

IRON-RICH PIGEONITES FROM ACID ROCKS IN THE TERTIARY IGNEOUS PROVINCE OF SCOTLAND

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ABSTRACT

Exceptionally iron-rich pigeonites, ranging up to $\text{Ca}_9\text{Mg}_{22}\text{Fe}_{69}$, have been identified in high-level acid intrusive rocks from the Isle of Rhum, Scotland. Electron microprobe analyses of the pigeonites are presented, together with comparative data on orthopyroxenes and Ca-rich clinopyroxenes co-existing with them, and analyses of the three pyroxene assemblage in a vitrophyric dacitic lava from Ben Hiant, Ardnamurchan, Scotland. Silica activity and oxygen fugacity are thought to predominate amongst the many factors controlling igneous iron-rich pyroxene parageneses.

INTRODUCTION

The hypabyssal acid and subacid intrusions of the British Tertiary Igneous Province often contain pyroxene and olivine as their principal mafic phenocrysts. Recent studies of these rocks have tended to concentrate on their more abundant feldspar phenocrysts, but Carmichael (1960, 1967) has given a detailed account of the olivine and pyroxene in a suite of acid vitrophyres. A number of other analyses of pyroxenes, amphiboles, and biotites from British Tertiary igneous rocks have been published (Hallimond, 1914; Anwar, 1955; Brown, 1956; Bell, 1966).

This account describes iron-rich pigeonites and associated pyroxenes from four Tertiary igneous rocks localities in Scotland. Since the pyroxenes are generally present in small amounts, all the analyses have been made with the electron microprobe; details of the analytical techniques are given in Appendix 2.

OCCURRENCES OF IRON-RICH PIGEONITES

Hallimond (1914) first noted iron-rich pigeonite in the Scottish Tertiary rocks, presenting an analysis of "uniaxial augite" from an inninmorite pitchstone from Mull (Table 1, no. 1). This rock can be classified in modern terms as a pigeonite ferrodacite, by use of the hitherto unpublished "Guide to the naming of volcanic rocks", prepared by the Associate Committee on Geology and Geophysics of Canada (Baragar and Irvine, personal communication, 1969). Rhombic pyroxene and "uniaxial enstatite-augite" were described by Richey and Thomas (1930) from pitchstones on Ben Hiant, Ardnamurchan, but these minerals were not analyzed. It is this occurrence, together with three examples from the Isle of Rhum, which are now considered.

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TABLE 1. ANALYSES AND CIPW NORMS OF ACID AND SUB-ACID ROCKS FROM THE SCOTTISH TERTIARY IGNEOUS PROVINCE

| | 1 | 2 | 3 | 4 | 5 | | 1 | 2 | 3 | 4 | 5 |
|--------------------------------|--------|-------|--------|--------|-------|----|-------|-------|-------|-------|-------|
| SiO ₂ | 64.13 | 66.06 | 70.20 | 68.76 | 69.39 | Q | 22.69 | 29.86 | 28.06 | 28.15 | 31.84 |
| Al ₂ O ₃ | 13.15 | 13.14 | 12.61 | 14.65 | 13.82 | or | 14.11 | 9.53 | 18.78 | 17.75 | 15.81 |
| Fe ₂ O ₃ | 1.08 | 2.27 | 2.89 | 1.90 | 2.70 | ab | 31.70 | 37.92 | 36.42 | 31.96 | 34.30 |
| FeO | 6.31 | 2.84 | 2.32 | 3.15 | 2.43 | an | 13.06 | 11.22 | 5.90 | 11.40 | 4.44 |
| MnO | 0.27 | 0.31 | 0.11 | 0.04 | 0.14 | C | — | 0.53 | — | 1.08 | 2.61 |
| MgO | 1.08 | 0.77 | 1.14 | 0.77 | 0.81 | di | 3.02 | — | 2.40 | — | — |
| CaO | 3.62 | 2.75 | 1.88 | 2.55 | 2.24 | hy | 10.72 | 4.24 | 2.66 | 4.99 | 3.09 |
| Na ₂ O | 3.64 | 4.28 | 4.28 | 3.76 | 4.06 | mt | 1.61 | 3.45 | 4.21 | 2.77 | 3.91 |
| K ₂ O | 2.32 | 1.54 | 3.16 | 2.99 | 2.68 | il | 2.33 | 2.15 | 1.30 | 1.47 | 1.54 |
| H ₂ O ⁺ | 2.71 | 3.38 | 0.51 | 0.70 | 0.24 | ap | 0.76 | 0.22 | 0.26 | 0.48 | 0.47 |
| H ₂ O ⁻ | 0.36 | 0.74 | 0.10 | — | — | cc | — | 0.88 | — | — | 0.24 |
| TiO ₂ | 1.19 | 1.08 | 0.68 | 0.77 | 0.81 | | | | | | |
| P ₂ O ₅ | 0.31 | 0.09 | 0.11 | 0.20 | 0.20 | | | | | | |
| CO ₂ | — | 0.37 | — | — | 0.88 | | | | | | |
| Others | 0.09 | 0.18 | 0.13 | — | 0.12 | | | | | | |
| Total | 100.26 | 99.84 | 100.12 | 100.24 | 99.82 | | | | | | |

1. Vitrophyric inninmorite. Intrusive sheet, Beinn an Lochain, Mull. (Richey and Thomas, 1930, table III, no. A).

2. Vitrophyric inninmorite. Lava, Ben Hiant, Ardnamurchan. (Richey and Thomas, 1930, table III, no. II).

3. Felsite. Cnapan Breaca, Rhum (Dunham, 1968, table 3, no. A).

4. Felsite (H 3318). Beinn nan Stac, Rhum (see Hughes, 1960, p. 117); New analysis: Geochemical Laboratories, Manchester University.

5. Granophyre, Long Loch, Rhum. (Dunham, 1968, table 3, no. C).

Pitchstone, Ben Hiant, Ardnamurchan. This is thought to be a lava or series of lava flows on the floor of a volcanic vent (Richey and Thomas, 1930). It consists of phenocrysts of plagioclase, ortho- and clinopyroxene, opaques, and apatite in a brown glass containing plagioclase and pyroxene microlites. The Geological Survey of Great Britain analysis of this lava is quoted in Table 1, no. 2. Petrographic data are given in Appendix 1. The three different pyroxenes identified in the specimen examined (MS 66) show the following inter-relationships. Firstly, each can be found as discrete phenocrysts; secondly, pigeonite sometimes forms cores to augite phenocrysts and; thirdly, pigeonite itself sometimes contains hypersthene cores.

Both augite and pigeonite vary in composition (Table 2, group 1). In part this results from compositional zoning, with marginal enrichment in Fe relative to Mg. However, one pigeonite crystal (Table 2, no. 3a) is considerably more magnesian than the others analysed in this rock. It forms the core of a composite grain, with a mantle of augite (Table 2, no. 3b). The analysed hypersthene (Table 2, no. 1a) is enclosed in pigeonite (Table 2, no. 1b), with a slightly higher Fe/Mg ratio than the hypersthene.

These complex grains, in which one pyroxene species jackets another and seals it from the residual liquid, are thought to be sequential rather than equilibrium features; giving indications of the course of pyroxene crystallization in the rock. The iron-enrichment of the outer pyroxene relative to the inner one supports this view. However, insufficient is known about the pre-extrusion P.T.X. history of this specimen to make any attempt to specify in detail what processes caused individual relationships, such as pigeonite surrounding hypersthene.

Porphyritic Felsite, West Minishal, Rhum. The felsite is from one of many similar boulders

TABLE 2. ELECTRON MICROPROBE ANALYSES OF PYROXENES IN SCOTTISH TERTIARY ACID AND SUB-ACID IGNEOUS ROCKS

| | GROUP 1 | | | | | | | | | | GROUP 2 | |
|--------------------------------|---|-------|-------|-------|-------|--------|-------|--------|------|---------|--------------------------|--|
| | Innimorrite pitchstone (MS 66), Ben Hiant, Ardmurchan | | | | | | | | | | Felsite, (DU 9870c) Rhum | |
| | 1a | 1b | 2 | 3a | 3b | 4 | 5 | 6 | 1-6 | 7 | | |
| SiO ₂ | 50.5 | 49.5 | 49.5 | 50.7 | 50.4 | 49.9 | 50.8 | 51.2 | | | | |
| Al ₂ O ₃ | 0.78 | 0.50 | 0.57 | 0.79 | 1.74 | 0.52 | 1.47 | 2.04 | | 1.10 | | |
| TiO ₂ | 0.40 | 0.30 | 0.33 | 0.41 | 0.80 | 0.35 | 0.75 | 0.79 | | 0.35 | | |
| FeO | 27.7 | 29.2 | 29.9 | 23.8 | 14.3 | 30.4 | 17.0 | 14.8 | 31.1 | 31.9 | | |
| MgO | 14.6 | 13.5 | 12.6 | 17.4 | 12.6 | 13.8 | 11.8 | 12.9 | 12.1 | 14.9 | | |
| CaO | 1.85 | 3.44 | 4.97 | 4.24 | 16.8 | 4.02 | 16.4 | 17.1 | 3.75 | 1.73 | | |
| Na ₂ O | 0.18 | 0.13 | 0.22 | 0.12 | 0.32 | 0.11 | 0.34 | 0.34 | | 0.01 | | |
| MnO | 1.32 | 1.64 | 1.63 | 1.31 | 0.84 | 1.61 | 0.96 | 0.87 | | 0.71 | | |
| | 97.33 | 98.21 | 99.72 | 98.77 | 97.80 | 100.71 | 99.52 | 100.04 | | | | |
| Si | 2.000 | 1.960 | 1.964 | 1.950 | 1.955 | 1.960 | 1.960 | 1.940 | | (1.989) | | |
| Al | 0.038 | 0.024 | 0.029 | 0.037 | 0.070 | 0.023 | 0.069 | 0.091 | | 0.052 | | |
| Ti | 0.012 | 0.010 | 0.010 | 0.012 | 0.023 | 0.010 | 0.021 | 0.023 | | 0.010 | | |
| Fe | 0.918 | 0.965 | 0.995 | 0.770 | 0.465 | 0.996 | 0.548 | 0.470 | | 1.050 | | |
| Mg | 0.861 | 0.796 | 0.742 | 1.020 | 0.723 | 0.802 | 0.672 | 0.695 | | 0.874 | | |
| Mn | 0.045 | 0.057 | 0.055 | 0.042 | 0.027 | 0.054 | 0.032 | 0.027 | | 0.024 | | |
| Ca | 0.082 | 0.145 | 0.210 | 0.176 | 0.700 | 0.169 | 0.672 | 0.695 | | 0.073 | | |
| Na | 0.014 | 0.010 | 0.014 | 0.009 | 0.023 | 0.009 | 0.023 | 0.023 | | 0.008 | | |
| Z | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | | | | |
| X+Y | 1.970 | 1.967 | 2.021 | 2.016 | 1.986 | 2.023 | 1.997 | 1.999 | | | | |
| Fe+Mn | 50.5 | 52.2 | 52.4 | 40.4 | 25.7 | 52.0 | 30.2 | 25.9 | 55.2 | 43.2 | | |
| Mg | 45.5 | 40.5 | 37.1 | 50.8 | 36.5 | 39.6 | 34.9 | 38.0 | 36.6 | 38.0 | | |
| Ca | 4.2 | 7.4 | 10.5 | 8.8 | 37.8 | 8.4 | 34.9 | 36.1 | 8.2 | 3.6 | | |

| | GROUP 3 Beinn nan Stac felsite, (H 3318) Rhum | | | | | | | | | | GROUP 4 Granophyre, (DU 990 ^d), Rhum | | | | | |
|--------------------------------|--|-------|-------|-------|--------|-------|--------|-------|-------|-------|---|-------|-------|-------|-------|--|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 1 | 2 | 3 | 4 | 5a | 5b | 5c | |
| SiO ₂ | 49.50 | 48.61 | 48.99 | 49.40 | 50.12 | 47.87 | 47.89 | 49.21 | 48.3 | 47.4 | 48.6 | 48.4 | 49.6 | 50.1 | 48.7 | |
| Al ₂ O ₃ | 0.58 | 0.53 | 0.43 | 0.68 | 0.59 | 0.28 | 0.30 | 0.61 | 0.50 | 0.43 | 0.53 | 0.50 | 0.97 | 0.68 | 0.46 | |
| TiO ₂ | 0.44 | 0.39 | 0.42 | 0.51 | 0.44 | 0.33 | 0.41 | 0.41 | 0.49 | 0.50 | 0.60 | 0.45 | 1.0 | 1.0 | 0.55 | |
| FeO | 31.20 | 31.05 | 32.22 | 29.40 | 31.18 | 36.50 | 37.18 | 23.57 | 36.2 | 36.3 | 37.0 | 36.1 | 24.9 | 22.4 | 33.9 | |
| MgO | 12.73 | 12.57 | 12.38 | 13.41 | 12.97 | 7.99 | 8.46 | 7.48 | 7.4 | 6.90 | 7.30 | 8.15 | 6.55 | 6.62 | 6.72 | |
| CaO | 3.96 | 4.21 | 3.29 | 4.08 | 4.26 | 4.00 | 3.89 | 16.93 | 3.74 | 3.97 | 3.66 | 3.75 | 13.9 | 14.9 | 5.80 | |
| Na ₂ O | | | | | | | | | 0.23 | 0.31 | 0.23 | 0.34 | 1.0 | 1.0 | 0.23 | |
| MnO | 1.58 | 1.53 | 1.60 | 1.43 | 1.59 | 2.28 | 2.25 | 1.31 | 1.50 | 1.40 | 1.68 | 1.40 | 0.90 | 0.97 | 1.60 | |
| | 99.99 | 98.88 | 99.33 | 99.38 | 101.15 | 99.25 | 100.27 | 99.52 | 98.36 | 97.21 | 99.60 | 99.09 | 98.82 | 97.67 | 97.96 | |
| Si | 1.963 | 1.954 | 1.964 | 1.970 | 1.962 | 1.976 | 1.961 | 1.966 | 1.998 | 1.993 | 1.991 | 1.986 | 1.989 | 2.014 | 2.012 | |
| Al | 0.027 | 0.025 | 0.021 | 0.032 | 0.027 | 0.014 | 0.014 | 0.029 | 0.025 | 0.021 | 0.025 | 0.024 | 0.046 | 0.033 | 0.023 | |
| Ti | 0.013 | 0.012 | 0.013 | 0.015 | 0.013 | 0.010 | 0.009 | 0.013 | 0.015 | 0.015 | 0.018 | 0.014 | 0.030 | 0.030 | 0.017 | |
| Fe | 1.035 | 1.044 | 1.080 | 0.971 | 1.021 | 1.260 | 1.273 | 0.787 | 1.253 | 1.277 | 1.268 | 1.239 | 0.835 | 0.753 | 1.171 | |
| Mg | 0.752 | 0.753 | 0.740 | 0.790 | 0.757 | 0.492 | 0.516 | 0.445 | 0.456 | 0.432 | 0.446 | 0.498 | 0.392 | 0.397 | 0.414 | |
| Mn | 0.053 | 0.052 | 0.054 | 0.048 | 0.053 | 0.079 | 0.078 | 0.044 | 0.052 | 0.050 | 0.058 | 0.049 | 0.031 | 0.033 | 0.056 | |
| Ca | 0.168 | 0.181 | 0.141 | 0.173 | 0.179 | 0.177 | 0.171 | 0.725 | 0.166 | 0.179 | 0.161 | 0.165 | 0.597 | 0.642 | 0.257 | |
| Na | | | | | | | | | 0.018 | 0.026 | 0.018 | 0.028 | 0.078 | 0.078 | 0.018 | |
| Fe+Mn | 54.32 | 54.0 | 56.3 | 51.4 | 53.6 | 66.7 | 66.4 | 41.5 | 67.7 | 68.5 | 68.6 | 66.0 | 46.7 | 43.1 | 64.6 | |
| Mg | 37.4 | 37.1 | 36.7 | 39.9 | 37.6 | 24.5 | 25.3 | 21.2 | 23.6 | 22.3 | 23.1 | 25.5 | 21.1 | 21.7 | 21.8 | |
| Ca | 8.4 | 8.9 | 7.0 | 8.7 | 8.8 | 8.8 | 8.3 | 36.3 | 8.7 | 9.2 | 8.3 | 8.5 | 32.2 | 35.2 | 13.6 | |

Notes: 1. All Fe as FeO.

2. Group 2, 1-6 is an average of 6 partial analyses of pigeonites (see Fig. 1). Full data from the authors on request.

3. Groups 1, 2 and 4 analysed by C. H. Emelius, Group 3 by the Microprobe Laboratory, University of Toronto.

4. Rock specimen number prefixes are: DU = Durham University Colln., H = Oxford University Colln., MS = R.N.T. Colln.

in the conglomerate underlying the lavas of West Minishal (Black, 1952). The rocks appear to have been derived during rapid weathering of the Long Loch-Cnapan Breaca felsites, which they resemble petrographically (Dunham, 1968; Dunham and Emeleus, 1967). The specimen (DU 9870c) contains phenocrysts of bipyramidal quartz, plagioclase, pyroxene, and opaques in a microcrystalline matrix. Petrographic details are given in Appendix 1. An analysis of a modally similar felsite from Rhum is given in Table 1, no. 3.

The rock contains pigeonite (Table 2, group 2) and very rare hypersthene phenocrysts. Extensive alteration of both phases precludes any conclusions about their textural interrelations. As in the Ben Hiant specimen, the pigeonite phenocrysts have a slightly higher Fe/Mg ratio than the hypersthene. Unfortunately the scarcity of hypersthene in both rocks prevents making enough analyses to be sure whether this Fe/Mg relationship remains when the compositional range of the mineral is known.

Porphyritic Felsite, Beinn nan Stac, Rhum. This forms a small sheet-like intrusion on the north side of Dibidil. Its general geology and petrography have been described by Hughes (1960). The specimen (H. 3318) examined contained phenocrysts of plagioclase (two generations; An₄₆ and An₂₉ cores), pigeonite, quartz, and opaques in a dull black microcrystalline matrix. Hypersthene phenocrysts have been recorded by Hughes (1960) but none was found in our specimen. A new analysis of this rock is presented in Table 1, no. 4; petrographic details in Appendix 1.

The pigeonite phenocrysts form stout 1 mm prisms, rimmed by occasional granules of ferroaugite, which also occurs separately. The compositions of seven pigeonite grains (Table 2, group 3) fall into two groups. It is possible that these represent the extremes of compositional Fe/Mg zoning; strongly zoned pigeonites have been observed in another sample from this intrusion (DU 13876). However, as there are two compositions of plagioclase phenocrysts in this rock, the possibility arises of two distinct pigeonite generations. This interpretation has been used in the construction of Figure 2.

Granophyre, Loch a 'Ghillie Reamhra, Rhum. The granophyre specimen (DU 9904) comes from the northern part of the large granitic intrusion in SW Rhum (Black, 1954; Dunham and Emeleus, 1967). The rock contains phenocrysts of plagioclase and pyroxene in a matrix of quartz, alkali feldspar, biotite, amphibole, and opaques. Petrographic details are given in Appendix 1. An analysis of a modally similar granophyre is given in Table 1, no. 5.

The pyroxene phenocrysts are ferroaugite and ferriiferous pigeonite; both often mantled and partly replaced by amphibole and opaques. The analyses (Table 2, group 4) show a spread in compositions, which is attributable to compositional zoning, since marginal enrichment in Fe was found in the less altered crystals. The average compositions of the pyroxenes (Figure 2) are the most iron-rich of the samples examined. In addition, they appear to show a smaller compositional gap between the Ca-rich and Ca-poor crystals than in the other specimens, although this is largely the result of low Ca in one ferroaugite (Figure 1, 5a) and high Ca in one pigeonite (Figure 1, 5c).

COMPARATIVE CHEMISTRY OF THE PYROXENES

The microprobe analytical data on a total of 30 pyroxene crystals from the four rocks are presented in Table 2. Variations in the atomic proportions of Fe (calculated as Fe²⁺), Mg, and Ca have been noted in the previous section (see Figures 1 and 2). There appears to be no positive or negative correlation of Al, Mn, Ti, and Na with increasing Fe content among these crystals. This is surprising in the case of Al and Mn, which

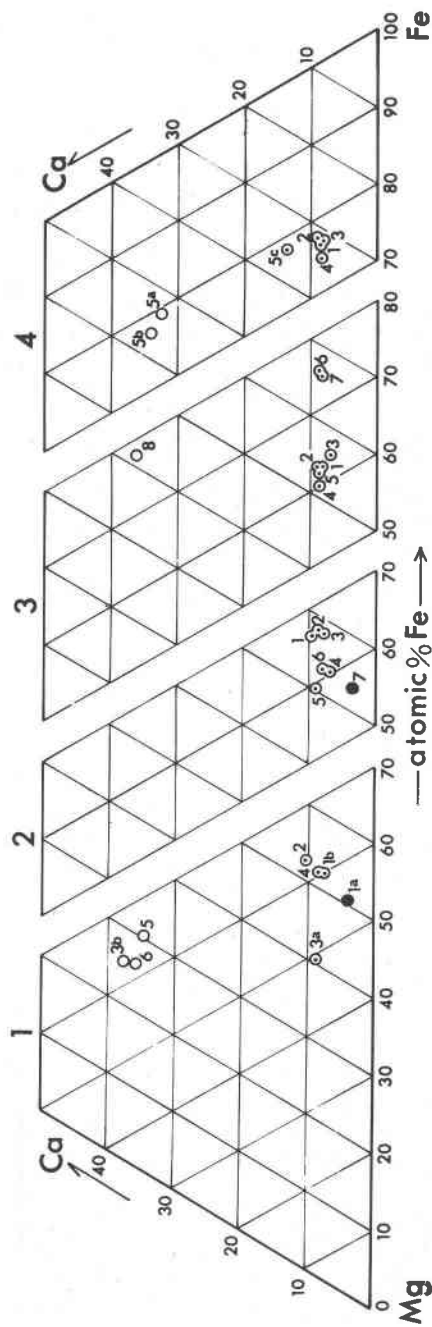


FIG. 1. Compositions of analysed pyroxenes from Hebridean Tertiary acid rocks. 1. Innimorite pitchstone, Ben Hiant, Ardnamurchan (MS 66); group 1, Table 2. 2. Porphyritic Felsite from boulder in conglomerate, Minishal, Rhum (DU 9870c); group 2, Table 2. 3. Porphyritic Felsite, Beinn nan Stac, Rhum (H 3318); group 3, Table 2. 4. Granophyre, Lochan a'Ghillie Reamhra, Rhum (DU 9904); group 4, Table 2. O, Ca-rich clinopyroxenes; \odot , pigeonites; \bullet , orthopyroxenes.

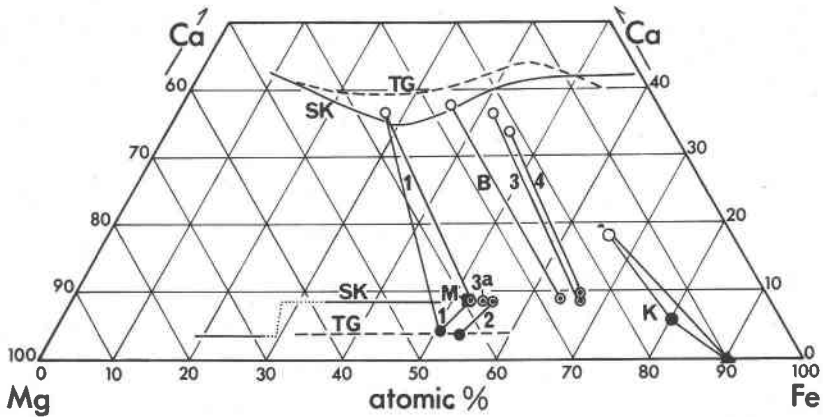


FIG. 2. Average compositions of pyroxenes from Hebridean Tertiary acid rocks in relation to pyroxene compositions in the Skaergaard Intrusion (Wager and Brown, 1967) and N. Atlantic Tertiary acid glasses (Carmichael, 1960). The Ben Hiant magnesium pigeonite (Table 2, group 1, no. 3a) has been omitted from assemblage 1 on this diagram, as it is thought to pre-date the main pyroxene crystallization period in the rock. The point labelled 3a on this figure is the average composition of the more magnesian pigeonite group in the Beinn nan Stac felsite (Table 2, group 3, nos. 1-5). Further discussion of these two complex specimens may be found in the text.

Key: 1, 2, 3, 4 as in Figure 1; ■ M, Analysed pigeonite, Mull (Hallimond, 1914); B, Pyroxenes from Beaver Bay, Minnesota, U.S.A. (Muir, 1954); SK, Trend of analysed pyroxenes, Skaergaard intrusion; TG, Trend of analysed pyroxenes from Tertiary acid glasses; K, Subcalcic ferroaugite, eulite and fayalite from dacite, Asio, Japan, (Kuno, 1969); pyroxene symbols as on Fig. 1; ▲, fayalite.

generally show good negative and positive correlations respectively with increasing Fe in pyroxenes.

Carmichael (1960, 1967) has analysed many Ca-rich clinopyroxenes and some orthopyroxenes from rocks in similar environments, hypabyssal and volcanic, to those of the specimens described here. The Rhum ferroaugites have similar Mn and Al, and higher Ti and Na contents than those studied by Carmichael, at the same range of Fe/Mg ratios. There is appreciably less Ca in the Rhum ferroaugites than is usual in igneous ferroaugites (Figure 2). However, the Rhum and Ardnamurchan augites have similar Ca contents to those in augites from the Skaergaard intrusion (Brown and Vincent, 1963).

The Rhum pigeonites are among the most iron-rich so far discovered. Iron-rich, Ca-poor igneous pyroxenes have been reported by Muir (1954) from the Beaver Bay diabase, Minnesota; by Edwards (1942) from the Mount Wellington sill; Tasmania; by Kuno (1969) from dacite in the Asio district, Japan; and by Philpotts (1966) from a quartz mangerite in

Southern Quebec, Canada. Some of these data have been plotted on Figure 2.

DISCUSSION

The average composition of the predominating iron-rich Ben Hiant pitchstone pigeonite ($\text{Ca}_8\text{Mg}_{40}\text{Fe}_{62}$) is virtually identical to that in the Mull inninmorite ($\text{Ca}_8\text{Mg}_{40}\text{Fe}_{62}$). The latter is unusual in containing pigeonite as its only pyroxene. These pigeonitic rocks of Mull clearly need further investigation. The jacketing relations among the three pyroxenes in MS 66 suggest that the orthopyroxene may have been the first of them to crystallize.

It should be clear from the descriptions and analyses given above that the pyroxenes in the rocks used in this study are rather complex, and do not approach equilibrium assemblages. Zoning of the crystals is as might be expected in a volcanic and subvolcanic environment. The tie-lines drawn on Figure 2 are between average compositions of groups of pyroxene analyses; giving approximately the same orientations as would have been obtained by separation and wet chemical analysis of the minerals.

Further evidence of disequilibrium is provided by the occurrence of two distinct compositional groups of pigeonite in the Ben Hiant and Beinn nan Stac specimens. Whether this feature can be ascribed to the intermingling of two chemically distinct magmas, a common occurrence in Tertiary Hebridean igneous rocks, or to intermittent pigeonite crystallization during the complex subvolcanic cooling history of a single magma, it underlines the point that the tie lines in Figure 2 are not based on equilibrium assemblages. When constructing this diagram only the more iron-rich pigeonite groups have been joined to the average augite compositions, because, unlike the more magnesium groups, these give tie-lines with similar orientations to those from previously-described augite-pigeonite assemblages.

The pigeonite phenocrysts in the Rhum rocks have compositions ranging up to the margin of the "no-pyroxene" field (Deer, Howie, and Zussman, 1963). Furthermore, one crystal in the granophyre shows a trend towards calcium-rich ferriferous pigeonite ($\text{Ca}_{14}\text{Mg}_{22}\text{Fe}_{64}$). The zoning in the pigeonites follows the normal pattern; from magnesian cores to iron-rich margins, as determined by the electron probe. Therefore, we assume that the precipitation of magnetite in these rocks was not sufficient to reverse the trend to iron-enrichment of the residual liquids during the crystallization process. Thus, the Rhum pyroxenes should give some clues as to the nature and compositional range of the closure of the two pyroxene fields.

The two main interrelated problems are: firstly, why should such iron-rich pyroxenes precipitate and, secondly, at what stage does pigeonite disappear and ferrohedenbergite+fayalite+quartz become the stable assemblage? Lindsley and Munoz (1969) have recently emphasized the importance of silica activity in controlling the compositions of pyroxenes. They predict that where $a(\text{SiO}_2)$ is high, reaching almost unity when a silica phase is precipitating (see Carmichael, Nicholls, and Smith, 1970), two pyroxenes should persist to very iron-rich compositions. Sparse high-quartz phenocrysts in the Rhum acid rocks indicate that $a(\text{SiO}_2)$ approached unity in them. Dunham (1968) has deduced that this quartz was co-precipitated with the iron-rich portions of the pyroxenes.

Carmichael *et al.* (1970) have taken up Lindsley and Munoz's point that $a(\text{SiO}_2)$ is but one of many parameters controlling pyroxene precipitation. They stress that, although a high $a(\text{SiO}_2)$ favours pyroxene at the expense of olivine, the oxygen fugacity must also play a vital part, wherever reactions involving iron take place. Thus, if $a(\text{SiO}_2)$ is held constant, it follows that $a(\text{Fe}_3\text{O}_4)$ must be high, if $f(\text{O}_2)$ is high. The presence of iron-rich pyroxenes in these rocks is a function of both high $a(\text{SiO}_2)$ and low $f(\text{O}_2)$.

The augites and ferroaugites in Scottish Tertiary acid glassy rocks studied by Carmichael (1960) are all much richer in calcium, for a given Fe/Mg ratio in the pyroxene, than those from the Rhum rocks. The more iron-rich calcium-rich pyroxenes described by him coexist with olivine. However, the tie-line joining the most magnesian of these pyroxene-olivine assemblages is still more iron-rich than any determined in the present study. It is notable that quartz is reported in only two of the phenocryst assemblages analysed by Carmichael (1960), and that in both cases the ferroaugite is less calcic than the main trend. However, the amount of CaO in Carmichael's rocks is less, for a given SiO_2 content, than in the Rhum acid rocks.

The phenocryst phases in both the specimens considered here and Carmichael's suite probably formed prior to emplacement in their present position. Hence another possible factor in the development of these pyroxenes may have been the length of time that the magma remained at depth before extrusion or emplacement. Lindsley and Munoz (1969) suggest that a metastable solvus in the pyroxene system, with a less calcic calcium-rich limb than in the stable system, may exist; outlining a two pyroxene field, rather than a pyroxene+fayalite+quartz assemblage. This might indicate that the pyroxenes in the pitchstone have more nearly equilibrated than those in the felsites and granophyres. It is still not clear which, if any, of these controls is the dominant one. However, many factors clearly influence the nature of the pyroxenes.

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APPENDIX 1

Petrographic notes

Ben Hiant pitchstone, Ardnamurchan. Generally referred to as "inninmorite", this rock closely resembles the icelandites (tholeiitic andesites) defined by Carmichael (1964), but is a little more siliceous than them. Our specimen (MS 66) contains 14.3% plagioclase, 4.7% pyroxene, and 1.3% Fe-Ti oxide phenocrysts, all of which occur singly or in clusters. The plagioclase phenocrysts (<3mm long) have uniform An₄₂ cores and sharply demarcated An₃₅ rims, determined optically using the twin orientation curves of Slemmons (1962). The orientations of the albite, albite-Carlsbad, Carlsbad, pericline, Ala, B and albite-Ala B twin laws present indicate high temperature optics. The augite crystals (<3 mm long; $2V_{\gamma}=48^{\circ}$) are generally larger than the pigeonites (<1 mm long; $2V_{\gamma}=2-8^{\circ}$). $2V_{\alpha}$ of a single hypersthene grain is 53° .

Porphyritic Felsite, conglomerate, West Minishal, Rhum. This rock is a typical Rhum felsite, resembling those described by Dunham (1968). The mode of specimen DU 9870 C is plagioclase phenocrysts (An₃₄₋₂₀) 17.8%, quartz with resorbed margins 0.4%, pyroxenes 4.4%, and Fe-Ti oxides 2.2%, in a microgranular groundmass. Much of the pyroxene is altered to aggregates of amphibole and opaques, a process which has gone to completion in many Rhum acid rocks.

Porphyritic Felsite, Beinn nan Stac, Rhum. This intrusion, described by Hughes (1960), is anomalous among Rhum acid rocks. Despite its normal-looking mode, with plagioclase phenocrysts 18.6%, quartz 1.7%, pyroxenes 5.0%, and Fe-Ti oxides 1.6% (in H 3318), the compositions of plagioclase cores fall into two distinct groups: An₄₅ and An₂₉ (volcanic optics). The margins of both types are zoned to An₁₈. Similar compositional grouping in the pyroxenes suggests a mixed (phenocryst-bearing) magma rock, a common phenomenon in the Tertiary Hebridean igneous province. The intermediate and ferriiferous pigeonites, often twinned on (110), have a range of $2V_{\gamma}$ from 3° to 20° . $2V_{\gamma}$ of the ferroaugite is 50° .

Granophyre, Loch a'Ghillie Reamhra, Rhum. This rock type is typical of the Rhum acid intrusives with micrographic groundmasses (Dunham, 1968). The mode of specimen DU 9904 is: plagioclase phenocrysts 25.0%, quartz 0.4%, pyroxenes 9.3%, and Fe-Ti oxides 3.1%. The ferroaugite sometimes contains minute, parallel lamellae (? exsolution; not resolved on the microprobe).

APPENDIX 2

Analytical Techniques

The pyroxenes were analyzed in polished thin sections using three microprobes, as follows: 1. ARL-EMX at the University of Toronto (for H 3318), operated by Dr. J. C.

Rucklidge, 2. ARL-EMX at the University of Chicago, and 3. Geoscan I at the University of Durham (for the other three specimens), operated by Dr. C. H. Emeleus.

Rucklidge used synthetic diopside, ferrosilite, and anorthite, and Mn metal as standards. He determined Mn at 25 kV, other elements at 15 kV, and corrected run count data for instrument drift, background, dead-time absorption, and fluorescence.

Emeleus used analysed Fe- and Ca-rich clinopyroxenes and the Mull "innimorite" pigeonite (see text) as standards. He determined all elements at 15 kV and corrected for instrument drift, background, and dead-time.

Considering the variety of machines and techniques used, the analyses are encouragingly concordant.

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