $-\log_{10}f_{O_2}$ (in atmos.) versus temperature for coexisting ilmenite-magnetite grains prior to exsolution. Also shown are buffer curves for sialic magmas in equilibrium with ilmenite and magnetite and olivine, pyroxene and hornblende and biotite at 1 atmos. pressure (after Carmichael, 1967).

HM hematite–magnetite, Ni–NiO Nickel–nickel oxide, QFM quartz–fayalite–magnetite buffer curves, calculated to 8 kb total pressure.

normally recorded for granulite-facies metamorphism; 850 °C is interpreted as the blocking temperature below which diffusion was unable to occur to form large-scale lamellae. A comparison may be made between this oxygen-fugacity curve and the curves determined by Carmichael (1967) (fig. 2) for acid lavas coexisting with different phenocryst phases. If an adjustment is made for the differences in bulk composition and pressure, some correspondence between the analysed points and the curve for hydrous silicates would be expected since hornblende is the earliest Fe-bearing silicate seen in the trondhjemite. However, correspondence is not found, implying that amphibole did not control the oxygen fugacity, either because it was not the main Fe-bearing phase at magmatic temperatures, or because the oxygen fugacity was externally controlled.

After the formation of broad high-temperature lamellae Ti diffusion continued on a smaller scale (2–3 μm) so that the lower-temperature history of these grains can be considered in terms of many independent microsystems. Limited diffusion continued across the boundaries of and within early magnetite and ilmenite lamellae. The compositions of small-scale exsolution lamellae in ilmenite and magnetite hosts have been determined. Lamellae of ilmenite in magnetite from different grains define separate log f_{O_2}–T curves for different grains. Lamellae of magnetite in ilmenite equilibrated at

lower temperatures and oxygen fugacities. Individual microsystems have equilibrated at different temperatures and oxygen fugacities within the same grain and similar microsystems in different grains have equilibrated at different temperatures and oxygen fugacities, suggesting that the rock itself has become a series of independent closed systems.

The compositions of phases either side of early high-temperature lamellar boundaries have been measured. Analyses from different rocks yield different oxygen-fugacity curves in the same temperature range (765 to 610 °C). Higher temperatures were obtained for grains 49/3 and 86/4, which have exsolved into broad-zoned lamellae with no small-scale exsolution. The sense of the zoning is such that R_2O_3 in ilmenite decreases as it approaches magnetite. The equilibration temperature and f_{O_2} at the grain boundary increases from the centre of the grain to the edge.

In HR. 56 ilmenite magnetite grains show broad-zoned lamellae with no late small exsolution lamellae. The sense of zoning is such that magnetite grains increase in ulvöspinel content towards ilmenite and ilmenite decreases in R_2O_3 towards magnetite (fig. 1B). Even though the grains are in disequilibrium, it is assumed that equilibrium was at least established close to the boundary between lamellae. Equilibration temperatures thus obtained are between 410 and 430 °C at an f_{O_2} between the Ni–NiO and QFM buffers. Ilmenite–magnetite grains coexist with a biotite richer in Ti and a hornblende depleted in Fe relative to those in samples yielding higher oxide temperatures suggesting that there was continuous Fe–Ti exchange between oxides and silicates as well as between ilmenite and magnetite.

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ILMENITE - MAGNETITE GEOTHERMOMETRY IN TRONDJEMITES
FROM THE SCOURIAN COMPLEX OF N.W.SCOTLAND

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Summary

Ilmenite-magnetite intergrowths from intrusive trondhjemites in the
Scourie complex, N.W. Scotland were analysed with the electron probe and
their equilibration temperatures and oxygen fugacities determined from the
experimental work of Buddington and Lindsley (1964).   Temperatures range
from 1000°C (possibly magmatic) down to 400°C; different parts of single
grains became closed systems at different temperatures and different grains
in the same rock show differing cooling histories.   The oxygen fugacity of
the magma was buffered by ilmenite, magnetite and possibly pyroxene slightly
above the Ni-NiO buffer for 8kb; on cooling the oxygen fugacity fell below
the QFM buffer curve for 8kb. and this is consistent with the loss of H_2O
from the system into hydrous silicates.

Introduction

The crystallisation history of four trondhjemite samples from the
Scourie complex, N.W. Scotland has been investigated using composite
ilmenite-magnetite grains.   A variety of compositions are present both as
large and small scale exsolution lamellae, which can be used to unravel
the complex cooling history of these rocks.

The samples were collected from Geodh'nan Sgadan bay near the
village of Upper Badcall, Sutherland, where intrusive trondhjemite sheets
one to two metres thick are seen to cut banded and homogeneous gabbro; the
geology of the area has been described recently by Davies (1976).   The
samples were collected from three different sheets about 8 metres apart
separated by gabbro.   A Scourie age is assumed for the trondhjemites and
gabbros because they are cut by undeformed, en echelon, Scourie dykes with
chilled margins.   The trondhjemites were intruded into the gabbro
synchronous with or prior to granulite facies metamorphism.   Quartzo-
feldspathic gneisses adjacent to the gabbro, although in part retrogressed
contain two pyroxenes.   Two pyroxene assemblages in the gabbro show
equilibration temperatures between 600°C - 680°C using the Nehru - Wyllie
equation (1974) and between 820°C - 870°C using the Wood - Banno (1973)
model.   An estimate of the pressure of equilibration can be obtained from
the method of Wood (1974); garnet-orthopyroxene pairs in adjacent gabbros
show equilibration pressures in the range 8-12kb. and a figure of 8kb. has
therefore been adopted as a conservative estimate in the recalculation of
the oxygen buffer curves.   The trondhjemites contain no pyroxene and the
earliest minerals that can be recognised are plagioclase (An_{30}), bluish-
grey quartz, hornblende and biotite.   Some hornblende grains are
poikiloblastic and seived with small grains of quartz; others occur as
small grains in a matrix of fine grained granular quartz suggesting that
they have grown from a pyroxene.   Similar granodiorite sheets on Scourie
More 3 km. to the north contain orthopyroxene as their main ferromagnesian
phase.   Later minerals include green biotite, chlorite, carbonate,
epidote and sphene.   Retrogression is localised and patchy.

The trondhjemites of Upper Badcall Bay have a complex history which
includes the following stages: i) magmatic (ii) granulite facies
metamorphism (iii) hydration and retrogression to amphibolite facies
(iv) slow cooling with uplift.

Sketches of the grains analysed are presented in Fig.1. Ilmenite-
magnetite grains in samples HR.49,53,86 display a complex exsolution
pattern (Fig.1A, Synopsis).   An original titanomagnetite exsolved into
large scale (up to 50 μm wide) ilmenite-magnetite lamellae, from which have
subsequently exsolved small scale lamellae (ca 4 μm wide) parallel to the
earlier lamellae.   The ilmenite-magnetite pairs form subhedral grains in
a granoblastic aggregate of plagioclase and quartz.   A small amount of
biotite overgrows some oxide grains.   Ilmenite-magnetite grains in sample
HR.56 are composed of broad zoned lamellae (Fig.1B, Synopsis); small scale
exsolution lamellae are not present.   Silicate grain boundaries are most
irregular and lower temperature minerals (chlorite and carbonate) are more
common.

Analytical Procedure

Analyses were made on polished thin sections using a Cambridge
Microscan V electron probe in the Department of Geology, at the University
of Leicester.   Operating conditions were 15kv and a specimen current of
0.02 μamps.   A spot size of less than 1 μm diameter was used.   Iron and
titanium were usually determined simultaneously.   Points were relocated
using X - Y coordinates.   Full ZAF and dead time corrections were applied
using the computer programe Magic IV of Colby (1971) modified by R. N.
Wilson.

Standards used were synthetic Fe_3O_4 for Fe (this gave   good
agreement with Fe metal, but was 3% lower than Fe determined using natural
ilmenite; a similar disrepancy is found using the computer program of Mason,
Frost and Reed, 1969), Ti, natural ilmenite (Ti 29.73, Fe 36.87, Mn 0.66,
Mg 066, Al 0.02); Cr, pure chromium metal; Mn, natural rhodonite (Si 21.83,
Al 0.09, Fe 2.80, Mn 31.58, Mg 0.34, Ca 5.59); Mg, synthetic MgO; Al,
natural jadeite (Si 27.80, Al 13.30, Fe 0.10 Na 11.20). Minimum detection
limits are Fe, 140 ppm., Ti, 60 ppm., and for minor elements from 100 ppm.,
to 240 ppm.

In order to obtain an average analysis of a grain which contains
minute exsolution lamellae of ilmenite either a defocused
beam (diameter ca. 20 μm) or a scanning beam over an area of up to 30 x
45 μm., free from surface irregularities on a stationary specimen were
used; this gives the pre-exsolution composition of the grain as regards
total cations.

Low totals in magnetites are thought to indicate that they are not
stoichiometric due to late stage alteration towards γ-maghemite.   Since
total iron is determined as FeO it is necessary to calculate the mole
fraction of ulvospinel in titanomagnatite on the basis of the TiO_2 content
which does not change with oxidation; the remaining Fe is made into
magnetite.   It is therefore possible to use these analyses to study
events prior to late oxidation.   An average analysis of a magnetite grain
containing lamellae of ilmenite will also have a low total, since the
method used to recast the analysis as Mgt-Usp$_{ss}$ does not take into account
subsequent oxidation of Fe^{2+} to Fe^{3+} during$_{ss}$ the exsolution of ilmenite
lamellae (Powell & Powell 1977).   For a grain with the composition
Usp$_{45}$Mgt$_{55}$ exsolving into Usp$_{26}$Mgt$_{74}$ and Ilm$_{65}R_2O_3$$_{35}$ in the proportion
3:1 an average grain analysis will be ca.1.0% too low.

Iron was allocated to Fe^{2+} and Fe^{3+} on the basis of mineral
stoichiometry and the mole fractions of ulvospinel and R_2O_3 (Fe_2O_3 +
Al_2O_3 + Cr_2O_3) were calculated using the method of Carmichael 1967.
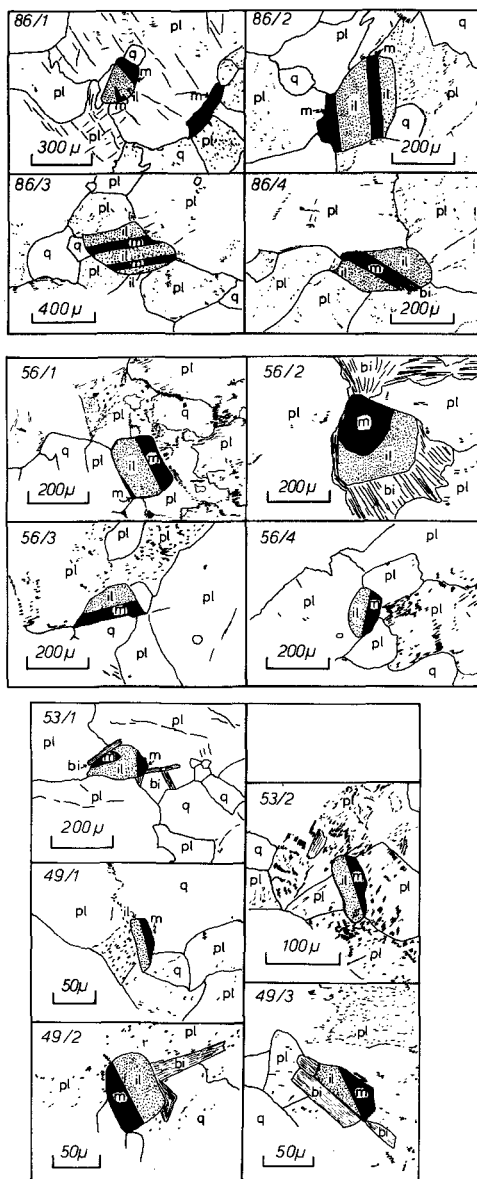

Fig. 1. a, b, c, sketches of oxide grains analysed showing only the
large ilmenite and magnetite lamellae; M, Magnetite; il, ilmenite;
pl, plagioclase; bi, biotite; q, quartz; the density of the stipple on
the plagioclase indicates the degree of sericitisation.

Thermometry and oxygen barometry

The experimental results of Buddington and Lindsley (1964) allow
the equilibration temperature and oxygen fugacity of coexisting ilmenite
and magnetite to be determined from their chemical composition. Subsequent
workers have shown that it is possible to determine liquidus temperatures
and oxygen fugacity for volcanic rocks (Carmichael, 1967; Anderson, 1968a)·
slowly cooled igneous and metamorphic rocks, however, have continued to
equilibrate below their solidus and show a range of temperatures and
oxygen fugacity conditions (Anderson, 1968b; Duchesne, 1972; Oliver,
1978).   Recent work by Bowles shows that the equilibration temperature
and oxygen fugacity estimated from compositions of ilmenite-magnetite
grains in slowly cooled gabbros may be a function of the silicate
environment, that different rocks from the same igneous complex may show
different cooling histories and that complex ilmenite-magnetite grains
may show a complex cooling history. (Bowles, 1976, 1977).

In the Scourian complex, O'Hara (1978) reports ilmenite-
magnetite intergrowths which suggest equilibration temperatures above 800°C
at an oxygen fugacity between the quartz - fayalite - magnetite and
magnetite - haematite buffers.

This paper presents 42 new pairs of analyses from 13 composite
ilmenite - magnetite grains (Fig.1, Table 1). Mole percent ulvospinel
and R_2O_3 values have been used to determine temperature and oxygen fugacity
at equilibration, from the experimental data of Buddington and Lindsley
(1964). These have been plotted on $-log_{10}fO_2$ vs. T°C. diagrams with
haematite - magnetite, NiO-Ni, and quartz$_{10}$- fayalite - magnetite oxygen
buffers calculated for 8 kb. total pressure from the data of Eugster and
Wones (1962) for reference (Figs.4-6, and Fig.2, Synopsis).

Treatment of minor elements

Since the experiments of Buddington and Lindsley (1964) were
confined to the pure $FeO-Fe_2O_3$ $-TiO_2$ system, their application to natural
Fe-Ti oxides is limited by the presence of impurities. Several
methods for recalculating analyses to minimise these effects have been
proposed and are reviewed by Bowles (1977b). For the purposes of
recalculating an analysis divalent elements are grouped together as RO,
trivalent elements as R_2O_3 and tetravalent elements as TO_2: RTO_3-R_2O_3 and
R_2TO_4-R_3O_4 stoichiometry is assumed. There are two types of
recalculation; firstly the method which assumes that the minor elements
form analogues of ulvospinel, magnetite, ilmenite and haematite and such
solid solutions behave as the pure Fe-Ti end-members (Carmichael 1967);
secondly the method which assumes that the minor elements are inert and so
are discarded (Anderson, 1968b, Buddington and Lindsley,1964). This
latter method arbitrarily groups together and discards RO and R_2O_3 as
spinel and RO and SiO_2 as silicate.

In this study the method of Carmichael has been adopted. The only
minor element of any significance is Mn in ilmenite, which rises to 4.6wt%
MnO. Using the recalculation procedure of Anderson (1968b) (the least
favourable alternative) ulvospinel differs by 0.18% Usp. and Fe_2O_3 differs
by 0.71% Fe_2O_3. These values make no
material difference to T and FO_2 derived from the Buddington and Lindsley
graph.

A plot of FeO vs MnO for ilmenite in acid and basic rocks from the
Scourian complex shows that Mn correlates inversely with Fe^{2+} in acid
rocks and positively with Fe^{2+} in basic rocks (Rollinson in prep.). This
suggests that Mn behaves differently in acid from basic rocks and that in
acid rocks Mn behaves as Fe^{2+}, favouring the recalculation procedure of
Carmichael (1967).

Equilibration of early broad lamellae

By using a scanning electron beam it is possible to obtain the
average composition of a broad lamellae which contains smaller exsolution
lamellae in order to estimate its composition prior to exsolution. A plot
of lamellae whose original composition has been determined in this way
shows that they lie on a curve slightly above the Ni-NiO buffer between
1010°C and 850°C (Fig.2, Synopsis). Temperatures of the order of 1000°C
are probably magmatic temperatures since they are higher than is normally
recorded for granulite facies metamorphism; 850°C is interpreted as the
blocking temperature, below which diffusion was unable to occur to form
large scale lamellae.

The interpretation of the log fO_2 - T curve defined by these
earliest phases is difficult. Carmichael and Nicholls (1967) have
pointed out that the oxygen fugacity of a melt may be externally
controlled by a volatile phase or the surroundings of the melt or,
internally buffered by crystal liquid equilibria, provided the mass of the
solid phases is sufficiently great compared with the mass of the gas.
Hornblende is the earliest ferromagnesian mineral seen that is likely to
have coexisted with Fe-Ti oxides, but it may not be primary. If a
comparison is made with the curves determined by Carmichael (1967) (Fig.2,
Synopsis) for oxygen fugacity in acid lavas coexisting with different
phenocryst phases and an adjustment is made for the difference in bulk
composition and pressure** between these and the Scourian rocks some
correspondence between the analysed points and the curve for hydrous
silicates would be expected if equilibria involving hornblende had been
controlling the oxygen fugacity. This is not found implying that
amphibole did not control the oxygen fugacity either because it was not
the main Fe bearing phase at magmatic temperatures or because the oxygen
fugacity was externally controlled.

Equilibration of small scale lamellae

After the formation of broad high temperature lamellae Ti diffusion
continued on a smaller scale (2-3 μm) so that the lower temperature
history of these grains can be considered in terms of many independent
microsystems (Fig.2). Limited diffusion continued across the boundaries
of and within early magnetite and ilmenite lamellae. The compositions of
small scale exsolution lamellae in ilmenite and magnetite hosts have been
determined and the results plotted in Figs. 3 and 4. For HR 86/1
lamellae of ilmenite plot between 765°C and 730°C along a buffer curve
close to the Ni-NiO buffer. Similar lamellae in HR.53 and 86/2 plot
between 1005°C and 950°C along a buffer curve parallel to the Ni-NiO
buffer but at a higher fO_2 than that for the equilibration of the high
temperature lamellae. Lamellae of magnetite in ilmenite plot at lower
temperatures below the QFM buffer curve in HR 86/1 and HR 53/2. Both
groups of points show decreasing oxygen fugacity with decreasing
temperature although they equilibrated at different temperatures.

Individual microsystems have equilibrated at different temperatures
and oxygen fugacities within the same grain and yet similar microsystems
in different grains have equilibrated at different temperatures and oxygen
fugacities suggesting that the rock itself has become a series of
independent closed systems. Similar findings have been made in the
gabbros of the Freetown complex, Sierra Leone (Bowles 1976, 1977).

In the case of magnetite lamellae in an ilmenite host it is
possible that the smaller lamellae (i.e.of the order of 2 μm wide) show
an excess of TiO_2 in the analysis. This is because a small (less than
1 μm) electron beam excites an area of up to 10 μm wide below the surface
of the specimen. In the case of magnetite in ilmenite Fe in the
magnetite will fluoresce Ti in the enclosing ilmenite. It is possible to
apply an extra fluorescence correction making some assumptions about the
orientation of the lamellae. Given a lamella 2 μm wide with vertical
sides and apparently 10.0 wt TiO_2 the maximum TiO_2 due to fluorescence of
the ilmenite is 2.5 wt% TiO_2 (S.J.B.Reed pers comm.). This has the
effect of changing the equilibration temperature from 714°C to 670°C and
$logfO_2$ from -17.2 to -18.0. There is therefore some uncertainty over
the position of points 17 to 22 on Fig.4, although their positions
relative to the QFM buffer curve remain unchanged. This does not affect
the main conclusions of this section which suggests that individual
microsystems within ilmenite-magnetite grains have behaved differently.

** The lower alkaline content of the trondhjemite will lower the curves,
whilst increased pressure will raise them by about 1 log unit(assuming
fO_2 is controlled by a reaction involving solid phases; if H_2O is involved
in the reaction, as in the case of hydrous silicates the curve will be
raised by a greater amount depending upon pH_2O); the net effect will be
that the position of the curves will be unchanged except for the hydrous
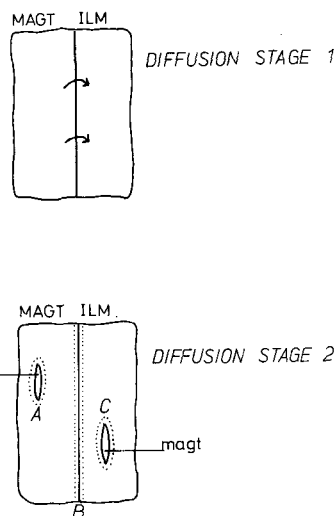silicates which will be slightly raised.

Fig. 2.   Model for diffusion in composite ilmenite magnetite grains at
high and low temperatures. Stage 1: the formation of ilmenite lamellae
from an originally homogeneous titanmagnetite. Stage 2: at lower
temperatures microsystems A (ilmenite and a rim of magnetite),
B (magnetite and ilmenite at the boundary of high temperature lamellae),
and C (magnetite and a rim of ilmenite) are the only systems that can be
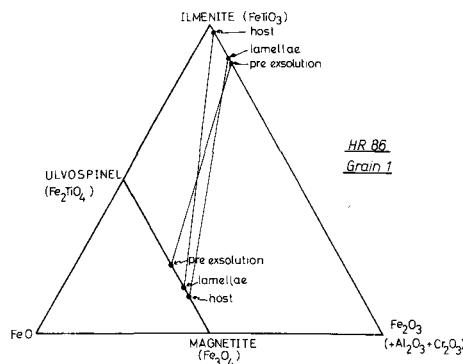in equilibrium.

Fig. 3.   Composition of phases plotted as mole percent in the system
$FeO-R_2O_3$ - $FeTiO_3$. The tie lines indicate coexisting phases.

Later diffusion across boundaries between early lamellae

The composition of phases either side of early high temperature
lamellae boundaries have been measured and the results plotted in Figs. 5
and 6. Analyses from HR.49 and 53 lie on the QFM buffer curve in the
temperature range 765°C to 610°C, whilst those for HR.86 plot in the same
temperature range at a lower fO_2 (Fig. 6). Equilibration temperatures
for HR.86/1 are the same as those for the equilibration of magnetite
lamellae in ilmenite. Separate buffer curves for different rocks were
described by Bowles (1976) who has pointed out that whilst there is a
real difference between two sets of analyses their exact position in
$log_{10}fO_2$ - T space is subject to the limits of experimental error quoted
by Buddington and Lindsley (1964). Consequently since there is a
real difference in the analyses of samples HR.49 and 53 and HR.56 the
separate buffer curves are regarded as meaningful. Grains 49/3 and
86/4 have exsolved into broad high temperature lamellae but are zoned and
contain no small scale exsolution lamellae. The sense of the zoning is
such that R_2O_3 in ilmenite decreases as it approaches magnetite. The
equilibration temperature and fO_2 at the grain boundary varies from the
centre of the grain (Fig. 5 points 24 and 25) to a higher temperature and
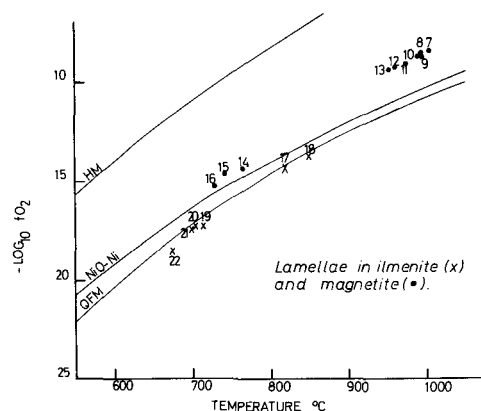fO_2 at the edge of the grain (Fig. 5 point 23).

Fig. 4. Plots of $-\log_{10}fO_2$ (in atmos.) versus temperature for coexisting ilmenite magnetite pairs occurring as lamellae and host in high temperature lamellae (systems A and C, Fig.3). 14-16, 19-22 (HR 86 grain 1), 7-1O (HR 86 grain 2), 11,13,18 (HR 53 grain 1), 12,17 (HR 53 grain 2). HM haematite-magnetite, Ni-NiO Nickel-Nickel Oxide, QFM quartz-fayalite-magnetite buffer curves calculated to 8 kb. after Eugster and Wones (1962).

Low temperature grains

In HR 56 ilmenite-magnetite grains show broad zoned lamellae with no late, small, exsolution lamellae. The sense of zoning is such that magnetite grains increase in ulvospinel content towards ilmenite and ilmenite decreases in R_2O_3 towards magnetite (Fig. 1B, Synopsis). Even though the grains are in disequilibrium it is assumed that equilibrium was at least established close to the boundary between lamellae. Equilibration temperatures thus obtained are between 410°C and 430°C at an fO_2 between the NiO-Ni and QFM buffers. Ilmenite-magnetite grains in HR 56 coexist with a biotite richer in Ti and a hornblende richer in Fe relative to those in samples HR.49, 53 and 86, suggesting that there was continuous Fe-Ti exchange between oxides and silicates as well as between ilmenite and magnetite.
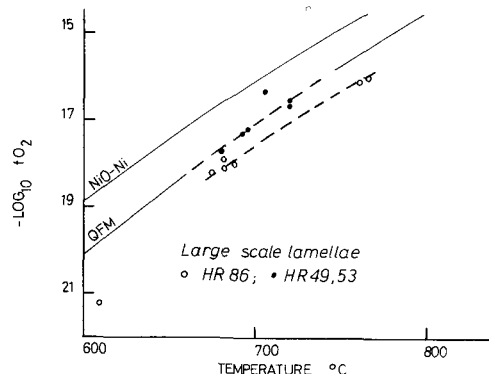

Figure 5. Plots of $-\log_{10}fO_2$ (in atmos.) versus temperatures for coexisting ilmenite magnetite pairs, measured close to the grain boundary between high temperature lamellae (system B in Fig.2). Buffer curves as in Fig. 4.

Conclusions and discussion

The present study shows that: (i) ilmenite-magnetite thermometry for intrusive trondhjemites in the Scourian complex yields reasonable magmatic temperatures. (ii) ilmenite-magnetite oxygen barometry suggests that the trondhjemites crystallised in equilibrium with pyroxene. (iii) the ilmenite-magnetite oxygen geothermometry is best interpreted in terms of the cooling history of the rock rather than separate metamorphic events. (iv) different parts of the same oxide grain become closed systems at different times. (v) different grains in the same rock show different cooling histories. (vi) different samples of similar rocks from the same locality may show greatly differing equilibration temperatures.

1. Discussion of equilibration temperatures. These may be read as blocking temperatures below which diffusion of Ti can no longer take place at the scale in question. Buddington and Lindsley (1964) suggest that the blocking temperature is a function of (a) the diffusion rate (i.e. the temperature of the system), (b) the amount of the guest phase present, and (c) the cooling rate (probably not very important in these slowly cooled rocks), (d) the presence of a fluid phase as catalyst.
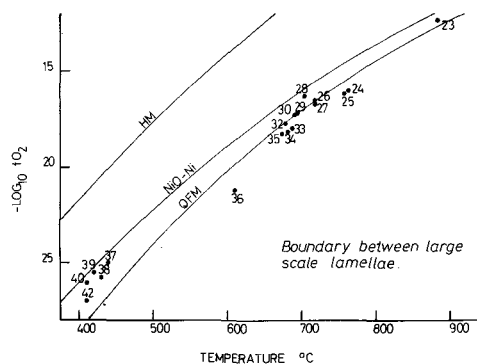

Figure 6. Plots of $-\log_{10}fO_2$ (in atmos.) versus temperature for co-existing ilmenite magnetite pairs, measured close to the grain boundary between high temperature lamellae in samples HR. 86. 53 and 49.

The blocking temperature for the large lamellae, which formed first, was determined principally by factors (a) and (b); on cooling, given that a certain amount of guest phase had exsolved a threshold is reached which prevents further diffusion on this scale, although it continues to take place on a smaller scale.

Factors determining the blocking temperature of the small-scale lamellae must include (a) and (b) but also in the case of ilmenite exsolving from magnetite the availability of oxygen (i.e. its mobility within magnetite and its availability within the system), since it is consumed in the reaction. This is not the case in the exsolution of small magnetite lamellae an ilmenite host, and may be why they equilibrate at a lower temperature (Fig. 4).

The low temperatures obtained from HR. 56 probably indicate the presence of a fluid phase which aided the diffusion of Fe and Ti between ilmenite, magnetite, biotite and hornblende.

2. Discussion of Oxygen Buffers. As the trondhjemite magma cooled the oxygen fugacity was probably controlled by the magma and crystallised phases. With further cooling possible oxygen buffers are: (i) water, (ii) the water-rock system, and (iii) the oxides themselves, since the production of ilmenite lamellae in magnetite involves a reaction which consumes oxygen and the production of titaniferous magnetite from ilmenite produces oxygen.

The difference in fO_2 and cooling history of HR.86/1 from HR.86/2 and HR.53 (Fig.4) is problematical. Bowles (1976) has shown that ilmenite-magnetite grains in different silicate environments in the same rock have different cooling histories. In these rocks however the silicate environment is identical. This would suggest the importance of a fluid phase in determining the history of these grains and indicates that early in the history of the rock fluids became isolated microsystems in equilibrium with their particular local environment. In the case of HR. 86 the microsystems may have been of the order of 1 cm. or less in average dimension.

If the only water in the system was that dissolved in the original magma and the trondhjemites have remained a closed system during cooling it is possible to show, using the model outlined in Buddington and Lindsley (1964), that the observed decrease in oxygen fugacity, across oxygen buffers, with falling temperature represents the loss of H_2O in the system to hydrous silicates.

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TABLE 1. CHEMICAL ANALYSES OF COEXISTING ILMENITE AND MAGNETITE.

ILMENITE

	Average grains						Magnetite host										Ilmenite host				
	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.
Rock/grain Anal. No.	HR 86/3 915/5	HR 53/1 925/17	HR 86/2 914/14	HR 53/2 925/12	HR 86/1 977/1	HR 49/2 924/13	HR 86/2 914/9	HR 86/2 914/6	HR 86/2 914/18	HR 86/2 914/2	HR 53/1 924/26	HR 53/2 925A5	HR 53/1 924/28	HR 86/1 977/16	HR 86/1 977/21	HR 86/1 977/20	HR 53/2 925/7	HR 53/1 924/30	HR 86/1 978/5	HR 86/1 978/2	HR 86/1 978/7
TiO_2	43.44	43.76	46.85	46.25	45.54	43.19	24.73	27.77	28.38	30.92	32.04	32.40	33.10	45.48	45.10	45.69	48.36	49.16	49.67	49.52	49.30
Al_2O_3	.37	.05	-	.02	.02	.01	-	-	-	-	.10	.04	.10	.08	.17	.16	.02	.02	.08	.03	.02
Cr_2O_3	-	.06	-	.03	.11	.00	-	-	-	-	.20	.10	.15	.17	.04	.00	.06	.03	.05		
'FeO'	53.14	51.90	52.71	51.08	50.72	49.78	68.96	64.09	67.47	63.39	60.57	62.40	59.90	49.52	49.94	48.95	1.73	1.48	1.17	1.17	1.12
MnO	1.29	1.31	-	1.59	1.05	3.02	-	-	-	-	.86	.94	1.01	.98	.98	.93	.00	.11	.22	.22	.23
MgO	-	.00	-	.00	.17	.04	-	-	-	-	.06	.00	.07	.19	.22	.23					
Total	98.25	97.11	99.56	98.97	97.59	96.04	93.70	91.86	95.84	94.31	93.67	95.97	94.21	96.33	96.38	95.99	96.19	98.07	98.23	98.25	97.95
FeO	37.76	38.02	42.13	39.98	39.59	35.71	22.24	24.97	25.52	27.80	27.80	28.16	28.62	39.57	39.22	39.37	41.74	42.51	43.09	42.95	42.79
Fe_2O_3	17.10	15.42	11.76	12.34	12.37	15.64	51.92	43.47	46.62	39.55	36.49	38.03	34.77	11.06	11.91	10.24	4.78	5.33	4.44	4.82	4.94
TOTAL	99.95	98.64	100.74	100.21	98.85	97.61	98.89	96.22	100.52	98.27	97.33	99.72	97.70	97.46	97.58	97.02	96.69	98.61	98.67	98.74	98.44
R_2O_3	16.91	15.12	11.16	11.83	12.09	15.35	51.23	43.92	45.11	39.02	36.35	37.16	34.56	11.05	11.87	10.27	4.78	5.18	4.38	4.71	4.85

MAGNETITE

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.
Anal. No.	915/13	924/25	914/13	925/20	977/5	924/12	914/8	914/5	914/17	914/3	924/27	925A6	924/19	977/29	977/15	977/19	925/10	924/19	978/6	978/1	978/8
TiO_2	15.96	15.35	15.99	15.30	14.77	11.15	8.68	8.73	9.10	9.10	8.44	7.55	8.14	8.91	8.16	7.92	15.59	17.84	10.38	9.60	9.08
Al_2O_3	.14	.05	-	.07	.11	.12	-	-	-	-	.05	.08	.05	.12	.12	.11	.04	.05	.07	.06	.10
Cr_2O_3	.14	-	.14	.21	.35	.12	-	-	-	-	.18	.30	.16	.32	.35	.31	.23	.20	.34	.28	.35
FeO	74.96	77.97	75.74	74.57	75.32	82.77	82.44	80.85	82.65	81.18	81.10	80.10	81.36	79.72	80.18	80.63	73.30	74.01	79.31	79.89	79.44
MnO	.32	.31	-	.24	.22	.73	-	-	-	-	.06	.08	.17	.06	.05	.10	.27	.41	.16	.23	.04
MgO	-	.02	-	.00	.04	.03	-	-	-	-	.02	.00	.02	.01	.00	.02	.00	.00	.01	.02	.00
Total	91.41	93.85	93.52	90.39	90.81	94.92	91.13	89.58	91.75	90.28	89.85	88.19	89.91	89.14	89.49	89.08	89.42	92.51	90.26	90.09	89.02
FeO	44.00	44.23	45.01	43.14	42.78	40.52	37.89	37.42	38.46	37.97	37.14	35.83	36.82	37.36	36.85	36.43	43.63	45.87	38.90	38.08	37.50
Fe_2O_3	34.41	37.50	36.13	34.93	36.16	46.95	49.51	48.27	49.11	48.02	48.75	49.20	49.50	47.08	48.85	49.12	33.04	31.27	44.91	46.47	46.61
TOTAL	94.85	97.60	97.13	93.89	94.43	99.62	96.08	94.42	96.67	95.09	94.63	93.04	94.86	93.86	94.38	94.01	92.80	95.64	94.77	94.74	93.68
Usp.	47.98	44.85	46.90	46.45	44.58	32.04	25.95	26.55	27.03	27.47	25.60	22.31	24.64	27.37	24.82	24.19	47.87	53.05	31.38	29.05	27.80
T°C	1010	980	935	930	922	850	1005	995	995	990	975	960	952	765	742	730	820	850	714	705	700
$-\log_{10} fO_2$	9.4	10.1	11.2	11.4	11.3	12.1	8.4	8.5	8.6	8.6	9.0	9.2	9.3	14.3	14.6	15.2	14.4	13.7	17.2	17.02	17.4

'FeO' total iron determined as FeO

ILMENITE

	Grain Boundary Pairs																				
	22.	23.	24.	25.	26.	27.	28.	29.	30.	31.	32.	33.	34.	35.	36.	37.	38.	39.	40.	41.	42.
Rock/grain Anal. No.	HR 86/1 978/4	HR 86/4 915/23	HR 86/2 915/21	HR 86/4 913/19	HR 49/3 924/17	HR 49/3 924/19	HR 49/2 925/7	HR 49/1 924/1	HR 53/31 924/30	HR 49/1 924/4	HR 53/2 925/9	HR 86/1 977/10	HR 86/1 977/12	HR 86/1 977/14	HR 86/2 914/21	HR 56/4 916/24	HR 56/3 916/17	HR 56/1 916/2	HR 56/2 916/13	HR 56/2 916/13	HR 56/1 916/1
TiO_2	49.81	46.03	46.96	46.57	47.94	48.05	47.57	47.41	49.16	47.62	48.55	49.89	50.01	49.65	51.34	50.06	50.42	49.66	48.87	48.87	50.38
Al_2O_3	.02	.06	.08	.04	.01	.01	.01	.01	.02	.02	.00	.02	.01	.01	-	.03	.04	.03	.21	.21	.09
Cr_2O_3	.04	-	-	-	.04	.00	.00	.00	.02	.04	.02	.03	.00	.01	-	-	-	-	-	-	-
'FeO'	46.72	46.86	44.65	46.99	46.46	46.25	46.92	43.74	47.31	43.74	46.98	47.22	47.32	47.23	48.23	47.61	45.59	49.30	44.09	44.09	48.31
MnO	1.16	1.06	1.71	1.29	2.05	2.13	3.15	4.60	1.48	4.43	1.64	1.06	1.10	1.12	-	1.75	3.15	1.45	4.42	4.42	1.48
MgO	.23	-	-	-	.07	.06	.04	.01	.11	.05	.00	.22	.23	.26	-	-	-	-	-	-	-
Total	97.98	94.97	93.35	97.89	96.57	96.51	97.70	95.78	98.07	95.96	97.21	98.44	98.70	98.25	99.47	99.45	99.10	100.14	98.10	98.10	100.26
FeO	43.21	40.32	40.50	43.27	40.91	40.94	39.52	37.96	42.51	38.29	42.00	43.40	43.45	43.05	46.08	43.24	42.15	43.19	39.49	39.49	43.81
Fe_2O_3	3.90	8.34	4.59	4.14	6.17	5.90	8.23	6.43	5.33	6.06	5.54	4.25	4.30	4.62	2.39	4.85	3.71	6.79	5.13	5.13	5.01
Total	98.37	95.81	93.79	98.30	97.19	97.09	98.51	96.41	98.61	96.58	97.76	98.86	99.13	98.72	99.71	99.94	99.47	101.12	98.10	98.10	100.76
R_2O_3	3.84	8.39	4.71	4.06	6.10	5.80	7.98	6.37	5.18	6.02	5.44	4.13	4.17	4.48	2.28	4.85	3.61	6.45	5.30	5.30	9.86

MAGNETITE

	22.	23.	24.	25.	26.	27.	28.	29.	30.	31.	32.	33.	34.	35.	36.	37.	38.	39.	40.	41.	42.
Anal. No.	978/3	915/24	915/20	915/20	924/16	924/16	925/8	924/2	924/27	924/3	925/16	977/9	977/11	977/13	914/17	916/25	916/18	916/5	916/9	916/10	916/6
TiO_2	9.58	15.20	15.15	15.15	9.45	9.45	8.69	7.69	8.44	7.78	7.53	9.33	8.96	8.30	9.10	.93	.87	.72	.47	.59	.56
Al_2O_3	.06	.22	.07	.07	.04	.04	.05	.05	.05	.08	.09	.11	.09	-	-	.32	.32	.28	.11	.16	.36
Cr_2O_3	.31	-	-	-	.16	.16	.13	.09	.18	.11	.30	.39	.36	.34	-	-	-	-	-	-	-
'FeO'	80.23	73.27	75.47	75.47	79.79	79.79	83.85	80.49	81.10	80.62	80.10	79.19	80.33	81.07	82.65	91.04	89.95	92.80	90.74	91.20	93.10
MnO	.28	.38	.25	.25	.06	.06	.13	.09	.06	.09	.08	.03	.11	.06	-	.07	.12	.10	.11	.16	.06
MgO	.06	-	-	-	.03	.03	.04	.04	.02	.08	.01	.01	.03	-	-	-	-	-	-	-	-
Total	90.54	89.07	90.95	90.95	89.55	89.55	92.88	88.44	89.85	88.65	88.19	89.02	89.89	89.87	91.75	91.36	91.26	93.91	91.41	92.08	94.09
FeO	38.10	42.49	43.19	43.19	37.92	37.92	38.31	35.99	37.14	36.19	35.63	37.72	37.57	37.08	38.46	31.56	31.10	31.86	30.80	31.13	31.83
Fe_2O_3	34.20	35.88	35.88	35.88	46.53	46.53	50.61	49.45	48.75	49.38	49.20	46.09	47.52	48.88	49.11	66.10	65.41	67.72	66.61	66.76	68.09
TOTAL	95.23	92.50	94.53	94.53	94.19	94.19	97.95	93.49	94.63	93.61	93.04	93.66	94.66	94.76	96.67	98.98	97.81	100.69	98.80	98.72	100.90
Usp.	28.83	46.79	45.69	45.69	28.77	28.77	25.47	23.65	25.60	23.88	23.31	28.56	27.14	25.15	27.03	2.72	2.57	2.07	1.39	1.73	1.60
T°C	675	885	765	760	720	720	705	695	695	693	680	687	682	675	610	440	430	420	410	410	410
$-\log_{10} fO_2$	18.5	12.3	16.0	16.1	16.5	16.6	16.3	17.2	17.2	17.3	17.7	18.0	18.1	18.2	21.2	25.0	25.8	25.5	26.0	26.0	27.0

'FeO' total iron determined as FeO