



THE PETROLOGY OF KENTALLENITE

by

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Thesis presented for the Degree of Doctor of Philosophy of the
University of Edinburgh in the Faculty of Science.

1968

ABSTRACT

Kentallenite is a peculiar basic intrusive igneous rock common in the Southwest Highlands of Scotland, and it is a member of the Scottish Caledonian calc-alkali suite. Detailed examination of its mineralogy (olivine, augite, biotite, plagioclase and orthoclase) suggests that kentallenite is an unusual assemblage of common minerals, and that its origin may therefore be explicable in terms of 'normal' means of evolution operating under 'abnormal' combinations of conditions.

Whole rock chemical data from kentallenites indicate the possibility of some control of their bulk composition by sorting and differential movement of olivine, but kentallenite compositions also straddle the low pressure thermal divide "zone" in the normative basalt tetrahedron, a trend that cannot be caused by olivine separation alone.

Geometrical and statistical treatment of bulk chemical data suggest that the scatter of kentallenites across the low pressure thermal divide zone is linear, and could be caused by separation of pargasitic hornblende from the parent magma. Amphibole is not, however, found as a primary phase in kentallenite.

Detailed consideration of the possible 'olivine' and 'amphibole' controls of evolution leads to the proposal of a petrogenetic model incorporating early fractionation of olivine from a picritic parent magma at depth, followed by uptake of water at the base of the orogenic crust and consequent pargasitic hornblende precipitation. Irruption of the magma from the base of the crust to a near-surface environment could result in breakdown of the amphibole, for which there is some mineralogical support.

Critical examination of current calc-alkaline evolutionary theories reveals their inadequacy to explain the distinctive features of the

suite. The petrogenetic model proposed for kentallenite is thought to be capable of explaining these features, and to offer a valid means of derivation of the calc-alkali suite as a whole by fractionation from a basaltic parent.

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Definition of rock-type.

In 1897 Teall described a peculiar intrusive basic igneous rock occurring at Kentallen, on the east side of Loch Linnhe south of Ballachulish (Figs. 1 and 2), which he compared to Brögger's olivine-monzonites. Hill and Kynaston recognised the rock-type to be sufficiently distinctive and widespread to merit a specific name, and proposed the name Kentallenite (after the type locality) for this rock, defining it as "a coarse or medium grained holocrystalline rock, consisting of olivine and augite, with orthoclase, plagioclase and biotite in varying proportions" (1900, p.532).

Form of intrusions and distribution.

Subsequent work (e.g. Kynaston et al., 1908; Bailey et al., 1916; Lee and Bailey, 1925; Bailey, 1958) has shown that kentallenite is intimately connected with the Appinite suite (Anderson, 1935'a'; Read, 1961) of the Scottish Southwest Highlands calc-alkali igneous province, and is the most common pyroxene-rich member of this dominantly hornblendic suite. It may be intruded in small plugs (Kentallen) or dykes (Loch Avich), but more commonly forms part of a larger intrusion (e.g. Colonsay; Appendix A).

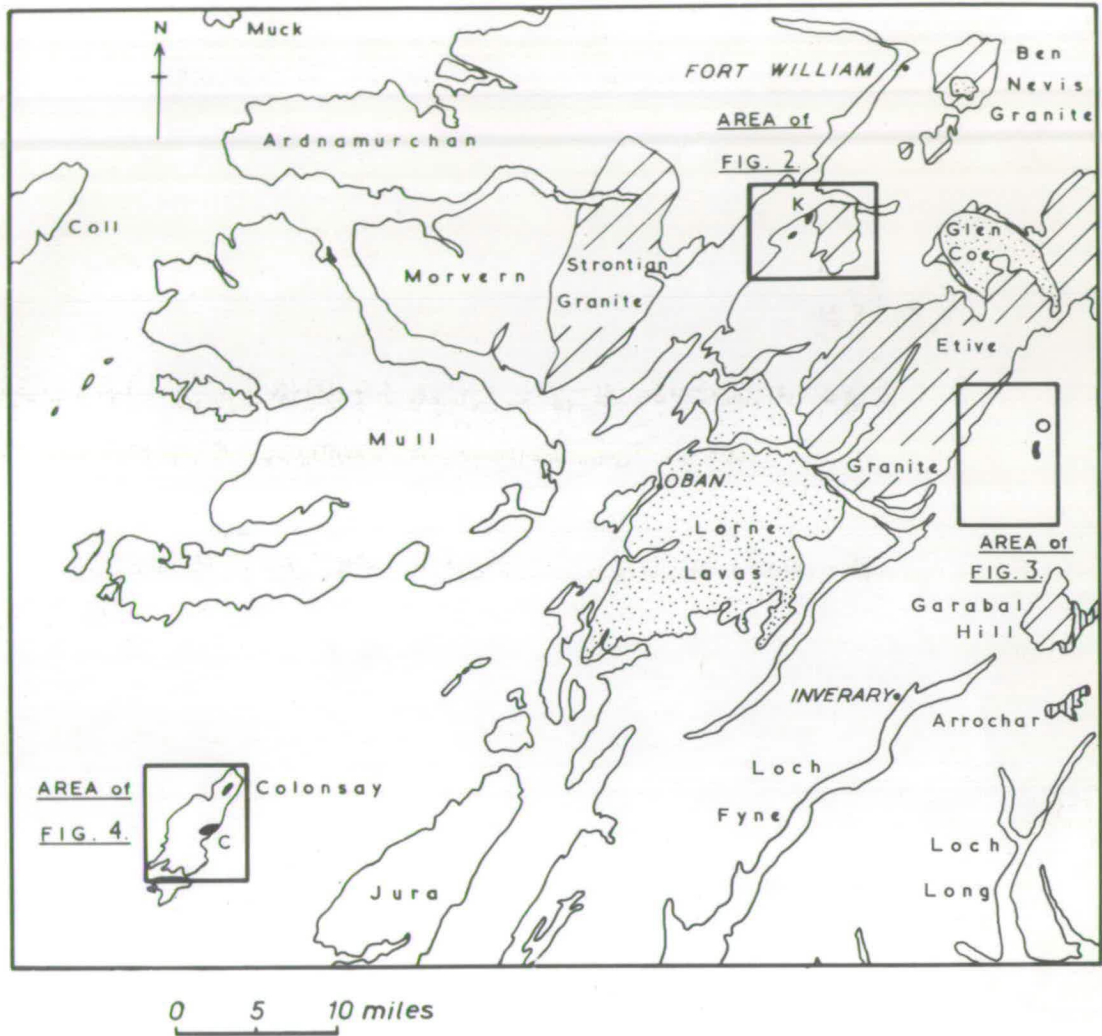
Hornblendic rocks similar to those of the appinite suite are recorded from the Northwest Highlands of Scotland (Read et al., 1925, 1926; Read, 1931 - Ach'uaine hybrids), from Donegal (e.g. French, 1966; Hall, 1967) and from several areas in Africa and the U.S.A. One kentallenite is known from Donegal (see Platten, 1966, p.179), and rocks similar to kentallenite have been found in Northern Japan (Onuki and Tiba, 1964) and in Rhodesia (Jamieson, pers. comm.); other than these occurrences kentallenite is believed to be restricted to Argyll.

FIGURE 1

General Geological Map of the Southwest Highlands of Scotland

(After H.M. Geological Survey, 10 mile Sheet 1)

The areas enlarged in Figures 2-4 are indicated.



Legend



Granite.



Volcanic rocks.



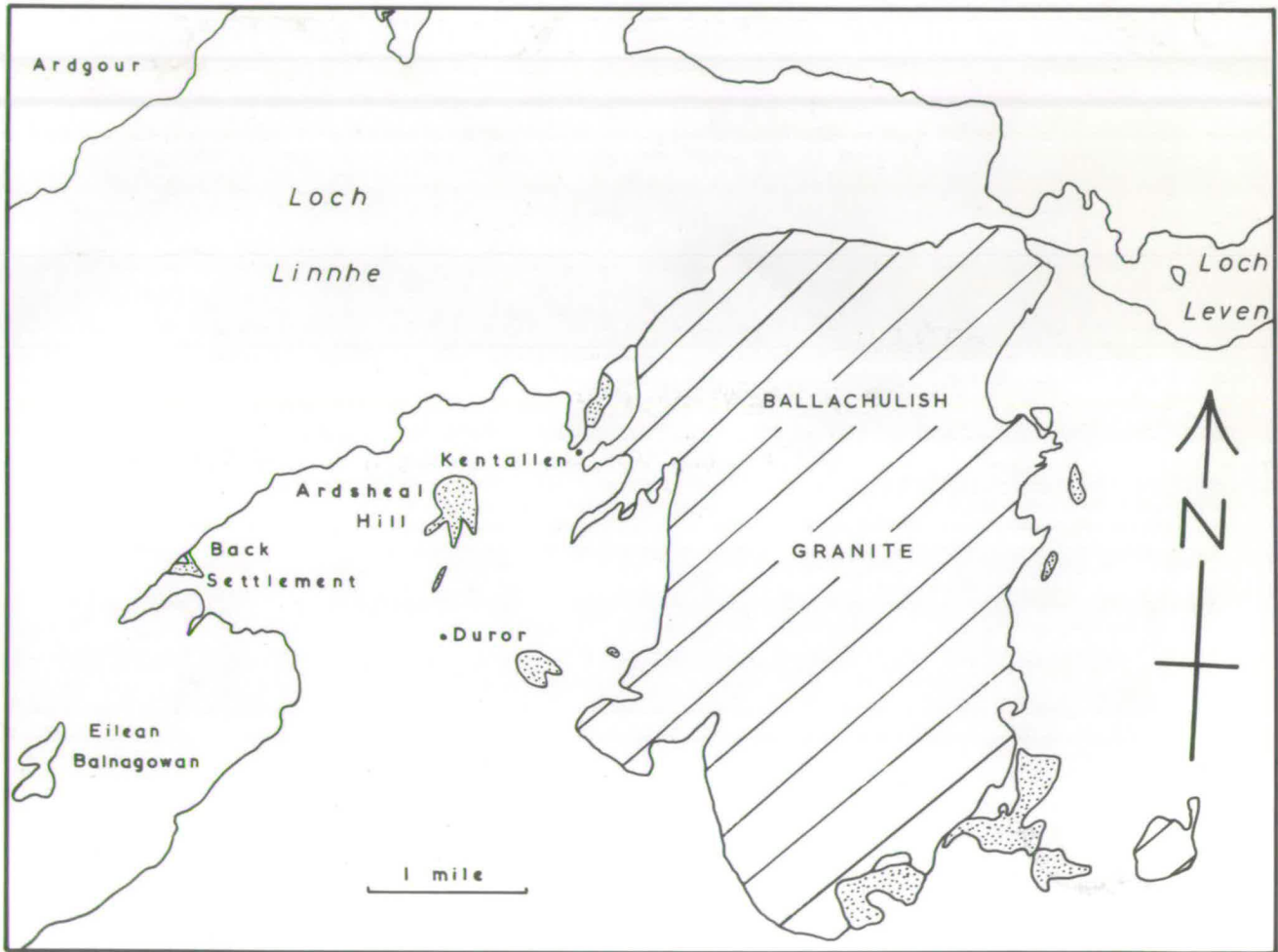
Basic bodies.

Figure 1

FIGURE 2

The Ballachulish Area

(After H.M. Geological Survey, 1 inch Sheet 53)



Legend



Granite.



Kentallenite, appinite, etc.

Figure 2

Field Associations.

1) The hypabyssal-plutonic association.

Hill and Kynaston (1900) and Bailey (1960) have noted the close association between the appinite suite and the four plutonic centres of Argyll (Ballachulish, Cruachan-Etive, Loch Avich and Ben Bhuidhe) and have shown that the basic rocks tend to be clustered round the acid plutons. These marginal rocks may be engulfed (Ballachulish), altered (Glen Ure) or cut (Kentallen) by the granites, indicating that they are older than the more acid rocks (Hill and Kynaston, 1900; Bowes, 1962; Platten, 1966; Appendix A).

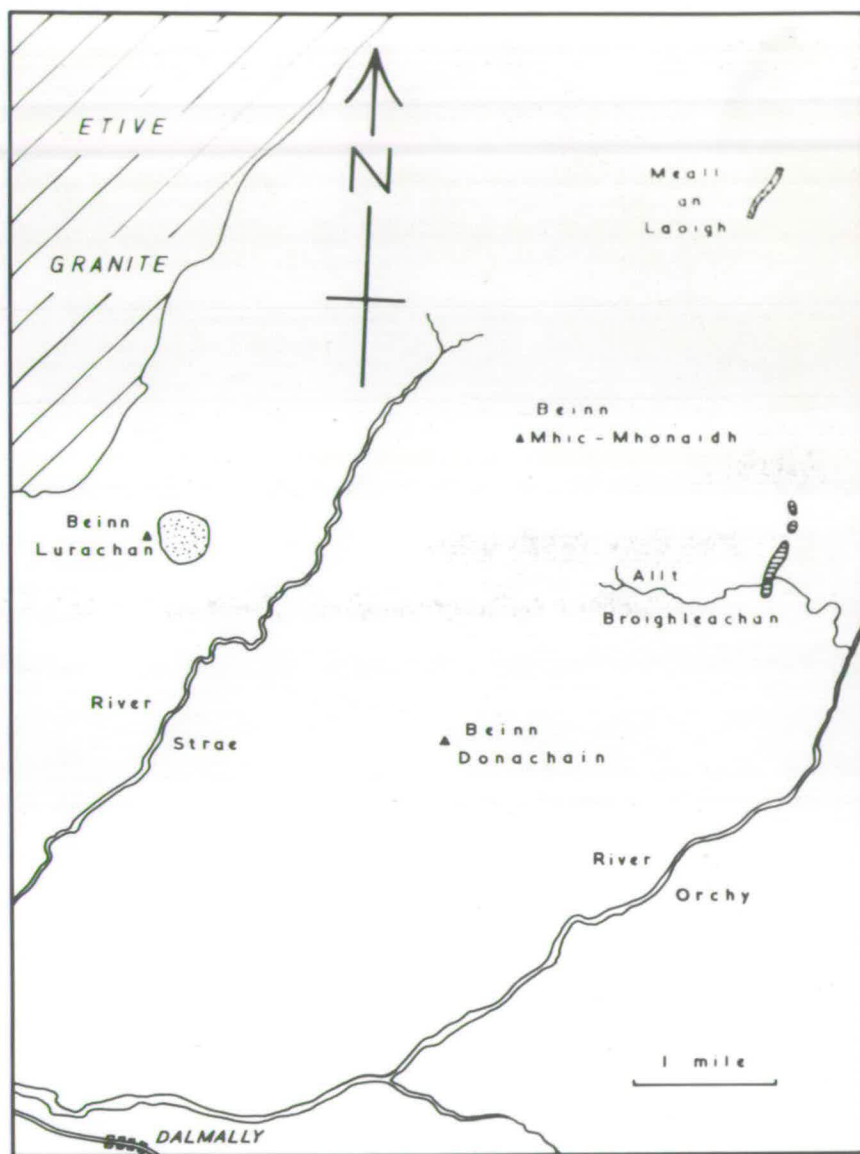
Walker (1927) and Anderson (1935'b') have shown that the satellitic basic stocks are often complex. Walker found eight rock-types in the summit complex of Ardsheal Hill (Figs. 1 and 2), including an olivine basalt containing large phenocrysts of clinopyroxene and small green olivines. This rock is similar to chilled kentallenite from Glen Creran (Bailey et al., 1916; Bailey, 1960), Kentallen (the 'lamprophyre' of Bowes, 1962; Platten, 1966, p.89), Glen Orchy (Figs. 1 and 3) and Scalasaig, Colonsay (Figs. 1 and 4; Appendix A), and is evidence for the existence of a kentallenite 'magma'. Close field and genetic relationships between kentallenite and appinite can be demonstrated at Ardsheal Hill (Walker, 1927), but although the Arrochar complex (Fig. 1) contains similar rock-types to those of Ardsheal Hill (Anderson, 1935'b'), the mutual relationships between kentallenite and appinite are obscure due to poor exposure. The Arrochar kentallenite is hypersthene-bearing, unlike that of Ardsheal Hill but similar to the Allt an t-Sithein body near Ben Bhuidhe (Hill and Kynaston, 1900), but the orthopyroxene may be a reaction product developed from olivine rather than a primary crystalline phase.

The Garabal Hill-Glen Fyne igneous complex (Fig. 1), composed dominantly of acid rock-types (Dakyns and Teall, 1892; Nockolds, 1941), is of

FIGURE 3

The Glen Orchy Area

(After H.M. Geological Survey, 1 inch Sheet 45)



Legend



Granite.



Diorite.



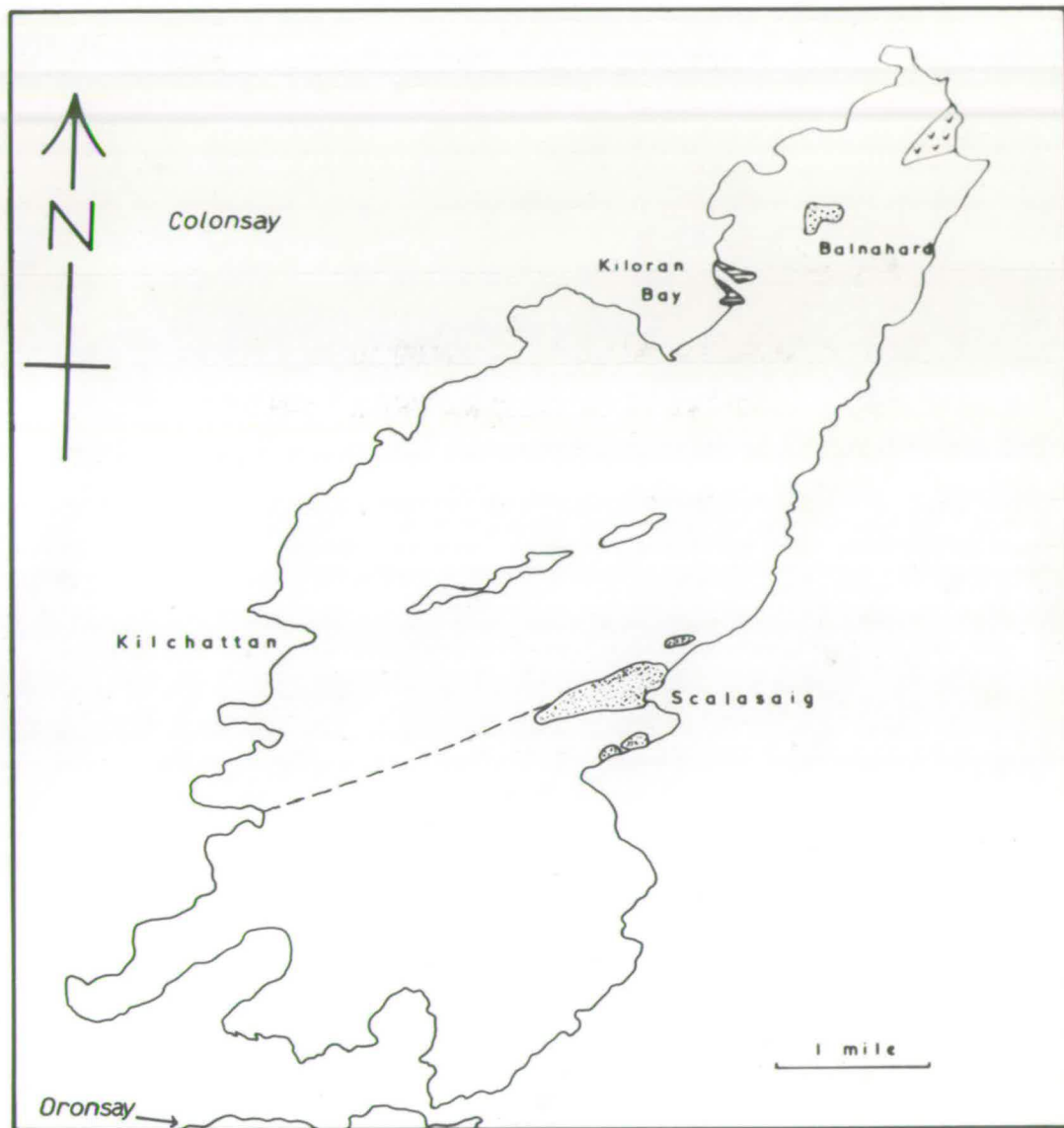
Kentallenite

Figure 3

FIGURE 4.

Colonsay, with part of Oronsay

(After Craig et al., 1911, plate 1)



Legend



Lewisian.



Syenite.



Kentallenite, diorite

Figure 4

similar size (5 miles long, up to 3 miles wide) to the Ballachulish granite complex (e.g. Bailey, 1960), and has a similar assemblage of basic bodies developed round it (cf. Ardsheal Hill and Ben Bhuidhe-Arrochar). Together with their immediately satellitic basic bodies, these two complexes show a range of chemical variation from ultrabasic (pyroxenites, 'dunites', peridotites) to acid (granodiorite, granite). Intrusion of the acidic magma at Garabal Hill probably exploited the area of weakness caused by initial emplacement of basic material (cf. Platten, 1966), but that at Ballachulish may have been emplaced by cauldron subsidence (Johnstone, 1966).

The major Caledonian igneous intrusions of the Southwest and Central Highlands have a distinct NE-SW linearity, in approximate parallelism with the 'grain' of the Dalradian metasediments (see Platten, 1966, p.194). Their emplacement may be controlled by crustal fracture under tension during relaxation of Caledonian stress (Westoll and Miller, 1968, in press).

2) The volcanic association.

Association of the appinite suite with the Old Red Sandstone (O.R.S.) Lorne Plateau Lavas has been suggested by several workers (e.g. Teall, 1897; Nockolds, 1941; Bailey, 1958; Platten, 1966), but the lavas were thought by Read (1961) to separate the "Forceful Newer Granites" (Ballachulish, Moor of Rannoch and Strontian) from the "Permitted Last Granites" (Glen Coe, Ben Nevis and Etive-Cruachan cauldron subsidences), and thus to post-date most members of the appinite suite (which are older than the Ballachulish granite).

There is, however, field, petrographic and chemical evidence that the Ballachulish complex is of Last Granite age. The distribution of rock-types within the complex and the contact relationships with the country rocks are similar to those of Ben Nevis (Bailey, 1960), and consistent with an origin by cauldron subsidence (Johnstone, 1966). In addition lamprophyre dykes of

the Etive or Ben Nevis swarms appear to cut only the earlier outer part of the Ballachulish complex, and to be cut by apophyses of the later central part of the intrusion (cf. Hill and Kynaston, 1900; Bowes, 1962), a relationship characteristic of Last Granite plutons (e.g. Etive-Cruachan and Ben Nevis). Further similarities between the Ballachulish body and the Glen Coe, Ben Nevis and Etive-Cruachan intrusions are shown by their petrographic characteristics (e.g. Bailey, 1960, p.225) and by chemical data (Bailey, 1960, Table 3). Age determinations cannot distinguish between the Forceful and Permitted Granites (Miller and Brown, 1965, p.130; Brown et al., 1968, p.267) and geological evidence is therefore considered decisive.

Thus it is likely that the Ballachulish complex is of Last Granite age and is later than the O.R.S. volcanicity. Some of the kentallenite-appinite pipes, which predate the granite, may then have acted as feeders to the lavas (see Platten, 1966), being exposed because of differences in erosion level north and south of the Pass of Brander Fault.

Explosion breccias (Bowes and Wright, 1961), generally pipe-like in form and composed almost entirely of fragments of country rock (Appendix A), are commonly associated with the appinite suite. Except for occasional small lamprophyre/appinite masses which may intrude them (e.g. at Back Settlement - Fig. 1; Bowes and Wright, 1961), they are normally free of igneous material, and their formation has been ascribed to gas streaming ahead of a volatile-rich appinite magma (Bowes and Wright, 1961, 1967; after Reynolds, 1954).

Postulated origins.

Early workers in the Southwest Highlands suggested derivation of the entire Scottish calc-alkali series by a process of differentiation acting at a depth upon a common parent (Dakyns and Teall, 1892; Hill and Kynaston, 1900).

This hypothesis has been supported by the chemical and mineralogical work of Nockolds (1941), Nockolds and Mitchell (1948) and Gill (1965), who chose a parent magma of andesitic type, and by strontium isotope data (Summerhayes, 1966). A similar theory, involving derivation from a hydrous basaltic magma, was advanced by Hall (1967) for the pyroxene-poor Donegal appinite suite.

Processes of hybridisation of basic material with acid magma (Read et al., 1925, 1926; Read, 1931, 1961; Nockolds, 1934; Joplin, 1959; French, 1966), and of acid material with basic magma (Platten, 1966), have been advanced to explain the large volumes of acid rock found in the Southwest Highlands, but they fail to explain the occurrence of the pyroxene-olivine bearing kentallenites. However Platten (1966) suggested that some basic magma was intruded at high level to form the basic bodies, the remainder assimilating granitic material at depth. A composite theory of origin was also suggested by Mathur (1951), who considered kentallenite to be derived from the parent magma by differentiation (cf. Nockolds, 1941), and appinites to result from reaction of kentallenite with the granitic residual liquid (cf. Nockolds, 1934). Transfusion of sedimentary rock by emanations from a primary hornblendite magma was suggested by Reynolds (1935, 1936) for the appinite suite. She proposed the formation of kentallenite by crystallisation of porphyroblasts of olivine and pyroxene within the sedimentary rocks, but the rocks which Reynolds described as containing porphyroblasts are chilled kentallenite (cf. Bailey, 1960; Platten, 1966), and thus indicative of igneous origin.

Purpose of the current work.

Kentallenite is a peculiar combination of 'early' (olivine, augite) and 'late' (biotite, orthoclase) minerals. This work was undertaken to elucidate the significance of this feature, and to re-examine the genesis of kentallenite in the light of current petrogenetic theory. Because of the

position of kentallenite at the basic end of the range of calc-alkaline variation in the Southwest Highlands, it was hoped that detailed chemical and mineralogical investigation of it would afford an insight into the early history of the calc-alkali series in general.

Twelve kentallenite localities were visited, and four were selected for examination on the basis of freshness and variety of rock-types. They were:

Kentallen	(the "type" locality),
Glen Orchy,	
Scalasaig)	} Colonsay.
Balnahard)	

Arrangement of the thesis.

The principle followed in the arrangement of the thesis was that of restriction of data to Appendices, rather than integration of them with the text. Little or no field, petrographic or chemical data are present in the text other than in diagram form, because inclusion of these data would disrupt the presentation of the main discussion and conclusions. Where necessary, however, reference is made in the text to the relevant Appendix.

Apart from this Introduction (Chapter 1), the thesis is composed of six chapters. The reasons for the order of the chapters should be clear from the notes on their contents given below.

Chapter 2 Mineralogy

This chapter is placed first because knowledge of the mineral chemistry is necessary for discussion in parts of the succeeding chapters. Following a brief outline of the microscopic features of the minerals their chemistry is examined, and it is concluded that kentallenites are

an unusual assemblage of normal minerals. It is therefore possible to consider 'normal' means of evolution in the genesis of the rock-type, but these may have operated under 'abnormal' combinations of conditions.

Chapter 3 Rock Chemistry

Diagrams of various kinds are used in this chapter to display the variation of the kentallenites, and to compare it with that shown by other calc-alkaline suites. The role of sorting and differential movement of olivine in controlling bulk composition is recognised.

Plots of kentallenite analyses demonstrate scatter of the compositions across the one atmosphere thermal divide in the normative basalt tetrahedron. Since olivine lies on this divide it cannot cause the scatter across it; some other means must be sought.

Chapter 4 Experimental Work

The validity of the one atmosphere thermal divide is examined in the light of published experimental work. Although a divide exists, its precise position under different physical conditions is uncertain. In practice, therefore, there will be a divide 'zone' rather than a 'plane'.

Kentallenites are thought to show sufficient variation to scatter across the enlarged divide 'zone', but there is no mineralogical evidence that the rocks crystallised at pressures sufficient to change the character of the divide.

Chapter 5 Geometrical and Statistical Treatment

Projections of kentallenite compositions into a four-component system analogous to the synthetic system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ are used in an attempt to define the major axes of variation of kentallenites. These

emphasise the olivine control observed in Chapter 3, and also disclose a marked linear trend across the divide 'zone'. Projection of natural mineral data from the Brae complex, Shetland, in these plots indicates that pargasite could be concerned in the development of the cross-trend. However, amphibole is not observed in kentallenite.

Principal component analysis performed on the data with the aid of a computer confirms the possible roles of olivine and pargasite as controls of kentallenite variation. The suggestion is made that an amphibole may have broken down in the relatively anhydrous environment of final crystallisation.

Chapter 6 Petrogenesis

The olivine and amphibole trends suggested in the previous chapter are considered in detail, and evidence for the possible pre-existence of amphibole is presented. A petrogenetic model is proposed, based upon the olivine and amphibole controls.

Chapter 7 Origin of the Calc-alkali suite

Critical examination of current calc-alkaline evolutionary theories reveals their inadequacy to explain the distinctive features of the suite. The petrogenetic model suggested in Chapter 6 is thought to be competent to explain these features, and to offer a valid means of derivation of the suite by fractionation from a basaltic parent.

The Appendices are lettered as follows:

Appendix A - Field relationships

Appendix B - Petrography of the minerals.

Appendix C - Analytical data. Modal and petrographic data of analysed rocks.

Appendix D - Methods. (Including X-ray diffraction and fluorescence, chemical analytical methods, R.I. and 2V procedure and mineral separation.)

CHAPTER 2MINERALOGYIntroduction

The position of kentallenite at the basic end of the range of variation of the Southwest Highland calc-alkali suite suggests that some features of its mineralogy may throw light upon the early history of this suite. Four olivines, two pyroxenes and four biotites were therefore separated from kentallenites and analysed; the methods employed in separation and analysis are recorded in Appendix D. In cases where separation was difficult, mineral compositions have been estimated by optical methods. Some of these data are used in the following chapters to aid in the explanation of the kentallenite trends of variation and, in conjunction with petrographic interpretations, to examine the processes controlling the early development of the calc-alkali series.

Petrographic summary

Kentallenite is usually fresh, and shows black olivine and green augite phenocrysts set in a matrix of poikilitic brown biotite, plagioclase and orthoclase. This matrix is fine-grained at the contact of the intrusion with the country rocks, but is elsewhere well crystallised. Textural evidence indicates that olivine probably started to crystallise before augite, but occasional accumulative textures of olivine and augite (Appendix B) and the presence of these minerals as phenocrysts indicate subsequent simultaneous crystallisation. Plagioclase phenocrysts are rarely present in chilled kentallenite, but plagioclase is the third phase to start crystallising, and may form large individuals comparable in size to the olivine and augite "phenocrysts" (i.e. 2-4mm) in central parts of the intrusions.

Where hornblende is a product of reaction between augite and the

magma it crystallises later than the plagioclase, but where it is a primary crystalline phase (e.g. in acidic rocks in Colonsay) it begins to crystallise before plagioclase. Both potash-bearing minerals are late-stage, the biotite forming large (up to $\frac{1}{2}$ ") plates which enclose plagioclase individuals and mould upon both olivine and pyroxene, the orthoclase crystallising from the last interstitial liquid and enclosing plagioclase. Accessory minerals rarely comprise more than 1-2% of the rock. Ore is never euhedral and is closely associated with olivine and biotite, but apatite forms elongate prisms, often pleochroic from pale violet to pink.

Approximate modal mineral contents of kentallenite (see also Appendix C) are:

olivine	-	15-40%
augite	-	10-30%
plagioclase	-	10-30%
biotite	-	5-15%
orthoclase	-	10-20%.

A more detailed treatment of petrography will be found in Appendix B.

Mineral chemistry

Olivine

Major elements.

Analytical and optical data for the separated olivines are presented in Table 1. Table 2 is a compilation of X-ray and optical data on fourteen olivines, including the chemically analysed samples.

The Fe_2O_3 values in Table 1 (determined by subtraction from total Fe_2O_3 using the method of Wilson (1955) for FeO) are higher than those normally recorded for magnesian olivines; e.g. 0.86% was found in olivine $Fe_{0.86}$ from Rhum (Brown, 1956), and <0.58% in olivines from peridotites (Ross et al.,

TABLE 1
OLIVINE DATA

<u>Mineral</u>	<u>K7 ol.</u>	<u>K8 ol.</u>	<u>O4 ol.</u>	<u>L4 ol.</u>
<u>Oxide (wt. %)</u>				
SiO ₂	39.2	38.9	39.4	38.4
TiO ₂	0.06	0.05	0.05	0.06
Al ₂ O ₃	0.32	0.25	0.22	0.14
Fe ₂ O ₃	1.97	1.92	2.12	1.92
FeO	18.2	17.9	17.9	19.7
MnO	0.37	0.39	0.34	0.41
MgO	40.6	39.7	39.9	37.9
CaO	0.37	0.36	0.40	0.40
Na ₂ O	-	-	-	-
H ₂ O	-	-	-	-
<u>Total</u>	101.1	99.6	100.3	99.0
<u>Element (p.p.m.)</u>				
Ni	1430	1360	1420	990
Sr	-	-	20	-
<u>Formula</u>	Fe _{78.4}	Fe _{78.2}	Fe _{78.2}	Fe _{75.9}
<u>R.I. - β</u>	1.686	1.687	1.683	1.694
<u>2V ∞</u>	90°	86°	89°	87°

K = Kentallen
O = Glen Orchy
L = Balnahard, Colonsay

For methods of measurement of
R.I. and 2V, see Appendix D.

TABLE 2

OLIVINE COMPOSITION COMPARISON

<u>Specimen No.</u>	<u>Method</u>		<u>2Vα</u> (All as Fo%)
	<u>Chemical</u>	<u>X.R.D.</u>	
K6		81.7	87
K7	78.4	77.6	85
K8	78.2	78.3	77
K17		75.8	81
K30E			83
K30H			77
A1		79.5	79
D6		79.5	87
O4	78.2	78.8	83
O11G			85
O11F			91
L4	75.9	77.9	79
C1G			83
C5C			79

K = Kentallen

A = Ardsheal Hill

D = Duror

O = Glen Orchy

L = Balnahard, Colonsay

C = Scalasaig, Colonsay

For determinative methods,
see Appendix D.

1954). However the values are lower than those originally obtained (Table 3) using the dichromate titration method (Peck, 1964) for FeO.

Kentallenite olivines are crowded with small opaque flakes flattened parallel to (100) of the crystals, and digestion of the olivine in hot 10% HCl left an opaque residue confirmed by X-ray diffraction as a spinel of the magnetite-magnesioferrite series (cf. Brown, 1956, p.19). The relatively high Fe_2O_3 values in Table 1 are therefore taken to reflect oxidation of ferrous iron in the olivine lattice (probably during thermal metamorphism), leading to exsolution of magnetite-magnesioferrite within the olivine. Forsterite contents of the olivines have been calculated on this assumption (Table 1, and Table 2, column 1).

Optical determinative methods (Tables 1 and 2) yield estimates of the parent host olivine compositions which are, as expected, slightly more magnesian (3-7%) than those indicated by the analyses recalculated with all the iron as Fe^{2+} . However values from the X-ray diffraction method fall within $\pm 3-4$ molecular percent of the chemical values, the quoted error of the method (Yoder and Sahama, 1957).

The olivines of kentallenite (Fe_{75-80}) are less magnesian than the earliest olivines precipitating from gabbroic layered intrusions (Wager and Brown, 1968) and may, therefore, have precipitated either from liquids less basic than basalt or from liquids of basaltic type which had previously precipitated olivine alone during their development.

Trace elements.

Nickel was determined in the olivines (Table 1) yielding a maximum value of 1430 ppm, rather lower than the values from olivines of similar Forsterite content from the Brae, Shetland, calc-alkaline complex

TABLE 3OLIVINE FeO DETERMINATIONSSpecimen No.

	<u>Method 1 (Peck)</u>	<u>Method 2 (Wilson)</u>	<u>Total Fe₂O₃</u>
K7	FeO 16.26%	18.17%	22.14%
	Fe ₂ O ₃ 4.09	1.97	
K8	FeO 16.13	17.93	21.82
	Fe ₂ O ₃ 3.92	1.92	
O4	FeO 15.68	17.91	22.00
	Fe ₂ O ₃ 4.60	2.12	
L4	FeO -	19.73	23.82
	Fe ₂ O ₃ -	1.92	

Method 1 - Peck L.C. U.S.G.S. Bulletin, 1170, 89p.p., 1964;
Analyst: N.D.S.W.

Method 2 - Wilson A.D. Bull. Geol. Surv. G.B., 9, 56-58, 1955;
Analyst: C.R.B.

($\text{Fo}_{78.9}$, $\text{Ni} = 2200$ ppm; Gill, 1965) and the Skaergaard intrusion ($\text{Fo} \sim 70$, $\text{Ni} = 2000$ ppm; Wager and Mitchell, 1951). This difference is probably attributable to a difference in parent magma composition.

Strontium has been determined in one olivine, but only one per cent contamination by plagioclase (see below) would explain the amount present, and it is not considered significant.

Augite

Major elements.

Analytical data for the clinopyroxenes are presented in Table 4. The similarity between the two analyses arises because it is possible to separate clean clinopyroxene only from the more basic and amphibole-poor rocks, i.e. rocks of approximately the same stage of evolution. Both pyroxenes are augites according to the classification of Poldervaart and Hess (1951, Fig. 1, p.474), but they plot close to the augite-salite (K8) and augite-endiopside (O4) boundaries; structural formulae were calculated with Z-group = 2 (after Bown, 1964). Electron-probe examination of the analysed clinopyroxenes^{**} showed that Fe/Mg ratios of the pyroxenes increases from core to margin, the normal type of zoning; no change was detected in calcium content across the pyroxenes.

An augite from Garabal Hill (Nockolds, 1941) with composition $\text{Ca}_{43.1}\text{Mg}_{44.7}\text{Fe}_{12.2}$ compares closely with the two analyses presented here, and four clinopyroxenes from the Brae complex, Shetland (Nos. C4, C5, C6 and C13; Gill, 1965), are very similar to the kentallenite minerals. The rocks from which these comparable pyroxenes were separated are all ultrabasic (augite-peridotite at Garabal Hill; olivine-, biotite- and hornblende-pyroxenites,

^{**}

By courtesy of Dr. Emeleus, University of Durham.

TABLE 4AUGITE DATA

<u>Mineral</u>	<u>K8 cpx.</u>	<u>04 cpx.</u>
<u>Oxide (wt.%)</u>		
SiO ₂	51.70	51.60
TiO ₂	0.70	0.64
Al ₂ O ₃	4.02	4.50
Fe ₂ O ₃	2.47	3.50
FeO	3.91	3.09
MnO	0.15	0.13
MgO	15.9	15.5
CaO	21.0	21.6
Na ₂ O	0.50	0.70
K ₂ O	0.06	0.17
Cr ₂ O ₃	0.39	0.48
Total	100.8	101.9
<u>Element (p.p.m.)</u>		
Ni	300	297
Sr	105	160
Zr	44	54
Ba	20	-
Cr	2550	2750
<u>Formula</u>		
Ca	45.0	43.9
Mg	44.9	46.1
Fe	10.1	10.0
<u>R.I. - β</u>	1.692	1.688
<u>2V_χ</u>	51°	46°

FIGURE 5

Comparison of kentallenite augites with other clinopyroxenes

This figure is a plot, in cation percent, of the kentallenite pyroxenes (K8, Ol₄) together with the most basic clinopyroxenes to crystallise from the Bushveld (B; Hess, 1949, 1960), Rhum (R; Brown, 1956), Skaergaard (Sk; from Brown, 1956) and Stillwater (St; Hess, 1949, 1960) layered intrusions, the Great Dyke (G; Hess, 1951) and the Lizard troctolite (L; Green, 1964).

Legend:

- o - Kentallenite augites
- - Other augites

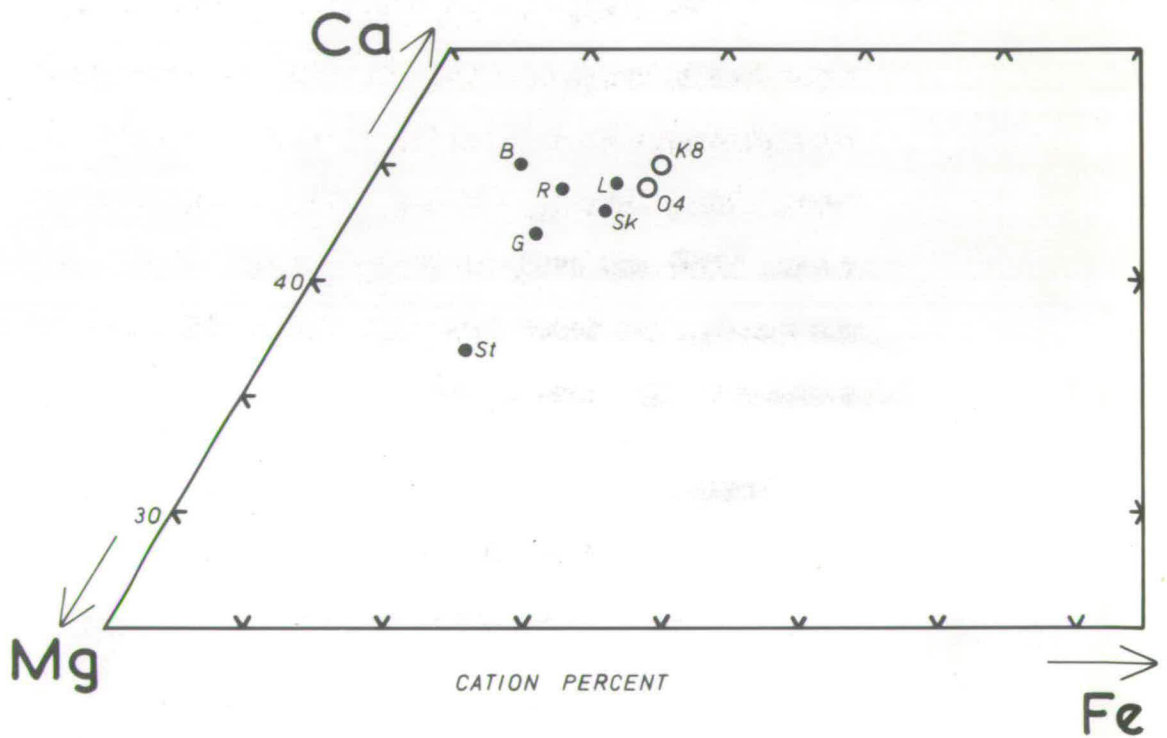
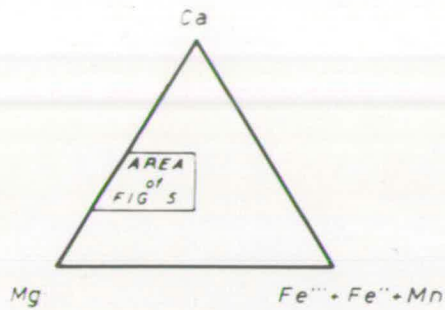


Figure 5

and websterite, from Brae), whereas the kentallenites are, chemically, basic. However the kentallenite pyroxenes are less magnesian than most ultrabasic pyroxenes (Fig. 5), suggesting that they are derived from a less basic magma than such pyroxenes (cf. discussion on olivines), and this implies that the ultrabasic rocks from which comparative data were taken (at Garabal Hill and Brae) are also crystal accumulates from a moderately evolved magma rather than early segregations from a basic liquid.

The analysed olivines (Table 1) co-existing with the analysed augites (Table 4) have a higher Fe/Mg ratio than the pyroxenes, in accordance with the data of Muir (1951). Both Al_2O_3 and TiO_2 contents of the kentallenite augites are closely comparable not only with those of other calc-alkaline augites but also with pyroxenes from the layered intrusions plotted in Fig. 5, and are consistent with crystallisation of the augites from a tholeiitic or high-alumina type of magma rather than one of alkaline affinities (Kushiro, 1960; LeBas, 1962).

Minor elements.

Chromium is the most abundant trace element in the kentallenite augites. The amounts of both chromium and nickel in these minerals are similar to those of the other pyroxenes with which major element comparison has been made. Strontium content (up to 160 ppm) exceeds that likely to be contributed by plagioclase contamination and is higher by a factor of three than that of the other augites for which Strontium data are available. It may reflect a higher content of strontium in the kentallenite parent magma.

Plagioclase

Major elements.

Plagioclase proved impossible to separate cleanly. Optical

TABLE 5

PLAGIOCLASE DATA

<u>Specimen No.</u>		<u>Composition (from X ^ 010)</u>	
		<u>Core</u>	<u>Margin</u>
K6	Kentallen Area	An ₆₀	
K8		An ₄₆	
K30E		An ₄₆	
K38A		An ₆₃	
A1		An ₄₅	
A2D		An ₆₇	
A7		An ₆₇	
A6		An ₅₅	
O2L	Glen Orchy	An ₇₂	An ₃₂
O4		An ₆₇	
L4	Balnahard, Colonsay	An ₈₇	An ₃₂
C1G	Scalasaig, Colonsay	An ₄₂	
C7K		An ₃₅	

methods were therefore used to determine feldspar compositions, and the results calculated from measurement of maximum extinction angle (X onto 010) are presented in Table 5. Compositional zoning of the kentallenite feldspars generally ranges from labradorite-bytownite ($\sim An_{70}$) to oligoclase-andesine ($\sim An_{30}$), values consistent with the range found in other Scottish calc-alkaline intrusions (Nockolds, 1941; Gill, 1965). The feldspar from Scalasaig, Colonsay, seems to be rather more albite-rich than that from the other intrusions and probably reflects the more 'evolved' nature of the rocks selected from there for analysis and feldspar determination.

Minor elements.

Trace element determinations on an impure separation of plagioclase from Balnahard, Colonsay, showed a high strontium content (~ 2200 ppm). Nockolds and Mitchell (1948) found ~ 3000 ppm strontium in plagioclase from the basic rocks at Garabal Hill, but Gill (1965) found only ~ 1000 ppm strontium in plagioclase from Brae. Rubidium content is low (40 ppm), and the moderately high barium content (620 ppm) of the plagioclase may be partly the result of contamination by orthoclase.

Hornblende

Major elements.

Separation of hornblende was not attempted because of intergrowth with augite in most of the kentallenites. Optical data have been obtained, however, from a secondary amphibole in Glen Orchy (011F), and from two primary amphiboles in Colonsay (Table 6). The higher 2V of 011F indicates that it has a higher Mg/Fe ratio than the Colonsay minerals (see Deer *et al.*, 1963'a', Figs. 76-78, pp.296-8), suggesting that the primary phases in Colonsay may have precipitated from a less magnesium-rich, and thus more differentiated, magma (cf. comments on Na_2O contents of feldspars).

TABLE 6

HORNBLLENDE DATA

<u>Specimen No.</u>	<u>2V α</u>
011F	91°
C6B	85°
C6E	84°

Minor elements.

Since no separation of hornblende was made, minor element analysis was not possible.

Biotite

Major elements.

Chemical and optical data for the analysed biotites are presented in Table 7; because of lack of sufficient sample one of the biotites (K7 brown) has been analysed only partially, and water has not been determined. Mg/Fe ratios of these micas indicate that they are phlogopites (after Heinrich et al., 1953; quoted by Deer et al., 1962'b'). The green variety of mica is secondary after the brown (Appendix B), and electron probe examination suggests that the colour change is mainly due to differences in TiO_2 content (cf. Hall, 1941; Hayama, 1959; Métais et al., 1962). In undeformed micas 2V is sensibly zero, but various degrees of distortion of the phlogopites may give rise to 2V values as high as 10° (Table 7).

Plots of the analysed micas in the $\text{MgO-FeO} + \text{MnO-Fe}_2\text{O}_3 + \text{TiO}_2$ diagram of Heinrich (1946), and in Nockolds' (1947) $\text{MgO-total Fe as FeO-Al}_2\text{O}_3$ diagram, Figs. 6 and 7, fall within or close to the fields appropriate to their paragenesis. The kentallenite micas are similar to some of those from Brae (Gill, 1965; e.g. B-2 and B-12), but the biotites from Garabal Hill (Nockolds, 1941), the most basic of which is from a pyroxene-mica-diorite (a more acidic rock-type than kentallenite), are more iron-rich than the kentallenite varieties (Table 8).

Minor elements.

Nickel contents of the analysed micas are high (Table 7), and comparable to those of the co-existing olivines (Table 1). This observation,

TABLE 7

BIOTITE DATA

<u>Mineral</u>	<u>K7 green bi.</u>	<u>K7 brown bi.</u>	<u>K8 bi.</u>	<u>L4 bi.</u>
<u>Oxide (wt. %)</u>				
SiO ₂	40.7	38.7	38.5	38.0
TiO ₂	0.54	3.86	4.76	4.39
Al ₂ O ₃	15.00	14.3	14.2	14.4
Fe ₂ O ₃	2.25	-	1.52	1.43
FeO	6.91	-	8.94	10.35
MnO	0.06	0.06	0.07	0.08
MgO	20.3	18.8	18.3	16.7
CaO	0.93	0.58	0.34	0.74
Na ₂ O	0.72	-	0.33	0.44
K ₂ O	8.85	-	9.45	9.14
H ₂ O	-	-	-	-
<u>Total (less H₂O)</u>	<u>96.3</u>	<u>-</u>	<u>96.4</u>	<u>95.7</u>
<u>Element (p.p.m.)</u>				
Ni	1250	1370	1378	862
Rb	275	315	370	345
Sr	170	100	75	115
Zr	92	32	45	80
Ba	320	2240	800	4370
<u>Mg:Fe ratios</u>	4.05	3.25	3.17	2.56
<u>R.I. - β</u>	1.605	1.633	1.638	1.631
<u>2V[∞]</u>	-	-	0-5°	0-10°

TABLE 8

COMPARATIVE BIOTITE DATA

<u>Mineral</u>	<u>Biotite from pyroxene- mica-diorite, Garabal Hill (Nockolds, 1941)</u>	<u>Biotite "B-2" from biotite-pyroxenite, Brae (Gill, 1965)</u>	<u>Biotite "B-12" from hypersthene-diorite, Brae (Gill, 1965)</u>	<u>K8</u>
<u>Oxide (%)</u>				
SiO ₂	39.4	38.6	38.8	38.5
TiO ₂	3.08	3.23	4.46	4.76
Al ₂ O ₃	10.6	16.6	14.7	14.2
Fe ₂ O ₃	1.53	1.13	2.61	1.52
FeO	11.0	6.87	9.50	8.94
MnO		0.04	0.05	0.07
MgO	16.9	20.9	16.7	18.3
CaO	1.08	0.25	0.46	0.34
Na ₂ O	-	0.91	0.12	0.33
K ₂ O	-	8.27	9.48	9.45
<u>Element (p.p.m.)</u>				
Ni	150	1800	1000	1378
Rb	1000	180	450	370
Sr	100	5	5	75
Zr	20	35	35	45
Ba	3000	1000	400	800

FIGURE 6

MgO—FeO + MnO —Fe₂O₃ + TiO₂ diagram

(After Heinrich, 1946)

The kentallenite biotites are plotted as filled circles in this diagram, and fall within Heinrich's 'basalt' field. The areas marked 'g' and 'p' in this figure are the areas appropriate to gabbroic and peridotitic biotites respectively.

FIGURE 7

MgO—total Fe as FeO—Al₂O₃ diagram

(After Nockolds, 1947)

The kentallenite biotites are plotted as filled circles in this diagram, and fall into the field of biotites associated with olivine and augite.

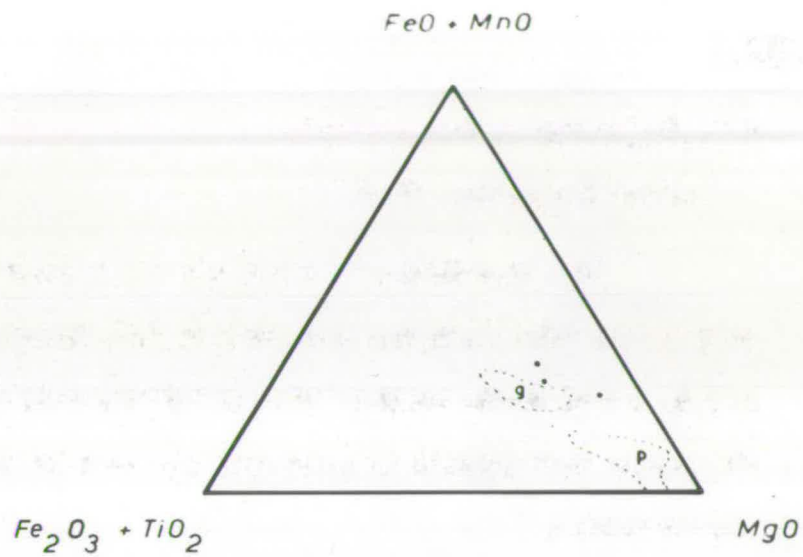


Figure 6

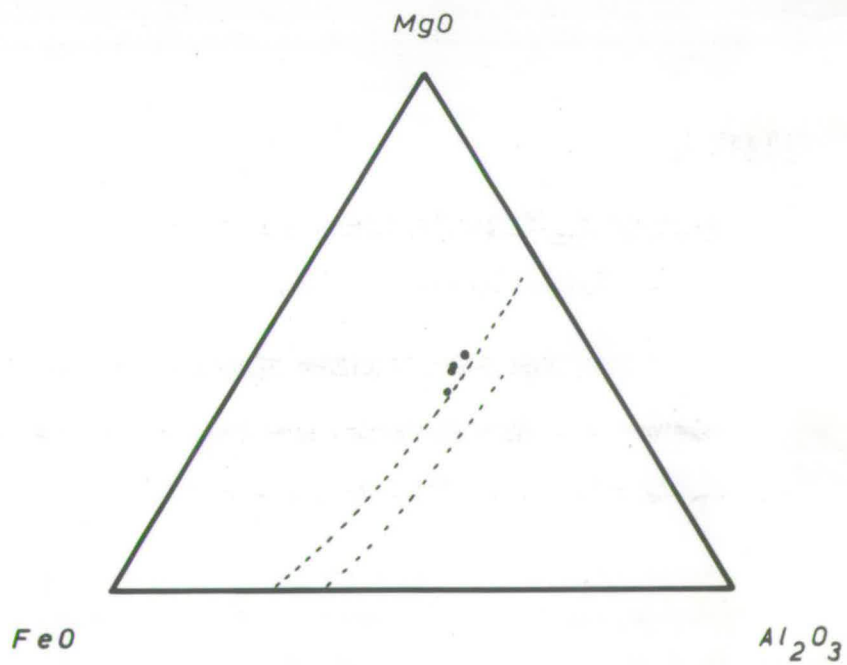


Figure 7

and textural evidence (Appendix B), suggests that phlogopite may be involved in a reaction relationship with olivine, being derived from breakdown of olivine and addition from the magma of the requisite K_2O , Al_2O_3 and (OH) to the released FeO , MgO , NiO and SiO_2 .

The differences evident in Table 8 between the trace element contents of the Garabal Hill biotite and those of Brae and Kentallen probably reflect the more fractionated nature of the magma from which the Garabal Hill micas separated.

Orthoclase

Major elements.

Separation of pure alkali feldspar was not attempted. 2V determinations on four alkali feldspars are presented in Table 9, and the values shown, together with the lack of microcline twinning, identify the feldspar as orthoclase (after Marfunin, 1961). The Colonsay orthoclases have a higher 2V than those from Kentallen and Glen Orchy, indicating that the Colonsay feldspars probably contain more sodium in solid solution than those from the other intrusions (see Deer et al., 1963'b', Fig. 28, p.58).

Minor elements.

An orthoclase concentrate (L4, from Colonsay) was analysed for several trace elements. The high concentration (~ 2500 ppm) of barium is in accord with Nockolds and Mitchell's data (1948; 2-5000ppm) on orthoclase from the medium granodiorite at Garabal Hill, and Gill's data (1965; 2500 ppm) from potash feldspar in a hypersthene diorite at Brae. Strontium content, approximately 2300 ppm, is similar to that of the 'co-existing' plagioclase (approx. 2200 ppm), a relationship consistent with that of Gill (1965) from Brae. Rubidium content of the orthoclase is low (100 ppm), probably as a result of early crystallisation of phlogopite; the mica may have depleted the magma in

TABLE 9

ORTHOCLASE DATA

<u>Specimen No.</u>	<u>2V α</u>
K30E	59°
04	58°
C5E	74°
C6B	79°

rubidium before orthoclase started to crystallise.

Ore

No chemical analysis of the ore present in kentallenite was attempted, but an X-ray fluorescence scan of a concentrate showed a high content of chromium, and as reflected light examination disclosed no chromite within the ore the chromium must be present in solid solution.

The ore has been identified as a spinel of the magnetite-magnesioferrite series both by reflected light and X-ray diffraction. Ilmenite exsolution lamellae are occasionally visible in polished section and have been confirmed by the electron probe; the ore associated with the olivine is, however, titanium-free.

Apatite

In an attempt to relate colour and pleochroism in apatite to manganese content (after Vasilieva, 1958; quoted in Deer *et al.*, 1962'c', p.332) several apatites were examined with the electron probe. No response was obtained for manganese, indicating that if it is the cause of the colour and pleochroism it must be effective in trace amounts (i.e. $< 0.05\%$, the limit of detection of Mn by the electron probe; C.H. Emeleus, pers. comm.).

No other analytical work was carried out on apatite.

Summary

The range of composition exhibited by the anhydrous mafic phases in kentallenite is considerably restricted, consequent upon the development of hydrous replacement and alteration products of them at an early stage in the crystallisation of the parent magma. The lack of hypersthene as a primary phase in kentallenite (contrast Brae complex; Gill, 1965) can probably be

attributed to suppression of it in favour of hornblende by the appreciable water content of crystallising kentallenite magma. Orthopyroxene and hornblende may therefore be "alternative" crystallisation products of the Scottish Caledonian parent magma (cf. Brae and Colonsay; see also Bailey, 1958), their relative importance being determined by water content at any given stage of magmatic evolution (see also discussion on Appinites, Chapter 6).

It has been shown in this chapter that the individual minerals of kentallenite are closely comparable with those of other rocks in the Scottish Caledonian calc-alkali suite. The peculiarity of kentallenite thus lies not in any oddity of its constituent minerals but in the assemblage as a whole, and it is possible that the origin of the rock-type may therefore be explicable in terms of normal processes acting under unusual, and possibly restricted, combinations of physical conditions.

Introduction.

Fifty-six rocks have been analysed, 31 from Kentallen (including single samples from Ardsheal Hill and Duror), 10 from Glen Orchy and 15 from Colonsay. All of those from Kentallen and Glen Orchy are kentallenites, but some of the analysed Colonsay rocks are diorites and contain hornblende as a primary crystalline phase (Chapter 2). Chilled phases of kentallenite have been analysed from the Kentallen area and Scalasaig, Colonsay, and picrites from Kentallen and Glen Orchy.

Because of the small size of kentallenite intrusions, and incomplete exposure, no attempt was made to sample for analysis on a grid system (cf. Mercy, 1963) and rocks were selected to show the maximum range of variation. However samples were analysed from traverses across each intrusion, but only at Glen Orchy and Colonsay, where transitions are visible in the field (Appendix A), do the analytical data show systematic variation with position in the intrusion.

The analyses have been plotted in various diagrams to aid in their interpretation, and these are discussed below; the data from which the diagrams are constructed may be found in Appendix C. Analysis of most major and all minor elements was performed by X-ray fluorescence (Rose et al., 1962; Aldermann and Kemp, 1958; see Appendix D).

Major Elements.

Fig. 8 (AFM plot) shows the affinity of the analysed kentallenites to a typical calc-alkaline trend (Brae, Shetland; Gill, 1965), and demonstrates the range of composition of kentallenites relative to this trend. Within this range, the Colonsay and Glen Orchy rocks tend to fall into separate groups, those in Colonsay having the higher proportion of alkalis, and the Kentallen samples also fall into two groups, matching those of Glen

FIGURE 8

AFM diagram of kentallenites

(cation percent)

$$A = Na + K$$

$$F = Fe^{3+} + Fe^{2+} + Mn$$

$$M = Mg$$

Kentallenites are plotted in this diagram according to the following legend:

- - Kentallen area rocks
- ⊙ - Ardsheal Hill
- + - Glen Orchy
- x - Scalasaig, Colonsay (C5, main intrusion)
- ⊗ - Scalasaig, Colonsay (C6, smaller appinitic diorite)

The Glen Orchy and Colonsay (C5) rocks are labelled in this diagram; see p.21 for discussion.

The dashed line is the approximate trend of the Brae, Shetland, rocks (compiled from the data of Gill, 1965).

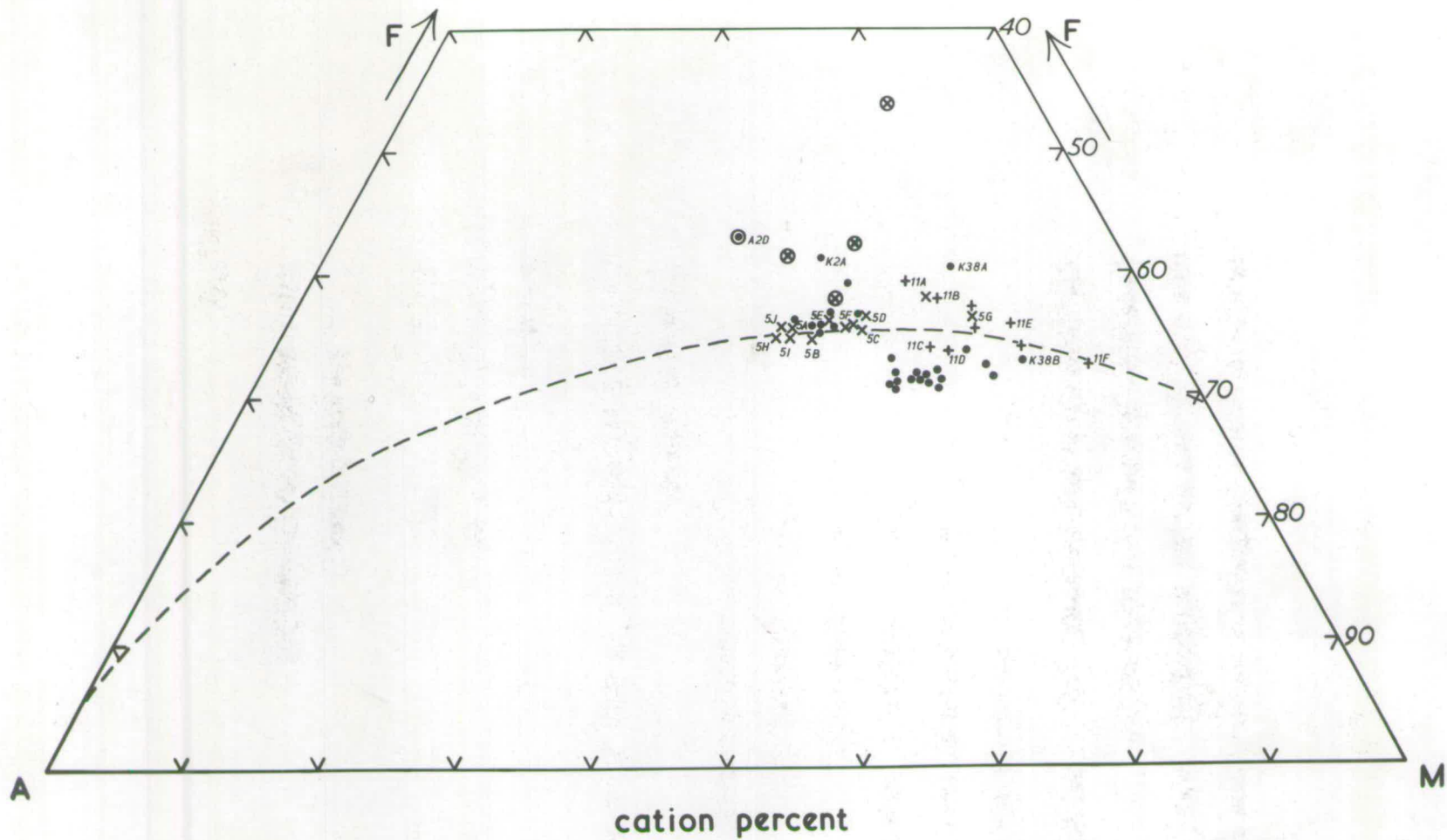


Figure 8

Orchy and Colonsay. These interrelationships, discussed further in Chapter 5, are preserved in other diagrams. The more hornblende-rich rocks from Colonsay (C6) have higher Fe/Mg ratios than the pyroxenic varieties (C5; cf. Onuki, 1966; Best and Mercy, 1967, p.470), and the picrites K38B and O11F are the most magnesian of the rocks analysed.

The AFM plot shows a systematic variation in bulk chemistry within the Glen Orchy and Scalasaig (C5) intrusions. The sequence 11F—11B (Fig. 8) represents the likely order of crystallisation in the main Glen Orchy mass; 11F is a picrite, and occurs at the lower contact of the intrusion in the stream section (Appendix A), 11B is from the upper contact and 11A is from the highest (topographic) outcrop of the intrusion, close to an area of aplite development (Appendix A). 5A—5J are rocks from the more pyroxenic Scalasaig intrusion (the main diorite; Appendix A) and show a similar trend to the Glen Orchy rocks. 5C and 5F are chills, and probably represent the original bulk composition of the magma. They plot in the middle of the range of variation at Scalasaig, the more accumulative marginal rocks (5D and 5G) plotting near the M-F join and the more acid central derivatives (5H, I and J) towards the alkali apex from that point. These relationships are observed in other figures, but in none of them are the trends as well defined as in Fig. 8.

The chills from the Kentallen area rocks (A2D, K2A and K38A) do not appear to represent the bulk compositions of kentallenite magmas. All plot away from the M apex of Fig. 8 from the main trend, suggesting that they are depleted in ferromagnesian minerals relative to the more coarsely crystalline kentallenites (see below). If kentallenites were intruded as crystal-liquid mushes, flowage differentiation (Smith and Kapp, 1963; Bhattacharji and Smith, 1964) could have depleted the marginal areas (i.e. the chills) in phenocrysts, concentrating them in picrites, and such a process would explain the

FIGURE 9

K-Na-Ca diagram of kentallenites
(cation percent)

Legend: as Figure 8, including dashed line for Brae trend.

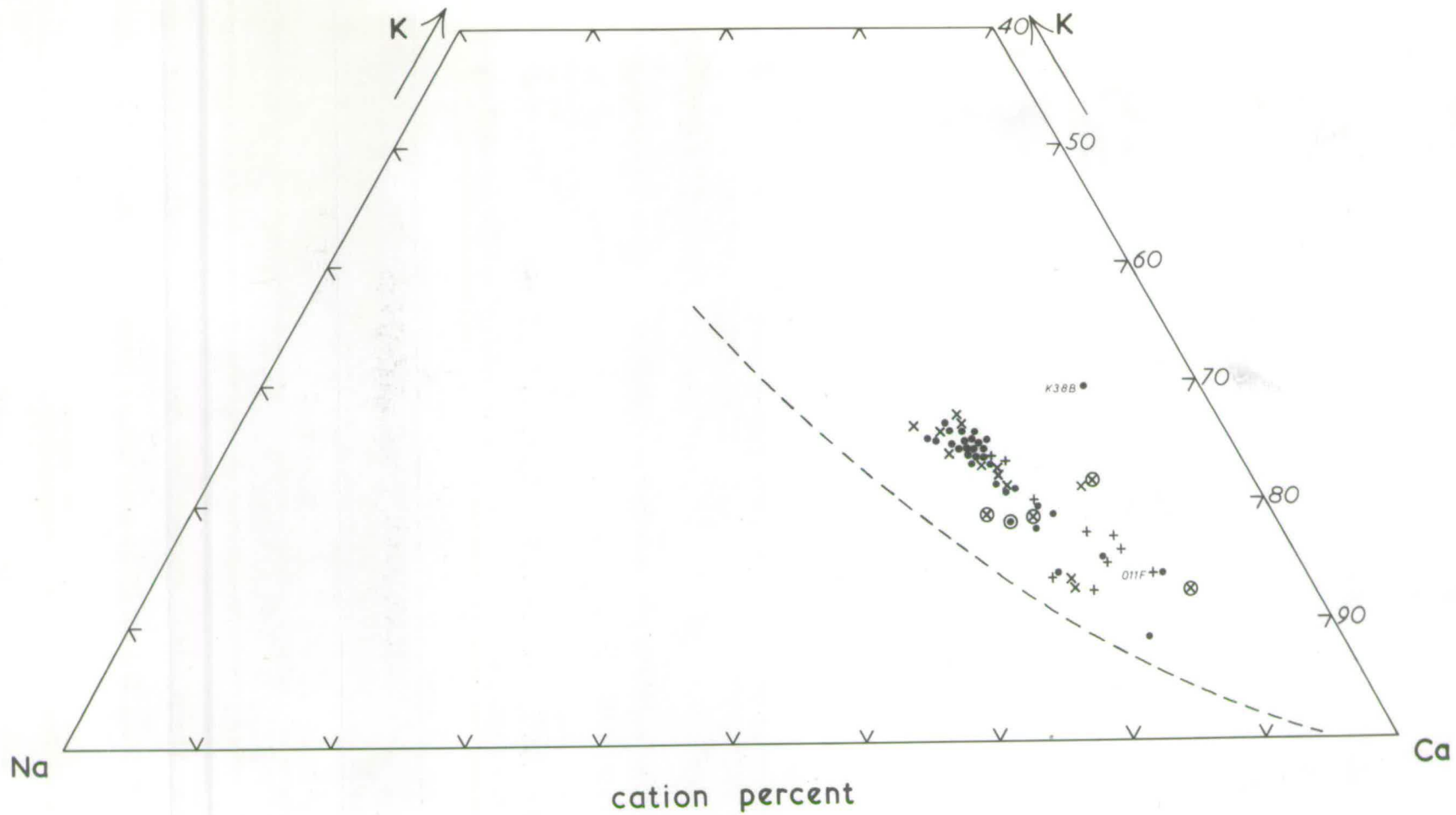


Figure 9

marginal position of picrites (e.g. K38B) within the kentallenite intrusions (Appendix A).^{**}

Kentallenites tend to have higher K_2O contents than the Brae suite (Fig. 9; K-Ca-Na plot), which is reflected in the abundance of biotite and orthoclase in kentallenite relative to the Shetland rocks. Rare kentallenite aplites, composed of micropertthite and biotite (Appendix B), are present at Kentallen and Glen Orchy, and indicate that the late stage residual liquids from kentallenite crystallisation are highly alkaline; chemical analysis^{***} gives 6.15% Na_2O , 6.74% K_2O . The divergence of picrite K38B from the kentallenite trend (Fig. 9) can be attributed to late-stage biotite crystallisation as alteration of olivine in the water rich marginal area of the intrusion (cf. Kennedy, 1955; see Appendices A and B).

Figs. 10, 11 and 12 illustrate the close chemical relationship between kentallenites and the Scottish Caledonian calc-alkali suite, and emphasise the connections suggested by other workers (e.g. Bailey, 1958). Nockolds and Mitchell (1948) have suggested that rocks with less than 25% Silicon (Fig. 12) in the Scottish suite are the result of crystal sorting or accumulation, and since all the analysed kentallenites contain less than 25% Silicon (Fig. 11), such a process may have operated in their development. The data plotted in Fig. 13 support this possibility; olivine control lines (Powers, 1955; also Murata and Richter, 1966) indicate that settling of

^{**} Alternatively the chills could represent the supernatant magma from which an olivine-pyroxene mush had accumulated at depth, and might have acted as a lubricant for the intrusion of these accumulates (+ interstitial liquid) as kentallenite.

^{***} Analyst; D. Strong, Edinburgh.

FIGURE 10

- a) AFM diagram)
b) K-Na-Ca diagram) (cation percent)

(After Nockolds and Allen, 1953)

The curve in each of these diagrams represents the Scottish Caledonian calc-alkaline trend, the area bounded by dashed lines the position of kentallenites.

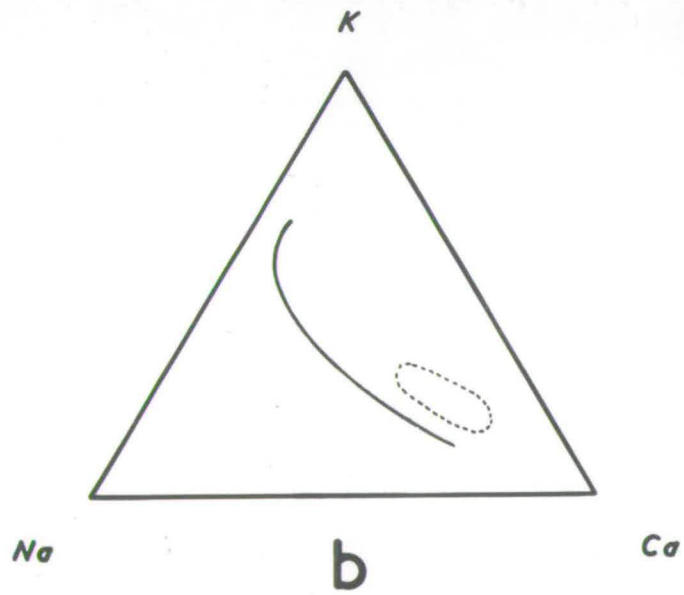
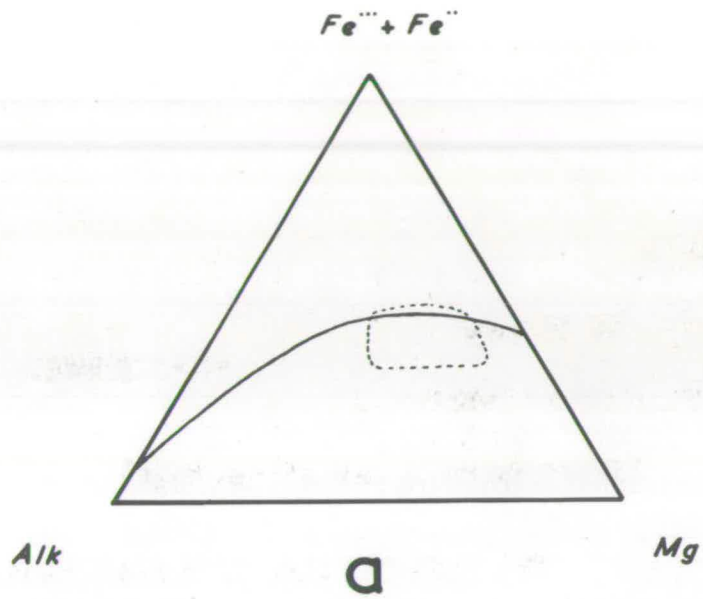


Figure 10

FIGURE 11

Variation diagram of kentallenites versus % Silicon
(cation percent)

Legend: as Figure 8

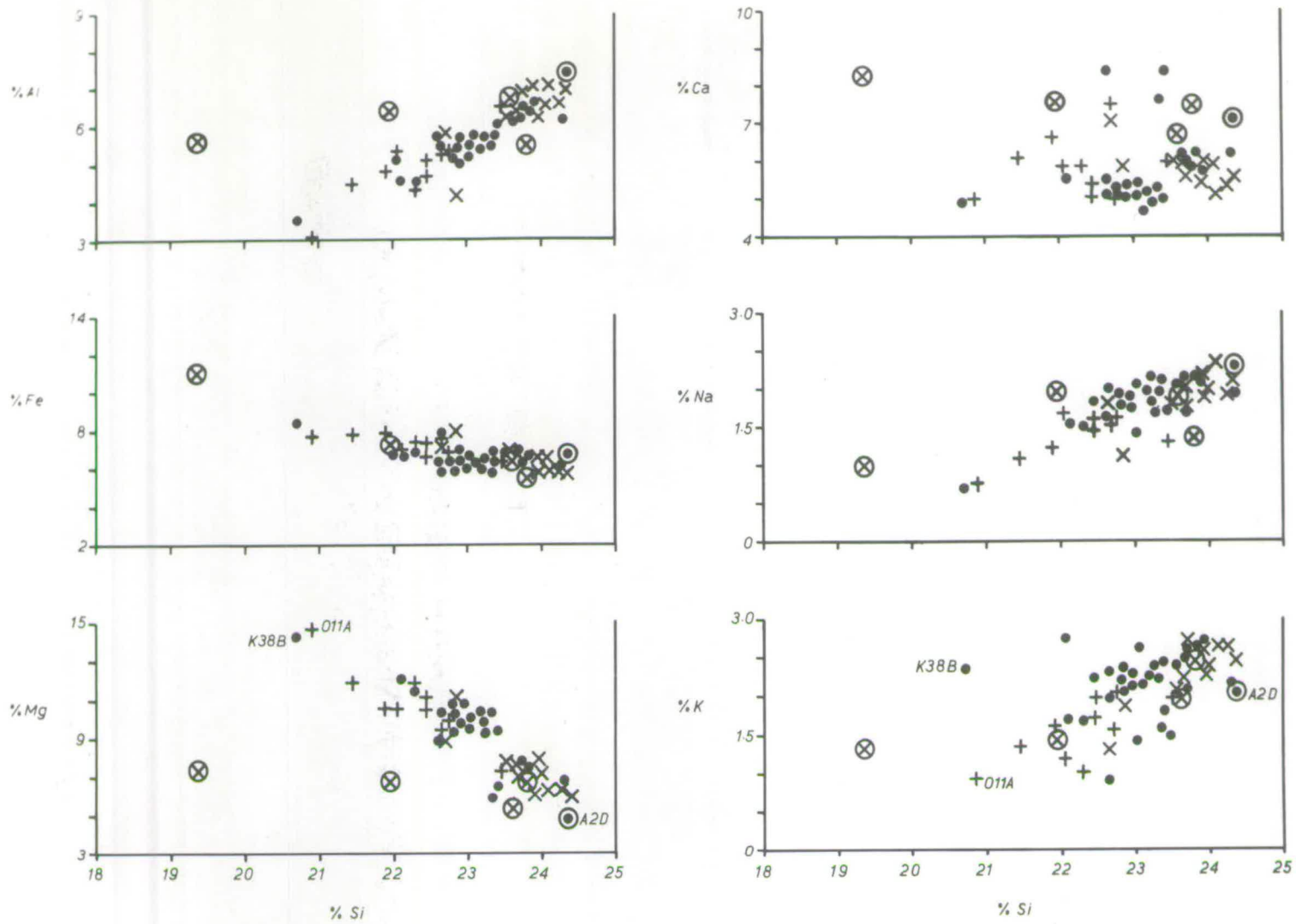


Figure II

FIGURE 12

Variation diagram of the Scottish calc-alkali suite versus

% Silicon

(cation percent)

The curves for each element (after Nockolds and Mitchell, 1948) represent the trends of variation shown by the entire Scottish calc-alkali suite, the areas bounded by dashed lines the limits of kentallenite variation.

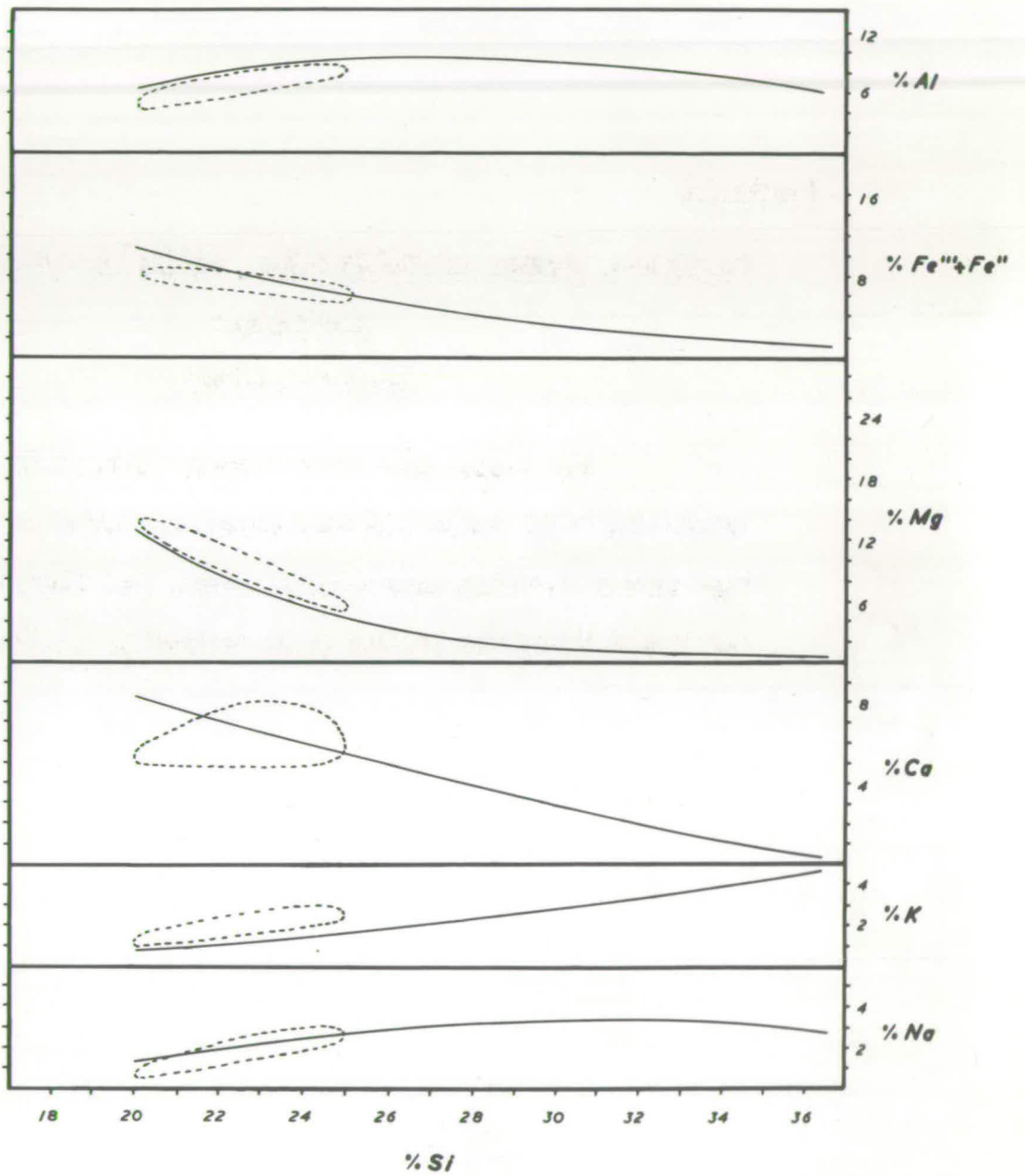


Figure 12

olivine may have caused some of the observed kentallenite variation.

Figs. 11 and 13 also support the conclusions of Nockolds (1941), Nockolds and Mitchell (1948) and Gill (1965) that calc-alkaline rocks tend to fall in the same relative positions in diagrams plotted using different indices of variation; e.g. K38B and O11F (picrites) fall at the basic end of the range of variation in both of these figures and A2D (chill) at the acid end, and the Colonsay and Glen Orchy rocks maintain their virtual isolation into two groups.

Minor Elements.

Compared with the values obtained by Nockolds and Mitchell (1948) on basic rocks from the Scottish Caledonian calc-alkali suite, kentallenites have higher nickel, chromium, strontium and barium contents, and rather lower rubidium (Table 10); the basic rocks from Brae (Gill, 1965) have less nickel, strontium and barium than kentallenites, but are otherwise comparable. These features are explicable in terms of the trace element concentrations of the minerals (Chapter 2), high nickel being related to olivine and biotite, high chromium to pyroxene, high strontium to both feldspars and high barium to biotite and orthoclase. However although barium is high in kentallenite, rubidium, also contained in biotite and orthoclase, is low, which suggests a low rubidium content in the parent magma (cf. Brae complex; Gill, 1965). The high strontium and nickel contents of kentallenite reflect the peculiar mineral assemblage of the rock; high strontium, normally concentrated in plagioclase and orthoclase (Nockolds and Mitchell, 1948; Chapter 2) and thus tending to rise with differentiation at least until the middle stages, is associated with high nickel, which is concentrated in olivine (and its biotite reaction product) and falls with differentiation. This suggests either that the kentallenite parent magma was unusually rich in strontium or that kentallenite may be the

TABLE 10

	Bras complex Gill, 1965	Kentallenites	Scottish Caledonian Nockolds and Mitchell, 1948
Ni	100-800 p.p.m.	300-800 p.p.m.	200-500 p.p.m.
Rb	20-120 p.p.m.	10-80 p.p.m.	< 100 p.p.m.
Sr	40-400 p.p.m.	800-1000 p.p.m.	50-1200 p.p.m.
Zr	5-160 p.p.m.	60-80 p.p.m.	< 100 p.p.m.
Ba	45-450 p.p.m.	600-1000 p.p.m.	< 200 p.p.m.
Cr	500-1600 p.p.m.	600-1200 p.p.m.	< 500 p.p.m.

FIGURE 13

Variation diagram of kentallenites versus % MgO
(weight percent)

Legend: as Figure 8, with the following addition;

0 - average kentallenite olivine.

Dashed lines are olivine control lines (cf. Powers, 1955).

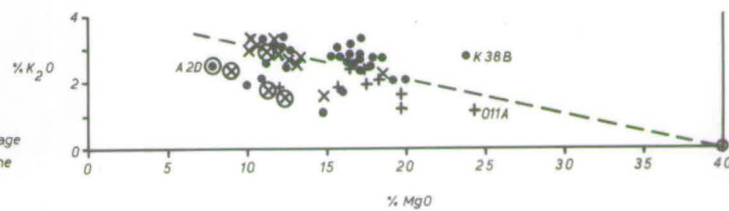
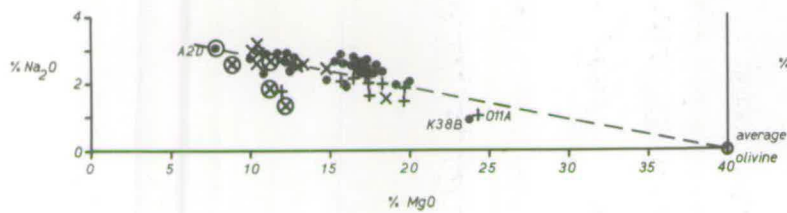
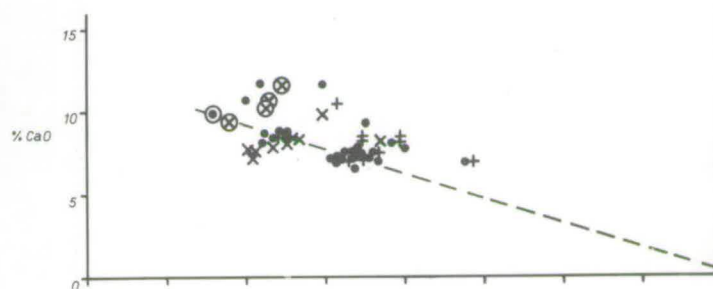
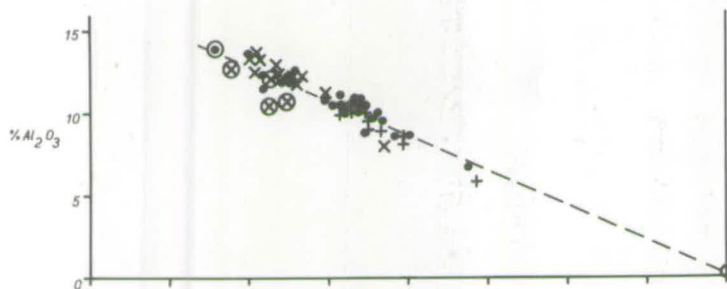
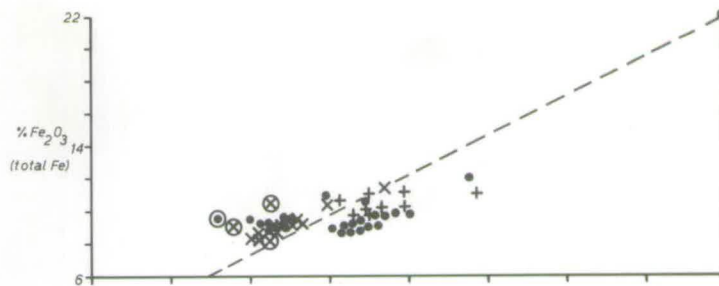
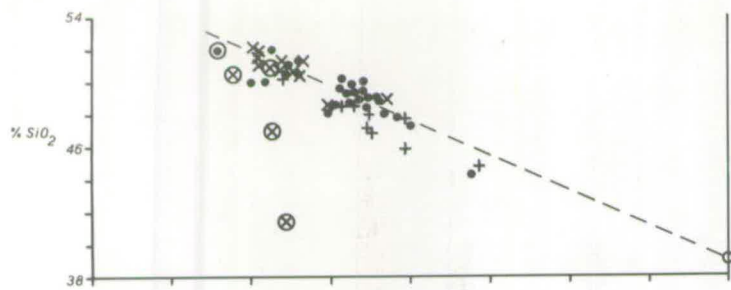


Figure 13

product of accumulation of olivine in a moderately 'evolved' magma. The latter alternative is consistent with the evidence from olivine control lines (Fig. 13), but mineralogical data (Chapter 2; Augite) suggests that the parent may have been strontium-rich.

Normative data.

The normative feldspar diagram (Fig. 14) shows the potassium-rich nature of kentallenite (see Fig. 9) with respect to rocks from the Brae complex. The Brae rocks which compare most closely in total alkali content with kentallenites are hypersthene diorites, more acidic than kentallenites. The highly potassic composition of K38B (Fig. 9) is also evident in Fig. 14.

With the exception of orthoclase the normative components of kentallenites are those of basalt, i.e. some members of a group including olivine, hypersthene, diopside, plagioclase, and nepheline, and representation of kentallenites in the simple basalt normative tetrahedron Quartz-Olivine-Diopside-Nepheline (e.g. Yoder and Tilley, 1962) will introduce little distortion and will permit relation of them to the important normative planes and joins of the basalt system, aiding in their interpretation. Weight percent projections from various normative minerals into planes within, or bounding, the tetrahedron are therefore used to examine the significant features of the chemistry of kentallenites.

Fig. 15, a projection from normative diopside into the planes olivine-plagioclase-nepheline and olivine-plagioclase-quartz (the diopside projections), shows that the major trend of kentallenite composition extends from olivine towards plagioclase along the join olivine-plagioclase-(diopside), the most basic rocks (K38B and O11F) lying towards the olivine end of the join (cf.

FIGURE 14

Normative feldspar diagram

(weight percent)

Legend: as Figure 8, including dashed line for Brae trend.

Abbreviations:

Or = Orthoclase

Ab = Albite

An = Anorthite.

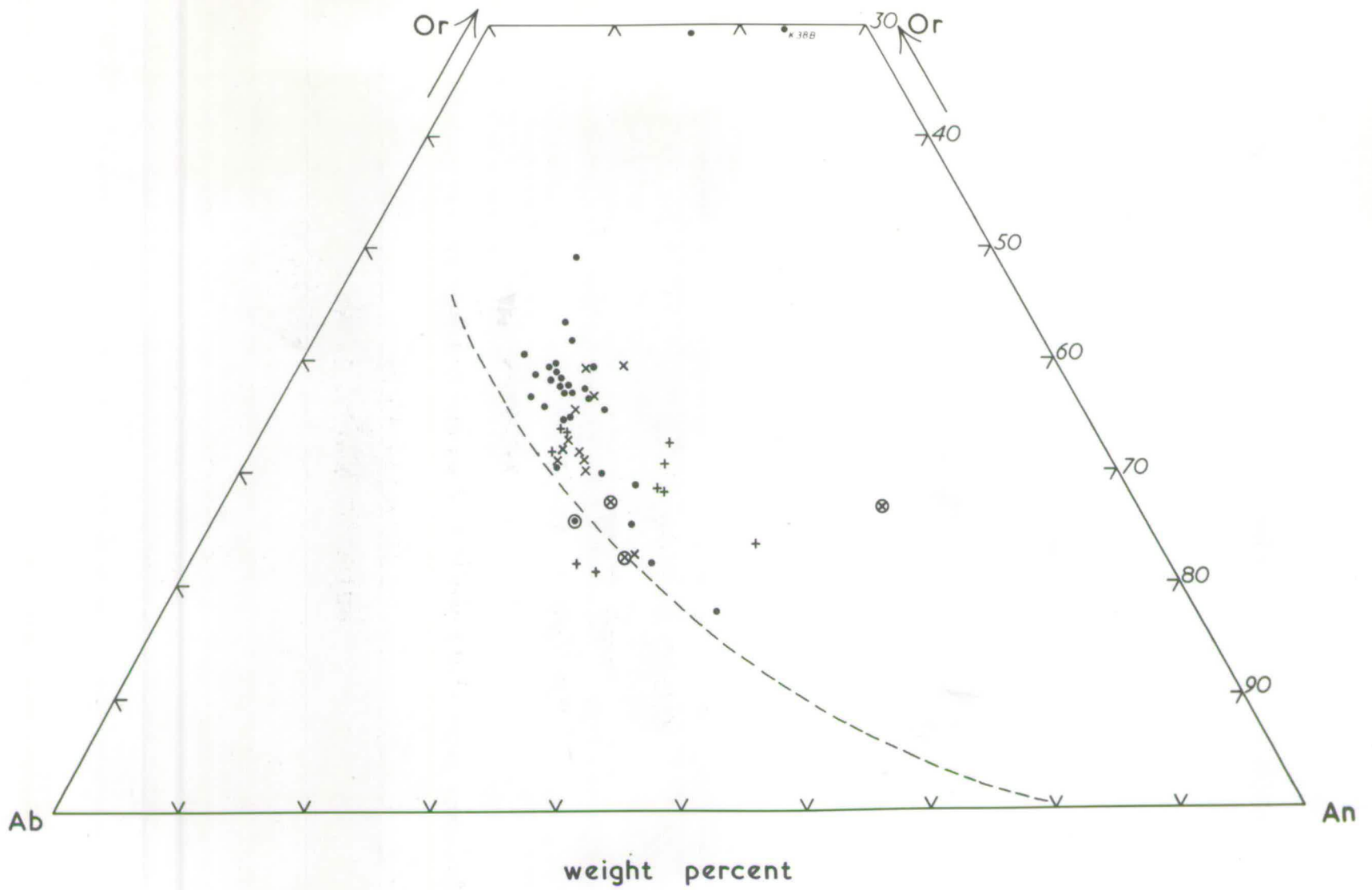


Figure 14

FIGURE 15

Normative Diopside projection

(weight percent)

Legend: as Figure 8.

Abbreviations:

Qz = Quartz

Plag = Plagioclase

Ne = Nepheline

Ol = Olivine.

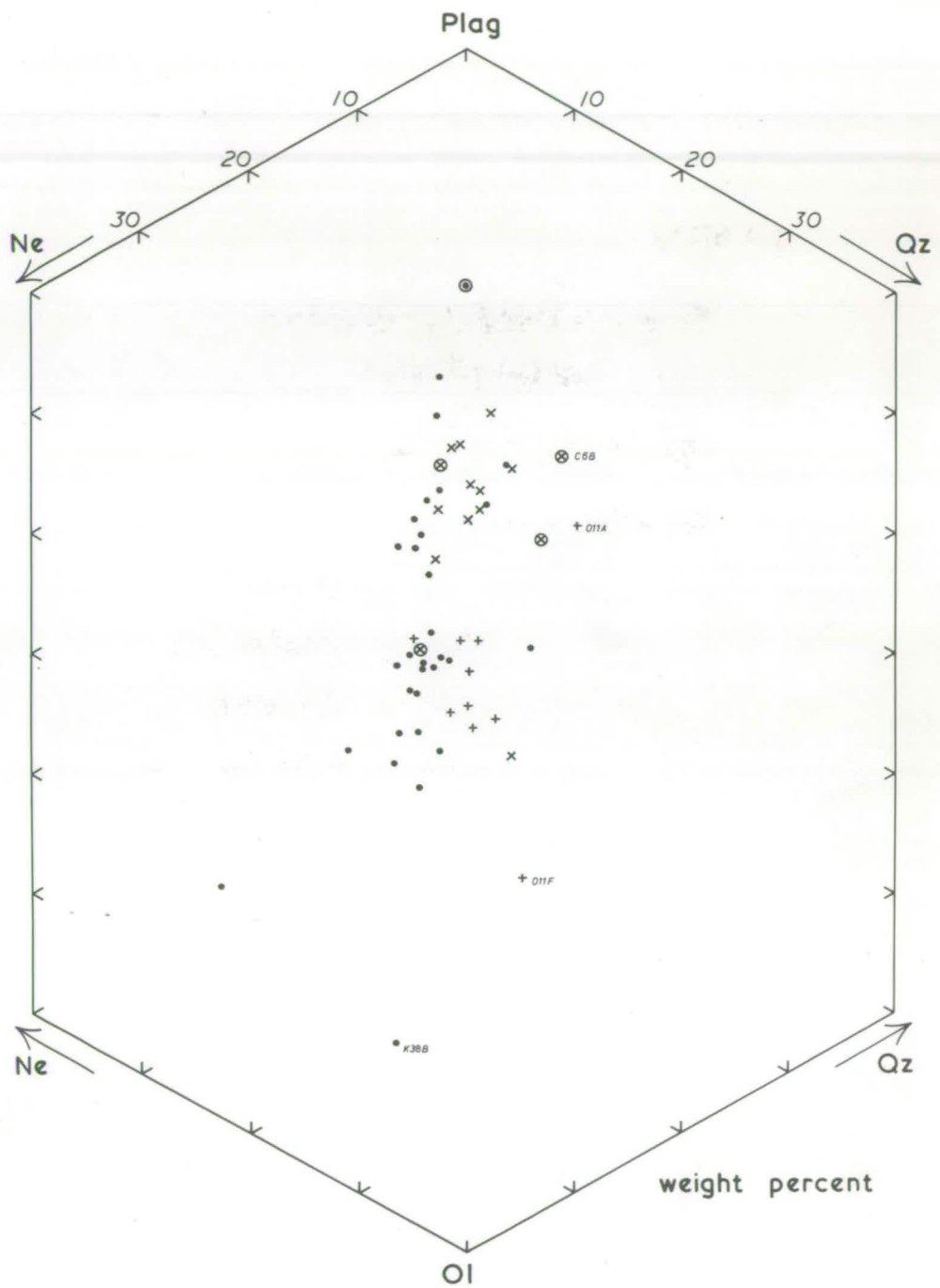


Figure 15

Fig. 13). Scatter of the kentallenite composition points across this join towards or away from quartz, however, is also apparent in Fig. 15, a feature emphasised by the olivine and plagioclase projections (Figs. 16 and 17 respectively), and in all of these projections the same two rocks (O11A and C6B) plot closest to the quartz apex.

They are also the most 'evolved' rocks of the data group, O11A occurring at the 'top' of the main Glen Orchy mass and C6B as a chill phase in the more hornblende-rich Scalasaig mass in Colonsay (Appendices A and B).

At least two evolutionary 'trends' therefore appear to be involved in the development of kentallenites. The major trend, evident in Figs. 11, 13 and 15 may be produced by olivine accumulation (giving rise to rocks such as A2D), but plotting of the data in Figs. 16 and 17 "removes" the influence of olivine and reveals a cross-trend to the olivine control which appears to result in enrichment in silica (leading to rocks such as O11A). The silica-enrichment trend of the Brae rocks (Gill, 1965) is also indicated on Fig. 17, and is of similar character to the kentallenite trend; it does not, however, overlap the diopside-plagioclase-olivine join.

Fig. 18 is a projection from the quartz and nepheline apices into the diopside-plagioclase-olivine join. Although some distortion is present in this projection, it also suggests the existence of two developmental processes, since although the kentallenite data tend to separate into two groups which may be related by a mechanism of differential olivine settling, evolution within the groups appears to be transverse to the olivine control lines (and approximately parallel to the Brae trend, included for comparison). For example, development within the more olivine-rich group is towards O11A, which has already been shown (Figs. 15, 16 and 17) to be one of the most acid analysed rocks. However, there is field evidence at Glen Orchy and Colonsay

FIGURE 16

Normative Olivine projection

(weight percent)

Legend: as Figure 8.

Abbreviations:

Qz = Quartz

Plag = Plagioclase

Ne = Nepheline

Di = Diopside

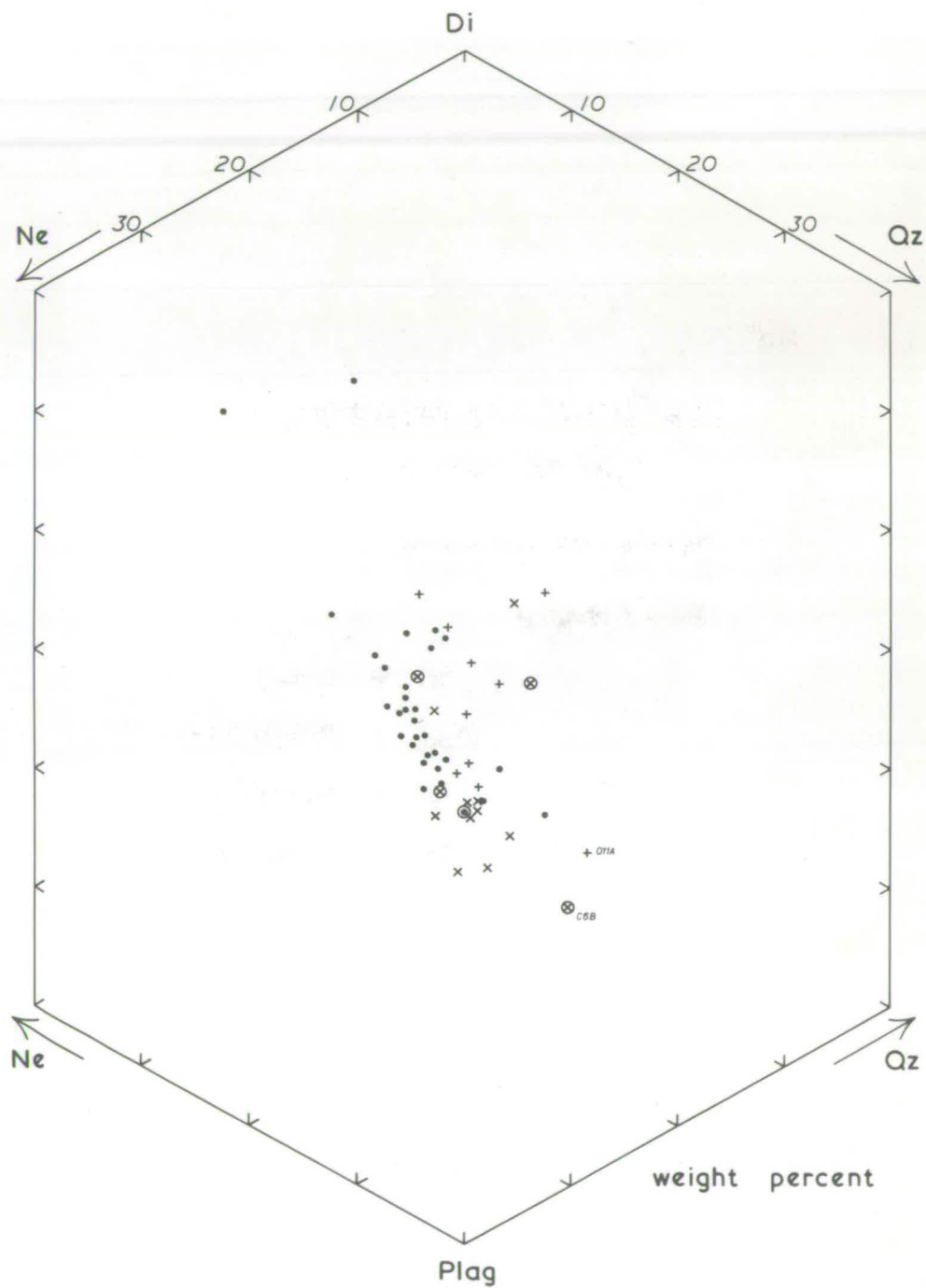


Figure 16

FIGURE 17

Normative Plagioclase projection

(weight percent)

Legend: as Figure 8, including dashed line for Brae trend.

Abbreviations: as Figures 15 and 16.

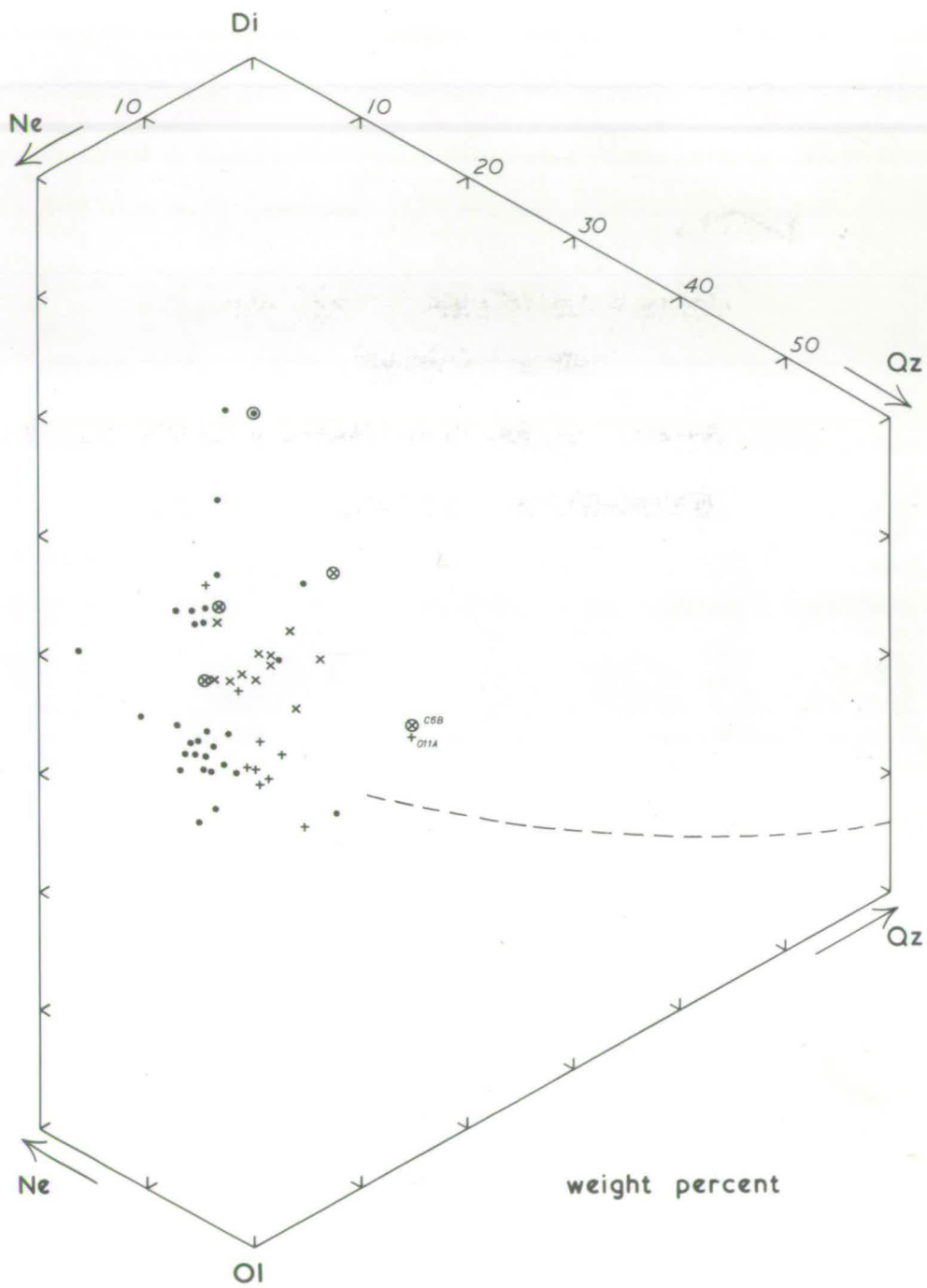


Figure 17

FIGURE 18

Normative Quartz and Nepheline projections

(weight percent)

Legend: as Figure 8, including dashed line for Brae trend.

Abbreviations: as Figures 15 and 16.

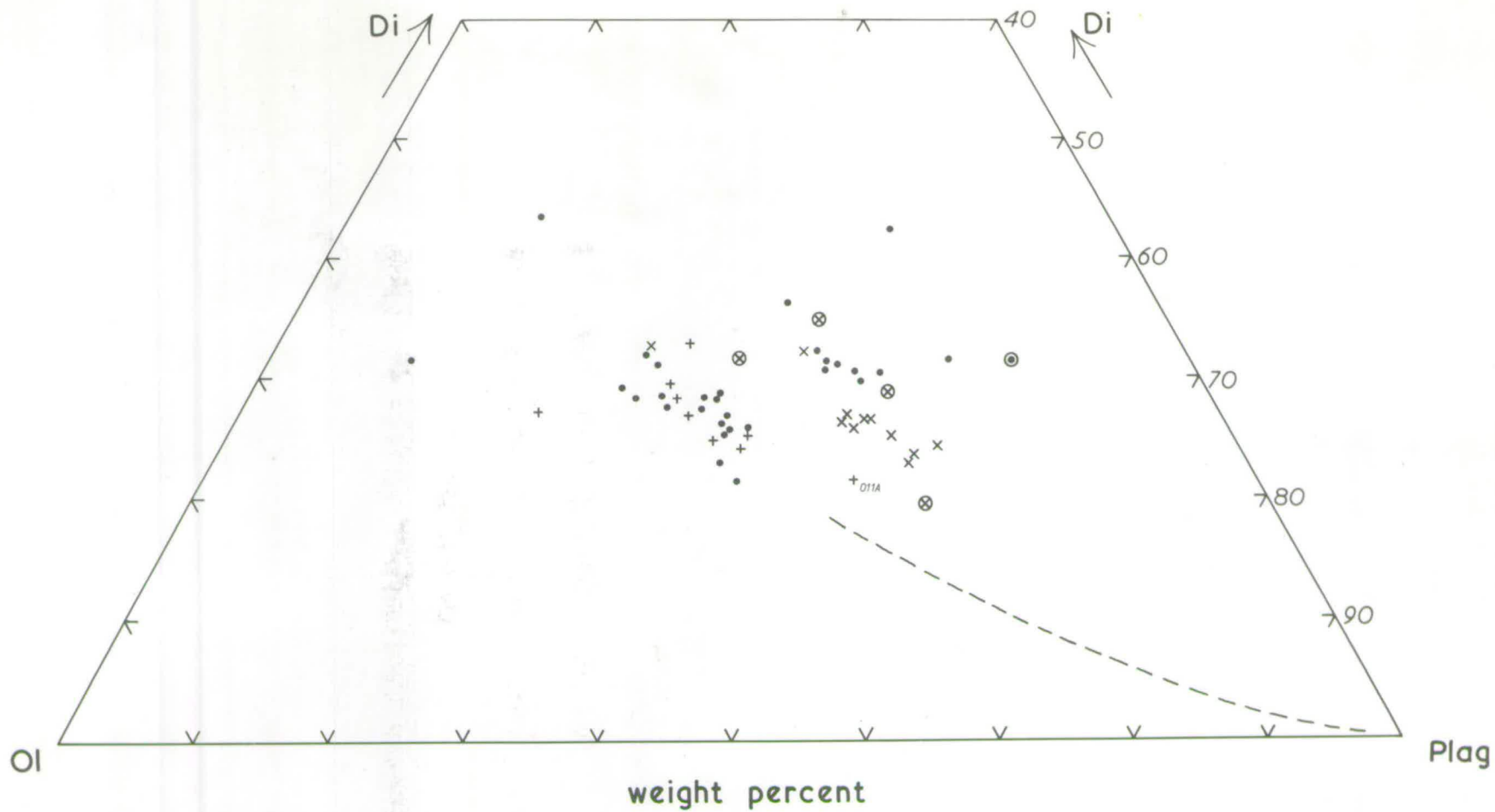


Figure 18

of some high-level fractionation of olivine and clinopyroxene (Appendix A), and while the scatter of kentallenite compositions across the diopside-plagioclase-olivine join (Figs. 16 and 17) cannot be the result of fractionation of two of the minerals which lie within that join, fractionation of olivine and clinopyroxene could produce trends such as those shown in Fig. 18. This third trend in kentallenite compositions is not apparent in the field at Kentallen, but has probably been effective to some degree during high-level crystallisation in all the intrusions examined.

The cross-trend in Figs. 15-17 penetrates the diopside-plagioclase-olivine join, which is close to the critical plane of silica under-saturation (Yoder and Tilley, 1962) in the normative basalt tetrahedron. This plane is an "equilibrium thermal divide" (Yoder and Tilley, 1962, pp.398-401), across which basaltic liquids cannot normally evolve during crystallisation, and an explanation must, therefore, be found for this behaviour of kentallenites. Some process other than olivine crystallisation must have operated during the development of kentallenite, since olivine lies in the plane across which the compositions scatter and cannot be the cause of such scatter.

Summary.

AFM and K-Na-Ca diagrams indicate a close chemical association between kentallenite and the Scottish Caledonian calc-alkali suite. Variation diagrams and trace element contents suggest that accumulation of olivine has exerted some control on the development of kentallenite from its parent magma. Projections of normative data, however, show that olivine, or olivine plus clinopyroxene, accumulation cannot explain all of the observed variation. The kentallenite compositions straddle the "equilibrium thermal divide" in the simple basalt normative tetrahedron, and some process other than separation of olivine is required to cause this scatter.

Introduction

The plane Diopside-Olivine-Plagioclase in the simplified basalt normative tetrahedron divides compositions showing nepheline in the norm from those showing hypersthene. The critical plane of silica undersaturation in the simple basalt system, which lies close to the Diopside-Olivine-Plagioclase plane, separates compositions whose residual liquids trend towards nepheline-bearing end products from those whose residual liquids trend towards silica-bearing end products; it is an "equilibrium thermal divide" (Yoder and Tilley, 1962).

Kentallenites show variation from 10.3% nepheline to 25.0% hypersthene in the norm (Appendix C), and thus straddle the plane Diopside-Olivine-Plagioclase in the simple basalt system. The range of this variation seems too great (Appendix C) to be explained by analytical error, and suggests that the "equilibrium thermal divide" is inoperative at some stage of kentallenite development. It is the purpose of this chapter to examine the experimental basis for the divide, the conditions of its stability, and the means available for breaching it at both low and high pressures.

Thermal divide at 1 atm. pressure.

For the divide to be effective, the stable assemblage in a crystallising liquid whose composition falls close to the divide must be diopside + olivine + plagioclase. The residual liquid from fractional or equilibrium crystallisation of this assemblage will then tend to move away from the divide, either towards nepheline- or hypersthene-normative compositions.

The positioning of the divide in a system is complicated by

solid solution in, and fractionation of the minerals of the divide assemblage. For example, in the system Forsterite-Diopside-Silica solid solution (ss) of forsterite and enstatite in diopside and of monticellite (or larnite at high pressure; Kushiro, 1964) in forsterite, and the presence of a thermal maximum in the boundary curve forsterite_{ss} + diopside_{ss} + liquid (contrast Schairer and Yoder, 1962) require positioning of the thermal divide athwart the join Forsterite-Diopside (Kushiro and Schairer, 1963), and some liquids containing normative hypersthene may give rise to nepheline-normative derivative residual liquids, and vice versa, even in equilibrium crystallisation. However, in this system the thermal maximum exists only on the curve forsterite_{ss} + diopside_{ss} + liquid, and will be an effective barrier only to liquids crystallising both forsterite_{ss} and diopside_{ss}. It will not control the development of a liquid close to the divide crystallising either forsterite_{ss} or diopside_{ss} alone, and the divide cannot be extended across the primary phase volumes of forsterite_{ss} or diopside_{ss} without knowledge of the fractionation and equilibrium crystallisation behaviour of the individual minerals, as shown by the following discussion.

The residual liquid derived from a liquid of initial composition X' (Fig. 19a) which crystallises forsterite_{ss} alone will, as a result of changing forsterite_{ss} composition during crystallisation, approach the forsterite_{ss} + diopside_{ss} + liquid curve along a path whose degree of curvature will depend upon the type of crystallisation taking place. If forsterite_{ss} remains in equilibrium and reacts with the liquid during crystallisation, the residual liquid composition will describe a path such as E_{X'}, and meet the forsterite_{ss} + diopside_{ss} + liquid curve to the right of the thermal maximum T, when diopside_{ss} will appear as second phase and the liquid will move down temperature towards A, crystallising both forsterite_{ss} + diopside_{ss}. If, on the other hand, forsterite_{ss} is removed from, and does not react with the liquid as it

FIGURE 19

Development of a thermal divide "zone"

For explanation, see pages 28-29.

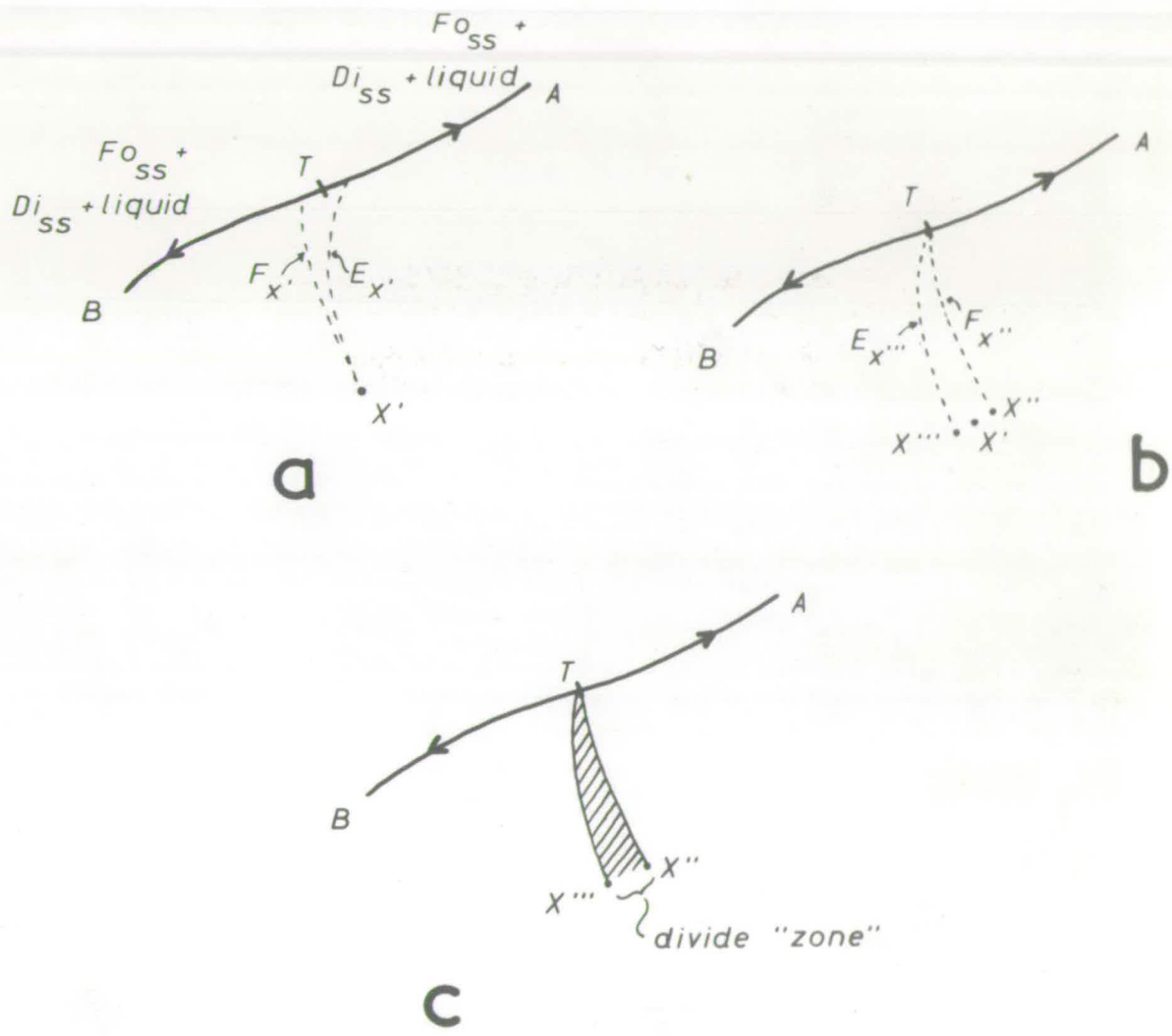


Figure 19

crystallises, the residual liquid will follow a path such as F_X , towards the forsterite_{ss} + diopside_{ss} + liquid curve, meeting that curve to the left of the thermal maximum T, and will proceed down temperature towards B, crystallising both forsterite_{ss} + diopside_{ss}. There will be a range of liquid compositions close to X' which may give rise to residual liquids which can attain the forsterite_{ss} + diopside_{ss} + liquid curve on either side of T, dependent on degree of fractionation, and this range of compositions will be restricted at one extreme by liquids such as X'', which cannot cross the divide by fractionation of forsterite_{ss} (curve $F_{X''}$, Fig. 19b), and at the other extreme by liquids such as X''', which are committed to the B-rich side of the divide under all conditions of crystallisation (curve $E_{X'''}$, Fig. 19b). The effective divide forsterite_{ss} + diopside_{ss} in the system Forsterite-Diopside-Silica will therefore be broadened into a "zone" (Fig. 19c) as it crosses the primary phase volumes of forsterite or diopside, the limits of which can be defined only by detailed experimental work.

The thermal divide plane forsterite_{ss} + diopside_{ss} + plagioclase_{ss} in the simple basalt system is also broadened into a zone as a result of possible fractionation of, for example, forsterite_{ss} + diopside_{ss} from a liquid whose composition lies close to the divide (O'Hara and Schairer, 1963, and unpublished), but the position of the divide zone is potentially more variable than in the system Forsterite-Diopside-Silica because of the more extensive mutual solid solution possibilities of minerals in the simple basalt system. Solid solution of enstatite (Boyd and Schairer, 1957, 1962, 1964) in diopside crystallising from a liquid close to the divide may result in production either of silica-undersaturated (O'Hara and Schairer, 1963) or silica-saturated (Schairer and Kushiro, 1964) end products, dependent upon initial liquid composition, and alumina substitution (either as Al_2O_3 or Ca-Tschermak's molecule) in crystallising

diopside may result in silica-enriched residua (Hytonen and Schairer, 1961; O'Hara and Schairer, 1963). Solid solution of 'iron albite' in plagioclase in iron-bearing systems may give rise to development of silica-undersaturated liquids from slightly silica-oversaturated liquids (Bailey and Schairer, 1964), but the mechanism can operate only in acid, oxidised systems and is thus not applicable to basalt development.

It should be emphasised that these mechanisms for breaching the divide and creating a divide zone are effective only in bulk compositions which initially lie close to the divide. Bulk compositions in the greater part of the simple basalt system are committed either to the silica-rich or silica-poor side of the divide, and residual liquids from their crystallisation cannot penetrate the divide at low pressures by the operation of processes involving solid solution in and fractionation of minerals in the divide plane. Although it is not possible to define the width of the divide zone in basalt compositions, kentallenites show a spread in normative composition (Appendix C) sufficient to overlap the range shown by a selection of tholeiitic and alkali basalts (Yoder and Tilley, 1962, Table 2). These basalts are associated with rock series which trend towards quartz-rich and nepheline-rich end points respectively, and must fall on opposite sides of the divide zone. It therefore seems likely that kentallenite compositions straddle the low pressure divide zone.

Fractionation of spinel from a liquid will enrich the liquid in silica, but bulk compositions from which it may be expected to crystallise are restricted in range at 1 atm. (Andersen, 1915; Osborn and Tait, 1952; Schairer and Yoder, 1960, 1961; Kushiro and Yoder, 1966), and the mechanism is unlikely to operate in normal basaltic liquids. Oxidation of a liquid during crystallisation (Kennedy, 1955; Osborn, 1959, 1962) may result in precipitation of magnetite, fractionation of which would lead to silica-enriched liquids. It

might be possible by this mechanism for a liquid on the nepheline-rich side of the divide to produce silica-saturated residua (Yoder and Tilley, 1962), but crystallisation of magnetite would have to occur early and in conjunction with other ferromagnesian phases. Otherwise the increased Mg/Fe ratio of the liquid would elevate the temperature of the divide above that of the liquid, and oxidation would lead to freezing without any liquid crossing the divide, although the final rock might be hypersthene- or quartz-normative. Some cases of hypersthene-normative rocks apparently derived from nepheline-normative liquids (Poldervaart, 1964) may be due to post-crystallisation oxidation (cf. Verhoogen, 1962; Watkins and Haggerty, 1967).

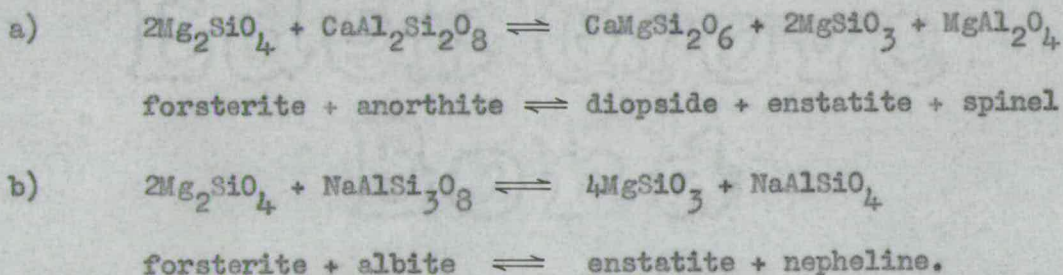
Thermal divide at elevated pressures.

a) In dry systems

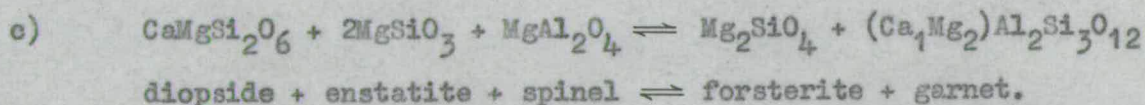
Movement of residual liquids across the position of the low pressure thermal divide is possible under conditions in which the divide no longer exists. Increase of pressure above 1 atm. causes contraction of the olivine primary phase volume in favour of that of orthopyroxene (Kushiro, 1964); enstatite melts congruently above ~ 2.3 kb (Boyd et al., 1964; Boyd and England, 1965), and crystallises from compositions in the divide plane at pressures in excess of ~ 9 kb (Yoder, 1964; Green and Ringwood, 1964; Kushiro, 1965'a'; O'Hara, 1965). At pressures around 9 kb fractionation of orthopyroxene from a silica-saturated liquid could give rise to silica-undersaturated residual liquids (cf. Holmes and Harwood, 1932; Powers, 1935), and solid solution of enstatite in diopside, which increases with pressure and temperature (Boyd and Schairer, 1962; Kushiro, 1964; O'Hara, 1963; Davis, 1963) would have a similar effect (Tilley and Yoder, 1964). Additionally, increase in solid solution of jadeite and Ca-Tschermak's molecule in diopside with pressure (Kushiro, 1965'c') will increase the range of silica-undersaturated compositions

from which fractionation of diopside could produce silica-saturated liquids, although solid solution of Ca-Tschermak's molecule in diopside decreases at very high pressure as a result of its uptake by garnet. The individual minerals of the low pressure thermal divide assemblage are still stable together at pressures around 9kb, but the divide is breached at these pressures as a result of incongruent melting of compositions in the divide to orthopyroxene (or sub-calcic augite) and liquid.

Higher pressures lead to breakdown of low pressure thermal divide minerals, forsterite + anorthite reacting to form 2 pyroxenes + spinel above ~9kb (Kushiro and Yoder, 1966) and forsterite + albite breaking down in favour of enstatite + nepheline at ~11kb (Kushiro, 1965'b' according to the following equations:



Residual liquids at these pressures (equivalent to the intermediate pressure regime of O'Hara, 1965) may evolve in either direction across the low pressure thermal divide. Further increase in pressure results in instability of the intermediate pressure assemblage 2 pyroxenes + spinel, which breaks down to forsterite + garnet, according to the equation:



The stable thermal divide in the system CMAS at ~30kb is the join orthopyroxene_{ss} + clinopyroxene_{ss} + garnet_{ss} (O'Hara, 1963; O'Hara and Yoder, 1963, 1967), and

since orthopyroxene and olivine are in reaction relationship with liquids at these high pressures, control of liquid evolution is effected by clinopyroxene_{ss} + garnet_{ss} (i.e. eclogite) fractionation (O'Hara and Yoder, 1963, 1967), which may cause residual liquids to penetrate the low pressure thermal divide. It is of interest to note that diopside_{ss} is important in the development of liquids at all pressures from that of their likely formation (~30kb, when it will be jadeite-rich) to lower, crustal pressures (when it is dominantly Ca-Tschermak's-rich; O'Hara and Schairer, 1963; Kushiro, 1965'c').

b) In wet systems

The principal hornblende end member compositions straddle the 1 atm. thermal and normative divides in the simple basalt system (Yoder and Tilley, 1962, Figs. 21-24); thus gain or removal of suitable hornblende may drive liquids either way through the low pressure thermal barrier. Sinking of early crystallising hornblende to the base of a magma chamber, and its resorption into the liquid, has been suggested as a means of deriving silica-undersaturated liquids from silica-oversaturated parents (Bowen, 1928), but the process requires crystallisation of a nepheline- or melilite-normative amphibole from a hypersthene-normative liquid. There is experimental evidence that amphibole may become the first silicate phase to crystallise from basaltic compositions at pressures slightly in excess of 10kb p_{H₂O} (Yoder and Tilley, 1962, Figs. 27-30 and p.453), but no data are available on the composition of such amphiboles and their effect on residual liquids cannot therefore be evaluated. Fractionation of amphibole of suitable composition from basaltic liquid may also cause derivative liquids to penetrate the low pressure thermal divide in either direction.

Crystallisation and resorption of biotite within a silica-saturated

magma could result in the production of leucite-bearing lavas (Bowen, 1928; Luth, 1967), and fractionation of biotite from a melt may have the reverse effect, producing silica-saturated liquids from silica-undersaturated parents (Luth, 1967).

Summary

A thermal divide exists close to the plane Diopside-Olivine-Plagioclase in the simple basalt normative tetrahedron at pressures between 1 atm. and approx. 9kb, but its precise position and effectiveness depend on the nature and composition of the crystallising phase assemblage. Mechanisms involving variable fractionation of, and solid solution in, the major phases of basalt are available for breaching the divide, but they can operate only in bulk compositions close to the divide, creating a divide zone. Compositions in most of the simple basalt tetrahedron cannot cross the divide zone at low pressures by any such fractionation or solid solution mechanism, but fractionation of spinel or magnetite from suitable silica-undersaturated liquids may give rise to silica-oversaturated residua. It is not possible to estimate the width of the divide zone at low pressures, but it seems likely that the scatter of kentalenite compositions overlaps it.

Increase in pressure leads to the development of new stable joins and minerals replacing the low pressure joins and minerals. Fractionation of orthopyroxene_{ss} and clinopyroxene_{ss} can carry liquids across the low pressure thermal divide towards silica-undersaturated and silica-saturated compositions respectively at pressures greater than ~9kb. Plagioclase no longer crystallises from liquids in the simple basalt system at high pressures. Spinel and garnet are the effective aluminous phases in liquid evolution, but only in certain bulk compositions and at certain pressures.

Since the major hornblende end-member compositions fall on either

side of the low pressure thermal divide, fractionation or resorption of amphibole in basaltic liquids may cause residual liquids to penetrate the divide zone in either direction, dependent upon the composition of the amphibole. A similar, but more restricted, effect will result from resorption or fractionation of biotite.

Mechanisms therefore exist at pressures greater than ~ 9 kb to control liquid evolution across the low pressure thermal divide either from nepheline-normative to hypersthene-normative compositions or vice versa. There is little mineralogical support in kentallenites for the operation of any of these mechanisms, but the probable scatter of kentallenite compositions across the low pressure divide zone suggests that one, or several, of them may have been effective at some stage in the development of kentallenite.

Introduction.

Several mechanisms are capable of causing scatter of rock compositions across the low pressure thermal divide "zone" in the simple basalt system (Chapter 4), but none is supported by mineralogical evidence in kentallenite. However, if any of these mechanisms has operated, some chemical evidence of it should be present, and kentallenite chemical data are examined by geometrical and statistical methods in this chapter in search of such evidence. Two methods of treatment of data have been employed, projection into a four-component system analogous to the synthetic system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (Tetrahedral projection) and Principal Component Analysis. Each method is discussed below.

Tetrahedral projection.

Three weight percent projections of data in the system $\text{K}_2\text{O-YO-R}_2\text{O}_3\text{-ZnO}_2$ (equivalent to C-M-A-S; Appendix C) are used in this section to demonstrate specific features of the chemistry of kentallenites. They are projections into the planes CA-M-S, CS-MS-A and $\text{C}_2\text{S}_3\text{-M}_2\text{S-AS}$, from or towards Diopside (CMS_2), Olivine (M_2S) and Enstatite (MS) respectively, and are considered in that order.

Diopside projection (Fig. 20).

This projection emphasises the strong olivine-controlled trend of kentallenite compositions established in Chapter 3, and shows the scatter of these compositions across the olivine-plagioclase-diopside thermal divide (cf. Fig. 15). As in the chemical variation diagrams and normative projections of Chapter 3, the picrites K38B and O11F lie at the basic end of the trend, the chill A2D at the acid end. Analysed olivines from Kentallen and Glen Orchy

FIGURE 20

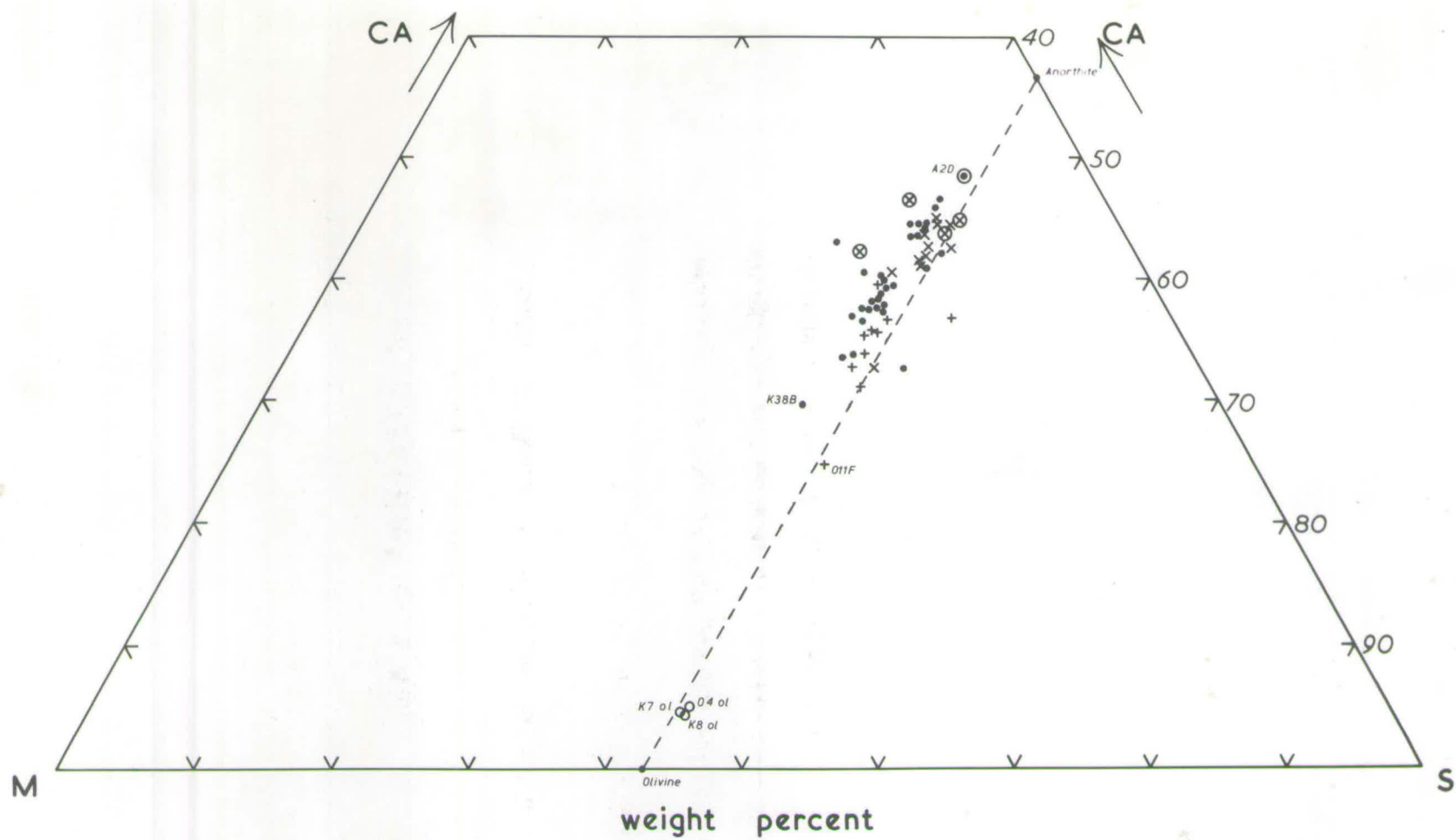
Diopside 'tetrahedral' projection

(weight percent)

Legend: as Figure 8, with the following addition;

O = kentallenite olivines.

'Olivine' and 'Anorthite' points are the composition points of the 'ideal' minerals. Dashed line is the trace of the normative divide Diopside-Olivine-Plagioclase.



are also plotted in Fig. 20.

The separation between Colonsay and Glen Orchy rock composition points in Fig. 20 (see also Fig. 8, Chapter 3) may result from crystallisation of different magma batches, but this is unlikely to explain the similar division of the Kentallen rocks. The most olivine-poor Kentallen rocks in Fig. 20 are generally from marginal facies, from which depletion in olivine and diopside by flowage differentiation during emplacement may have taken place, resulting in the formation of near-marginal picrites and phenocryst-poor 'chills' (after Smith and Kapp, 1963; see Chapter 3).

Olivine projection (Fig. 21).

Projection of data from the olivine composition point reveals a strong linear trend of kentallenite compositions across the low pressure thermal divide (cf. Figs. 16 and 17, Chapter 3). This must reflect some event in the developmental history of kentallenite, and is not the result of crystallisation of either of the phenocryst minerals of kentallenite (olivine and diopside; Appendix B) plotted in Fig. 21; nor can it be ascribed to fractionation of enstatite (possible from the geometry of Fig. 21) because O11A, the rock closest to the enstatite apex of Fig. 21, is considered to be the most "evolved" rock in the kentallenite series on geological grounds (Chapter 3). Since hydrous minerals such as biotite and hornblende may cause liquids to penetrate the low pressure thermal divide (Chapter 4), biotites from kentallenite and early hornblendes from Brae (Gill, 1965) and Garabal Hill (Nockolds, 1941) have been plotted on Fig. 21 to examine the potential effect of their separation or accumulation.

The pargasite from Brae is close to the composition required for its separation to cause the linear trend of kentallenite compositions across the divide, and this suggests that pargasite was a crystallising phase at some

FIGURE 21

Olivine 'tetrahedral' projection

(weight percent)

Legend: as Figure 8, with the following additions;

- O-K7, K8, O4Bi - kentallenite biotites
- O-Brae - Brae pargasite (from Gill,
1965)
- O-Garabal - Garabal Hill hornblende
(from Nockolds, 1941).

'Olivine-Plagioclase p.p.' is the piercing point of the 'ideal' olivine-plagioclase join in the plane CS-MS-A. The dashed line is the trace of the normative divide. 'Diopside' is the composition point of the 'ideal' mineral.

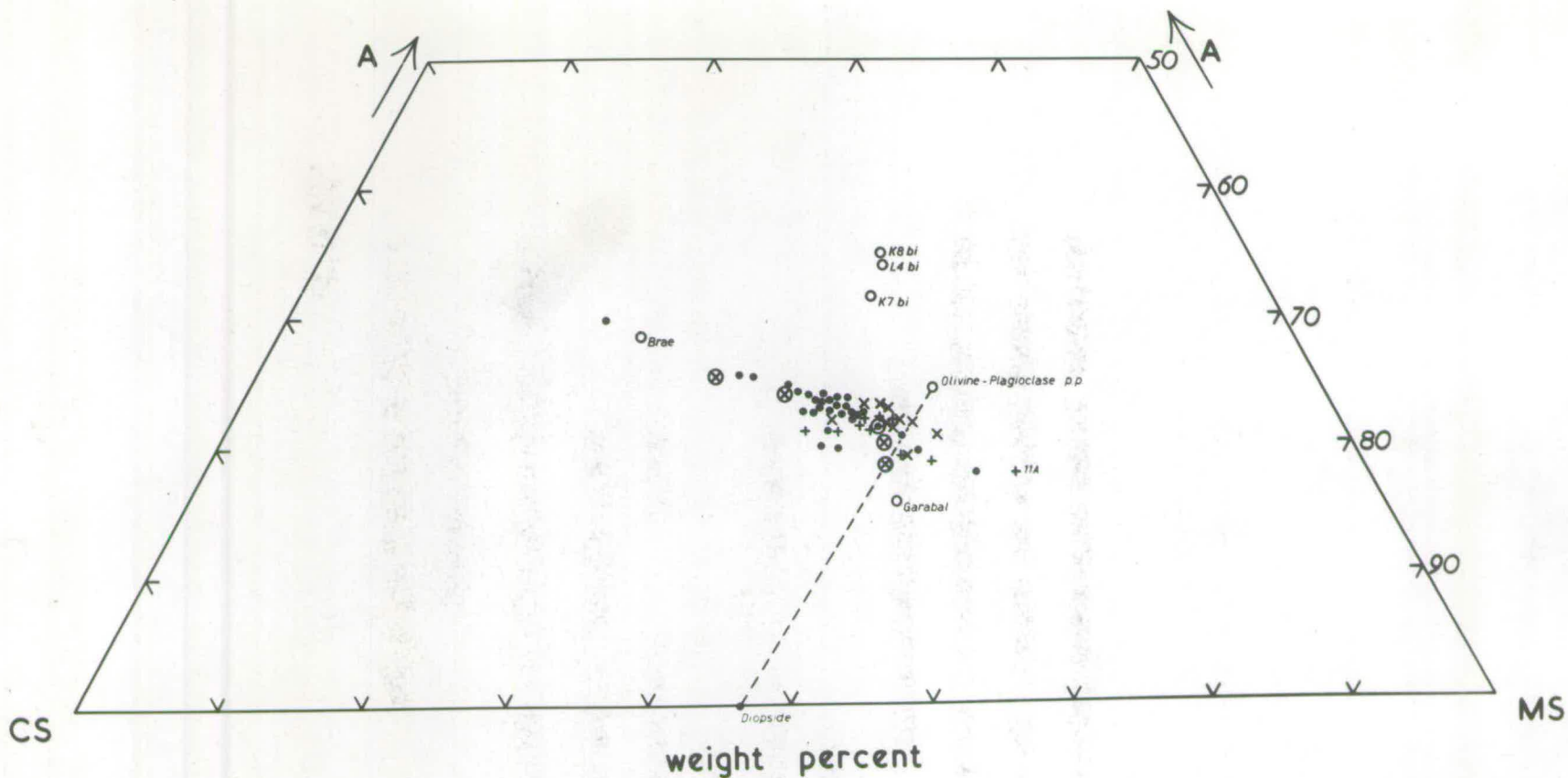


Figure 21

FIGURE 22

Enstatite 'tetrahedral' projection

(weight percent)

Legend: as Figure 8, with the following additions;

●-K7, K8, O4 - kentallenite olivines

0 - Brae pargasite (from Gill, 1965).

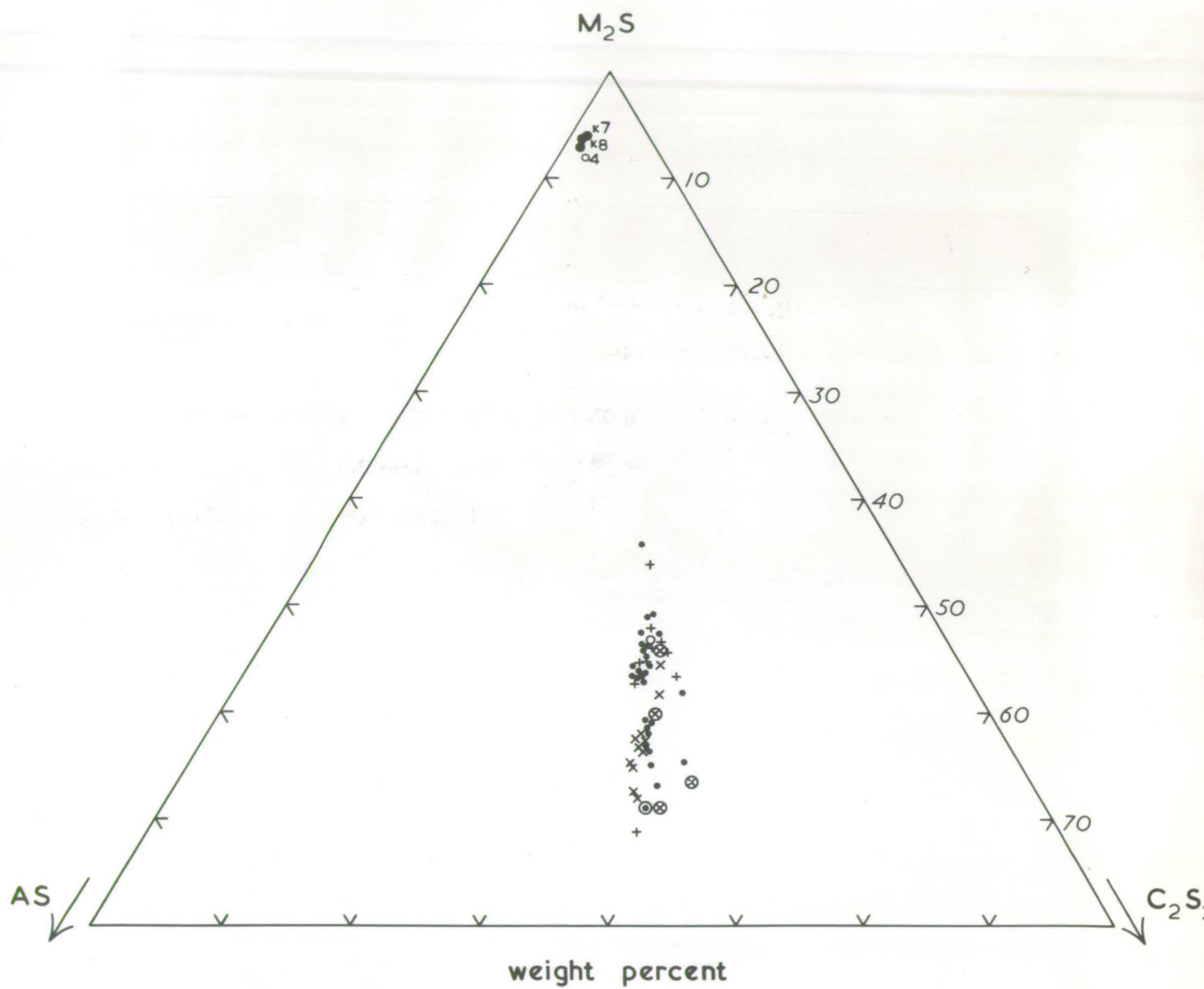


Figure 22

stage in the development of kentallenite from its parent magma. It is not present in the mineral assemblage of kentallenite, but there is some mineralogical support for its earlier existence in kentallenite magma, reviewed below (Chapter 6; Appendix B).

Enstatite projection (Fig. 22).

In the enstatite projection the olivine and hornblende trends are coincidentally superimposed, and the extremely linear trend in Fig. 22 shows that kentallenite, olivine and pargasite compositions are coplanar, and emphasises that the greater part of the variation in kentallenites could be explained by olivine and pargasite fractionation from the parent magma.

Principal Component Analysis.

Processing of data for tetrahedral projections involves some redistribution of oxide components for ease of calculation (Appendix C), and might give rise to some errors of interpretation. Principal component analysis, which can be treated as multidimensional projection, does not require such redistribution since computers can handle large volumes of data, and the kentallenite major element data (with the exception of P_2O_5 and MnO) were therefore entered in a principal component analysis computer program** to verify the trends suggested by tetrahedral projection.

The first three transformed axes of the analysis (i.e. the first three principal components of the data cloud in polydimensional space; see, e.g. Kendall, 1957), whose directions in polydimensional space are defined by eigenvectors (the direction cosines of transformed axes), account for a total variance of .802 (Table 11). This means that 80.2% of kentallenite

**

Program written by R.F. Cheeney, Edinburgh.

Table 11

VARIANCES AND EIGENVECTORS OF PRINCIPAL COMPONENTS

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O
0.449	-0.417	0.156	-0.366	0.325	0.258	0.364	-0.009	-0.427	-0.284	0.316
0.222	0.080	-0.519	-0.253	0.073	-0.446	0.381	-0.506	0.020	0.203	0.114
0.131	0.309	-0.365	-0.310	-0.257	-0.183	0.035	0.487	-0.118	-0.566	-0.050
0.072	0.123	0.074	0.200	-0.406	-0.064	-0.231	-0.206	-0.132	-0.120	0.802
0.060	-0.104	-0.119	-0.128	-0.686	0.524	0.196	-0.297	-0.090	0.032	-0.277
0.030	0.279	0.335	-0.431	-0.162	-0.170	-0.061	0.202	-0.451	0.567	-0.016
0.019	0.145	-0.543	0.331	0.257	0.312	-0.231	0.043	-0.570	0.174	-0.024
0.009	0.357	0.367	0.203	0.079	-0.195	0.044	-0.465	-0.378	-0.415	-0.346
0.007	-0.571	-0.023	0.395	-0.298	-0.485	0.155	0.210	-0.320	0.048	-0.145
0.001	0.382	0.103	0.395	-0.006	0.150	0.739	0.271	0.063	0.131	0.155

chemical variation can be represented in terms of these axes, i.e. in a three-dimensional space. It should be emphasised that the axes, which are mutually at right angles, are not necessarily geologically meaningful, as they are selected by the computer purely on statistical grounds.

The transformed variable of a chemical analysis of a rock or mineral is the projection of the analysis on one of the axes, and is equal to the scalar product of the analysis by the eigenvector for that axis. Any rock or mineral may be represented in terms of transformed variables by multiplication of its chemical analysis by the appropriate eigenvectors, and may thus be plotted in relation to the kentallenite analyses. The average Kentallen olivine and the Brae pargasite have been calculated and inserted in Figs. 23, 24 and 25.

Figs. 23 and 24, the plots of transformed variables 1 and 2, and 1 and 3 respectively, illustrate a precisely similar olivine-controlled trend of kentallenite variation to those discussed above (Figs. 20 and 22) and in Chapter 3 (Fig. 15). In Fig. 25 (Transformed variables 2 and 3), which is close to an olivine 'projection' (cf. Fig. 21), lines have been drawn to separate hypersthene- from nepheline-normative compositions in Glen Orchy, Scalasaig (Colonsay) and the olivine-poor section of Kentallen, the hypersthene-rich side of each line being remote from pargasite. These lines are all of similar "type", and suggest that crystallisation of pargasite from, or accumulation of pargasite into the parent magmas of each intrusion may have caused their evolution from nepheline- to hypersthene-normative compositions, or vice versa, across the thermal divide.

Separate principal component analyses were performed for each intrusion, in general merely confirming the features of the total kentallenite principal component analysis, but plots of transformed variables at Glen Orchy fortuitously show the effect of pargasite crystallisation. Figs. 26 and 27

FIGURE 23

Principal Component Analysis of kentallenites

1) Plot of transformed variables 1 and 2.

Legend: as Figure 8, with the following additions;

●--average olivine - average kentallenite olivine

O--Brae pargasite - Brae pargasite (from Gill, 1965)

Positive and negative ends of the axes are marked.

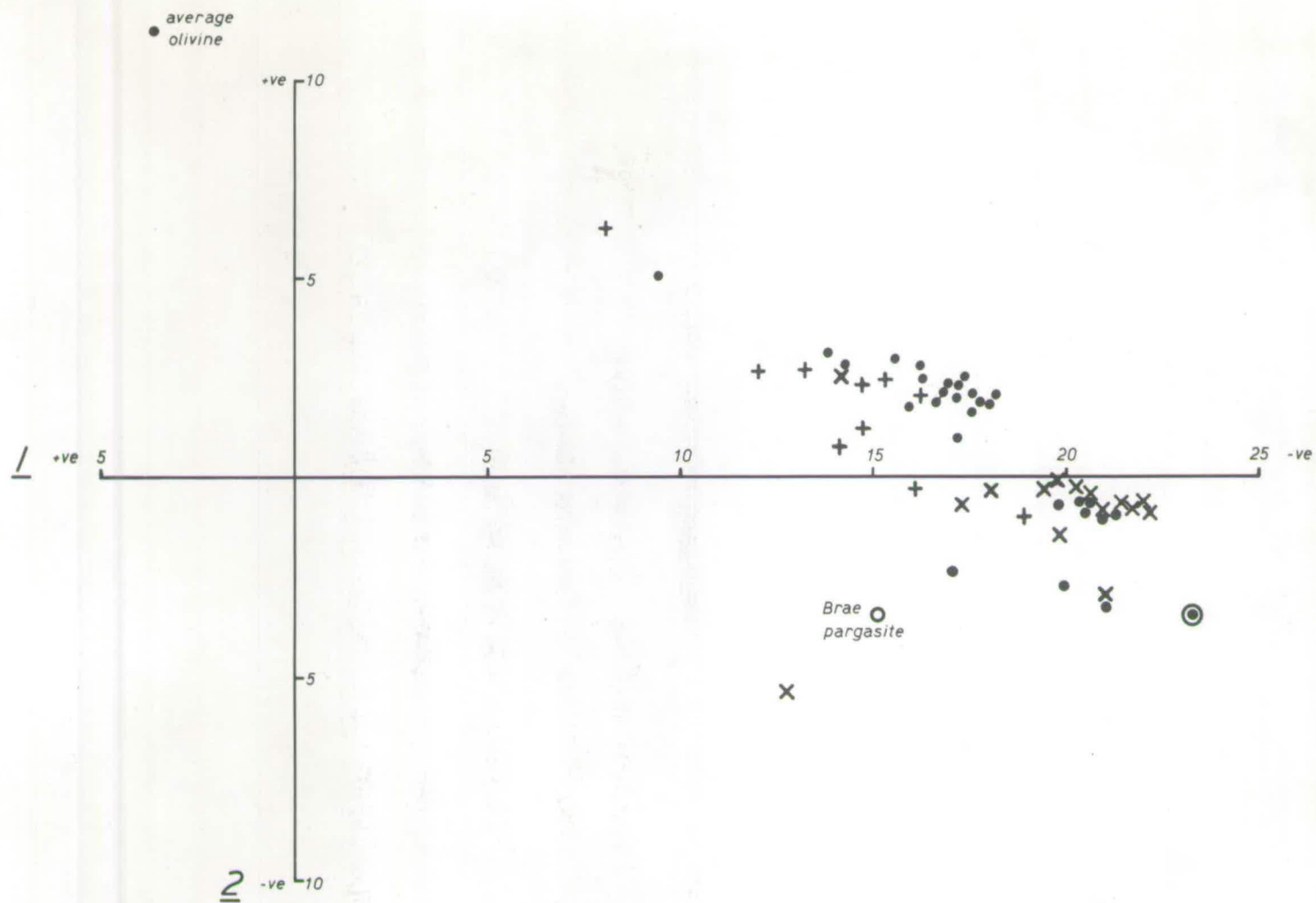


Figure 23

FIGURE 24

Principal Component Analysis of kentallenites

2) Plot of transformed variables 1 and 3.

Legend: as Figure 23.

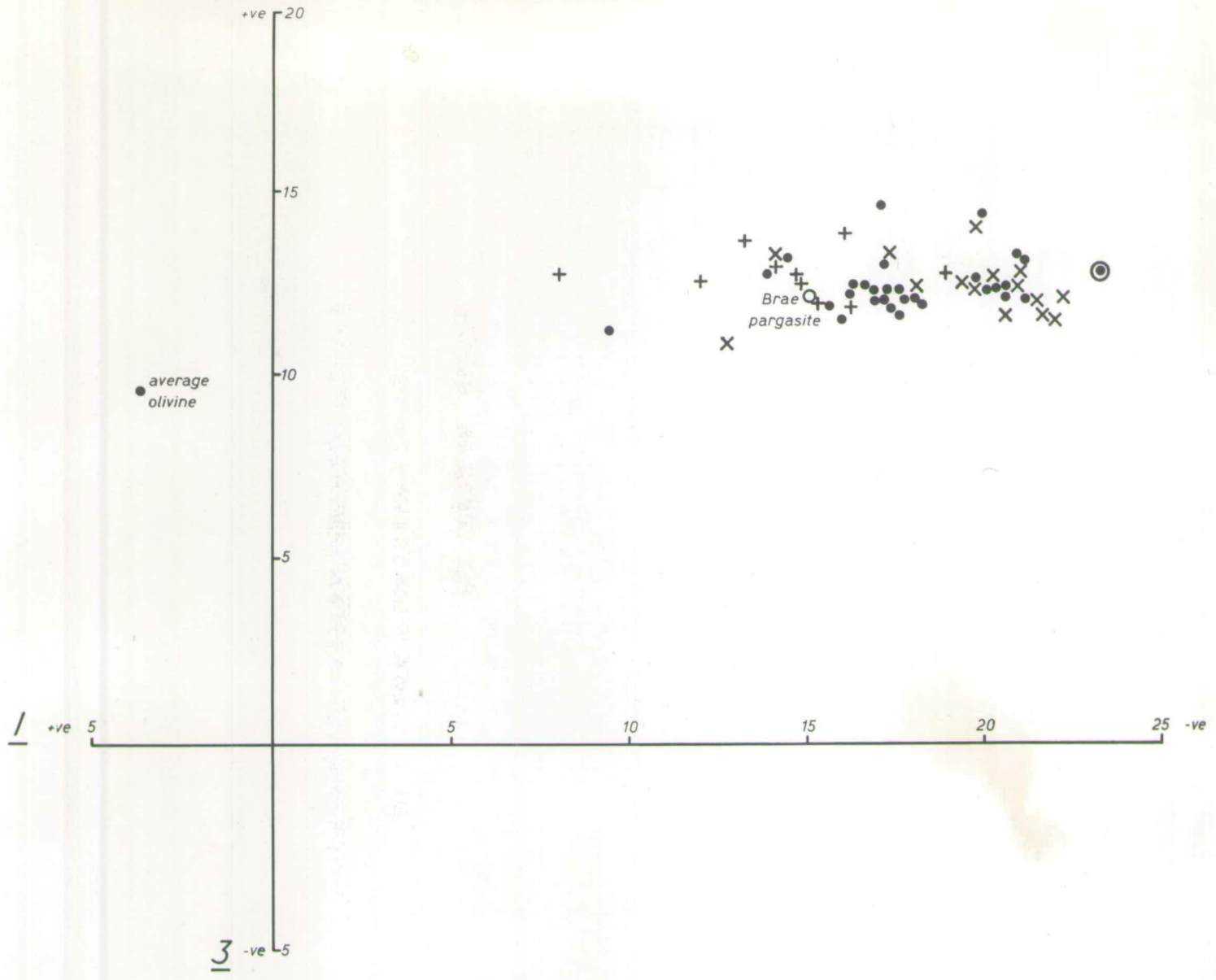


Figure 24

FIGURE 25

Principal Component Analysis of kentallenites

3) Plot of transformed variables 2 and 3.

Legend: as Figure 23.

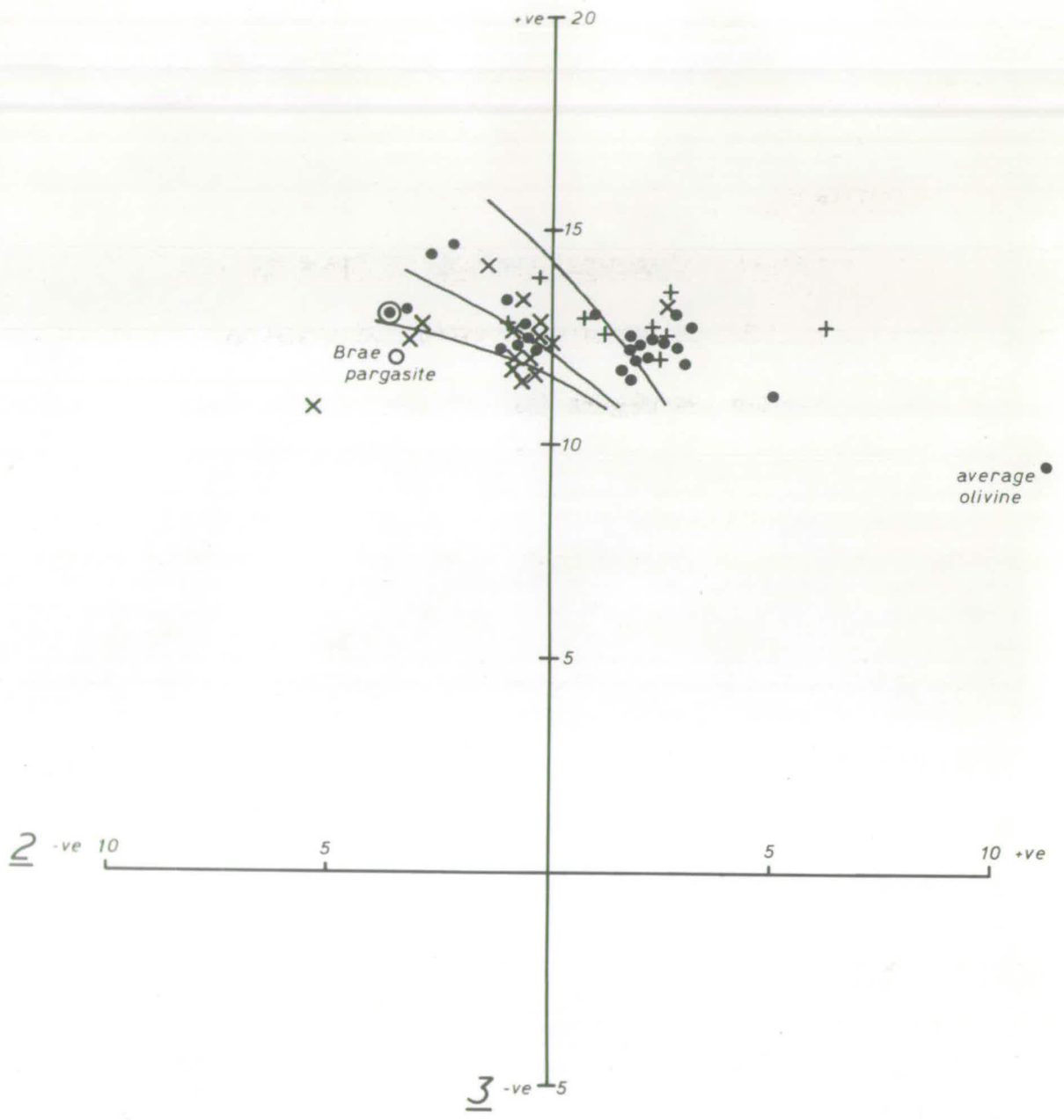


Figure 25

(transformed variables 1 and 2, 2 and 3 respectively) show a separation between nepheline- and hypersthene-normative compositions, and the boundaries between them have been drawn in each figure. These boundaries have been placed as close as possible to the estimated normative 'divide' (Ne=Hyp=0), and their concavity towards the Brae pargasite in both figures provides support for the suggestion of pargasite crystallisation as the mechanism for breaching the low pressure thermal divide.

Summary.

Tetrahedral projections and Principal Component Analysis confirm the role of olivine in kentallenite evolution and provide very strong evidence that crystallisation of pargasite from kentallenite parent magma was the mechanism effective in breaching the low pressure thermal divide and causing the observed scatter of compositions across it. There is clear mineralogical evidence only for olivine crystallisation in kentallenites, but it is possible that a hydrous mineral such as pargasite might break down if the magma from which it was crystallising was emplaced in a relatively dry upper crustal environment. Alternatively, pargasite might have accumulated in depth.

FIGURE 26

Glen Orchy Principal Component Analysis

1) Plot of transformed variables 1 and 2.

Legend:

- + - Hypersthene normative specimen.
- - Nepheline normative specimen.
- 0 - Brae pargasite (from Gill, 1965).

The solid-dashed curve separates hypersthene-
from nepheline-normative compositions, and lies close to
the normative divide (see p.40). The negative and positive
ends of axes 1 and 2 respectively are indicated.

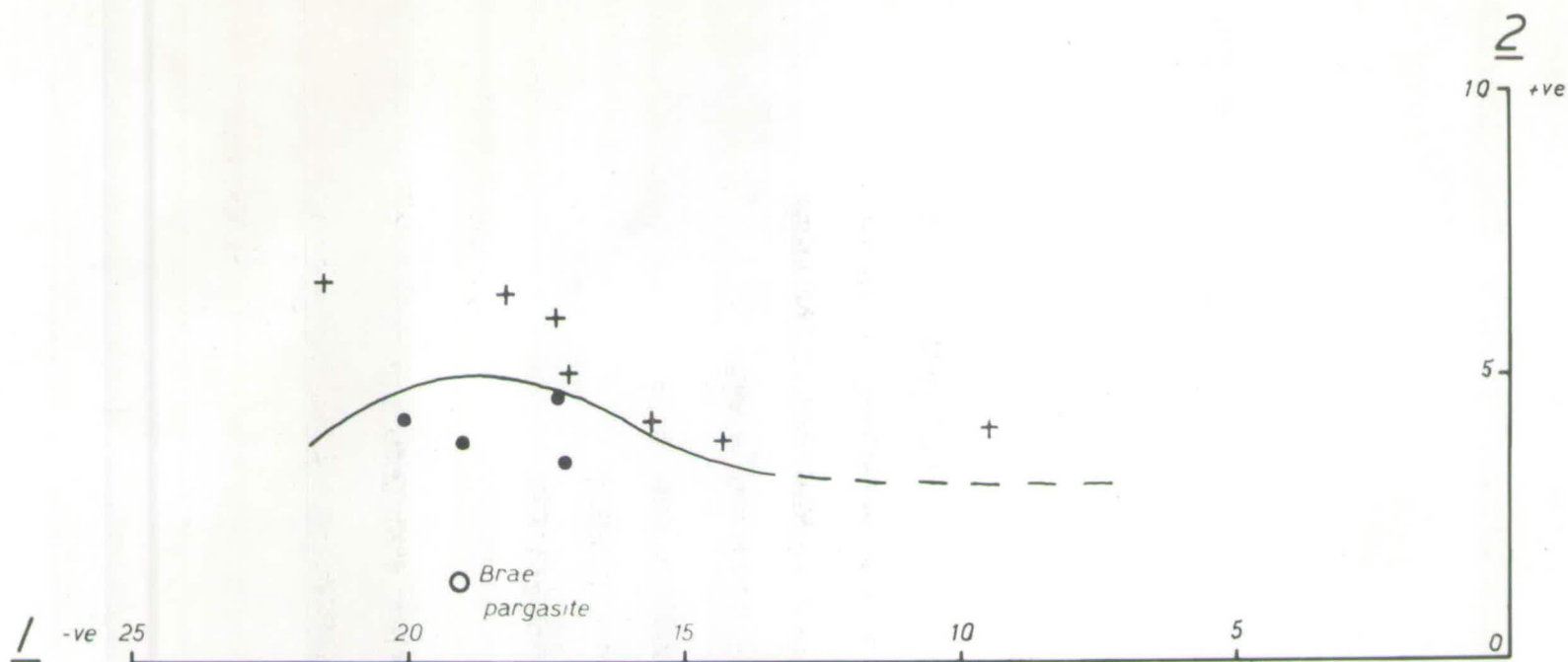


Figure 26

FIGURE 27

Glen Orchy Principal Component Analysis

2) Plot of transformed variables $\underline{2}$ and $\underline{3}$.

Legend: as Figure 26.

The negative and positive ends of axis $\underline{2}$, and the positive end of axis $\underline{3}$, are marked on the figure.

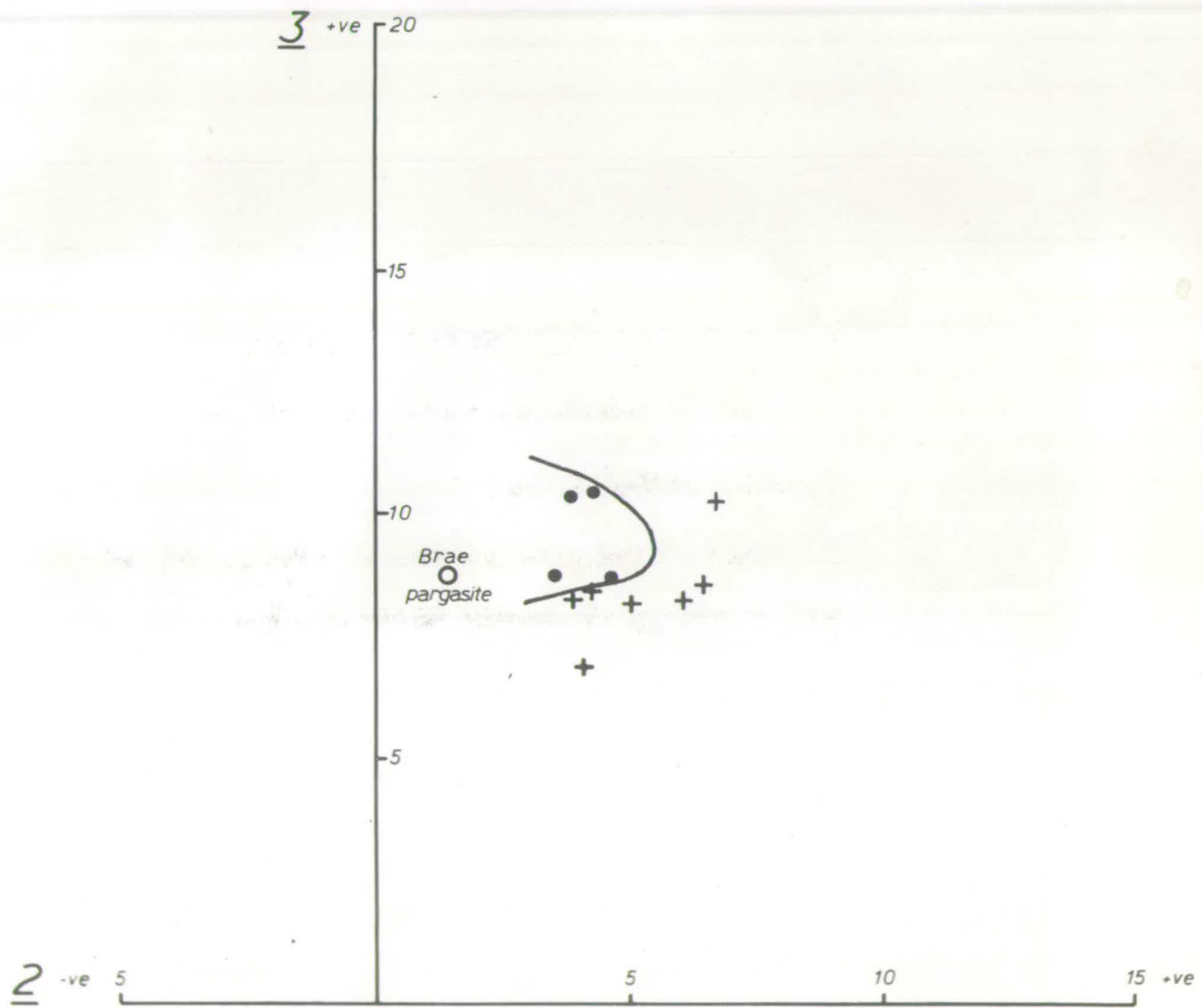


Figure 27

Introduction

In this chapter the operation of the olivine and amphibole "controls" discussed in the last chapter is examined. For simplicity of treatment the mechanisms are treated individually, although their operation may partly have overlapped.

No phase equilibria studies have been performed on kentallenites. However at least 90% of most kentallenite analyses can be expressed in terms of the synthetic system CMAS if iron is allowed to substitute for magnesium, and kentallenites are close to many basalts in bulk chemical composition. Analogies can therefore be drawn from experimental studies of natural basalts, and simplified basalts in the system CMAS, to aid in the understanding of kentallenite evolution.

The major chemical difference between kentallenites and basalts, that of K_2O content, is also discussed in this chapter, and its significance in the development of the kentallenite kindred examined.

Olivine Trend

Linear trends in igneous rock chemistry result either from the mixing of two homogeneous end-member phases or from the separation of one homogeneous phase in differing amounts from another. Mechanisms competent to explain the range and type of variation shown by kentallenites can be restricted to the following:

- 1) Mingling of two extreme end-member liquids in differing proportions.
- 2) Progressive contamination of a liquid by solution of a solid, the locus of liquids dissolved from which is linear.
- 3) Production of successive batches of partial melt from a single-phase source rock or a multiphase rock, the locus of liquids in equilibrium

with which is linear.

- 4) Evolution from a parent liquid at one end of a series towards derivatives at the other by fractional crystallisation of a single phase of fixed composition or a combination of such phases in fixed proportions.
- 5) Development of both extremes by a process of melting and fractional crystallisation acting upon a composition intermediate between the extremes, subject to the linearity conditions already stated.

Examination of the diopside and quartz normative projections (Figs. 15 and 18) shows that the extreme end-member compositions required to explain kentallenite variation are close to dunite and high-alumina basalt in composition. The mechanisms are, therefore, interpreted in terms of these compositions.

Case 1: Mingling of two end-member liquids.

A process of mingling and mixing of two end-member liquids, postulated for the Ach'uaiane Hybrid suite of Northwest Scotland (Read et al., 1925, 1926; see also Chapter 1), was extended to cover some Southwest Highland basic rocks by Mercy (1963). However Read et al (1925) supposed that a granitic magma mixed with an olivine-pyroxene-hornblendite magma (or rock; see next section) to produce the hybrid suite of Sutherland, and a process involving these extreme compositions cannot be applicable to kentallenites.

Basalt magmas, particularly high-alumina basalt magmas, are common in orogenic belts. Experimental study of the system $MgO-FeO-SiO_2$ (Bowen and Schairer, 1935), however, has demonstrated that dunite magmas are unlikely to exist at temperatures less than $\sim 1900^\circ C$ at any pressure in the absence of water. Field evidence suggests low intrusion temperatures for most dunite bodies, and lowering of the melting point of dunite by high water

content (i.e. the existence of serpentinite magma; Hess, 1938) has been proposed. Experimental work in hydrous systems does not support this suggestion, and "there seems no escape from the conclusion that ultramafics can be intruded only in the solid state" (Bowen and Tuttle, 1949, p.440; also Kitahara et al., 1966; Scarfe and Wyllie, 1967'a' and 'b'), and that a process requiring the existence of a dunite magma cannot operate.

Case 2: Contamination of a liquid by a solid.

An assimilative mechanism has been applied to the development of the basic and intermediate rocks of the calc-alkali Appinite suite of Scotland by Read et al. (1925, 1926; Read, 1961; also Nockolds, 1934; Joplin, 1959). In the broader aspect of the calc-alkali series, with which kentallenites and appinites are connected (see Chapter 1), similar assimilative theories have been widely favoured (e.g. Nockolds, 1934; Reynolds, 1935, 1936; Tilley, 1950; Joplin, 1959; Wilkinson, 1966). In all of these cases, with the necessity of explaining large volumes of acidic material, one of the proposed end-members is usually granitic or siliceous "material", and a process involving such a composition is, as pointed out above, inadequate to explain the occurrence of the basic pyroxene-olivine rocks of the kentallenite kindred. The failure of this mechanism to explain the occurrence of the basic bodies throws doubt on its acceptance as a major theory of origin of the calc-alkali suite as a whole (see Chapter 7).

Field and petrographic evidence render it unlikely that hybridisation of solid dunite and basaltic liquid has been effective in producing kentallenite variation. If solid dunite was an end-member of the series, some evidence of its original intrusion, and xenoliths and relics of it caught up in kentallenite at any level of outcrop, would be expected. With the exception of "dunite" recorded from Garabal Hill (Nockolds, 1941), probably the result of

crystal accumulation from a basaltic magma (see Case 5), there is no record of highly olivine-rich inclusions or intrusions within the Scottish calc-alkali province. Nor is there any indication of physical disintegration of dunite and strewing of olivine crystals throughout a hybrid liquid (cf. Nockolds, 1933), since mineral disequilibrium between olivine and kentalenite liquid is not pronounced. Although kentalenite olivines may be rimmed by orthopyroxene-hornblende coronas (Appendix B), this is attributed to post-crystallisation oxidation (after Shand, 1945; Murthy, 1958; O'Hara and Stewart, 1966). Olivine crystals in the chills are never rimmed, are rarely aggregated, and may often be nearly euhedral, features which are not suggestive of xenocrystal origin (cf. Jamieson, 1966).

Case 3: Successive partial melts.

Basalt magmas are thought to result ultimately from partial melting processes operating in the upper mantle (Bowen, 1928; Yoder and Tilley, 1962). By analogy, a similar ultimate source may be sought for kentalenite.

Field, petrographic and chemical evidence indicate that for a process of successive partial melting to be effective in generating kentalenite the initial partial melt of the upper mantle at some pressure must be highly olivine-rich (approx. 40% normative olivine + hypersthene; Appendix C) and become less so with increase in degree of fusion.

The initial partial melt in the system CMAS becomes more olivine-rich with increase of pressure (e.g. O'Hara, 1965) and at 40kb (equivalent to ~120km depth) has the normative composition Anorthite 32.4; Diopside 21.8; Enstatite 26.0; Olivine 19.9% (Davis and Schairer, 1965). The 40kb partial melt in CMAS, probably a close approach to the composition of the 40kb partial

melt of the upper mantle, is thus rich enough in normative olivine + hypersthene to give rise directly to the most olivine-rich kentallenite. However, because garnet and clinopyroxene are the first phases to disappear on melting a garnet peridotite at high pressures (O'Hara, 1963; O'Hara and Yoder, 1967; Ito and Kennedy, 1967), increase in degree of melting will produce liquids richer in olivine and orthopyroxene than the initial melt, the reverse order to that required.

Partial melting of mantle peridotite under successive reductions of pressure would produce successively less olivine-rich liquids, but these would not bear a linear relationship to another (O'Hara, 1965; 1968, in press). Thus a process involving derivation of successive partial melts from mantle peridotite is inadequate to explain the variation shown by kentallenites.

Case 4: Evolution from one end of the series to the other.

Discussion of Case 3 has shown that liquid dunite is unlikely to be formed in the mantle, and that the kentallenite sequence cannot be derived from the olivine-rich end. Bulk rock compositions as olivine-rich as those found at Kentallen and Glen Orchy could, however, be formed by accumulation of olivine from a less basic liquid, e.g. basalt or andesite.

Laboratory melting experiments at one atmosphere have shown that all the major silicate phases begin to crystallise in most natural basalts within a small temperature interval ($<80^{\circ}\text{C}$ - Yoder and Tilley, 1962; $<50^{\circ}\text{C}$ - Tilley et al., 1963, 1964, 1965, 1967). Thus the compositions of most basalts lie close to the "4-phase curve" of Yoder and Tilley (1962, p.396), but if this were the case in all basalts there would be no way of producing a rock series of basaltic affinity whose major variation could be explained in terms of fractionation of a single mineral (cf. O'Hara, 1965).

There are, however, some basalts whose compositions do appear to be controlled by accumulation of a single mineral, usually olivine (Macdonald, 1944; Powers, 1955; Murata and Richter, 1961, 1966; Richter and Moore, 1966), and whose bulk compositions do not lie close to the "4-phase curve" at atmospheric pressure (cf. O'Hara, 1965). For example the picrite basalt of the 1840 flank eruption of Kilauea is an olivine-enriched derivative of the lava batch which supplied the 1840 summit eruption (Macdonald, 1944; also Murata and Richter, 1966). Relative densities (Clark, 1966) indicate that in order for a basalt to accumulate olivine alone it must be the only mafic mineral crystallising from the magma. This can occur only if the liquid lies in the olivine primary phase volume, and the 1840 Kilauean parent magma must therefore have been held for some considerable time within this volume.

However, if olivine has accumulated in a magma column, the bulk composition lying at the olivine-poor end of the trend of variation will not represent the original parent liquid. This composition must be an olivine-depleted derivative of the parent, although if accumulation has occurred by elutriation of a very small amount of olivine (e.g. $\frac{1}{2}\%$) from a through-flowing magma the departure of that bulk composition from that of the original parent could be very small. Case 4, which suggests that the kentallenite series is derived from the basaltic end of the sequence of variation, cannot therefore apply, and the logical alternative is that suggested in Case 5, evolution by olivine depletion and accumulation from a composition lying between the extremes.

Case 5: Development from a composition intermediate between the extremes.

The temperature interval between the olivine liquidus and the onset of cotectic crystallisation (the liquidus interval) in the 1840 Kilauean picrite basalt is $\sim 270^{\circ}\text{C}$, whereas the olivine-poor summit eruption has a liquidus interval of $\sim 70^{\circ}\text{C}$ (Yoder et al., 1963). If the parent of these

basalts is assumed to lie approximately half-way between the two olivine-bearing extremes, it would have a liquidus interval of around 170°C , which contrasts strongly with the liquidus intervals quoted by Yoder and Tilley (1962, $<80^{\circ}\text{C}$) and Tilley *et al.*, (1963, $<50^{\circ}\text{C}$) for basalts close to the "4-phase curve", and would have precipitated olivine alone throughout this interval. A similar mode of origin can be proposed for the major variation in the kentallenite series, the observed sequence evolving from an 'intermediate' parent by separation of olivine alone. Since most common basalts are erupted on or close to the "4-phase curve" (Yoder and Tilley, 1962; see O'Hara, 1965), a magma which is not near-cotectic at the time of emplacement in the upper crust is aberrant to the normal pattern, and requires explanation.

Consider a liquid generated by partial melting of upper mantle material at a depth of 100-120km (equivalent to a pressure of 30-40kb). Such a liquid is likely to be picritic in character and will lie close to the olivine-enstatite-plagioclase and the olivine-diopside-plagioclase planes in the simplified basalt system (O'Hara, 1965, Fig. 8; Davis and Schairer, 1965; O'Hara and Yoder, 1967, Fig. 5). If this liquid is abruptly propelled to low pressure (~ 10 -15kb or less; see O'Hara, 1965, Figs. 10-12), it will lie in the olivine primary phase volume and can attain the low pressure cotectic curve only by precipitation of olivine (see O'Hara, 1965, Figs. 8-12).^{**} During this process the bulk composition will remain close to the olivine-enstatite-plagioclase and olivine-diopside-plagioclase planes, merely moving away from olivine. By this means rocks (e.g. kentallenites) and liquids (e.g. Kilauea, 1840, 1959) which show evidence of crystallisation of olivine alone

^{**} The projections shown in Figs. 8-12 (O'Hara, 1965) show only that the liquid will lie in the clinopyroxene + olivine + liquid volume, but it seems likely, from the probable configuration of the clinopyroxene-olivine boundary surface at intermediate pressures (O'Hara, 1968, in press), that a liquid generated at 30-40kb will lie in the olivine primary phase volume at pressures of around 10-15kb.

for a considerable temperature interval can be obtained.

Summary

Of the five hypotheses proposed to explain the origin of the major variation shown by the kentallenites, the only one consistent with all the available data is that involving derivation of the sequence by fractional crystallisation and accumulation of olivine from a parent magma intermediate between the two extreme compositions - Case 5. It is thought that the dominance of olivine crystallisation from this liquid is consequent upon its rapid movement from the zone of initial melting (30-40kb) to an area of much lower pressure (~10-15kb). Under these conditions the liquid will move towards the low pressure cotectic curve by precipitation of olivine alone through a substantial temperature interval.

Amphibole Trend.

The amphibole trend of the kentallenite sequence has been attributed (Chapter 5) to separation of pargasite from the parent magma, and although kentallenites are not amphibole-bearing rocks the chemical evidence in favour of pargasite separation is so strong that consideration must be given to the possibility that such a process has operated.

Kentallenites show evidence of being intruded in a relatively "dry" state, and it is only in the later stages of crystallisation that water content builds up sufficiently (or the temperature falls low enough - Luth, 1967) to allow biotite to form. Evidence from Ben Nevis (e.g. Bailey, 1960) and Glen Coe (Ferguson, 1966) suggests that the kentallenite plugs rose to within 6000 ft. of the O.R.S. land surface, and some may (Flatten, 1966) have been feeders to the lavas; in either case the volatile content of the parent liquid will have had easy access to the surface. Since pH_2O would have been

less than 1kb, hornblende would not have been stable at "basaltic" eruption or emplacement temperatures of 1100-1200°C (Yoder and Tilley, Figs. 27-30), and if it had been crystallising at depth from a water-rich kentallenite parent magma it would not be expected to survive transportation in this magma to a near-surface, low p_{H_2O} , environment of crystallisation.

Reaction between a mineral within its normal pressure-temperature-composition stability range and a liquid to produce a second mineral is often incomplete, and some evidence normally remains to show that reaction has taken place. Outside its normal pressure-temperature-composition stability range, however, a mineral will break down more rapidly and completely, and evidence of its former existence may be scarce. A hydrous mineral, such as pargasite, transported to an environment of low p_{H_2O} and slow cooling, might be expected to break down completely. Only under conditions of rapid cooling, for example in lavas, would pre-existing phenocrysts of amphibole or biotite be partly or wholly preserved (e.g. Turner and Verhoogen, 1960, p.277).

Pargasite has not been found either as xenoliths or a primary crystalline phase in kentallenites, but examination of thin sections of these rocks has disclosed several examples of possible breakdown products of hornblende (Plates 24-27). These are fine-grained aggregates which occur most frequently in chilled kentallenite, and are composed of clinopyroxene, plagioclase and some olivine. They occasionally show nearly hexagonal outlines (Appendix B). These aggregates cannot be considered unequivocal evidence for the prior existence of amphibole in these rocks, but the 'breakdown' texture implies the pre-existence of some mineral and the six-sided outline and composition are consistent with it being an amphibole. The amphibole, however, must have been pargasitic in composition in order for the proposed separation mechanism (see Chapter 5) to have been effective. The amphibole trend of kentallenite variation spreads across the "equilibrium thermal divide"

Forsterite-Diopside-Plagioclase in the "simple" basalt normative tetrahedron (see Yoder and Tilley, 1962), and pargasite is the only amphibole whose separation from the kentalenite parent magma is capable of causing this scatter. The 'breakdown' aggregates cannot be separated for analysis, and thus direct determination of the composition of the "amphibole" is not possible.

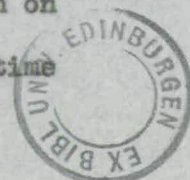
If the aggregates are the result of breakdown of pargasite above its liquidus at high temperatures ($> 1030^{\circ}\text{C}$) due to fall in pH_2O , the assemblage likely to result is Aluminous-diopside + Forsterite + Spinel + liquid + vapour; low temperature breakdown ($< 1030^{\circ}\text{C}$) will give rise to Aluminous-diopside + Forsterite + Nepheline + Spinel + Anorthite + vapour (Boyd, 1956; also Gilbert, 1966). Neither Spinel nor Nepheline has been detected in the aggregates, but if any interchange of material between pargasite and liquid took place during breakdown, the potential Spinel and/or Nepheline might have been removed from the amphibole. This is difficult to evaluate, but detailed electron-probe examination should give information on the alumina contents of the pyroxenes in the aggregates, which would aid in their interpretation. Discussion of the likely composition of early crystallising amphiboles must therefore at present be mainly by analogy with data from other complexes.

Most analyses of hornblende from the calc-alkali suite of Scotland (e.g. Nockolds, 1941; Nockolds and Mitchell, 1948) are from intermediate members of the suite, and are not pargasitic. However an amphibole separated from a hornblendite inclusion in gabbro of the Brae calc-alkaline complex, Shetland (Gill, 1965), is very close to pargasite in composition, and has been used in the data projections and principal component analysis plots of Chapter 5; it is strikingly close to the composition required by these plots to explain the scatter across the 1 atmosphere thermal divide. In order to cause this scatter, pargasite must be a primary phase crystallising from a liquid, and

although the pargasite in some ultrabasic rocks appears to be secondary in origin (Mackenzie, 1960; Green, 1964), that at Brae is thought to be primary (Gill, 1965, p.214, and pers. comm.), in common with those from St. Paul's Rocks peridotites (Melson et al., 1967) and Finero, N. Italy (Vogt, 1962). Pargasitic hornblende-gabbroic inclusions in calc-alkaline basalts from Japan have also been recorded, and the paragenesis of these inclusions suggests that they are high-pressure relics from an early stage in the crystallisation history of the rocks (Yamazaki et al., 1966). Pargasite appears, therefore, to be the stable amphibole in basic hydrous environments, which is encouraging to an hypothesis which requires early crystallisation of pargasite from basic magma.

Nevertheless, the strongest conclusion permitted by the evidence available is only that crystallisation of pargasite is competent to exert a control on the early evolution of a hydrous kentalenite parent magma; whether or not it is operative as a mechanism cannot yet be confirmed mineralogically, but its occurrence as an early crystallising phase in other calc-alkali suites lends support to the hypothesis.

The available evidence is also consistent with assimilation of pre-existing pargasitic amphibole exerting a control on magmatic evolution. If the proposed contaminant be solid hornblendite, however, xenoliths of it would be expected to occur in kentalenites, and these are not seen. This does not contradict the earlier discussion on resorption of hornblende, since xenoliths are commonly armoured against attack by rims of reaction products, and require mechanical disintegration to aid their complete disappearance. It is more likely that any material "assimilated" would be in the form of a sludge of hornblende (\pm olivine) crystals, which would be remobilised and resorbed on intrusion. This is an extension of the previous discussion on magmatic crystallisation, and implies that the magma remained for some time



either in the hornblende primary phase volume or in the olivine + hornblende + liquid equilibrium.

Uptake of water may suppress crystallisation of olivine in favour of hornblende at intermediate pressures (Yoder and Tilley, 1962, Figs. 27-30 and pp.448-455). Thus a melt intruded from depth into the base of the crust during orogenesis, and picking up water, might crystallise hornblende as the only primary phase in place of olivine (at pressures greater than about 10kb - Yoder and Tilley, 1962), and olivine would then react with the liquid. The ultimate stage in such a process would be a crystal mush composed entirely of hornblende, fractionation of which from the parent liquid could lead to derivatives on both sides of the one atmosphere thermal divide. Irruption of the derivatives to dry upper crustal levels, accompanied by the breakdown of hornblende and reprecipitation of olivine, would give rise to the features seen in kentallenites.

There is, however, no need to postulate the appearance of hornblende as ^aprimary phase at intermediate pressures. It could be the second phase after olivine, at a slightly lower p_{H_2O} (cf. Yoder and Tilley, 1962, Figs. 27-30), as a result of uptake of water by the magma shortly before it becomes cotectic. At a suitable pressure ($\sim 8-12$ kb; see Yoder and Tilley, 1962) hornblende and not pyroxene would be the second mafic phase to crystallise from a basaltic parent magma, and cotectic crystallisation of olivine and a suitable hornblende could then carry the residual liquid "across" the divide from Nepheline-normative to Hypersthene-normative compositions, producing the scatter seen in the plots discussed in Chapter 4. Irruption from depth would then produce the features seen in kentallenite, as mentioned for the previous, "hornblende first" hypothesis.

The difference between the "hornblende first" and "hornblende

second" hypotheses is one of degree, and would be controlled by the depth (and thus the pressure) at which water was taken up by a melt. The latter is preferred in the present case, but it is appreciated that there is no conclusive evidence against the other. Hornblendite inclusions at Brae, Shetland (Gill, 1965), suggest that perhaps a "hornblende first" type of fractionation was effective there, but the occurrence of hornblende gabbroic xenoliths in Japanese calc-alkaline rocks (Yamazaki *et al.*, 1966) is evidence that cotectic crystallisation involving pargasitic hornblende has taken place in at least one province.

Summary

Primary pargasite is absent from kentallenites, but it is suggested on chemical grounds that crystallisation of pargasitic hornblende (probably cotectic with olivine) has caused the compositional scatter of kentallenites across the one atmosphere thermal divide. In support of this, probable breakdown products of pargasite are observed, leading to the suggestion that irruption of a parent magma crystallising pargasite from intermediate pressures (~8-12kb) to a near-surface environment has resulted in instability of the amphibole, which has broken down to aggregates of diopside-plagioclase-olivine, rarely preserved. That early hornblendes in orogenic rock suites may be pargasitic is confirmed both by Scottish and Japanese examples.

Potash Content

The major non-basaltic chemical feature of kentallenites is their high K_2O content (cf. Bowes *et al.*, 1964, p.969). Most basalts have 0.1-0.7% K_2O (see Yoder and Tilley, 1962, Table 2, for representative examples) and kentallenites generally have between 2 and 3%; a few exceed 3%. A mode of origin for kentallenite involving "basaltic" magma such as that proposed above,

must also explain their high K_2O contents relative to those of "normal" basalts.

Mechanisms for the generation of high K_2O contents in basic igneous rocks may be concerned with the genesis of the original parent (Control by partial melting), with some process operating during its ascent from depth (e.g. Zone Refining) or with enrichment as a consequence of crystallisation behaviour (Control by fractional crystallisation); perhaps even with all three. Each of these possibilities is now examined in detail.

Control by Partial Melting

It is likely that the upper mantle is composed of eclogite-facies mineral assemblages (e.g. O'Hara and Mercy, 1963, Fig. 23), which probably contain less than 0.10% K_2O (Ito and Kennedy, 1967). A thirty-fold enrichment of K_2O would therefore be necessary to produce the kentallenite values by partial melting, and this would require the complete melting of a discrete potash-rich minor phase in the lowest melting fraction (first 3%) of the upper mantle.

Oxburgh (1964) suggested concentration of potash in minor amphibole in the upper mantle. Primary amphibole has not been recorded in nodules or inclusions of presumed upper mantle garnet peridotite (A.F. Williams, 1932; Nixon *et al.*, 1963; Carswell, 1966) but its postulated occurrence at depth does not contradict available experimental data (cf. Ernst, 1962; see, however, Davis *et al.*, 1965). Phlogopite was rejected as a possible potash-rich minor phase in the upper mantle by Oxburgh on the grounds of its "wrong" K:Na ratio (>7:1). However, eclogite-facies clinopyroxenes have very high Na:K ratios (e.g. Yoder and Tilley, 1962, Tables 37, 39 and 41), and various mixtures of phlogopite and clinopyroxene in a parent peridotite could produce any required K:Na ratio in a partial melt. Phlogopite, unlike amphibole, has been recorded as a discrete crystalline phase from peridotite inclusions in kimberlite

(Williams, 1932). Experimental work on phlogopite has been mainly confined to pressures less than 5kb (Yoder and Eugster, 1954; Wones and Eugster, 1965; Luth, 1967) and there are few data on its possible stability in the mantle. Some work at higher pressures (41-96kb; Kushiro *et al.*, 1967), suggests the potential stability of phlogopite down to depths of 150-200km beneath the continents, but the control of experimental conditions in this study seems inadequate for the conclusions drawn from it.

It seems unlikely that very small amounts of partial melt liquid could be extracted from upper mantle rocks by any mechanism (cf. Harris, 1957). If a 5% partial melt is the least amount of liquid that can be extracted from peridotite, and all the K_2O is concentrated in this 5% as a result of complete melting of potash-bearing amphibole or phlogopite, there will be only approximately 1-2% K_2O present in the liquid. Although sufficient for normal basalts, this is not potash-rich enough to give rise directly to kentallenites; a further, or different, process is required.

Zone Refining

Harris (1957) envisaged a molten "zone" moving up through the mantle by dissolving minerals above it and reprecipitating them beneath, the non-diadochic minor elements (K, Rb, Cs etc.) being retained in the melt. If the minor elements are concentrated in "minute grains of accessory minerals along the crystal boundaries" (Harris, 1957, p.200), however, the process may involve only grain-boundary melting. The most abundant of the minor elements is K_2O , and its ultimate concentration in the melt as a result of this process will depend both upon the distance travelled through the mantle and the distribution factor of potassium between melt and solid (see Dickinson and Hatherton, 1967); Harris suggests that at least a hundred-fold enrichment would be attainable.

Operation of the mechanism of Zone Refining is critically dependent upon Harris' assumption that the mantle at all depths is very close to its melting temperature. Recent experiments, however, have shown that only at pressures of 30-40kb is the upper mantle close to its melting temperature (Ito and Kennedy, 1967; D.H. Green and Ringwood, 1967'b'). At pressures less than 30-40kb the temperature gap between melt and environment is likely to be such that a partial melt liquid would be shielded from reaction with its roof and wall rocks by development of a chilled envelope; Zone Refining could not then operate.

Hybridisation and assimilation, related in some respects to Zone Refining, have previously been shown inadequate to explain the overall chemistry of kentallenites; they cannot therefore be involved in the generation of high K_2O contents. It is possible that alkalis were introduced to the magma with the influx of water required for pargasite crystallisation. Experimental work suggests, however, that Na is likely to be more soluble than K in a hydrous vapour phase in the crust (Khitrov, 1962; Luth and Tuttle, 1967). Thus enrichment of K relative to Na will probably not take place by such a mechanism.

Some other process, concerned more with "closed system" fractionation, must therefore be sought.

Control by Fractional Crystallisation

a) At high pressure.

Experimental work suggests that the initial partial melt of mantle peridotite at 30-40kb is probably a hypersthene-normative picrite (O'Hara and Yoder, 1963, 1967; Davis and Schairer, 1965). Because of reaction relations between crystals and liquids at high pressures, involving disappearance of enstatite and olivine from the crystallising assemblage (O'Hara and Yoder, 1963, 1967; O'Hara, 1965; Davis and Schairer, 1965; Green and Ringwood, 1967'b'),

liquid crystallising at high pressure changes in composition on cooling principally by precipitation of clinopyroxene and garnet, i.e. eclogite (O'Hara and Yoder, 1963, 1967).

The composition of the primary partial melt of peridotite at high pressures is thought to lie close to the clinopyroxene-garnet join, and to the likely composition of the clinopyroxene + garnet mixture which will crystallise from it on cooling (O'Hara and Yoder, 1963, 1967; O'Hara, 1965). Extensive fractionation of eclogite from the primary partial melt will thus give rise to a derivative liquid little different in major element concentration from the original bulk composition, with the following exception. Because only Na, of the alkalis, is taken into the mineral phases of eclogite (as jadeite, in omphacite), the K:Na ratio of the residual liquid will rise on fractionation of eclogite from it (cf. Holmes and Harwood, 1932). The longer a partial melt liquid remains at high pressure, therefore, the more likely it is to develop a high K:Na ratio (see O'Hara, 1965).

b) At transitional pressures.

If a partial melt liquid is irrupted from depth to shallower levels in the manner suggested earlier in this chapter, only olivine will separate from it as it cools. Olivine does not take K or Na into its structure, and its fractionation from a liquid can only increase the proportion of total alkalis in the residual melt.

c) At lower pressure.

The stable phases crystallising from a basaltic melt on the cotectic curve at low to moderate pressures are olivine + clinopyroxene + plagioclase, i.e. olivine gabbro. If the composition of the cotectic

liquid lies close to the olivine gabbro divide plane, as would be likely for the Southwest Highland rocks, a situation analogous to that existing at high pressure obtains; extensive fractionation of olivine gabbro will not greatly alter the major element concentrations of the liquid, with the exception of that of K_2O . Na is taken into plagioclase in considerable excess over K, and in the absence of sufficient water (or a suitable bulk composition) to stabilise phlogopite and/or hornblende (cf. Oxburgh, 1964), K_2O content of the residual liquid must rise with olivine gabbro fractionation. As with eclogite fractionation, the time spent crystallising olivine gabbro will control the ultimate K_2O content of the liquid.

d) Discussion.

Either high or low pressure closed-system fractionation schemes are competent to explain the high K_2O contents of kentallenites (and possibly of other potassic mafic rock suites - e.g. Ruwenzori, Uganda : Holmes and Harwood, 1932; O'Hara and Yoder, 1963; O'Hara, 1965). Both processes will have similar geochemical consequences, and major element chemistry is therefore of little help in deciding which of the two alternatives has been effective. Knowledge of the trace element spectra both of the proposed derivatives (kentallenites) and residua (gabbro or eclogite) is insufficient to aid in interpretation.

Some comments on the possible crystallisation history of these rocks can, however, be made from consideration of the geometry of data plots (e.g. clinopyroxene normative projection, Fig. 15, repeated here as Fig. 28). The initial partial melt of garnet peridotite at 30-40 kb lies to the quartz-rich side of the plagioclase-olivine-diopside join and within the volume plagioclase-olivine-diopside-enstatite (O'Hara, 1965; Davis and Schairer, 1965) in the simple basalt normative tetrahedron. Massive fractionation of eclogite from

FIGURE 28

Normative Diopside projection

(weight percent)

As Figure 15.

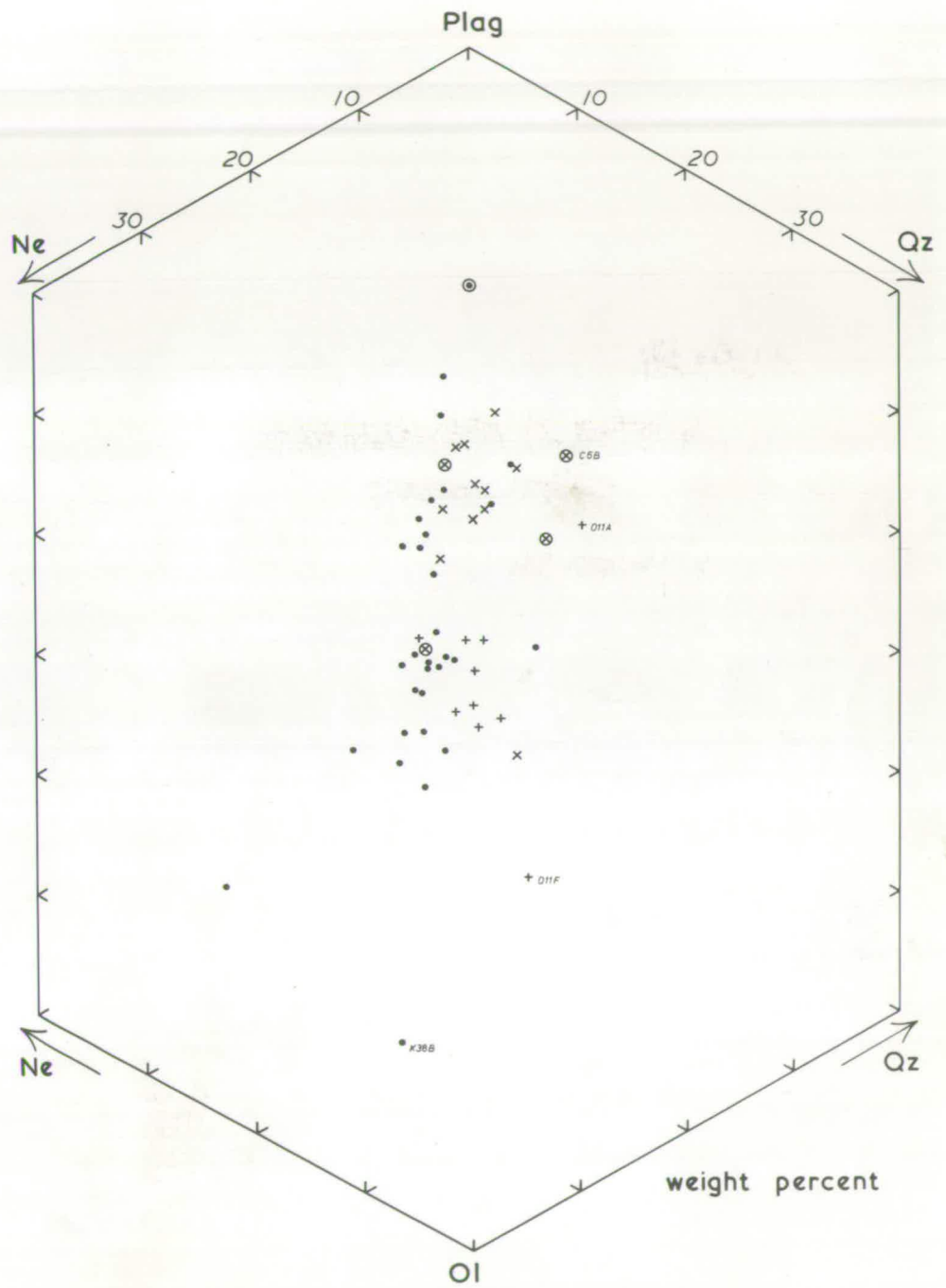


Figure 28

a liquid of this composition will move the residual liquid towards nepheline-normative compositions (O'Hara and Yoder, 1963, 1967; O'Hara, 1965), i.e. towards the plagioclase-olivine-diopside join, while increasing its K:Na ratio. If a residual liquid whose bulk composition lies close to the plagioclase-olivine-diopside join as a result of eclogite fractionation is irrupted to shallower levels (e.g. $\sim 8-12\text{kb} - 25-35\text{km}$), it will crystallise olivine alone as it approaches the cotectic curve existing at that pressure (see Olivine section, this chapter), a sequence of events consistent with the features of Fig. 28.

This is not, however, the only high-pressure fractionation scheme which can explain the features of Fig. 28. Experimental evidence suggests that the primary partial melt composition point of garnet (i.e. aluminous) peridotite migrates in predictable fashion with falling pressure, describing an arcuate course (in the simplified basalt normative tetrahedron) across the plagioclase-olivine-diopside join towards nepheline at some intermediate pressure ($\sim 20\text{kb}$). At lower pressures ($\sim 5-10\text{kb}$) it recrosses the join towards quartz (O'Hara, 1965; 1968, in press). It is therefore possible for the composition of the initial partial melt of aluminous peridotite to lie "in" the plagioclase-olivine-diopside join at two different pressures, $\sim 20\text{kb}$ and $\sim 5-10\text{kb}$. A $\sim 20\text{kb}$ partial melt, irrupted to shallower levels immediately on formation, would fractionate by precipitation of olivine alone and would display precisely the same characteristics in Fig. 28 as the $30-40\text{ kb}$ partial melt plus eclogite fractionation discussed above.

There are, however, limitations inherent in interpretations from data plots, one of the most important of which is that K_2O content is not shown in Fig. 28. This is critical to the case discussed above, since the major, perhaps the only, difference in bulk composition between the products of $30-40\text{kb}$ partial melting plus eclogite fractionation and direct $\sim 20\text{kb}$ partial

melting is that the former should be much the richer in K_2O and the non-diadochic minor elements. There is no direct evidence to support one high pressure mechanism at the expense of the other, but demonstration that gabbroic fractionation at low to moderate pressures was not effective in enriching the liquid in K_2O would favour the concept of 30-40kb partial melting followed by eclogite fractionation.

A ~ 5-10kb partial melt will fractionate towards quartz (or nepheline) by precipitation of olivine + plagioclase + clinopyroxene on rapid reduction of pressure. This gabbroic fractionation scheme cannot explain the olivine-controlled linearity of kentallenite compositions discussed earlier in this chapter, but might act upon a liquid irrupted from high pressure to these lower pressures, enriching it in K_2O in the manner suggested earlier. There is, however, no evidence in favour of extensive olivine + clinopyroxene + plagioclase cotectic crystallisation in the kentallenite parent, since kentallenite chills contain phenocrysts only of olivine and clinopyroxene. It is possible that plagioclase has been removed by flotation or eruption from the kentallenite parent magma, which would be consistent with the partly accumulative nature of kentallenite, but some evidence of early plagioclase crystallisation would then be expected. None is found.

Kentallenites do not contain xenoliths either of eclogite or gabbro, but gabbroic xenoliths are found in Japan (Yamazaki et al., 1966), Soufrière (Wager, 1962) and the Western U.S.A. (H. Williams, 1931); eclogite has not been recorded from these suites. While this is strong evidence in favour of gabbroic fractionation taking place in these suites, it cannot be considered strong evidence against eclogite fractionation since eclogite would not be expected to survive as such in a magma irrupted from high to low pressures (cf. earlier discussion of hornblende).

At present, therefore, it can only be said that the high K_2O content of kentallenites could be due to eclogite fractionation at the depth of initial partial melting, possibly in conjunction with gabbroic fractionation at shallower depths.

Summary

The major non-basaltic feature of kentallenite is its high K_2O content. It is suggested that 'closed-system' processes, involving selective partial melting together with high (and possibly low) pressure fractionation, are competent to explain the relatively high concentrations of K_2O . No appeal need be made to external, 'open-system', processes such as Zone Refining or assimilation.

Petrogenetic Model

On the basis of the foregoing discussion, the following tentative petrogenetic model for kentallenite is suggested:

- 1) Partial melting of upper mantle garnet peridotite at a depth of between 100 and 120km (equivalent to 30-40kb pressure) in an orogenic environment, producing a hypersthene-normative picritic liquid.
- 2) Probable fractionation of eclogite from this liquid at, or close to, its depth of origin, effecting a rise in the K:Na ratio without greatly altering the remaining bulk composition.
- 3) Irruption of the residual liquid of such fractionation to the base of the 'orogenic' crust, a depth of approximately 25-35km (equivalent to ~8-12kb pressure), and fractionation of olivine alone from the liquid to produce a high-alumina

basaltic type of magma.

- 4) Uptake of H_2O by the high-alumina basaltic liquid at pressures of ~8-12kb, resulting in the appearance of pargasitic hornblende as second crystalline phase (after, and with, olivine), fractionation of which assemblage would cause the observed scatter of kentallenite compositions across the one atmosphere thermal divide in the simplified basalt system.
- 5) Irruption of the residual liquid from the base of the crust to a near-surface environment, causing complete breakdown of pargasite due to volatile loss.
- 6) Crystallisation, in a relatively dry upper crustal environment, of the potash-rich derivative liquid from high and intermediate pressure fractionation as kentallenite, compositional trends in this environment possibly being influenced by olivine + diopside fractionation (Chapter 3).

Kentallenite may have formed either in feeder pipes supplying the Lorne Plateau lavas or as separate hypabyssal intrusions which failed to reach the surface. Appinites may owe their hydrous mineralogy and close association with kentallenite (see Walker, 1927) to crystallisation within such hypabyssal intrusions. Loss of volatiles from, and chilling of the roof and walls of an intrusive pipe would produce a crystalline 'envelope' of kentallenite within which water pressure might build up, as a result of anhydrous mineral crystallisation, to levels that could allow hornblende to reprecipitate from the liquid (cf. Platten, 1966; Hall, 1967; see also Summary of Chapter 2). (Early pargasite might then be preserved in the cores of hornblende individuals, and confirmation of this would be impressive support for the model as a whole.) Explosion breccias (Bowes and Wright, 1961, 1967), common features of the appinite suite, can be interpreted as the result either

of volatile loss from the kentallenite magma at shallow depth (e.g. Back Settlement; Bowes and Wright, 1964) or of rupture of the 'envelope' and consequent marginal gas-streaming round a crystallising kentallenite-appinite pipe (e.g. Kentallen north contact; see Appendix A). Erosion level would control which member of a pipe sequence outcropped at the surface.

The high modal olivine content of kentallenite, the composition of that olivine (Fe_{75-80} - see Chapter 2) and the partly accumulative textures (Appendix B) suggest that much of the olivine present may have sunk out of a larger body of basaltic magma. The lack of widespread high-grade thermal aureoles round most of these plugs (Appendix A; see also Platten, 1966) and the occurrence of appinite in close association with them does not support the hypothesis that most of the plugs are remnants of feeder pipes to the Lorne Lavas. Some (e.g. Barnamuc; Platten, 1966) may be feeders, but the high olivine content and possible hornblende 'ghosts' in the Kentallen, Glen Orchy and Colonsay intrusions more probably reflect intrusion of "magma" as a liquid-crystal mush containing olivine and hornblende crystals accumulated in a magma-chamber at greater depth (see also Chapter 3).

Introduction

The kentallenite-appinite suite is part of the Scottish Caledonian calc-alkali province (see Chapter 1), and although kentallenite is uncommon in other calc-alkali suites its close field and chemical relationships to the Southwest Highland rocks demand discussion of its petrogenesis within the broader framework of genesis of the calc-alkali series in general. Most previous work in the Southwest Highlands has been concerned with the spread of rock-types ranging from dunite (Garabal Hill) to granite (Ben Nevis, Starav). The present examination has concentrated on the "window" into early evolutionary history provided by rocks near the basic end of the range of variation in this suite and has produced evidence which may be of importance in discussion of the origin of the calc-alkali series as a whole.

Hypotheses advanced to explain the origin of the calc-alkali suite can be grouped into five categories. They are:

- 1) Gas Transfer.
- 2) Assimilation of crustal rocks by basaltic or granitic magma.
- 3) Partial melting (palingenesis) of crustal rocks.
- 4) Direct derivation by partial melting of basalt, eclogite or peridotite in the mantle.
- 5) Fractionation from a basaltic parent.

Each of these is now examined in detail, from the dual standpoint of their agreement with current petrological thought and consistency with the occurrence of kentallenite.

Gas Transfer.

Gas transfer has been invoked (e.g. Stanton, 1967) to explain

the development of the calc-alkali suite. The numerical approach favoured by Stanton demonstrates that the compositions of calc-alkali volcanic suites fall into two linear arrays on diagrams such as FeO:MgO vs Total alk:MgO, and that these arrays intersect at a point of "inflection" corresponding to the "composition" of Nockolds' (1954) average tholeiite or Daly's (1933) plateau basalt. Stanton concluded that these features were most easily explained by a process of gas transfer with differential loss acting on a tholeiitic or plateau basaltic parent producing andesitic derivatives and refractory residues of dunite and peridotite.

Examination of the data, however, suggests that the points of inflection in Stanton's diagrams are the result of changing fractional crystallisation type rather than of gas transfer. It can be shown that the basic-ultrabasic linear array could be caused by olivine fractionation from a picritic parent, and the intermediate-acid array by subsequent gabbroic fractionation acting on the residual liquids. Although Stanton considered, and rejected, a process of fractionation of a mineral extract of changing composition from the parent, he did not discuss the possibility of changing type of fractionation. Since a change in type of fractionation from dunite to gabbro close to the point of inflection would effect the changes attributed to gas transfer, it is considered the more likely process, and gas transfer is rejected as a major means of calc-alkaline evolution.

Assimilation

Assimilation does not appear to be competent to explain the origin of kentallenite (see Chapter 6), but it is often invoked as a mechanism for the generation of the calc-alkali suite and thus merits discussion.

Batholithic granites are often associated with orogenic belts (e.g. Western U.S.A., Indonesia, Japan) and have been thought to bulk too large

to be derived directly from basalt (Turner and Verhoogen, 1960). Assimilation, of granitic crustal material by basic magma (e.g. Holmes, 1932; Walker and Poldervaart, 1949; Tilley, 1950; Kuno, 1953) or of basic material by granitic magma (e.g. Read et al., 1925, 1926; Nockolds, 1934; Joplin, 1959), has been suggested to counter this "anomaly", but recent work has shown that many batholiths may be floored at no great depth in the crust (Hamilton and Myers, 1967); thus the volume "anomaly" may not be so severe as was thought. Nevertheless, theoretical and experimental evidence (e.g. Bowen, 1928) does indicate that addition of granitic material to fractionating basalt magma will increase the quantity of the final acid differentiate, provided the magma is already committed to the silica-rich side of the one-atmosphere thermal divide (Yoder and Tilley, 1962), or is very close to the divide on the nepheline-rich side. Liquids deeply committed to the nepheline-rich side of the divide cannot pass through the divide by assimilation of siliceous material (e.g. Gribble and O'Hara, 1967).

Assimilation cannot, however, explain the voluminous intermediate rock-types (e.g. andesites, diorites, granodiorites) found in calc-alkali provinces, unless fractionation is not operating on the contaminated liquid, an unlikely event in a large body of magma crystallising minerals of differing density and reaction rates. Hence the basic liquid - solid granite (or siliceous sediment) assimilation theory should probably be discarded as a general theory of origin of the calc-alkali suite; it may, however, have local importance (e.g. Garabal Hill porphyritic granodiorite; Nockolds, 1941).

Features shown by the intermediate rocks at Garabal Hill (position on variation diagrams, relative abundances, etc.) led Nockolds (1941; see p.496) to abandon an acidic liquid - basic rock assimilation hypothesis (Nockolds, 1934) for the generation of calc-alkaline rocks in favour of fractional crystallisation of a pyroxene-mica-diorite (i.e. andesite) parent magma (cf. Dakyns and Teall,

1892; Hill and Kynaston, 1900), a conclusion supported by Gill (1965) from the Brae calc-alkaline complex, Shetland. Nockolds' (1934) assimilation hypothesis, reiterated in modified form by Joplin (1959), also fails to explain the origin of the basic rocks of the suite; there is no way in which olivine-pyroxene bearing rocks can be generated by this mechanism, since "any magma will tend to make inclusions over into the phase or phases with which it is saturated" (Bowen, 1928, p.197). "Attenuated granodioritic magmas" (Joplin, 1959) do not contain augite or magnesian olivine (cf. Chapter 2).

Holmes' inference (1932) that the calc-alkali suite is not normally a product of differentiation of basalt because it is not developed on Hawaii is probably correct, but the corollary, lack of andesites or their plutonic equivalents from the oceans, is demonstrably not true. They occur, for example, in the Bonin-Mariana and Aleutian arcs, neither of which is underlain by appreciable sialic crust (e.g. Gorshkov, 1962; Lewis, 1967), and their occurrence in these environments is inconsistent with assimilative theories of origin. Although trapped trench-sediments could be a source of contamination to an ascending basaltic magma, such contamination would occur at high levels in the crust and homogenisation of the product, and its freedom from xenoliths, would not be expected. Trace element data on andesites from Japan and New Zealand are also thought to exclude an origin by assimilation, contamination or mixing of acid and basic material (Taylor and White, 1965; 1966; Taylor, 1967'a' and 'b'), but are consistent with derivation from a primary andesite magma (Taylor and White, 1965; 1966; after O'Hara, 1965). However O'Hara (1967) has thrown doubt on the practical importance of this hypothesis (see section 4 below).

Among the criteria used in attempts to clarify the origin of andesites and their associated rocks is the Strontium isotopic ratio Sr^{87}/Sr^{86} .

Because of the potential importance of this ratio in determining the ultimate source of calc-alkaline (and other) rocks, its validity is examined here in some detail. Originally discussed in connection with the composition of the upper mantle (Gast, 1960), the ratio Sr^{87}/Sr^{86} was applied by Faure and Hurley (1963) to the problem of the origin of basalts and other igneous rocks. The significance of the Sr^{87}/Sr^{86} ratio lies in the Sr^{87} isotope. It is generated by radioactive decay from Rb^{87} , and its concentration in a rock, expressed as the Sr^{87}/Sr^{86} ratio, is thus a function both of initial Rb^{87} content and time. If the age of a sample, its Rb and Sr contents, the Rb^{87} half-life and the present Sr^{87}/Sr^{86} ratio are known, the initial Sr^{87}/Sr^{86} ratio (i.e. at the time of formation of the sample) can be calculated.

Most basalts have an initial Sr^{87}/Sr^{86} ratio of between .702 and .707 (Faure and Hurley, 1963; corrected after Anon, 1964), and these are thought to be the characteristic values of the upper mantle, the source region of basalts. Small variations in initial Sr^{87}/Sr^{86} ratios in oceanic basalts from different areas, which can be attributed to slight inhomogeneities in the upper mantle, have, however, been found (Powell et al., 1965; Hedge, 1966). Crustal rocks and sediments tend to have higher values (.710-.740; e.g. Hamilton, 1963; Aldrich et al., 1964; Moorbath and Bell, 1965) than those of basalts, and thus a rock generated by the operation of processes such as assimilation, contamination or partial melting involving sialic crust with such Sr^{87}/Sr^{86} ratios would have a higher initial Sr^{87}/Sr^{86} ratio than one derived from the upper mantle. Some ancient gneisses, however, have very low Sr^{87}/Sr^{86} ratios (e.g. \sim .700 in Keewatin Precambrian - Hedge and Walthall, 1963; .700-.706 in the Lewisian of Northwest Scotland - Evans, 1965); processes of magma generation or development involving such gneisses would be isotopically indistinguishable from those involving mantle rocks.

Where geological evidence of contamination or assimilation is present (e.g. Red Hills, Skye - Wager et al., 1965; Garabal Hill xenolithic granodiorite - Nockolds, 1941) the initial Sr87/Sr86 ratios are markedly higher than those associated with basaltic rocks (Moorbath and Bell, 1965; Summerhayes, 1966, respectively), but clear evidence of geological contamination is uncommon. Often the isotopic data are ambiguous in their meaning, since there is no uniform standard, or "threshold value", beyond which a rock can be said to be "contaminated". As the following example shows, there may not even be unanimity on a "threshold value" within the same laboratory (in this case M.I.T.); Hurley et al., (1965) considered that initial Sr87/Sr86 ratios of approximately .704-.710 were indicative of crustal fusion, whereas Fairbairn et al. (1967) thought that ratios of approximately .704-.715 were derived from the upper mantle.

There is also evidence that Sr isotopes do not behave entirely as expected in some circumstances, notably under conditions of strong fractionation. Initial Sr87/Sr86 ratios of .710-.730 are recorded in granophyres at Skaergaard (Hamilton, 1963), where the country rock has only .712-.716; variations are found in Hawaiian and other oceanic lavas, in general showing an increase in the ratio with fractionation (Gast et al., 1964; Lessing and Catanzaro, 1964) or "erring" on the high side (Bence and Hurley, 1967; but see, for example, Hamilton, 1965 'a' and 'b', and MacDougall and Compston, 1965, for contrary views); and ratios as extreme as 2.47 have been recorded in Lithium pegmatites (Riley, 1967; also Brookins et al., 1964). Considerable caution must therefore be exercised in interpretation of high initial Sr87/Sr86 ratios where there is no geological evidence of contamination (e.g. Gast et al., 1964; Riley, 1967), and it would appear that one can be confident of interpretation only when low values, consistent with derivation of a rock from the mantle, are found. If the Rb/Sr ratio, and thus Sr87, decreases with depth in the crust,

however (Hedge and Walthall, 1963; Heier, 1964, 1965; Evans, 1965), a low initial value of Sr^{87}/Sr^{86} need not be diagnostic of mantle origin.

Strontium isotope ratios have been determined on calc-alkaline rocks in various environments, both in continental provinces (e.g. Davis et al., 1965; Hurley et al., 1965; Summerhayes, 1966) and island arc systems (Compston, quoted by Taylor and White, 1965). All yield low values even for the acidic members of complexes (but see Hurley et al., 1965; their data are ambiguous), and since some of these results are from oceanic areas they tend to support derivation of the rocks from the oceanic mantle without contamination by sialic crust. More isotopic data on calc-alkaline rocks are required, however, before any firm conclusions can be reached by this method.

Partial melting of crustal rocks.

In his examination of the Cascades province of the western U.S.A., Waters (1955) proposed derivation of andesites by fractional crystallisation of hydrous tholeiitic basalt and production of granites by subsequent partial melting of rocks within the downbuckled tectogene. This latter suggestion has been endorsed both from the theoretical (Turner and Verhoogen, 1960) and experimental (Winkler and von Platen, 1961'a' and 'b'; Wyllie and Tuttle, 1961) viewpoints, and has led to a revival of interest in the process of palingenesis of crustal rocks (Mercy, 1963; Den Tex, 1965; Kleeman, 1965; Taneda, 1966).

Winkler and von Platen (1961, 'a' and 'b') obtained aplitic and tonalitic partial melts from greywackes and high-grade meta-sediments, the precise composition of the melts being dependent not only on the pressure but also on the composition (particularly the Albite:Orthoclase ratio) of the parent rock. The hydrothermal melting of shales (Winkler and von Platen, 1961'b'; Wyllie and Tuttle, 1961) resulted in a more acidic initial melt (granite-granodiorite)

than that derived from the metasediments, probably due to low Ab:Or ratios, and even 50% melting of shales did not produce a liquid more basic than granodiorite. Since liquids at this degree of partial melting (50%) are chemically very unlike normal igneous rocks (and become more so with further fusion), Wyllie and Tuttle concluded that this mechanism could not produce basaltic, or andesitic, magmas.

Experimental demonstration of the acidity of initial partial melts of crustal rocks, however, held the promise of solving the apparent volume problem of the orogenic acidic rocks. Thus Mercy stated: "There seems little doubt that petrological opinion is deviating from a purely metasomatic and replacement hypothesis for the origin of granite and inclining towards a mainly magmatic hypothesis based on palingenesis of continental basement rocks and on partial melting of metasedimentary rocks" (1963, p.207), and he pointed out that temperatures and pressures (7-800°C; ~2kb; see Wyllie and Tuttle, 1961) sufficient to produce partial melts of country rock would be attained in high-grade regional metamorphism. Mercy's hypothesis requires, however, that the partial melting products be homogenised with respect to distribution of major elements; he observed (1963) that not only do the individual Caledonian granites differentiate in the same manner (by fractional crystallisation; see Anderson, 1937), but that they have similar relative proportions of the elements Mg, Fe, Na, K and Ca. This is equivalent to stating that the partial melts (and the degree of partial melting) from widely differing areas, and thus probably from widely differing rock-types, are closely similar, a conclusion at variance with the experimental data of Winkler and von Platen (1961'a' and 'b') and Wyllie and Tuttle (1961).

Palingenesis may account for the origin of some granites and granodiorites, but it cannot explain the occurrence of basic rocks in the calc-

alkaline series (see Wyllie and Tuttle, 1961). This complication was avoided by Mercy (1963), who denied any genetic connection between the Scottish Caledonian granites and the Appinite suite, favouring the Read-Joplin hypothesis of contaminative origin for the basic rocks (which was discussed, and rejected, in Chapter 6). Apart from any 'direct' evidence against the theory (e.g. Strontium isotopes), successful demonstration that the acidic and basic rocks of the calc-alkali suite are genetically related will demolish the palinogenetic arguments of Mercy (1963). Let us therefore examine his proposals in the light of evidence from Scottish calc-alkaline complexes.

Smooth and continuous trends on variation diagrams produced by plotting major element analyses of Scottish Caledonian calc-alkaline rocks (including those from Garabal Hill) led Nockolds (1941) to suggest fractional crystallisation as the mechanism controlling evolution of the entire series, and to choose pyroxene-mica-diorite as the parent magma to the suite. Further work on trace elements (Nockolds and Mitchell, 1948) has supported this view, which was also endorsed by Bailey (1958). Mercy (1963) has questioned the sampling techniques used by Nockolds and Bailey, and criticised their 'lumping' of data from several individual, and thus possibly different, intrusions, but data from Garabal Hill (Nockolds, 1941) and the Brae complex, Shetland (Gill, 1965), each produce similar continuous trends of variation to the overall trend produced by Nockolds (1941) and Nockolds and Mitchell (1948), suggesting that Mercy's criticisms do not apply. The kentallenite data are too restricted in composition to provide a major contribution to these trends, but they are consistent with them.

Methods of interpretation which rely on trends of variation are, however, open to criticism on several grounds, the most fundamental being that diagrams alone are merely illustrative, not diagnostic, of modes of origin.

In order to establish a genetic connection between acidic and basic rocks of a complex, data are required from a mineral (or minerals) occurring in all members of the complex, and zoned in such a fashion that there is chemical overlap between zones of the mineral in the successive rocks. Alternatively it may be established by the presence of an unusual trace element or trace element spectrum, or the unusual abundance of a common trace element, throughout the complex.

Insufficient mineralogical data are available from Scottish calc-alkaline rocks to provide evidence of a common origin for the series, but the Brae complex (Gill, 1965), which itself shows as wide a range of chemical variation as the Scottish calc-alkali suite as a whole, has a trace element spectrum which suggests consanguinity of basic and acidic rock-types. Both Cr and Ni remain unusually high in intermediate rocks (up to 850 ppm Cr; up to 220 ppm Ni) and acidic rocks (up to 400 ppm Cr; up to 80 ppm Ni), and Sr, Ba and Rb tend to be depleted throughout the series. Gill attributes these features to unusual concentrations of the elements in the parent magma, and states; "That these features are retained in acid, intermediate, basic and ultrabasic rock types must be regarded as proof of their derivation from a common parent" (1965, p.259). Thus palingenesis cannot be invoked at Brae and, by analogy, is unlikely to apply to the rest of the Scottish calc-alkali suite.

Strontium isotope data suggest that calc-alkaline rocks may be derived from partial melting of the mantle rather than by palingenesis of the crust (e.g. Davis et al., 1964; Compston, quoted by Taylor and White, 1965). The only Sr isotope data obtained from the Scottish calc-alkali suite are from Garabal Hill (Summerhayes, 1966). The average initial Sr⁸⁷/Sr⁸⁶ ratio of rocks ranging in composition from peridotite to pegmatite at Garabal Hill (excluding "geologically contaminated" rocks) is $.705 \pm .003$, consistent with derivation of the complex from the mantle. However, much of the Sr isotopic case against

crustal derivation of acidic members of the suite would collapse if the crust is zoned with respect to Sr87/Sr86 ratio (see discussion in section 2 of this chapter), although field relationships, and the consistency of the Sr isotope data at Garabal Hill would still point to the adequacy of other processes to produce considerable volumes of acidic material.

Direct derivation by partial melting of basalt, eclogite or peridotite.

a) Derivation from 'basalt'.

Hamilton proposed derivation of high-alumina basalt, andesite and dacite by a process of partial melting of the "basaltic component of the mantle" (1964, p.636) at pressures less than those appropriate to the basalt-eclogite transition. In areas of high upper mantle temperature Hamilton suggested that the basalt-eclogite transition might be depressed to a depth of ~60km (a maximum of ~17kb; Yoder and Tilley, 1962; Cohen et al., 1967), and that initial melting temperature of the mantle would be reached at shallower depths than this, giving rise to a partial melt rich in normative plagioclase.

The operation of this mechanism requires hydration of the parent rock to lower the melting point of plagioclase relative to that of pyroxene, and presence of plagioclase in the primary assemblage. If these conditions are met, Hamilton's theory is consistent with available experimental data (Yoder and Tilley, 1962; Yoder, 1965, 1967), although it fails to explain, for example, the highly olivine-rich rocks of the Southwest Highlands; let us examine the conditions required.

There are no data on the water content of mantle rocks, but it has been suggested, from seismic velocities (Ringwood, 1962), that the upper mantle may be sufficiently hydrous (0.5-0.8% H₂O - Ringwood, 1966) to allow the formation of amphibole only at depths shallower than about 20km, which would restrict the occurrence of amphibole to the mantle underlying oceanic areas.

If this estimate of depth is realistic (for others see Green and Ringwood, 1963, 1967; Davis et al., 1965), the maximum temperatures attainable in hydrated upper mantle are approximately 300-400°C (Ringwood et al., 1964), inadequate for partial melting of likely mantle rocks (cf. Yoder and Willey, 1962; Ito and Kennedy, 1967).

It is possible (see Chapter 6) that the upper mantle is composed dominantly of garnet peridotite; at shallow depths the garnet in the assemblage will break down in favour of spinel or alumina-rich pyroxene (Boyd and MacGregor, 1964). Some of the garnet peridotite nodules in kimberlite pipes are thought to represent the closest available approach to unmodified samples of the upper mantle (O'Hara and Mercy, 1963), and plagioclase is not observed in such nodules at any pressure under dry conditions (Ito and Kennedy, 1967). However, the amount likely to be present could be less than the limit of detection. If plagioclase is absent from the assemblage, and if this is a general feature of upper mantle rocks (but see Ringwood, 1962; Green and Ringwood, 1963, for an alternative view), Hamilton's mechanism for derivation of high-alumina basalt and calc-alkaline rocks cannot function. However arguments against this hypothesis are clearly not strong; possibly the strongest is the likely adequacy of another process in deriving the calc-alkali suite (see section 5 of this chapter).

b) Derivation from eclogite.

A model for the origin of the calc-alkali igneous rock suite by partial melting of quartz-eclogite, which had sunk from the surface to a considerable depth in the mantle, was advanced by T.H. Green and Ringwood (1966). Their experiments suggested that the initial partial melting product of quartz eclogite at 25-40kb pressure (i.e. ~100-120km depth) was of andesitic composition under dry conditions, and granodioritic if wet.

A parent andesite could differentiate to produce granodiorite and granite, but T.H. Green and Ringwood preferred the more acidic members of the calc-alkali suite to be generated by partial melting of eclogite under wet conditions. This is inconsistent with the field relationships found in the British Caledonides (including the Southwest Highlands, the Newry and Galloway centres, and the Brae complex, Shetland) where the basic rocks are always intruded before the acidic varieties, for the following reason. Since eclogite is unlikely to take in water at great depth in the mantle (see discussion at end of previous section), it must have obtained it in a near surface environment and carried it down to depth if a wet melting mechanism is to operate. Partial melting will then take place with generation of granodiorite first, followed, on dehydration, by progressively more basic melts, the opposite sequence to their intrusion in the crust. Derivation of the acidic rocks by differentiation from a parent andesite does not conflict with the field data (see Nockolds, 1941). However the likely presence of eclogite (whether wet or dry) at depth in the mantle has not yet been considered; it is clearly critical to T.H. Green and Ringwood's hypothesis, and is discussed now.

D.H. Green and Ringwood concluded, from an experimental investigation of the basalt-eclogite transition, that "eclogite mineralogy is stable in dry basaltic rocks along normal geothermal gradients throughout the entire crust" (1966-1967'a', p.767; ** see also Ringwood and Green, 1964). This proposal, at variance with other published evidence on the transition (Yoder and Tilley, 1962, Fig. 43, p.498; Cohen et al., 1967), is based upon extrapolation

** This paper appeared in A.N.U. publication 444 in 1966, but was not published by Geochim. Cosmochim. Acta until 1967. It will be referred to as "D.H. Green and Ringwood, 1966-1967'a'", throughout this section.)

of data obtained at temperatures above 1000°C and pressures greater than 10kb to the pressure-temperature conditions existing near the surface of the earth. It is carefully examined here because of its important petrological and geophysical implications.

According to Ringwood and D.H. Green (1966) basalts and gabbros in crustal rocks owe their basaltic mineralogy to kinetic rather than thermodynamic stability, and will become transformed to eclogite under suitable conditions of cooling. Such "crustal" eclogites could sink through the crust, dragging it down to form a geosyncline, and because they are of higher density than the likely upper mantle rocks (Ringwood and D.H. Green, 1966), could also sink deep into the mantle, where they might undergo partial fusion to produce andesitic magmas as discussed above.

Examination of D.H. Green and Ringwood's (1966-1967'a') experimental results, however, suggests that their data (Fig. 29; reproduced from Fig. 7, D.H. Green and Ringwood, A.N.U. Publication 444, 1966) are not adequate to support the conclusions based upon them. For example, the gradients of the transition zone boundaries, which are of critical importance to the extrapolations proposed by D.H. Green and Ringwood, are interpretations of incomplete data obtained under conditions where Cohen et al. experienced "considerable difficulty" in performing consistent subsolidus reactions (1967, pp.499-500). Additionally the boundaries are drawn as straight lines in an environment where curvature, induced by variable mutual solid solution of the coexisting minerals, might be expected. Close bracketing runs on the boundaries would be required to establish whether or not curvature exists, and these have not been performed. The same authors, however, noted curvature of the upper transition zone boundary in other experiments (D.H. Green and Ringwood, 1967'c', Fig. 1), and it should be emphasised that any curvature of

FIGURE 29

Experimental results of D.H. Green and Ringwood

(Reproduced from Figure 7, D.H. Green
and Ringwood, ANU Publication 444, 1966).

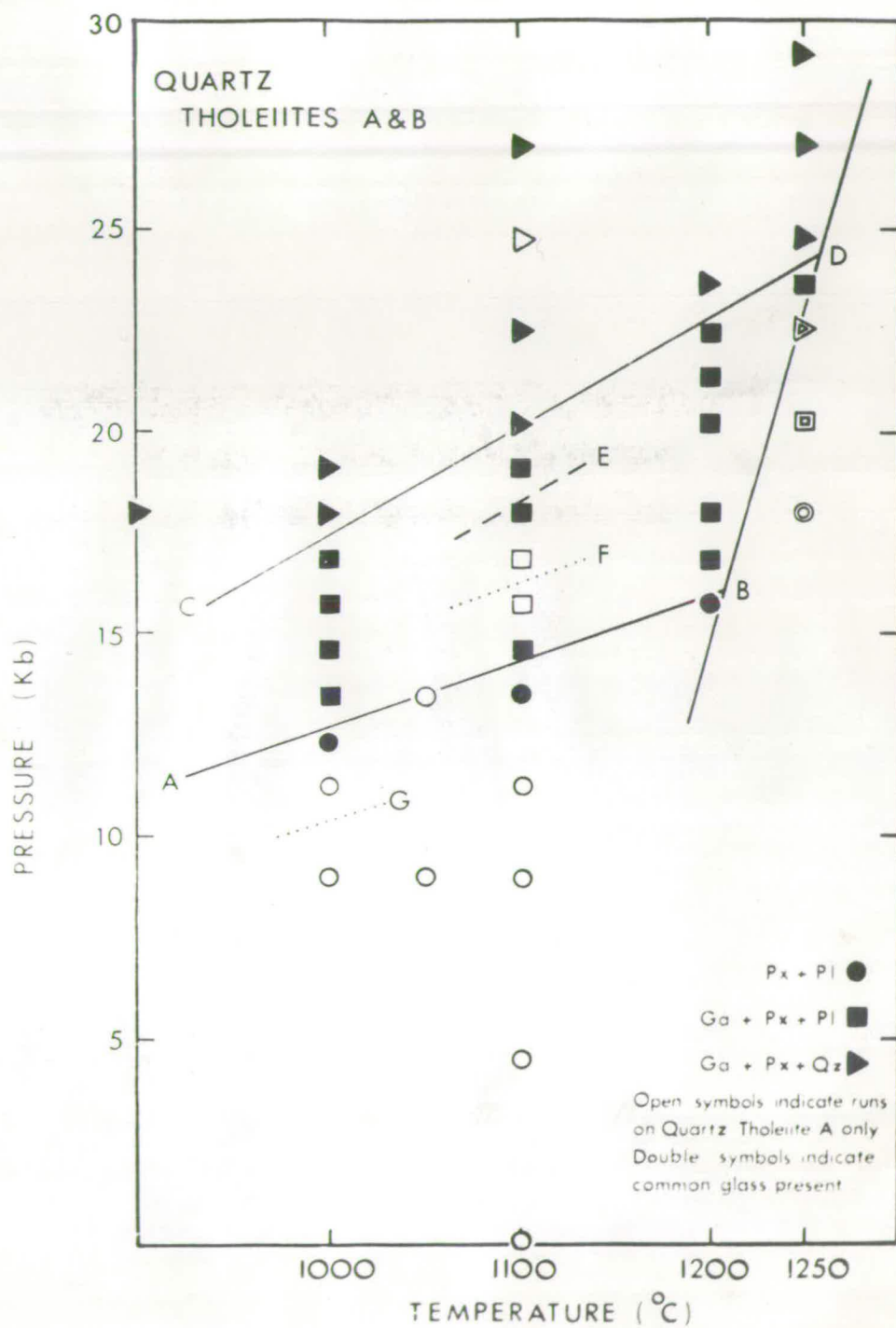


Figure 29

the kind observed in the later work will act against the hypothesis of crustal eclogite transformation.

Ringwood and D.H. Green (1966) have attempted to support their chosen transition zone boundary gradients by comparison of them with known gradients in simple systems closely related to the basalt-eclogite transformation. For purposes of comparison Ringwood and D.H. Green averaged the gradients of their upper and lower transition zone boundaries, thus removing any direct relationship between them and the experimental data, because of the "appreciable uncertainty" (1966, p.399) of boundary gradients determined over small temperature intervals. A similar "appreciable uncertainty" may be attributed to the process of extrapolation performed by Ringwood and D.H. Green. In addition, some selectivity in Ringwood and D.H. Green's choice of gradients to compare with those of the transition zone boundaries is apparent. For example, only the upper transition zone boundary curves, which have a slope of very much higher dP/dT than the lower boundary curves, have been taken from the data of Kushiro and Yoder (1965). The majority of curves (including those of Kushiro and Yoder) selected to support the eclogite transition zone boundary gradients have been determined only at high pressures and temperatures. Extrapolation of them to low pressures and temperatures may involve as much uncertainty as the extrapolation of the transition zone gradients themselves, and they cannot therefore be considered strong support for the slope of the transition zone boundary gradients chosen by Ringwood and D.H. Green.

D.H. Green and Ringwood's (1966-1967'a') experimental data on partial melting of eclogite at high pressures appear to be consistent with other, related, work (Cohen et al., 1967), but the data obtained on the basalt-eclogite transition are inadequate to support their conclusion that eclogite is stable in the crust. Hence it is concluded that partial melting of eclogite, as proposed

by T.H. Green and Ringwood (1966), cannot yet be regarded as an acceptable method of derivation for the calc-alkali igneous rock suite.

c) Derivation from peridotite.

By interpretation based on the experimental results of Yoder and Chinner (1960), O'Hara (1965) proposed derivation of andesite by direct partial melting of mantle peridotite under water saturated conditions. Yoder and Chinner (1960, Fig. 25) showed that a synthetic mixture on the grossular-pyroxene join containing about 19 wt% of grossular would crystallise in a water saturated environment at 10kb by the precipitation of spinel at $\sim 1360^{\circ}\text{C}$, joined by forsterite at $\sim 1230^{\circ}\text{C}$ and by both pyroxenes simultaneously at $\sim 980^{\circ}\text{C}$. O'Hara presented a simplified construction based on 16% grossular (thus introducing a small error), to show that if the liquid in equilibrium with forsterite, spinel, 2 pyroxenes (i.e. spinel peridotite) and vapour at $\sim 980^{\circ}\text{C}$ "resembles an igneous rock at all, i.e. if it does not contain normative corundum" (1965, p.35), it will have a high content of normative quartz and a high hypersthene:diopside ratio in the norm. It will, therefore, be 'andesitic', provided the vapour phase is not enriched in, for example, SiO_2 and/or alkalis relative to the condensed phases, an assumption that can be strongly challenged (cf. Tuttle and Bowen, 1958; Luth and Tuttle, 1967). If the liquid is 'andesitic', it will fractionate by crystallisation of 2 pyroxenes + spinel at 10kb (see Fig. 25, Yoder and Chinner, 1960), which will result in movement of the residual liquid towards more quartz-rich compositions until amphibole starts to crystallise at $\sim 910^{\circ}\text{C}$, the composition discussed going solid shortly thereafter. (For a diagrammatic summary of the behaviour of this liquid, see O'Hara, 1965, Fig.13.)

If upper mantle rocks contain plagioclase (see discussion in an earlier part of this section), qualitative support of O'Hara's (1965) mechanism for producing relatively acidic liquids from the upper mantle is provided by

experiments in the synthetic systems Diopside-Anorthite- H_2O (Yoder, 1965, Figs. 8 and 9) and Anorthite-Forsterite- H_2O (Yoder, 1967, Fig. 4.9), the results of which suggest that the first liquids formed in the water saturated systems at pressures close to 10kb and 7.5kb respectively are rich in silica and anorthite. Support for the existence of a primary andesitic magma has also come both from geophysical interpretations (Dickinson, 1967) and geochemical data (Taylor and White, 1965, 1966).

Crystallisation from a primary andesite magma, however, cannot account for the compositional scatter shown by kentallenites, since olivine is never the only phase crystallising from the proposed liquid and thus cannot be a major control of its evolution (see Chapter 6). In addition, the composition of the liquid in the "equilibrium" spinel + 2 pyroxenes + amphibole + liquid + vapour "must lie to the silica-rich side of the plane two pyroxenes + anorthite" (O'Hara, 1965, p.36) which is that side of the plane remote from kentallenite compositions. Such a liquid cannot be concerned with kentallenite development.

Peridotites equilibrated at pressures of 10-20kb and temperatures of 800-900°C should be prominent among alpine-type peridotites if a process of wet partial melting of peridotite is active in the generation of andesites. O'Hara has since suggested that the apparent general lack of such peridotites "might then be a pointer to the relative unimportance of this mechanism in the generation of andesite provinces" (O'Hara, 1967, p.403). Although further sampling of alpine-type peridotites may disclose the required rocks, presently available data do not support the hypothesis of andesite derivation by wet partial melting of peridotite.

Fractionation from a basaltic parent.

The calc-alkali suite differs from 'normal' basaltic series in its abundance of intermediate to acid rocks and lack of iron-enrichment during

fractionation. These features must be explained by any hypothesis which would derive calc-alkaline rocks from a basaltic parent.

Field and chemical data from the Southwest Highlands of Scotland (e.g. Dalryns and Teall, 1892; Nockolds, 1941; Nockolds and Mitchell, 1948) have suggested that the Scottish Caledonian calc-alkali suite has been derived by crystal fractionation from an intermediate parent, pyroxene-mica-diorite, a conclusion which has been extrapolated to other provinces (Nockolds and Allen, 1953). An intermediate parent magma would be capable of explaining the characteristic features of the calc-alkali suite, but the ultimate source of the intermediate liquid remains unexplored by this hypothesis.

Several recent workers, recognising the "intimate field relations of basalt and andesite" (Turner and Verhoogen, 1960, p.284; also Tilley, 1950), have favoured derivation of the intermediate and acid rocks of the calc-alkali suite by fractionation of basaltic parent magmas under special conditions. Thus the Andean volcano Puyehue gives evidence of development of calc-alkaline rocks from high-alumina basalt (Katsui and Katz, 1967), as does the Cascades volcanic province (Waters, 1962), and calc-alkaline rocks in Japan are apparently developed from tholeiitic, high-alumina or alkali-basaltic parents (Kuno, 1965). In all of these cases the special conditions under which fractionation is thought to have taken place are those associated with high water content; i.e. high p_{H_2O} and, possibly, high oxygen fugacity.

The potential importance of oxygen fugacity (f_{O_2}) in controlling crystallisation trends of basaltic liquids was first appreciated by Kennedy (1955). He suggested that, because Fe^{3+} -bearing phases melt at higher temperatures than either Fe^{2+} - or Mg-bearing phases, crystallisation under a 'high' f_{O_2} would give rise to extensive iron-oxide precipitation from a magma, thus depleting the residual liquid in iron and enriching it in silica. The

dioritic and granitic liquids produced by such a process would contrast strongly with the Fe-rich residual liquids resulting from crystallisation at 'low' fO_2 .

Support for Kennedy's observations was provided by Osborn (1959, 1962). As a result of experiments in the system $MgO-FeO-Fe_2O_3-SiO_2$ Osborn divided basalt crystallisation into two types similar to those of Kennedy (1955), but emphasised the importance of control, rather than magnitude, of fO_2 . Osborn's Type 1, crystallisation at "constant total composition", takes place with fall in fO_2 which was thought by Osborn to be controlled by the crystallising assemblage itself. It gives rise to ferrogabbroic late differentiates in dry, non-orogenic environments (e.g. Skaergaard). Type 2, crystallisation at "constant fO_2 ", requires fO_2 to be imposed upon the assemblage by an external agent (e.g. water), and Osborn suggested that crystallisation of this type in wet, orogenic, environments would give rise to the calc-alkali rock series (e.g. Cascades). Because type 2 crystallisation implies addition of oxygen to the system, it is "open", and type 1 "closed" with respect to oxygen (see Osborn, 1963, p.4). As the closed and open system distinctions are essential to Osborn's hypothesis for the origin of the calc-alkali suite, it is necessary to discuss the possible occurrence of such systems in nature.

A system crystallising at constant total composition is, according to Osborn (1963), a closed system. This requires that no exchange of H_2 or O_2 takes place between the system and its surroundings and implies that fO_2 must be internally controlled. However, Thompson has noted that "the distinction between a closed and open system is ... dependent in large part on what one chooses to define as the limits of the system" (1955, p.80), and that although closed systems are easier to treat thermodynamically, it is difficult to find a geological system big enough to remain completely closed. It is therefore likely that any natural system will be at least "semi-open" (Korzhinsky,

1950), and if so it is likely to be completely open with regard to the important controls of oxygen fugacity (i.e. O_2 , and particularly H_2). One may then question the existence of a completely closed system with respect to fO_2 anywhere in the crust.

Eugster and Wones (1962) considered that the attainment of H_2 equilibrium between experimental charges and their buffers indicated that the systems were closed to all components. As these workers note, such systems are in "local equilibrium" (see Thompson, 1959), but they cannot be considered "closed" since equilibrium of H_2 between a charge and its buffer requires the charge to be "open" with respect to H_2 . Thus the fH_2 (and fO_2) of a charge will be externally buffered.

By analogy, the same may be true of a magma intruded into the crust. Although initial crystallisation of the intruded magma would be controlled by its own fO_2 , equilibration with the country rocks, and crystallisation under the control of the country rock fO_2 , should be rapidly attained if the system is not closed to volatiles. In most cases the country rock assemblage probably contains magnetite (rather than haematite or wüstite) as oxide phase, and equilibrium with a solid-solid buffer assemblage of this kind (e.g. quartz-fayalite-magnetite-water - QFM) will vary with temperature (see Eugster, 1959, Fig. 6). The equilibrium crystallisation path in such a system will be the same as that required by Osborn's type 1 (i.e. fO_2 will fall with crystallisation), although the fO_2 of the liquid is being controlled by a solid assemblage outside the magma and not by the crystallising assemblage. Thus crystallisation of Osborn's type 1 does not require the system to be internally buffered.

Crystallisation of type 2 requires O_2 to be progressively added to the system or H_2 to be progressively lost from it; Osborn (1959) suggested addition of oxygen derived from the breakdown of water to the system. In

general (Eugster, 1959) the composition of water vapour in a rock is in equilibrium with the assemblage of minerals stable in that rock, and Eugster has noted that although "geologists often suspect that water itself can be oxidising, the oxygen being derived from thermal dissociation" (1959, p.424), the effect of water added to a system will depend on the fO_2 of the system and of the water, and on the buffering capacity of the system. Only if water equilibrated at relatively high fO_2 is introduced to the system in sufficient quantities to overcome the buffering effect of the solid assemblage and act as a buffer itself, will oxidation take place.

Since the fO_2 of pure water is higher than that of most solid-solid buffer assemblages and drops less rapidly with fall in temperature than the fO_2 of such buffers (see Fig. 30), a magma crystallising in equilibrium with a pure water buffer will be oxidised, and become progressively more oxidised as crystallisation proceeds, relative to most solid-solid buffers. This is a close approach to the conditions required by Osborn (1959) for type 2 crystallisation. To maintain fO_2 constant with falling temperature, or to increase it, however, would require either further addition of oxygen to the system with crystallisation, or loss of hydrogen. It appears, therefore, that crystallisation of both types 1 and 2 is likely to take place in semi-open systems, the difference between the two being dependent on the type of external buffering operative.

Expansion of Osborn's (1959) data from $MgO-FeO-Fe_2O_3-SiO_2$ to more complex systems by Roeder and Osborn (1966) and Presnall (1966) has increased the relevance of the experimental work to natural systems. However these workers have shown that the lower limit of fO_2 effective in type 2 crystallisation is $\sim 10^{-8}$ atm., which undermines Osborn's belief (1959, 1962) in the importance of control of fO_2 , as it appears to be of little importance whether or not fO_2 is constant provided it remains above 10^{-8} atm. (i.e. 'high'), a conclusion consistent with Kennedy's earlier (1955) work.

Fudali et al. (1961) and Fudali (1965) have shown that the fO_2 s

FIGURE 30

The fO_2 of H_2O

(After Carmichael, 1967, Figure 2)

Legend:

HM - haematite-magnetite buffer.

H_2O - pure water buffer

QFM - quartz-fayalite-magnetite buffer.

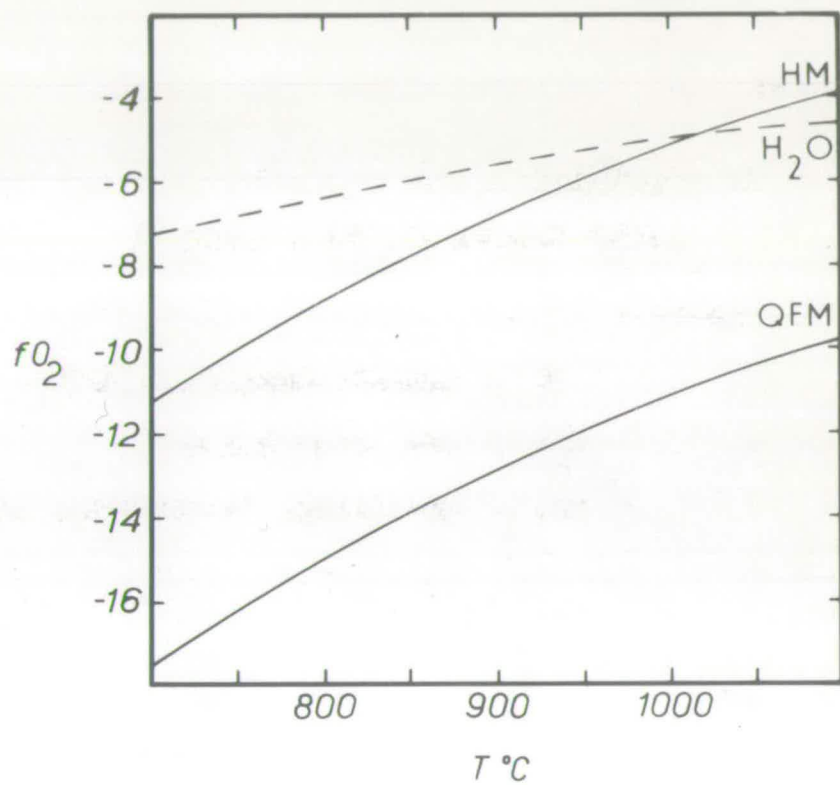


Figure 30

in equilibrium with the original ferrous/ferric iron ratios of 9 volcanic rocks (tholeiites, high-alumina basalts and andesites) are approximately 10^{-9} - $10^{-6.5}$ atm. at 1200°C , i.e. close to the QFM buffer. Direct determination of $f\text{O}_2$ on cooling Hawaiian tholeiite (Sato and Wright, 1966) indicates a value of approximately $10^{-8.5}$ atm. at liquidus temperatures, supporting Fudali's data, and $f\text{O}_2$ drops parallel to the QFM buffer with falling temperature. Evidence of initial crystallisation of calc-alkaline and other acidic rocks close to the QFM buffer at much lower temperatures (800 - 1000°C) and $f\text{O}_2$'s (10^{-11} - 10^{-15}) suggests that there is "no indication that the fugacity of oxygen remains constant during fractionation in the Cascade orogenic volcanic series" (Carmichael, 1967, p.60). It seems, therefore, that although an $f\text{O}_2$ of $\sim 10^{-8}$ is attained at basaltic liquidus temperatures it will fall during the crystallisation of most volcanic rocks, including calc-alkaline ones, in a manner suggesting that $f\text{O}_2$ is controlled either by a country rock buffer or by the internal buffering of the crystallising assemblages (i.e. type 1 crystallisation).

There are some examples of crystallisation under conditions of high, and relatively constant, $f\text{O}_2$, but all occur in closely sub-surface environments where water equilibrated with the atmosphere might have access to the magmas. Thus plutonic rocks in the cauldron subsidences of the Oslo Fjord (Czamanske, 1965) and Ben Nevis (Haslam, 1968), granites in the Sierra Nevada (Wones and Eugster, 1965) and some salic volcanic rocks from the western U.S.A. (Carmichael, 1967) show mineralogical features consistent with crystallisation under oxidising conditions. It has been inferred from experimental data (Muan and Osborn, 1956; Wones and Eugster, 1965) that fractional crystallisation of liquids at constant $f\text{O}_2$ will result in Mg-enrichment in the mafic minerals, instead of the more common Fe-enrichment, and the plutonic and volcanic rocks mentioned above show this feature since biotites and amphiboles become more magnesian in successive differentiates. There is no evidence for the occurrence

of a similar effect in the more basic rocks of these, or other, areas and Carmichael (1967) has pointed out that such evidence should be present in a series of rocks generated by a high fO_2 mechanism.

Carmichael's data (1967) showed that the oxide phases in most of the salic volcanics which he examined were equilibrated at or near to the QFM buffer, and that they were the first ferromagnesian phases to crystallise. This does not imply that the acid rocks were derived from more basic material by precipitation of oxides, the mechanism proposed by Osborn (1959, 1962); if the acid rocks are derived from basaltic liquids at depth they will have had a longer time to become equilibrated with the QFM buffer (if this is the country rock assemblage) than their basaltic parents, and will lie close to the buffer at liquidus temperatures. Basalts do not generally precipitate an oxide phase first (e.g. Yoder and Tilley, 1962, pp.383-4; Sato and Wright, 1966), which suggests that they are not on or above the QFM buffer at their liquidus temperatures, and that they reach this buffer only after precipitating olivine \pm pyroxene \pm plagioclase. Columbia River basalt, which contains oxide minerals only in the ground-mass, requires an fO_2 greater than that of the QFM buffer to precipitate magnetite first (Hamilton et al., 1964). Evidence that salic rocks initially equilibrated at or near QFM can therefore be construed as support for the concept of control of crystallisation under the influence of the country rock buffer assemblage, in a semi-open system.

The high fO_2 mechanism for derivation of the calc-alkali igneous suite (Osborn, 1959, 1962) is theoretically and experimentally valid under suitable conditions, and has been invoked by several workers (e.g. Best, 1963; Carmichael, 1964; Kuno, 1965; Taneda, 1966), but it appears that such conditions are not realised in nature. In addition to the arguments against the process presented above, T.H. Green and Ringwood have noted that "calc-alkaline rocks are not invariably strongly oxidised nor is there evidence for early

formed magnetite crystals" (1966, p.315), a conclusion emphasised by other workers (see Turner and Verhoogen, 1960, pp.272-288; Best and Mercy, 1967; Carmichael and Nicholls, 1967). There is no mineralogical evidence for the operation of the process in the Scottish Caledonian calc-alkali province; early oxide minerals are not present either in Shetland (Gill, 1965; pers. comm.) or in the Southwest Highland rocks (e.g. Appendix B). Because of the wide range of rock-types exhibited in the Scottish province, the lack of evidence from any part of the series in favour of "early" oxide mineral crystallisation must be considered a powerful argument against the mechanism.

It seems, therefore, that Osborn's high fO_2 hypothesis should be rejected as a major means of deriving the calc-alkali series from a basaltic parent. It may possibly operate in isolated instances (e.g. Thingmuli; Carmichael, 1964), although the magnetite which appears in such cases can probably be interpreted as an effect of another process (discussed below) rather than the cause of an Osborn-type evolution.

Hornblende fractionation and calc-alkaline evolution.

It has been pointed out that the calc-alkali series is characterised by an abundance of intermediate and acid rocks, a lack of iron-enrichment during fractionation and localisation within orogenic belts. From the water expected in orogenic belts Osborn (1959) derived high fO_2 to provide a possible mechanism for explaining the chemical features of calc-alkaline rocks. A more "direct" use of water content is applied in this section in an attempt to explain the calc-alkaline characteristics.

Osborn's high fO_2 process was concerned primarily with absolute removal of iron from the system. Oxidation, and precipitation of the iron as oxide was the method chosen, but it should be emphasised that oxidation as such is only a means of obtaining iron in a conveniently removable form and is not

a required characteristic of a calc-alkaline evolutionary process. Any method which will remove iron from the system, and increase SiO_2 concentration in the residual liquids, is germane to the problem.

In Chapter 6 it was concluded that pargasitic amphibole crystallised from kentallenite parent magma as a consequence of hydration of that magma at the base of the orogenic crust. Fractionation of highly undersaturated pargasite from a basaltic parent magma will drive residual liquids towards more siliceous compositions, and generate larger quantities of intermediate and acid rocks than would form from a basaltic parent under normal, dry, conditions. Amphiboles from ultrabasic and basic nodules in calc-alkaline rocks, probably representative of early deep-seated crystallisation, are pargasitic in composition (Engel, 1959; Gill, 1965; Yamazaki *et al.*, 1966) and contain much more iron than co-existing clinopyroxenes (Gill, 1965; Onuki, 1966), a feature that persists in calc-alkaline hornblendes to more acidic compositions (see Best and Mercy, 1967). It is not possible to determine directly whether or not the pargasitic hornblendes contain more iron than the magma from which they crystallised, but the relationship between the amphiboles and the general trend of evolution of non-accumulative calc-alkaline rocks can be depicted in AFM diagrams such as Fig. 31 (which is drawn for the Brae, Shetland, examples; data from Gill, 1965). AFM diagrams, it should be emphasised, depict only ratios, but not only do the pargasitic amphiboles (from Engel, 1959; Gill, 1965; Yamazaki *et al.*, 1966) plot towards the iron apex from the general trend in Fig. 31, they also contain a higher amount of iron than the rocks comprising the trend. The values of total iron (as FeO) of all the amphiboles and several of the rocks are inserted on Fig. 31, to show this feature.

In the Scottish Caledonian calc-alkali province, therefore, of which Brae is a representative example, a mechanism involving early fractionation

FIGURE 31

AFM diagram of Brae rocks

(cation percent)

Legend:

- 5.04 - Brae rock, 5.04%
total iron as FeO.
- 8.41, 8.74 - Amphiboles 5B, 5A
from Gill (1965).
- 10.76, 11.01, 11.41 - Amphiboles SG2, SG1 and
KJ1 from Yamazaki et al.,
(1966).
- 13.86, 15.10 - Amphiboles HM2, HM54 from
Engel (1959).

For discussion, see p.88.

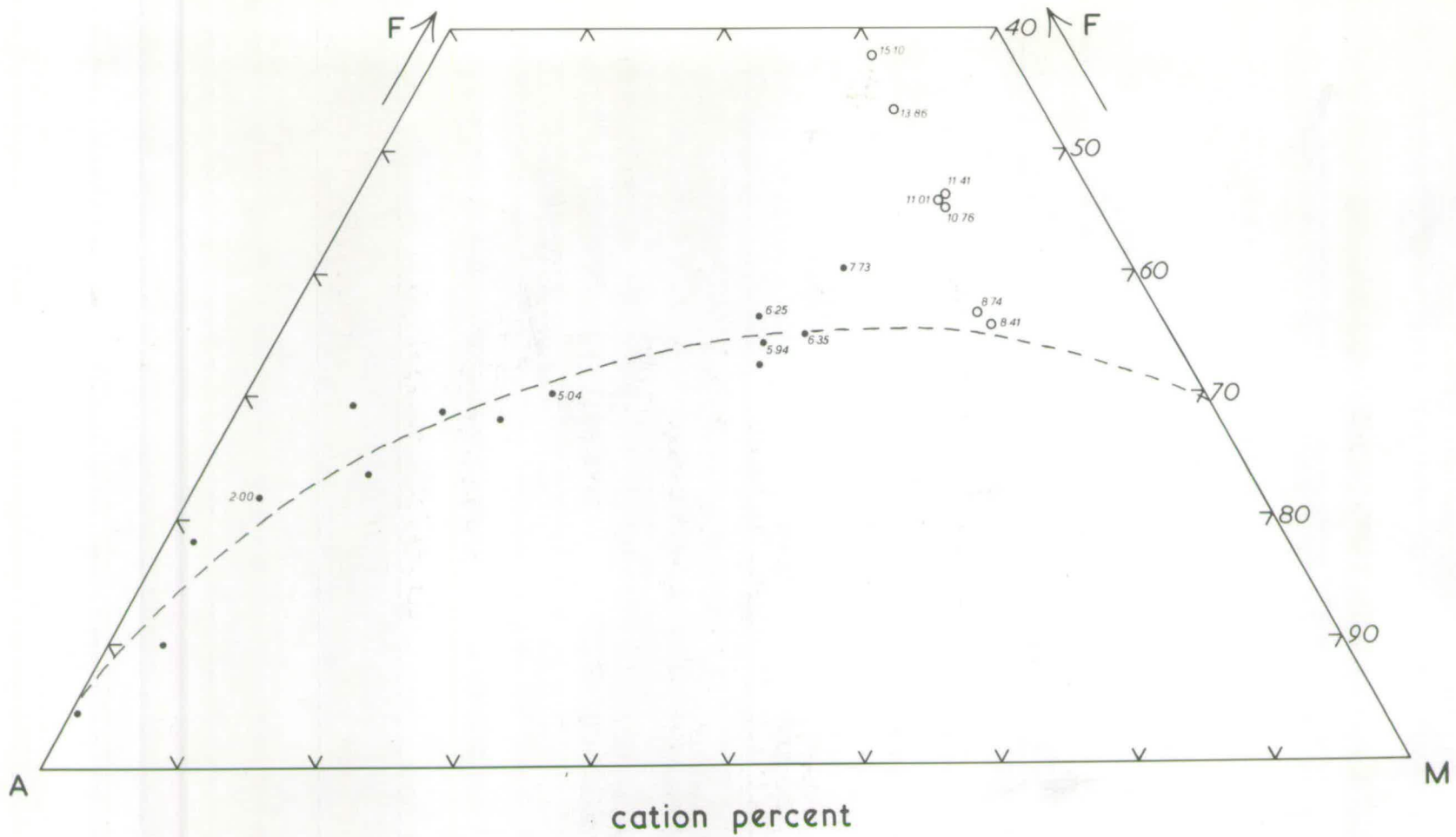


Figure 31

of pargasitic hornblende from a hydrous basaltic melt is competent to explain the large amounts of intermediate and acid rocks, and the lack of iron enrichment, which are the dominant characteristics of the calc-alkali suite.

A similar process has been proposed by Best and Mercy for the Guadalupe complex, California, but they pointed out (1967, p.470) that "this hornblende effect cannot account for all the chemical and mineralogical aspects of the calc-alkaline trend". The writer would agree with this comment, but believes that early crystallisation of pargasite in the manner proposed above is the method most likely to be effective in the development of the major features of the calc-alkali suite from parental basalt.

Tilley (1950) considered such an hypothesis for the origin of the calc-alkali series, but rejected it because of lack of evidence for hornblende crystallisation as a general process in calc-alkaline evolution. Discussion in Chapter 6 has shown that this lack is to be expected because of breakdown of the amphibole. Principal component analysis of chemical data may provide some indication of pargasite crystallisation, but careful search in the more basic members of calc-alkali provinces should disclose some xenoliths or xenocrysts of amphibole or its breakdown products. If found (as in Japan and Shetland), they would be qualitative confirmation of the proposed mechanism.

APPENDIX AFIELD RELATIONSHIPSKentallen (Fig. 32)

The Kentallen body, approximately 1/3 mile long and 1/4 mile wide, is intruded into Dalradian rocks of the Cuil Bay Synform (Bailey, 1960, p.42). Since the intrusion of kentallenite the country rocks (Appin Phyllites) have been metamorphosed in the thermal aureole of the Ballachulish granite with production of cordierite, which has overprinted and obliterated any contact metamorphism due to the kentallenite. In otherwise unmetamorphosed areas, however, kentallenite may produce cordierite-bearing hornfelses and, rarely, evidence of partial melting (e.g. Barnamuc; Platten, 1966) in the country rocks.

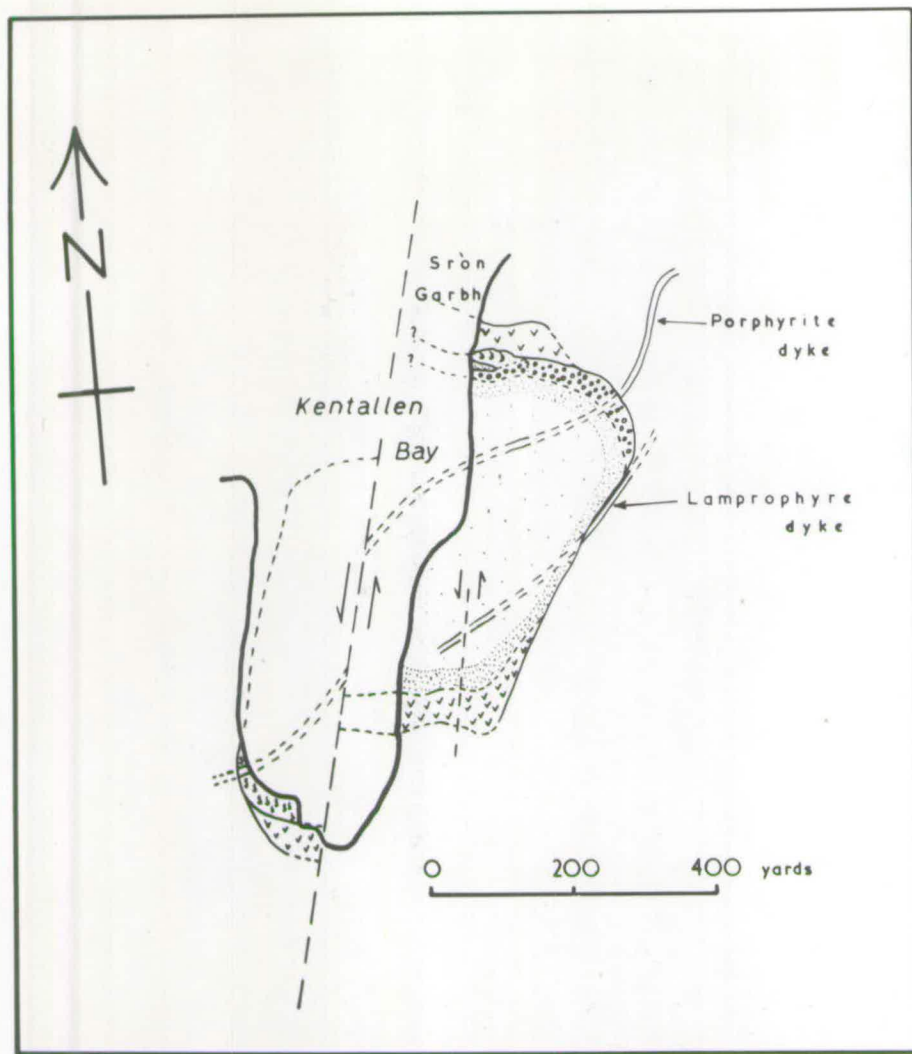
Several faults (see Fig. 32) cut the intrusion, causing a variable degree of shattering; the sinistral fault in Kentallen Bay (throw approx. 150 yards) has severely brecciated that part of the Kentallen intrusion lying west of the bay whereas the sinistral fault in the railway cutting (throw approx. 5 yards) causes little obvious disturbance. Numerous lamprophyre and porphyrite dykes cut the intrusion. Exposure of the kentallenite is good in the rail and road cuttings, and at the northern and southwestern margins; elsewhere it is poor, because of glacial drift cover.

Contact relationships.

The northern contact of the Kentallen intrusion displays the age relationships between kentallenite, lamprophyre and granite, and will be described in detail. At Sròn Garbh, on the shore of Loch Linnhe below the small railway cutting, chilled kentallenite is cut by a lamprophyre dyke, which is in turn cut by granite veins (probably from the Ballachulish body; Figs. 33 and 34), giving the age sequence kentallenite-lamprophyre-granite

FIGURE 32

Field map of the Kentallen intrusion



Legend







- 
Brecciated country rock
- 
Marginal diorite
- 
Picritic facies
- 
Fine-grained kentallenite
- 
Fault-shattered kentallenite
- 
"Normal" medium-grained kentallenite

Figure 32

(cf. Bowes, 1962). The lamprophyre dyke which cuts the chill can be followed through the chill into the kentallenite picrite (Figs. 33 and 34), and is mineralogically distinct from the chill. Bowes (1962) thought this dyke to be an apophysis of the chill, itself misidentified as lamprophyre. To the north of the chill an intrusion of appinitic diorite, also cut by the lamprophyre and granite veins, contains xenoliths of chilled kentallenite (Fig. 33, Plate 1). It is thus younger than the kentallenite, an age relationship that was not recognised by Bowes (1962) or Bowes and Wright (1967). The diorite also contains xenoliths of quartzite (Plate 2) mineralogically identical to the Appin Quartzite which lies at a depth of 500-800 ft. beneath this outcrop, and these xenoliths must have been carried up that distance. The Appin Phyllites to the north of the contact with diorite are severely folded and shattered for a distance of approx. 10 yards, and some igneous material has been introduced to them (Fig. 33). The shattering is similar to that seen in the explosion breccia at Back Settlement (Bowes and Wright, 1961), and is attributed to gas streaming. To the south of the chill a kentallenite picrite separates the chill from more normal kentallenite, a feature observed elsewhere along the northern, and possibly southern, margins of the body.

These features suggest the following sequence of events:

intrusion of kentallenite as a "damp" crystal mush, the chilled outer margins being depleted in olivine and diopside phenocrysts before consolidation by a process of flowage differentiation (Smith and Kapp, 1963) to give rise to the near marginal kentallenite picrite (see Chapter 3); crystallisation of olivine and diopside from kentallenite magma at depth in the pipe within an impervious "envelope" of crystalline kentallenite, resulting in build up of volatile pressure (see Chapter 6); fracture of the "envelope" at depth and subsequent gas streaming and intrusion of the diorite to the north of the contact, brecciating the country rock and carrying up xenoliths of quartzite

FIGURE 33

Map of Northern contact at Sròn Garbh, Kentallen

FIGURE 34

Detail of part of Figure 33

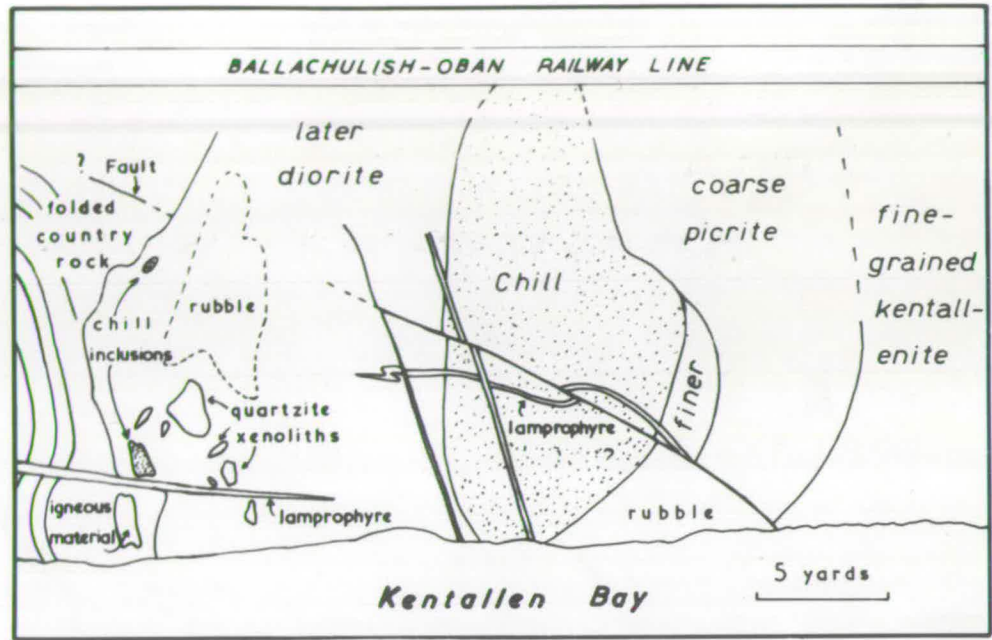


Figure 33

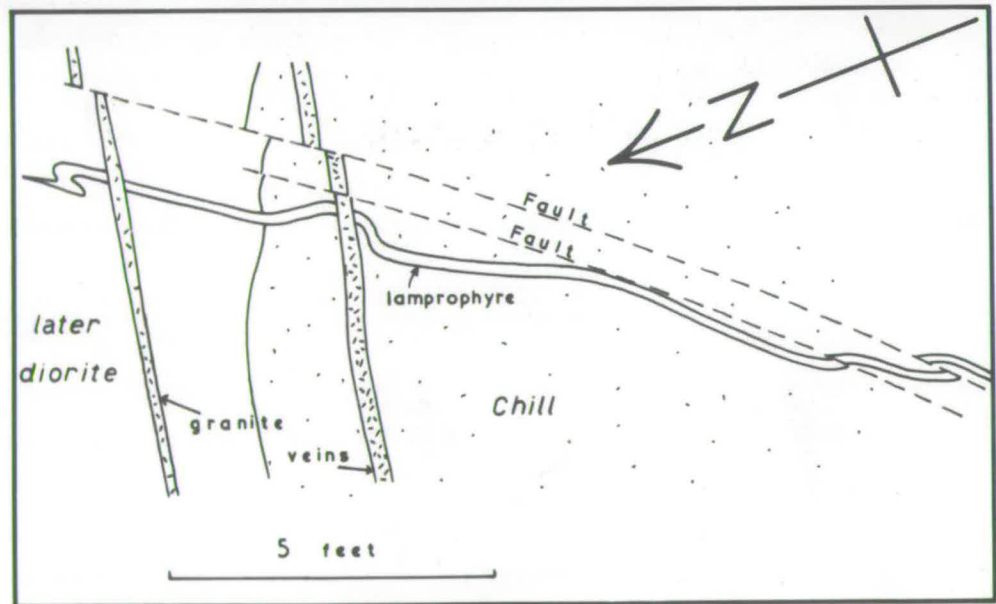


Figure 34

PLATE 1

Chilled kentallenite inclusion in appinitic diorite, North contact, Kentallen.

Scale given by 2 lb. hammer.

PLATE 2

Xenoliths of Appin Quartzite in appinitic diorite, North contact, Kentallen.

Scale given by 2 lb. hammer.

PLATE 3

Chilled kentallenite inclusions in diorite breccia, Scalasaig, Colonsay.

Scale given by 2 lb. hammer.

PLATE 4

Xenoliths of country rock phyllite in diorite breccia, Scalasaig, Colonsay.

Scale given by 7 lb. hammer.



PLATE 1



PLATE 2



PLATE 3



PLATE 4

and kentallenite chill; intrusion of lamprophyre dyke after consolidation of the diorite; intrusion of granite veins.

The eastern contact of kentallenite with the country rock is complicated by the later intrusion of a lamprophyre dyke along part of it (Fig. 32). The Appin Limestone outside the contact is thermally metamorphosed to a skarn composed of variable proportions of forsterite, diopside, grossular, spinel and wollastonite, but it is not possible to determine the relative importance of kentallenite and lamprophyre in the production of these assemblages. No larnite, spurrite or tilleyite were found in the skarns. Calc-silicate skarns also occur at the southern end of the intrusion, which is poorly exposed and confused in detail. Some chilled kentallenite, possibly erratic, occurs "inside" (i.e. to the north of) these skarns.

The southwest portion of the Kentallen intrusion is severely shattered by a fault, probably associated with the Great Glen Fault, which passes through Kentallen Bay, but the rock-types present can be identified as kentallenite despite alteration. There is also evidence of gas streaming and brecciation in this area, and the contact is obscure; the western contact lies beneath Kentallen Bay. Bowes and Wright (1967) do not observe the fault, but they identify a new pipe, St. Moluag's pipe, to the south of Kentallen Bay; the exposures which comprise this pipe are all glacial erratics, probably derived from the main Kentallen intrusion.

Internal variation.

No systematic internal variation has been detected within the Kentallen body, with the exception of slight increase in biotite content centrally. Rare aplite veins (composed of biotite and microperthite) are evident in erratics near the eastern contact, and some rocks near the northeastern margin show evidence of late-stage gas streaming, with the development of pale amphibole

from pyroxene and olivine. Small impure dolomite xenoliths, metamorphosed to Forsterite-Diopside-Spinel assemblages (pseudo olivine nodules), are occasionally present internally.

Ardsheal Hill

The summit complex of Ardsheal Hill (Walker, 1927) was visited to collect chilled kentallenite for analysis. No attempt to map the complex was made.

Duror

The kentallenite at Duror, south of Kentallen, is severely altered and shattered by the southward continuation of the Kentallen Bay Fault. One sample was collected for analysis, but no mapping was undertaken.

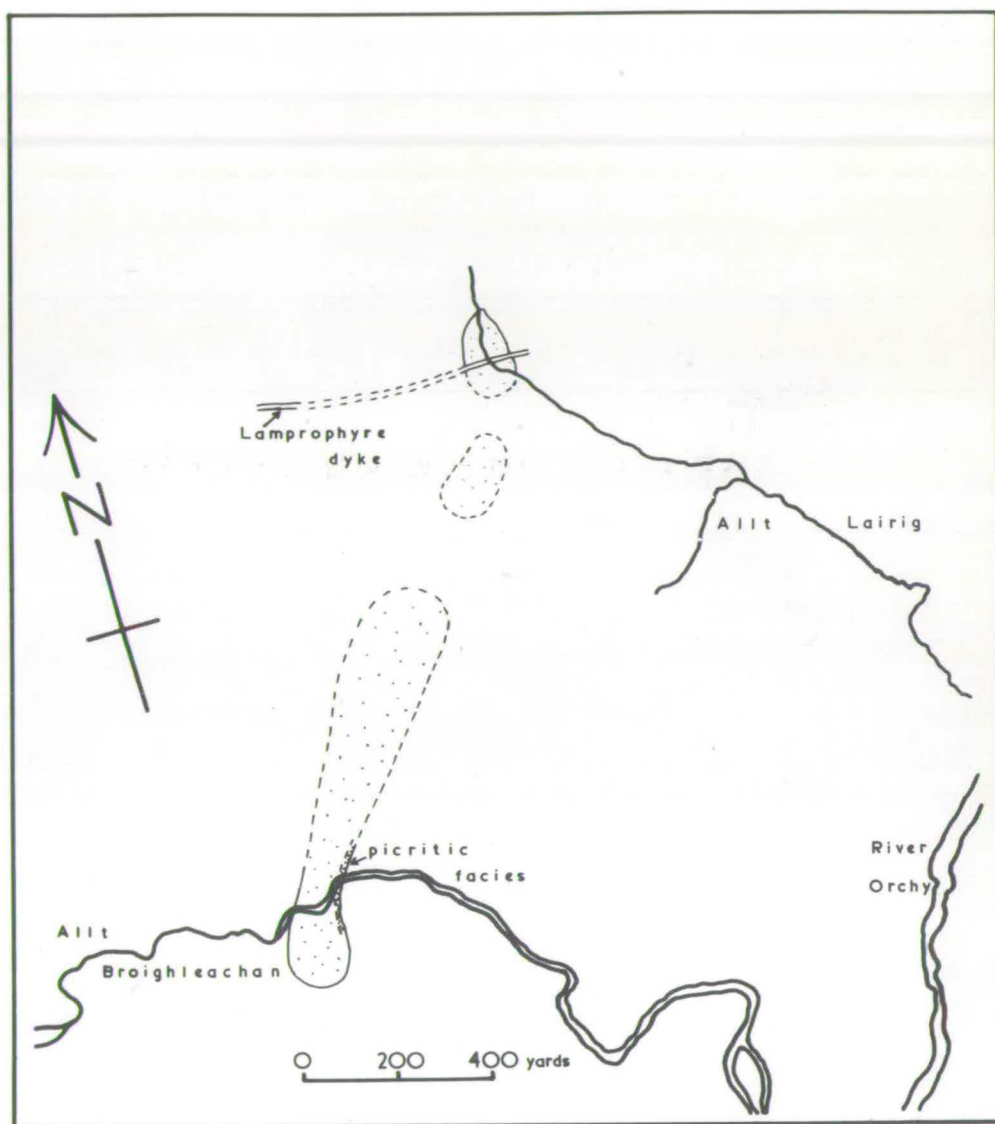
Glen Orchy (Fig. 35)

With the exception of a stream section through part of the mass, the Glen Orchy kentallenite is very poorly exposed. Glaciation of Glen Orchy was intense, and boulders of kentallenite, almost certainly derived from Glen Orchy have been found in Dalmally, approximately 8 miles southwest of the area. Glaciated pavements, with perched blocks, also occur south of the main intrusion. Mapping can therefore be performed only where stream erosion shows rocks to be in situ.

Available evidence indicates that there may be three separate intrusions in Glen Orchy, possibly parts of a "fingered" sheet, aligned approximately parallel to Glen Strae (Fig. 35), but only the northern and southern masses are clearly in situ. The most southerly mass, which outcrops in Allt Broighleachan, may be up to $\frac{1}{2}$ mile long and 100 yards wide, but the size of the northern mass, occurring in a corrie on Lairig Hill, is indeterminate and complicated by brecciation. There is considerable net-veining of

FIGURE 35

Field map of the Glen Orchy intrusions



Legend


 Probable limit of kentallenite outcrop.

Figure 35

the Dalradian country rock, attributed to gas streaming, close to the margins of the kentallenite intrusions, and the country rock is hornfelsed for up to 30 yards from the contacts; cordierite is sparsely developed within this zone.

The eastern contact of the most southerly kentallenite body is faulted against hornfels, and the fault continues to the north along the eastern contact, causing severe shattering and brecciation in the most northerly mass. An east-west lamprophyre (vogesite) dyke cuts through the northern mass in the corrie; no other dykes can be seen to cut the kentallenite.

Contact relationships.

The western contact of the southern body is sharp, and abuts against breccia, but all other contacts of kentallenite with the country rock are faulted or unexposed. It is probable that the kentallenite "sheet" dips steeply to the west, but meaningful measurements of the angle of dip cannot be made. Chilled kentallenite is present in erratic blocks, and a marginal picrite similar to that at Kentallen occurs in situ at the eastern, lower, margin of the body. The picrite may have formed partly by crystal settling in the inclined kentallenite sheet rather than by flowage differentiation, since there is no equivalent on the western, upper, side of the mass (cf. Kentallen).

Brecciation of the country rocks by gas streaming occurs at the western contact, and is closely connected with net-veining. Although the brecciation is not so severe as that at Kentallen it is more widespread, and the difference in degree may be attributed to the more psammitic rock-types of Glen Orchy, which would fracture less easily than the phyllites at Kentallen.

Internal variation.

The stream section through the more southerly kentallenite body

in Glen Orchy shows a transition from picrite at the eastern end to a leucocratic kentallenite at the western end, a sequence also evident in the chemical data (Chapter 3). Although some of the features of this variation may have been inherited from depth (see Chapter 6), the sequence seen in the stream section may be largely the result of high level fractionation, particularly of olivine and clinopyroxene.

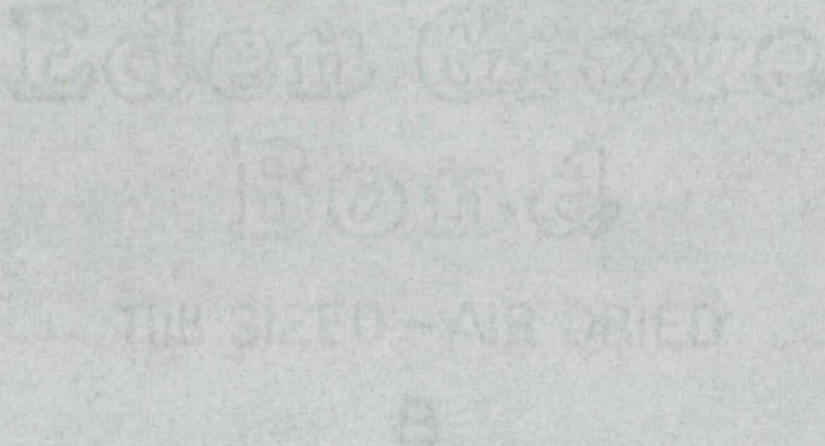
The kentallenite in the stream section occasionally contains rounded xenoliths, approximately 1 foot in diameter, of finer grained kentallenite, which show a greater amount of orthopyroxene reaction product after olivine in thin section than the more coarse grained host. They may be pieces torn or foundered from an early crystallising, dry, kentallenite liquid (cf. Chapter 2), possibly parts of a chilled phase. Aplite veins, identical to those occurring at Kentallen, are found in the middle intrusion, and are the most 'evolved' rock occurring in Glen Orchy. The most northerly body is in a similar state of alteration to the southwest part of the Kentallen intrusion; consequently no chemical work has been performed on it, but thin section examination confirms that it is kentallenite.

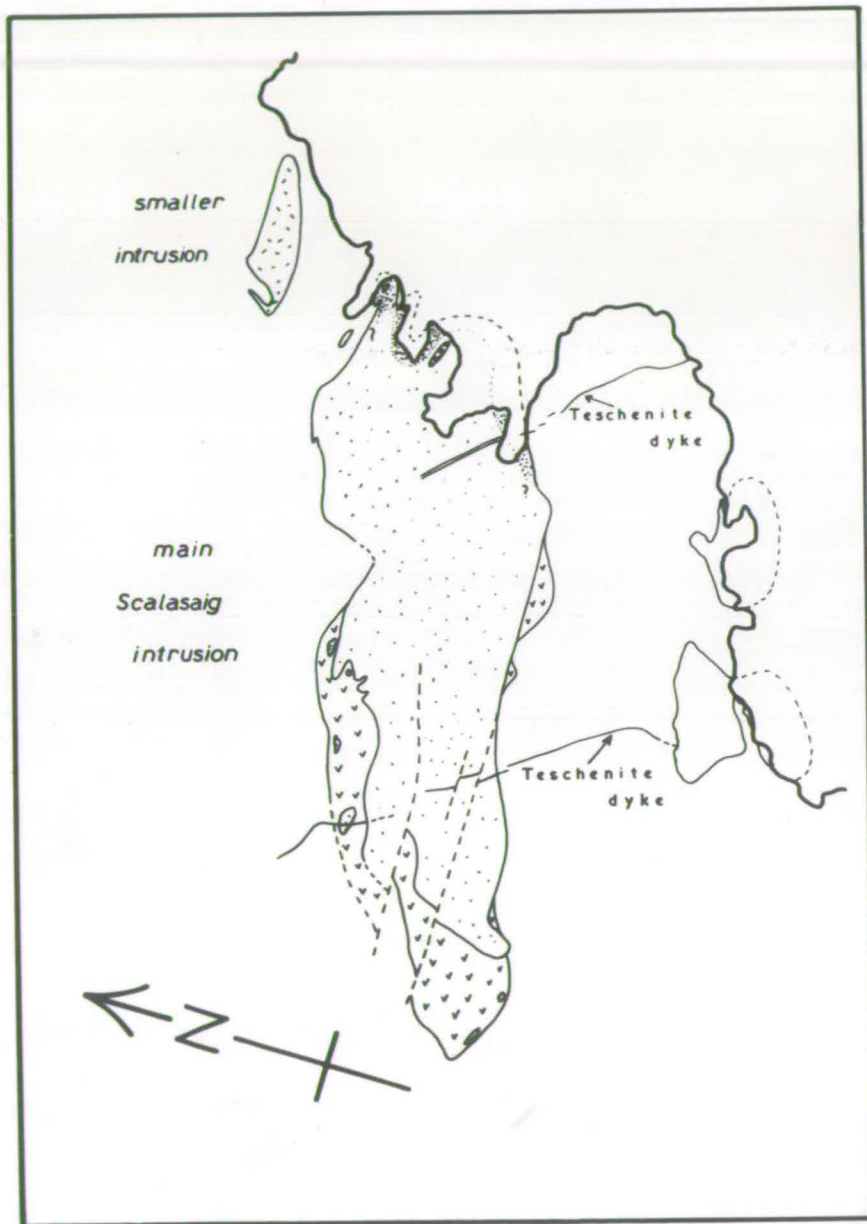
Colonsay (Fig. 36)

Three intrusions have been examined in Colonsay, two at Scalasaig in the centre of the island and one at Balnahard in the north. All are intruded into Torridonian sedimentary rocks, and garnet and cordierite may be developed within their thermal aureoles. The largest of these intrusions, the main Scalasaig augite-diorite (Fig. 36) is elliptical in shape and is exposed for approximately $3/4$ mile from east to west, and $1/4$ mile from north to south. The smaller Scalasaig mass, which lies to the north of the main body (Fig. 36), is only $1/6$ mile long, and the poorly exposed Balnahard kentallenite is approximately $1/3$ mile across.

FIGURE 36

Field map of the Colonsay intrusions





Legend






-  Brecciated country rock
-  Chilled kentallenite
-  "Normal" kentallenite
-  Augite - diorite
-  Appinitic diorite.

Figure 36

Post-intrusion faulting is well developed in the main Scalasaig mass and glacial erosion has exploited the fault planes, creating gullies visible in aerial photographs. Teschenite (= crinanite of Craig et al., 1911) dykes cut the main intrusion at Scalasaig, and a lamprophyre (vogesite) dyke is closely associated with the Balnahard body. The main mass at Scalasaig, upon which most work was performed, is described in detail; the smaller Scalasaig intrusion, and the Balnahard kentallenite, were sampled but not mapped, partly because of poor exposure.

Main Scalasaig intrusion

Contact relationships.

Chilled phases of kentallenite are well developed at the eastern and northern contacts of the main Scalasaig intrusion. That on the eastern margin is very wide (approx. 50 yards) and may be dipping at a shallow angle to the west, lying just inside the margin of the intrusion. Part of the eastern contact with the country rocks may be present on the headland at the north-eastern end of the intrusion, but the chill contains inclusions of phyllites (showing 2nd folds; contrast Wright, 1908) and larger rafts of limestone in this area, and the "contact" may be merely the western margin of a 'raft' of country rock. The eastern limit of the intrusion is, however, probably close offshore. Chills are poorly represented on the southern and western margins of the intrusion, but they may have been sheared out or brecciated by the fault present along the southern margin.

Outside the contacts, particularly on the northern and western margins, a diorite breccia is intruded, and blocks of quartzite are caught up in it, and in the chilled phases of the main intrusion, in a similar manner to their occurrence in the marginal diorite at Kentallen. Reynolds (1936)

observed abundant quartzite xenoliths in the Kiloran Bay syenite, on the west coast of Colonsay, which she attributed to uplift from depth by fluidisation or gas streaming. It has been shown, however (Craig et al., 1911; Stewart, 1962), that the Colonsay Torridonian succession does not contain quartzite, and that its base rests upon Lewisian gneiss in the north of the island. If the Lewisian gneiss is in situ, and is not a thrust slice (see Stewart, 1962), there can be no quartzite at depth and it cannot have ascended in either the Kiloran or Scalasaig pipes; it must therefore have descended from an overlying horizon, since eroded. The most likely source for the xenoliths is the Islay Quartzite outcropping to the south on Islay and Jura, which might have overlapped Colonsay at the time of pipe formation. Comparison of the xenoliths with Islay Quartzite** supports the possibility of their derivation from that horizon, but there is not enough mineralogical evidence to confirm it.

The diorite breccia, which contains xenoliths of chill (Plate 3) and country rock phyllite (Plate 4) in addition to quartzite, may be quite local in extent, and the limit marked in Fig. 36 is the outer limit within which brecciation may occur. The occurrence of quartzite as xenoliths in the chilled phase of the main Scalasaig intrusion, and of the chilled phase as xenoliths in the diorite breccia, suggests two "generations" of brecciation and gas streaming, one contemporaneous with initial intrusion, the other later. Faulting within the intrusion is post-brecciation in age.

A hornblendic "picritic" facies may occur locally inside the chill, but it is not as well developed as at Kentallen; thin section examination shows it to be largely an alteration product of near-marginal kentallenite.

** Supplied by J.L. Roberts, Newcastle-upon-Tyne.

Internal variation.

The main Scalasaig intrusion shows an inward transition from marginal olivine- plus clinopyroxene-bearing chill through true kentallenite to augite-diorite (whose pyroxenes become progressively overgrown with hornblende towards the centre of the intrusion), which probably results from differentiation in situ. Biotite and orthoclase also increase in abundance towards the centre, reflected by a slight increase in potash content (Appendix C). Crystallisation at depth (Chapter 6) may have controlled compositional variation in the intruded liquid, or liquid-crystal mush, but high level fractionation has probably been important in producing the observed gradation within the intrusion.

Fresh kentallenite occurs only immediately 'inside' the chill at the eastern end of the intrusion; elsewhere it is absent or severely altered.

Small Scalasaig intrusion

This body, which lies approximately 300 yards north of the main Scalasaig intrusion, crystallises hornblende and biotite as the only ferromagnesian minerals and is thus appinitic (cf. Bailey *et al.*, 1916; Bailey, 1960). The intrusion hornfelses the country rock flags, chills slightly against them, and becomes amphibolitic in parts internally. Four samples were collected for analysis.

Balnahard

Exposure of the Balnahard kentallenite is extremely poor, being confined to the southern margin and occasional knobs rising above the raised beach deposits to the north. An altered chill is present, and the country rocks have been metamorphosed with the production of garnet and cordierite. One sample was collected for analysis.

APPENDIX BPETROGRAPHY OF THE MINERALS

This appendix consists of petrographic descriptions of the minerals of kentallenite, but no mention is made of their chemistry since this has been treated in Chapter 2. Modal mineral contents of the analysed rocks and a summary of their petrographic characteristics are presented in table form following the chemical data of Appendix C (Tables 15 and 16).

Mineral descriptionsOlivine.

Olivine generally appears black in hand specimen, due to exsolution of magnetite in minute spidery plates flattened parallel to (100) of the olivine crystals (Plate 5; cf. Judd, 1885; Brown, 1956). Magnetite is also present in cracks throughout the olivine, and both occurrences are ascribed to post-crystallisation oxidation of olivine, probably the result of thermal metamorphism (Chapter 2). The unzoned olivine phenocrysts (up to 4 mm in diameter) are usually rounded or subhedral in central parts of the intrusions (Plate 6), probably as a result of reaction with the liquid to form orthopyroxene (rare) or biotite, but they may be euhedral, and occasionally skeletal, in chilled margins (Plate 7). Olivine may rarely be enclosed, partly (Plate 8) or completely (Plate 9), by clinopyroxene and since enclosure of clinopyroxene by olivine is not observed this indicates that olivine started to crystallise first.

In unchilled kentallenite olivine may exhibit a corona structure against plagioclase, usually composed of two rims, the inner one invariably of orthopyroxene and the outer of hornblende and, often, biotite (Plate 10); no

PLATE 5

Exsolution of magnetite within olivine.

Scale bar = 0.1 mm.

PLATE 6

Rounded olivine in normal kentallenite.

Scale bar = 1 mm.

PLATE 7

Euhedral olivine in chilled kentallenite.

Scale bar = 1 mm.

PLATE 8

Olivine partly enclosed by clinopyroxene.

Note lack of corona on the enclosed part of the olivine.

Scale bar = 1 mm.

PLATE 9

Olivine completely enclosed by clinopyroxene.

Note absence of corona.

Scale bar = 1 mm.



PLATE 5

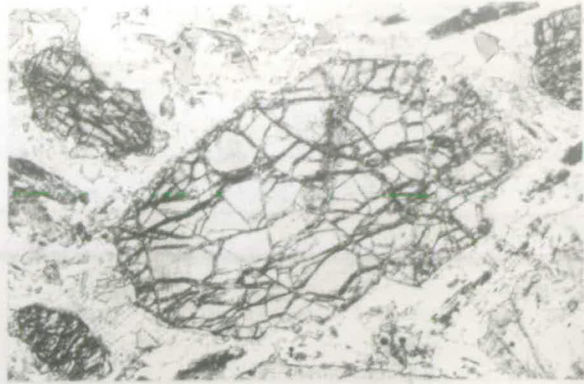


PLATE 6

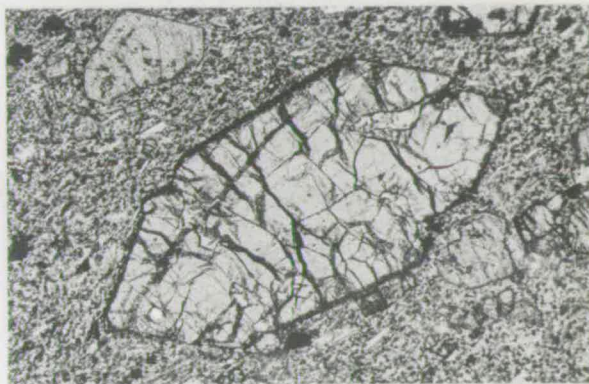


PLATE 7

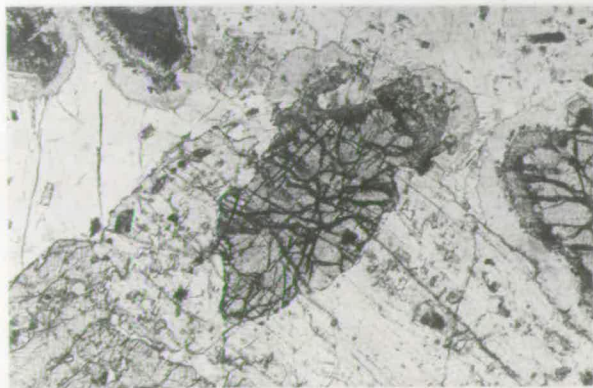


PLATE 8

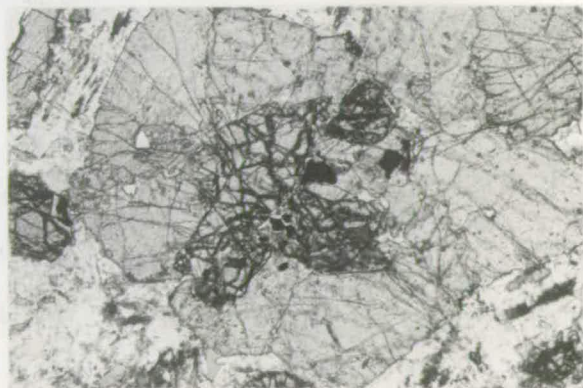
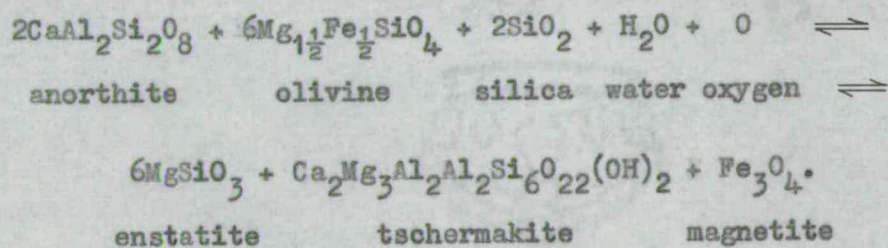


PLATE 9

spinel occurs in these coronas (contrast, for example, Mason, 1967). Sometimes only one rim is developed, which is then composed of hornblende (cf. Murthy, 1958). Of these rims the orthopyroxene is derived largely from the olivine and the hornblende predominantly from the feldspar, and reaction must have taken place in the solid state since not only do the rims form exclusively at plagioclase-olivine interfaces but they are interrupted by (Plate 11), and may not form beneath (Plate 12) pre-existing biotite moulded onto the olivine. The outer hornblende rim usually contains granular orthopyroxene at its inner margin (see Plate 12), but not if it is the only rim present. There appears to be a positive correlation between the occurrence of exsolution of magnetite within the olivine and development of the corona structures, suggesting a genetic connection, and a possible origin could involve introduction of silica, water and excess oxygen during thermal metamorphism resulting in reaction according to the equation:



Electron probe analysis (cf. Mason, 1967), which has not been performed, might help to verify this reaction.

Development of small, anhedral, orthopyroxene crystals as a result of reaction between olivine and the magma is occasionally observed, most commonly in fine-grained inclusions within the Glen Orchy mass (Appendix A). Orthopyroxene is never a primary phase in kentallenite.

Alteration of olivine to tremolite-actinolite may be observed

PLATE 10

Double corona on olivine.

The lighter, outer, corona is composed of amphibole, the darker inner one of orthopyroxene.

Scale bar = 1 mm.

PLATE 11

Interruption of hornblende rim by biotite moulded onto the olivine

Note that the orthopyroxene rim is still present.

Scale bar = 1 mm.

PLATE 12.

Absence of rims beneath pre-existing biotite.

The centre of this plate shows a "triple" corona of orthopyroxene-granular orthopyroxene-hornblende. To the right and left of this area no rim is formed beneath the enclosing biotite, the orthopyroxene rim thinning gradually to the right, more abruptly to the left.

Scale bar = 1 mm.

PLATE 13

Radial cracks in feldspar round partially serpentinised olivine.

Scale bar = 1 mm.



PLATE 10

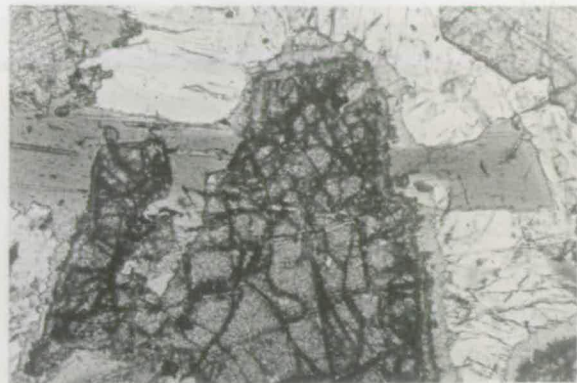


PLATE 11

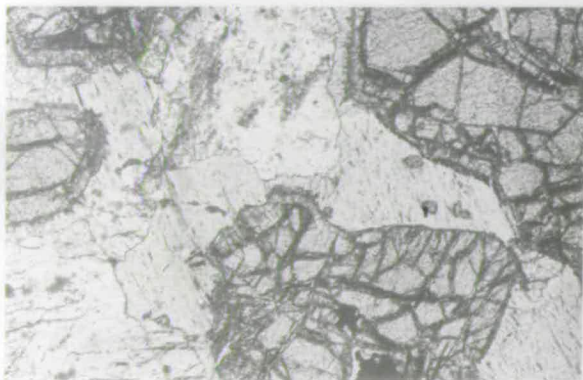


PLATE 12



PLATE 13

in chilled kentallenite, due to later marginal hydrothermal activity. Serpentinisation is rare, and appears to result from weathering processes close to the surface; cracks radiating from serpentinised olivines across, for example, feldspar (Plate 13), indicate that the serpentinisation is not a constant volume process.

Augite.

The pale green augite of kentallenite is usually euhedral, both in chills (Plate 14) and the more coarsely crystalline rocks (where it may reach a size of 4-6 mm), but it may be rounded and partly replaced by hornblende, particularly in Colonsay. Broken crystals (Plate 15) are common, and indicate the possibility of intrusion of kentallenite as a crystal mush, and meshworks of olivine and clinopyroxene, indicative of accumulation, are occasionally visible in thin section. Augite may also occur in glomeroporphyritic aggregates (Plate 16), when it may be twinned; otherwise twinning is rare.

Thin oscillatory zones, possibly due to repeated supercooling and crystallisation, may be observed at the margins of the crystals, but their cores are generally homogeneous. Electron probe traverses across augite crystals from core to margin show gradual increases in Fe/Mg ratio, with no detectable variation in Calcium content. Transition from the core to the marginal zoning may be marked by a zone of inclusions of the other minerals, most commonly olivine (Plate 17; cf. Platten, 1966), and occasionally an augite individual may be completely "spongy" with inclusions (Plate 18). The inclusions may result from trapping of interstitial liquid within the pyroxene during rapid growth (possibly in chilling), and its subsequent crystallisation within the mineral. Such a process would account for the occasional euhedral biotite terminations observed in such inclusions (Plate 19), but cannot explain the annuli of olivine crystals which may occur in (see Plate 17) or around (Plate 20)

PLATE 14

Euhedral augite in chilled kentalenite.

Scale bar = 1 mm.

PLATE 15

Broken pyroxene crystal.

Note the abrupt terminations of the zones, indicative of fracture.

Scale bar = 1 mm.

PLATE 16

Glomeroporphyritic aggregate of augite crystals.

Scale bar = 1 mm.

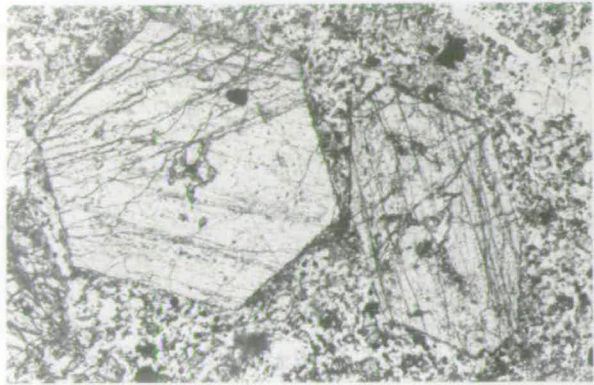


PLATE 14



PLATE 15

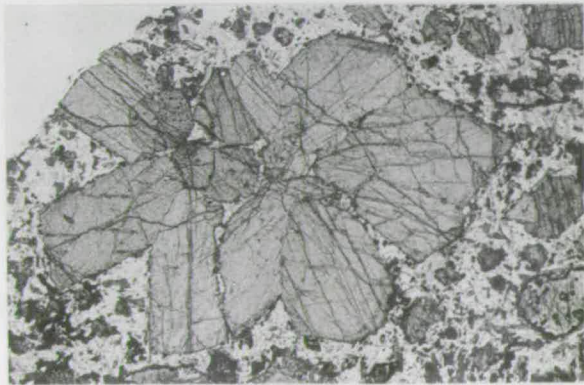


PLATE 16

PLATE 17

Annular zone of olivine inclusions in augite.

Scale bar = 1 mm.

PLATE 18

'Spongy' pyroxene.

Scale bar = 1 mm.

PLATE 19

Euhedral biotite terminations within 'spongy' pyroxene.

Scale bar = 0.1 mm.

PLATE 20

Annulus of olivine crystals around augite individual.

It is possible that this is an intermediate stage in the generation of the zones of inclusions such as those seen in Plate 17.

Scale bar = 1 mm.



PLATE 17

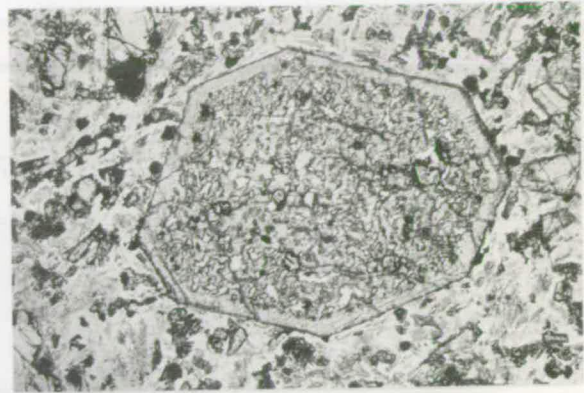


PLATE 18

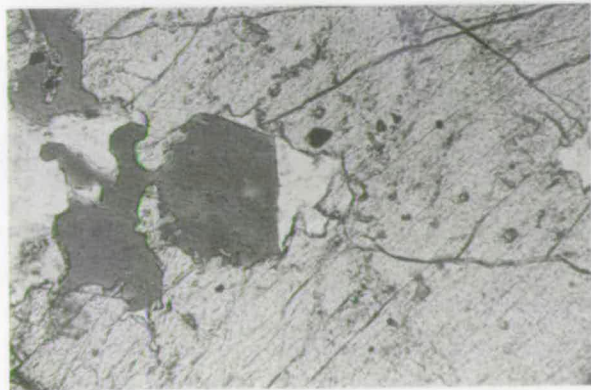


PLATE 19

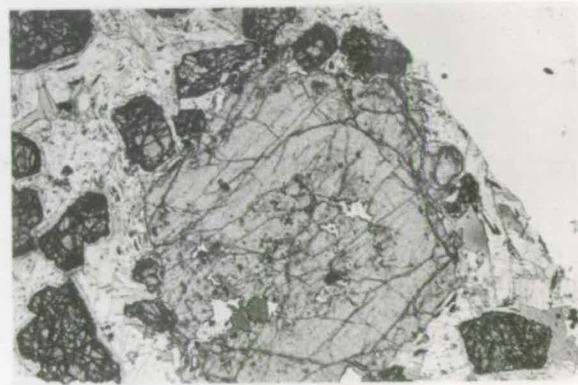


PLATE 20

augite individuals; these seem to result from growth of olivine directly onto the surface of the pyroxene, and probably require very stable conditions for their formation.

Alteration of augite to hornblende or fibrous amphibole is frequent in Colonsay and in hydrothermally altered chills at Kentallen, but is scarce elsewhere.

Hornblende.

Amphibole occurs at Kentallen and Glen Orchy only as a rare magmatic alteration product of augite, and is pale green in colour, but is more abundant in Colonsay where a dark green to green-brown hornblende may occur as the primary mafic phase in place of augite. When replacing augite, hornblende often mimics the pyroxene habit (Plate 21), occasionally to the extent of duplicating twinning (Plate 22). This replacement is often structurally controlled, the pyroxene and amphibole sharing $[010]$ and $[001]$ crystallographic axes. Rhythmic overgrowths of tremolite-actinolite, attributed to crystallisation under conditions of successive build-up and release of pressure (Bowes *et al.*, 1964), grow occasionally on primary or secondary hornblende (Plate 23).

Peculiar aggregates of pyroxene crystals, often with feldspathic "cores" (Plates 24-27), occur occasionally in kentallenite, particularly in the chills, and may be breakdown products of some pre-existing mineral. They differ from the glomeroporphyritic aggregates of Plate 16 in their finer grain size and lack of zoning and in the absence of euhedral outgrowths to the pyroxene individuals. Occasional six-sided aggregates (Plate 27) suggest that the original mineral may have been amphibole, and discussion in Chapter 6 has shown that amphibole would be expected to break down in the relatively dry environment of high level kentallenite crystallisation. To satisfy the conditions of the petrogenetic model proposed in Chapter 6, however, these

PLATE 21

Hornblende replacement mimicing the original pyroxene terminations.

The central part of the crystal is unaltered augite.

Scale bar = 1 mm.

PLATE 22

Replacement hornblende duplicating twinning in 'host' augite.

The section is arranged such that the darker part of the central twin (in hornblende) is distinct from the lighter part (in pyroxene).

Scale bar = 1 mm.

PLATE 23

Rhythmic amphibole overgrowths.

Scale bar = 1 mm.



PLATE 21



PLATE 22

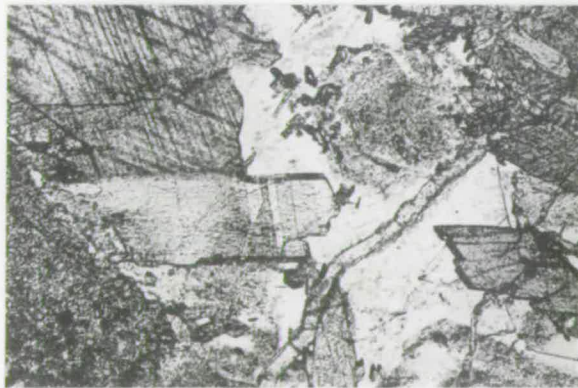


PLATE 23

PLATE 24-27 (inclusive)

Possible breakdown products of amphibole.

Scale bars = 1 mm.

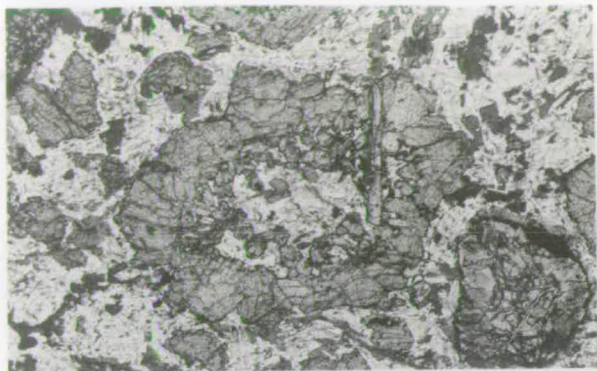


PLATE 24

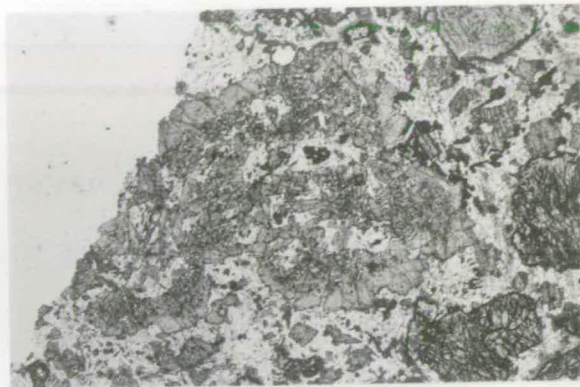


PLATE 25

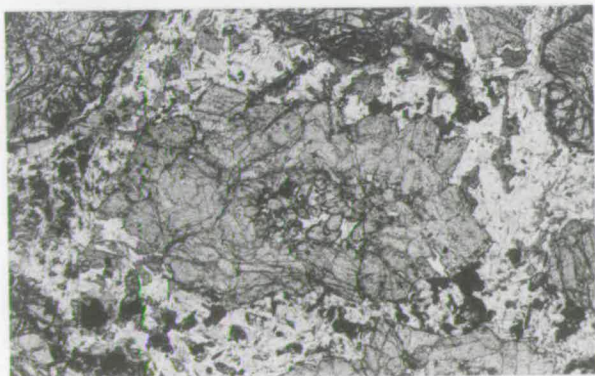


PLATE 26

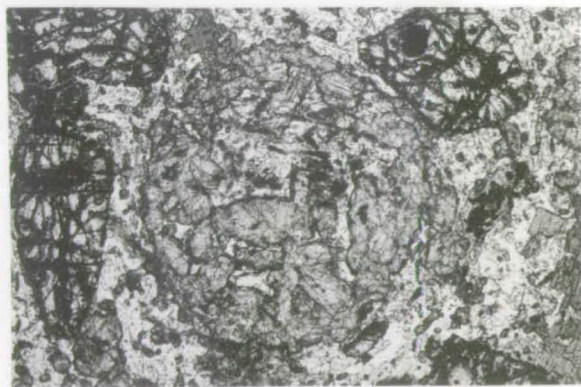


PLATE 27

aggregates should represent the breakdown of pargasite, and should contain nepheline or spinel. These undersaturated phases have not been found but, as discussed in Chapter 6, potential spinel or nepheline might have been removed from the amphibole (or saturated with SiO_2) during breakdown. Electron probe examination should aid in the interpretation of these aggregates. It has been noted that pargasite is unstable in the presence of quartz (Boyd, 1959; Deer *et al.*, 1963a) and would break down to diopside + enstatite + labradorite. However kentallenite liquids are not siliceous enough to produce this assemblage, and since pargasite is thought to have crystallised initially from the kentallenite parent magma, subsequent breakdown to this assemblage in that liquid cannot be proposed.

Biotite.

Reddish-brown biotite is characteristically poikilitic in kentallenite, and may develop this texture to such an extreme as to appear in thin section as a group of physically isolated individuals in optical continuity. Biotite is usually closely associated with olivine and magnetite (Plate 28) and its high nickel content (Chapter 2) supports the textural evidence of its late magmatic development.

Alteration to green biotite accompanied by exsolution of rutile may be observed in thin section, particularly in a rock which has been subjected to later thermal metamorphism (e.g. at Kentallen). The colour change is partly due to a fall in TiO_2 content (confirmed by electron probe), but loss of iron is also evident on alteration from brown to pale green micas (Chapter 2). However electron probe examination shows that the greatest change in iron content occurs between the dark green and light green micas, and TiO_2 loss seems therefore to be the major cause of the brown-green transition (cf. Hall, 1941; Hayama, 1959; Métais et al., 1962).

PLATE 28

Association of biotite with olivine.

Scale bar = 1 mm.

PLATE 29

Euhedral plagioclase enclosed in orthoclase.

Scale bar = 1 mm.

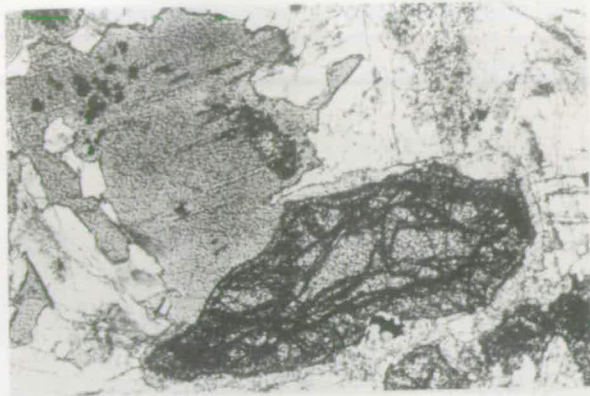


PLATE 28

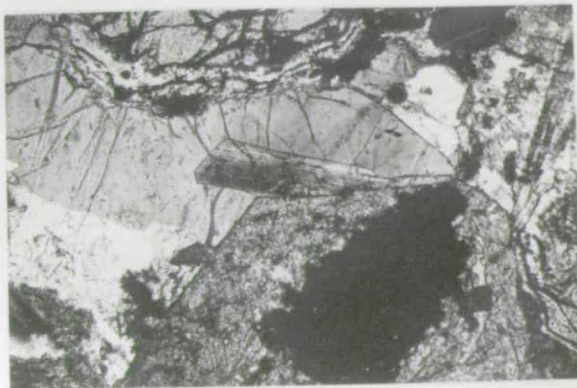


PLATE 29

Plagioclase.

This mineral is rarely euhedral unless partly or completely enclosed in biotite or orthoclase (Plate 29), although it may grow to moderate size (2-4mm). Normal zoning is marked in the plagioclase, and oscillatory zoning may occasionally be observed in thin section. Albite and/or Pericline twinning are ubiquitous. In intrusions which have been exposed to post-crystallisation thermal metamorphism (Kentallen and, to a lesser extent, Glen Orchy) the feldspars are clouded, possibly due to exsolution of iron (Poldervaart and Gilkey, 1954), but otherwise they are clear.

Orthoclase.

Alkali feldspar crystallises either as overgrowths on plagioclase, when it sometimes shows Carlsbad twinning and may grow in optical continuity with the plagioclase (Plate 30), as pools of clear feldspar enclosing several plagioclase individuals (Plate 31), or as a generally untwinned interstitial residuum between any of the minerals in the rock (Plate 32). It may, particularly in the kentallenite aplites, be perthitic (Plate 33), and may occasionally show microcline twinning. To identify it in interstitial areas a sodium cobaltinitrite stain (Chayes, 1952; Bailey and Stevens, 1960) was used. Thermal metamorphism does not cause clouding in kentallenite orthoclase.

Apatite.

The characteristic habit of apatite in kentallenite is that of long needles, often with median holes. Such "tube" apatites have been recorded as experimental quench products, and from basic rocks in the Kerrco volcanic succession of Rhodesia (Wyllie et al., 1962), being interpreted as indicative of crystallisation of the host rocks direct from a liquid. Apatite needles in kentallenite may be pleochroic from pale pink to violet, and inclusion of

PLATE 30

Carlsbad-twinned orthoclase in optically continuous overgrowth
on plagioclase.

Scale bar = 1 mm.

PLATE 31

Pool of clear orthoclase enclosing several plagioclase
individuals.

Scale bar = 1 mm.

PLATE 32

Untwinned interstitial residuum of orthoclase.

Scale bar = 1 mm.

PLATE 33

Perthitic orthoclase in kentallenite aplite.

Scale bar = 1 mm.



PLATE 30



PLATE 31



PLATE 32

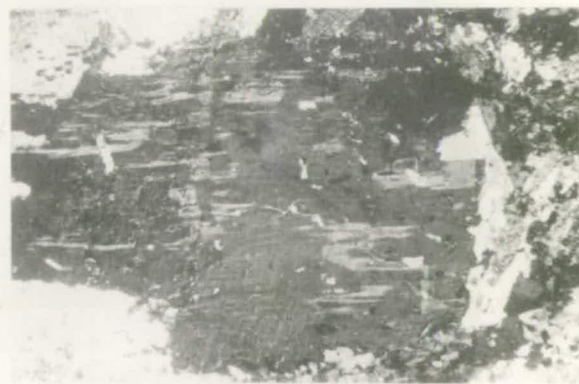


PLATE 33

them within biotite produces pleochroic haloes.

Ore.

The magnetite in kentallenite is never euhedral, and is always interstitial to the other minerals. It is often associated with biotite, and with olivine, usually forming a membrane between the olivine and the biotite moulding upon it; the reverse situation of biotite between magnetite and olivine may sometimes be seen. Broad ilmenite lamellae may be exsolved from the magnetite, and larger discrete blebs of ilmenite are occasionally visible in polished section. Small chalcopyrite and pyrite blebs occur rarely.

APPENDIX CANALYTICAL DATA

Fifty-six rocks have been analysed by X-ray fluorescence and by wet chemical methods (Appendix D) for major and minor elements (Tables 12 and 13 respectively). C.I.P.W. norms have been calculated from the major element analyses, and these are presented in Table 14. Details of the modal mineralogy of the analysed rocks, and their petrographic characteristics, are also given in table form (Tables 15 and 16 respectively).

Precision and accuracy of analyses.

Tables 17 and 18 contain data^{**} on the precision and accuracy of the X-ray fluorescence methods used for major element analysis of kentallenites. The standard and relative deviations listed in Table 17 were derived from analytical data on seven separate fusions of a single sample. In Table 18 the preferred accurate values of major elements in G-1 and W-1 standards according to Fleischer and Stevens (1962) and Ingamells and Suhr (1963) are compared with the values obtained from X-ray fluorescence analysis of G-1 and W-1 at Edinburgh. Good agreement (and thus good accuracy) is apparent for SiO_2 , TiO_2 , total Fe_2O_3 , MnO , MgO and CaO , but Al_2O_3 is slightly high in the Edinburgh samples. This error may be attributable to mass absorption factors, despite the allowance made for these in the preparation of material for analysis (see Appendix D).

The relative deviation of the wet chemical methods used for the analysis of the Alkalis, FeO and H_2O are estimated at 1%, 0.5% and 10% respectively, and the accuracies at $\pm 1\%$, $\pm 5\%$ and $\pm 10\%$ respectively (M.J. Saunders, pers. comm.).

^{**} These tables are compiled from the data of B.G. Jamieson, Edinburgh, whose permission to include them here is gratefully acknowledged.

Table 12 contains several rocks whose analyses do not sum to acceptable totals (99.5 - 100.5%). Although they must be in error, they are included in the tables, and in the diagrams of Chapters 3 and 5, since they conform with the rest of the data and cannot be distinguished from them in the diagrams.

Normative spread.

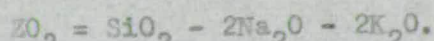
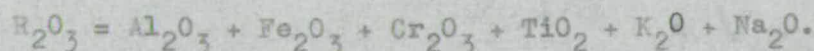
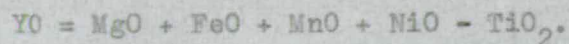
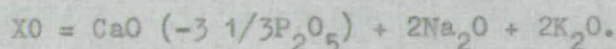
Kentallenites show a spread of normative compositions from 10.3% Nepheline to 25.0% Hypersthene (Table 14). To examine the possibility that analytical error is the cause of this scatter, the norm of a typical kentallenite (K8) was calculated in three ways:

- 1) as in Table 14;
- 2) with all iron oxidised to Fe_2O_3 ;
- 3) with the addition of 1% of Na_2O .

It should be emphasised that 2) and 3) are extreme examples chosen to set unrealistic limits for least and most undersaturated possibilities, and bear no relationship to the likely errors of FeO and Alkali determinations in these rocks (see above). Nevertheless, the maximum spread generated by the oxidation of iron and addition of Na_2O is only from 10.2 to 1.6% Nepheline (i.e. approx. 9%), insufficient to cause the scatter observed in kentallenite compositions.

Tetrahedral projection.

Representation of analytical data in the system $\text{XO-YO-R}_2\text{O}_3\text{-ZO}_2$ (devised by M.J. O'Hara, Edinburgh) is performed as follows:



Abbreviations used in Tables 12-16.

Letters are locality indicators.

K = Kentallen

L = Balnahard, Colonsay

D = Duror

C5 = Scalasaig, Colonsay; main intrusion

A = Ardsheal Hill

C6 = Scalasaig, Colonsay; small appinitic

O = Glen Orchy

diorite

Table 12

MAJOR ELEMENT DATA

	K1B & C	K1D	K2A	K2E	K3D	K8	K14C
Oxide wt. %							
SiO ₂	52.0	50.8	50.0	50.1	49.3	49.7	50.9
TiO ₂	0.64	0.63	0.73	0.66	0.57	0.56	0.64
Al ₂ O ₃	11.7	12.1	13.6	11.4	10.4	10.6	12.1
Fe ₂ O ₃	2.33	2.93	3.07	2.78	2.51	2.57	2.54
FeO	5.91	5.56	5.83	5.70	5.97	5.60	6.01
MnO	0.15	0.16	0.14	0.15	0.14	0.14	0.14
MgO	11.2	11.8	9.99	10.8	16.5	15.7	12.2
CaO	8.71	8.43	10.7	11.7	7.37	7.07	8.49
Na ₂ O	2.62	2.79	2.82	2.33	2.77	2.87	2.83
K ₂ O	2.59	2.97	1.90	2.18	3.15	2.89	3.18
P ₂ O ₅	0.34	0.41	0.41	0.40	0.34	0.30	0.34
CO ₂							
H ₂ O	1.41	1.26	1.19	1.33	0.95	1.67	0.77
Total	99.9	99.8	100.4	99.5	100.0	99.7	100.1
Total Fe as Fe ₂ O ₃	8.89	9.10	9.54	9.11	9.14	8.79	9.21
$\frac{\text{Fe} + \text{Mn}}{\text{Fe} + \text{Mn} + \text{Mg}}$ (cation %)	0.48	0.48	0.53	0.50	0.39	0.40	0.47

Table 12 Cont.

	K14E	K14G	K16B	K18D	K18E	K22A	K22D
Oxide wt. %							
SiO ₂	50.7	51.1	50.7	47.1	48.0	47.3	48.5
TiO ₂	0.59	0.60	0.63	0.83	0.55	0.53	0.52
Al ₂ O ₃	11.9	12.2	12.1	9.76	9.51	8.63	10.4
Fe ₂ O ₃	2.63	2.42	2.54	3.95	3.19	2.97	2.50
FeO	6.03	6.02	5.94	5.90	5.83	6.24	5.90
MnO	0.15	0.14	0.15	0.18	0.16	0.16	0.14
MgO	12.2	11.0	11.7	17.3	18.3	20.0	17.2
CaO	8.42	8.11	8.39	8.29	6.99	7.76	7.69
Na ₂ O	2.75	2.83	2.86	2.71	2.44	2.06	2.43
K ₂ O	3.06	3.30	3.09	3.32	2.69	2.06	2.40
P ₂ O ₅	0.42	0.36	0.42	0.39	0.30	0.31	0.27
CO ₂							
H ₂ O	0.90	0.83	1.13	0.78	1.60	2.02	1.68
Total	99.8	98.9	99.7	100.5	99.6	100.0	99.6
Total Fe as Fe ₂ O ₃	9.37	9.10	9.13	10.5	9.66	9.90	9.05
<u>Fe + Mn</u> Fe + Mn + Mg (cation %)	0.48	0.49	0.48	0.42	0.38	0.37	0.38

Table 12 Cont.

	K22F	K22G	K30A	K30B	K30C	K30D	K30E
Oxide wt. %							
SiO ₂	50.7	47.8	49.8	48.8	48.5	50.0	49.0
TiO ₂	0.63	0.53	0.58	0.56	0.56	0.58	0.56
Al ₂ O ₃	12.0	8.48	10.5	9.89	10.6	10.8	10.6
Fe ₂ O ₃	2.43	3.08	2.99	2.96	2.65	2.82	2.90
FeO	6.18	6.16	5.47	5.63	5.65	5.38	5.56
MnO	0.15	0.15	0.13	0.14	0.14	0.14	0.15
MgO	12.5	19.2	17.0	18.0	15.4	15.7	16.4
CaO	8.48	8.10	7.35	7.32	7.11	7.06	7.29
Na ₂ O	2.43	1.99	2.33	2.47	2.65	2.66	2.54
K ₂ O	2.53	2.04	2.81	2.71	2.79	2.93	2.72
P ₂ O ₅	0.28	0.25	0.40	0.29	0.36	0.34	0.39
CO ₂							
H ₂ O	1.71	2.03	1.70	1.88	1.66	1.86	1.96
Total	100.0	99.8	101.1	100.7	98.1	100.3	100.1
Total Fe as Fe ₂ O ₃	9.29	9.92	9.06	9.21	8.92	8.79	9.07
<u>Fe + Mn</u> Fe + Mn + Mg (cat ion %)	0.47	0.38	0.39	0.38	0.41	0.40	0.40

Table 12 Cont.

	K30F	K30G	K30H	K30I	K30J	K30K	K38A
Oxide wt. %							
SiO ₂	49.0	48.9	49.5	48.9	50.6	49.3	48.4
TiO ₂	0.45	0.57	0.55	0.55	0.64	0.58	0.60
Al ₂ O ₃	9.70	10.2	10.7	10.0	11.9	10.1	10.8
Fe ₂ O ₃	2.64	3.09	2.67	2.65	2.45	1.09	2.53
FeO	6.36	5.36	5.85	5.86	6.25	7.09	7.53
MnO	0.15	0.14	0.15	0.15	0.14	0.14	0.17
MgO	17.8	16.3	16.9	16.8	12.5	16.0	14.8
CaO	7.23	7.31	6.60	7.35	8.58	7.22	11.7
Na ₂ O	2.42	2.48	2.63	2.54	2.73	1.98	2.13
K ₂ O	2.61	2.79	2.68	2.59	2.99	1.73	1.12
P ₂ O ₅	0.31	0.31	0.26	0.27	0.39	0.25	0.39
CO ₂							
H ₂ O	1.63	2.25	1.67	1.69	0.81	1.18	0.42
Total	100.3	99.7	100.2	99.4	100.0	96.7	100.6
Total Fe as Fe ₂ O ₃	9.70	9.04	9.16	9.16	9.39	8.96	10.9
$\frac{\text{Fe} + \text{Mn}}{\text{Fe} + \text{Mn} + \text{Mg}}$ (cation %)	0.39	0.40	0.39	0.39	0.47	0.40	0.46

Table 12 Cont.

	K38B	D6	A2D	04	05I	06B	06E
Oxide wt. %							
SiO ₂	44.3	49.7	52.1	48.0	46.9	47.7	47.2
TiO ₂	0.99	0.56	0.77	0.62	0.83	0.68	0.81
Al ₂ O ₃	6.65	10.3	13.9	8.90	9.03	8.15	10.0
Fe ₂ O ₃	4.30	2.53	3.38	2.76	3.15	3.04	2.86
FeO	6.91	5.85	5.64	6.80	7.14	6.57	6.65
MnO	0.16	0.14	0.16	0.16	0.19	0.17	0.18
MgO	23.8	16.3	7.88	18.3	17.5	19.7	17.3
CaO	6.85	7.15	9.94	7.53	9.26	8.19	8.21
Na ₂ O	0.91	2.55	3.10	2.01	1.63	1.86	2.26
K ₂ O	28.3	2.72	2.50	2.07	1.93	1.23	1.42
P ₂ O ₅	0.08	0.39	0.33	0.25	0.30	0.21	0.28
CO ₂							
H ₂ O	2.34	1.35	0.33	2.16	2.21	2.82	3.14
Total	100.1	99.5	100.0	99.6	100.1	100.3	100.3
Total Fe as Fe ₂ O ₃	12.0	9.02	9.64	10.3	11.1	10.3	10.2
$\frac{\text{Fe} + \text{Mn}}{\text{Fe} + \text{Mn} + \text{Mg}}$ (cat ion %)	0.37	0.40	0.59	0.40	0.43	0.38	0.41

Table 12 Cont.

	011A	011B	011C	011D	011E	011F	L4
Oxide wt. %							
SiO ₂	50.2	48.5	48.7	48.1	45.9	44.7	48.5
TiO ₂	0.66	0.53	0.72	0.68	0.77	0.50	0.65
Al ₂ O ₃	12.3	9.89	10.1	9.60	8.46	5.80	11.0
Fe ₂ O ₃	2.11	3.37	3.11	3.12	4.31	4.82	3.32
FeO	6.35	6.64	6.04	6.14	6.22	5.64	6.35
MnO	0.15	0.17	0.16	0.16	0.18	0.16	0.16
MgO	12.1	15.7	16.5	17.4	19.7	24.3	14.8
CaO	8.38	10.5	7.04	7.08	8.50	6.98	9.83
Na ₂ O	1.75	2.08	2.18	2.08	1.48	1.03	2.44
K ₂ O	1.83	1.88	2.48	2.38	1.62	1.12	1.58
P ₂ O ₅	0.26	0.26	0.27	0.26	0.20	0.12	0.24
CO ₂							
H ₂ O	3.34	2.23	2.49	2.70	3.48	5.05	1.14
Total	99.4	101.8	99.8	99.7	100.8	100.2	100.0
Total Fe as Fe ₂ O ₃	9.16	10.7	9.81	9.94	11.2	11.1	10.4
$\frac{\text{Fe} + \text{Mn}}{\text{Fe} + \text{Mn} + \text{Mg}}$ (cation %)	0.47	0.48	0.41	0.40	0.40	0.35	0.45

Table 12 Cont.

	C5A	C5B	C5C	C5D	C5E	C5F	C5G
Oxide wt. %							
SiO ₂	51.9	50.7	51.2	50.4	51.3	50.6	48.8
TiO ₂	0.69	0.67	0.65	0.63	0.68	0.66	0.58
Al ₂ O ₃	12.4	12.8	12.1	11.8	12.3	12.0	7.86
Fe ₂ O ₃	1.98	2.31	2.75	2.91	2.45	3.18	4.13
FeO	5.82	5.78	5.94	5.94	6.03	5.39	6.53
MnO	0.13	0.14	0.16	0.15	0.15	0.15	0.16
MgO	10.4	11.7	13.2	12.9	11.9	12.6	18.5
CaO	7.43	7.76	8.34	8.35	8.27	8.26	8.18
Na ₂ O	2.57	2.70	2.56	2.49	2.68	2.53	1.53
K ₂ O	3.20	3.27	2.76	2.52	2.86	2.68	2.26
P ₂ O ₅	0.32	0.34	0.35	0.32	0.41	0.36	0.26
CO ₂							
H ₂ O	2.31	2.40	0.58	1.55	0.63	1.67	2.02
Total	99.2	100.6	100.6	100.0	99.7	100.1	100.8
Total Fe as Fe ₂ O ₃	8.44	8.73	9.34	9.50	9.14	9.16	11.4
<u>Fe + Mn</u> Fe + Mn + Mg (cat ion %)	0.49	0.47	0.45	0.46	0.48	0.46	0.42

Table 12 Cont.

	C5H	C5I	C5J	C6A	C6B	C6D	C6E
Oxide wt. %							
SiO ₂	51.6	51.1	52.1	47.0	50.5	41.4	50.9
TiO ₂	0.67	0.65	0.62	1.26	0.84	1.52	0.78
Al ₂ O ₃	13.3	13.3	13.2	12.1	12.6	10.6	10.4
Fe ₂ O ₃	2.20	2.20	2.50	3.05	1.86	3.63	2.06
FeO	5.58	5.52	5.29	6.76	6.54	11.1	5.51
MnO	0.15	0.13	0.13	0.14	0.15	0.17	0.14
MgO	10.4	10.5	10.1	11.3	8.91	12.2	11.2
CaO	7.16	7.55	7.74	10.6	9.38	11.6	10.5
Na ₂ O	3.14	2.91	2.96	2.66	2.56	1.33	1.83
K ₂ O	3.19	3.13	2.96	1.74	2.37	1.58	2.96
P ₂ O ₅	0.29	0.32	0.32	0.24	0.31	0.37	0.12
CO ₂				1.23	1.91	1.33	1.53
H ₂ O	2.05	2.06	1.84	1.95	2.50	2.66	2.07
Total	99.2	99.4	99.7	100.0	100.4	99.5	100.0
Total Fe as Fe ₂ O ₃	8.39	8.33	8.32	10.6	9.12	15.9	8.18
<u>Fe + Mn</u> Fe + Mn + Mg (cation %)	0.49	0.48	0.49	0.52	0.55	0.60	0.46

Table 13MINOR ELEMENT DATA

	K1B & C	K1D	K2A	K2E	K3D	K8	K14C	K14E	K14G
Elements p.p.m.									
Ni	370	390	140	180	400	720	380	390	370
Rb	69	74	44	56	80	67	72	75	81
Sr	750	810	1040	790	890	720	870	910	850
Zr	100	72	66	62	86	80	88	66	86
Ba	840	970	960	700	940	700	920	1000	870

Table 13 Cont.

	K16B	K18D	K18E	K22A	K22D	K22F	K22G	K30A	K30B
Elements p.p.m.									
Ni	380	360	810	920	810	820	890	770	770
Rb	78	85	64	53	56	65	45	69	64
Sr	820	900	670	620	810	650	610	710	730
Zr	78	80	58	50	68	68	40	72	66
Ba	880	960	780	640	660	670	660	800	800

Table 13 Cont.

	K30C	K30D	K30E	K30F	K30G	K30H	K30I	K30J	K30K
Elements p.p.m.									
Ni	710	720	760	800	740	750	780	370	480
Rb	71	71	66	64	65	66	69	70	29
Sr	770	780	740	590	700	700	690	870	870
Zr	76	74	66	70	64	68	77	82	50
Ba	840	800	780	670	630	750	780	850	600

Table 13 Cont.

	K38A	K38B	D6	A2D	04	05I	06B	06E	011A
Elements p.p.m.									
Ni	310	960	720	73	800	660	880	740	830
Rb	13	86	66	57	46	45	36	39	49
Sr	1100	200	710	1030	520	740	480	680	530
Zr	130	31	82	156	50	70	72	88	106
Ba	780	1450	760	920	410	500	430	510	390

Table 13 Cont.

	011B	011C	011D	011E	011F	L4	C5A	C5B	C5C
Elements p.p.m.									
Ni	690	680	770	860	1200	450	350	370	410
Rb	56	67	68	48	33	31	72	82	66
Sr	730	660	620	490	270	820	780	690	730
Zr	119	127	132	94	67	60	129	114	136
Ba	590	510	450	470	310	590	1280	710	780

Table 13 Cont.

	C5D	C5E	C5F	C5G	C5H	C5I	C5J
Elements p.p.m.							
Ni	420	360	420	690	310	330	330
Rb	60	64	61	54	81	72	72
Sr	750	760	710	360	810	850	860
Zr	120	142	125	91	144	154	152
Ba	740	790	730	570	980	960	860

Table 13 Cont.

	C6A	C6B	C6D	C6E
Elements p.p.m.				
Ni	200	160	190	240
Rb	24	51	42	70
Sr	600	600	470	530
Zr	102	109	85	101
Ba	560	1020	400	1240

Table 14NORMATIVE MINERAL DATA

	K1B & C	K1D	K2A	K2E	K3D	K8	K14C
Normative Minerals wt. %							
Orthoclase	15.6	17.8	11.3	13.1	18.8	17.4	18.9
Albite	22.6	21.4	21.5	17.7	12.9	18.1	18.0
Anorthite	12.6	12.0	19.1	14.5	6.62	7.52	11.1
Nepheline		1.37	1.40	1.29	5.85	3.61	3.31
Diopside	23.3	22.1	25.3	33.5	22.3	20.8	23.2
Hypersthene	7.17						
Olivine	13.3	18.9	14.5	13.6	28.0	26.9	19.8
Magnetite	3.44	4.31	4.49	4.10	3.67	3.80	3.70
Ilmenite	1.24	1.21	1.40	1.28	1.09	1.09	1.22
Apatite	0.82	0.98	0.98	0.96	0.81	0.73	0.81
Calcite							
Water	1.41	1.26	1.19	1.33	0.95	1.67	0.77

Table 14 Cont.

	K14E	K14G	K16B	K18D	K18E	K22A	K22D
Normative Minerals wt. %							
Orthoclase	18.3	19.9	18.6	19.7	16.2	12.4	14.5
Albite	19.6	20.9	19.9	4.01	14.0	13.1	15.6
Anorthite	11.1	11.1	11.1	4.67	7.20	8.38	10.7
Nepheline	2.14	1.88	2.55	10.3	3.83	2.52	2.95
Diopside	22.7	22.0	22.7	26.9	20.7	22.8	21.0
Hypersthene							
Olivine	20.2	18.6	19.3	26.3	31.5	34.6	30.0
Magnetite	3.86	3.57	3.74	5.74	4.72	4.39	3.70
Ilmenite	1.13	1.16	1.22	1.58	1.07	1.03	1.01
Apatite	1.01	0.87	1.01	0.93	0.73	0.75	0.65
Calcite							
Water	0.90	0.83	1.13	0.78	1.60	2.02	1.68

Table 14 Cont.

	K22F	K22G	K30A	K30B	K30C	K30D	K30E
Normative Minerals wt. %							
Orthoclase	15.2	12.3	16.7	16.2	17.1	17.6	16.4
Albite	20.9	14.7	18.2	14.7	17.8	19.5	17.7
Anorthite	14.7	8.37	9.87	7.99	9.20	9.02	9.57
Nepheline		1.38	0.89	3.51	2.98	1.81	2.30
Diopside	21.0	24.6	19.1	21.2	19.8	19.3	19.6
Hypersthene	3.56						
Olivine	19.2	32.4	28.9	30.3	27.2	26.7	28.2
Magnetite	3.59	4.57	4.36	4.34	3.99	4.16	4.29
Ilmenite	1.22	1.03	1.11	1.08	1.10	1.12	1.08
Apatite	0.67	0.61	0.95	0.70	0.88	0.82	0.94
Calcite							
Water	1.71	2.03	1.70	1.88	1.66	1.86	1.96

Table 14 Cont.

	K30F	K30G	K30H	K30I	K30J	K30K	K38A
Normative Minerals wt. %							
Orthoclase	15.6	16.9	16.1	15.7	17.8	10.7	6.60
Albite	16.0	17.4	19.2	16.9	18.6	17.5	14.4
Anorthite	8.01	8.65	9.49	8.54	11.4	14.3	16.6
Nepheline	2.61	2.26	1.83	2.74	2.57		1.94
Diopside	20.9	20.9	17.5	21.4	23.2	17.2	31.2
Hypersthene						14.8	
Olivine	31.4	27.4	30.3	29.1	20.8	22.1	23.6
Magnetite	3.88	4.60	3.93	3.93	3.58	1.65	3.66
Ilmenite	0.87	1.11	1.06	1.07	1.23	1.15	1.14
Apatite	0.74	0.75	0.63	0.65	0.93	0.62	0.92
Calcite							
Water	1.63	2.25	1.67	1.69	0.81	1.18	0.42

Table 14 Cont.

	K38B	D6	A2D	04	05I	06B	06E
Normative Minerals wt. %							
Orthoclase	17.1	16.4	14.8	12.6	11.7	7.45	8.63
Albite	1.60	19.3	26.3	17.5	12.5	16.1	18.9
Anorthite	5.84	8.84	16.7	9.39	11.9	10.5	13.4
Nepheline	3.40	1.44			0.87		0.40
Diopside	22.4	19.6	24.5	21.7	26.3	23.6	21.1
Hypersthene				0.13		5.90	
Olivine	41.1	28.7	10.5	32.9	29.8	30.1	31.0
Magnetite	6.38	3.73	4.92	4.11	4.67	4.52	4.26
Ilmenite	1.92	1.08	1.47	1.21	1.61	1.32	1.58
Apatite	0.19	0.94	0.78	0.61	0.73	0.51	0.68
Calcite							
Water	2.34	1.35	0.33	2.16	2.21	2.82	3.14

Table 14 Cont.

	011A	011B	011C	011D	011E	011F	L4
Normative Minerals wt. %							
Orthoclase	11.3	11.2	15.1	14.5	9.84	6.96	9.44
Albite	15.4	13.1	19.0	18.2	12.9	9.16	17.7
Anorthite	21.2	12.2	10.8	10.1	12.0	8.30	14.6
Nepheline		2.50					1.72
Diopside	16.3	30.6	18.5	19.3	23.7	21.5	26.3
Hypersthene	25.0		2.14	0.69	1.09	11.2	
Olivine	5.68	23.9	27.9	30.6	32.1	34.3	23.5
Magnetite	3.19	4.91	4.64	4.67	6.42	7.35	4.87
Ilmenite	1.31	1.01	1.41	1.33	1.50	1.00	1.25
Apatite	0.64	0.62	0.66	0.64	0.49	0.30	0.57
Calcite							
Water	3.34	2.23	2.49	2.70	3.48	5.05	1.14

Table 14 Cont.

	C5A	C5B	C5C	C5D	C5E	C5F	C5G
Normative Minerals wt. %							
Orthoclase	19.5	19.7	16.3	15.1	17.1	16.1	13.5
Albite	22.5	20.6	21.6	21.4	22.9	21.7	13.1
Anorthite	13.3	13.3	13.4	13.8	13.2	13.8	8.00
Nepheline		1.47					
Diopside	18.2	18.9	20.4	20.9	20.4	20.2	24.8
Hypersthene	8.77		0.08	2.37	0.69	2.43	7.97
Olivine	12.7	20.5	22.2	20.2	19.9	18.9	24.8
Magnetite	2.97	3.41	3.98	4.29	3.59	4.68	6.06
Ilmenite	1.35	1.30	1.23	1.22	1.30	1.27	1.11
Apatite	0.78	0.82	0.83	0.77	0.98	0.87	0.62
Calcite							
Water	2.31	2.40	0.58	1.55	0.63	1.67	2.02

Table 14 Cont.

	C5H	C5I	C5J	C6A	C6B	C6D	C6E
Normative Minerals wt. %							
Orthoclase	19.3	19.0	17.9	10.5	14.3	9.65	17.9
Albite	25.7	24.6	25.6	20.4	22.1	7.22	15.8
Anorthite	13.0	14.3	14.3	16.2	16.3	18.9	11.7
Nepheline	0.82	0.37		1.37		2.39	
Diopside	17.1	17.6	18.2	22.3	13.6	23.6	24.6
Hypersthene			4.37		20.2		14.9
Olivine	18.7	18.8	14.0	18.8	3.98	25.8	6.73
Magnetite	3.27	3.28	3.70	4.51	2.75	5.44	3.05
Ilmenite	1.30	1.27	1.20	2.44	1.63	2.98	1.51
Apatite	0.70	0.78	0.77	0.58	0.75	0.91	0.29
Calcite				2.85	4.44	3.13	3.55
Water	2.05	2.06	1.84	1.95	2.50	2.66	2.07

The modal analyses presented in Table 15 were obtained by counting 1000 points on one thin section of each sample, and are quoted to the nearest percent. Accuracy is estimated at $\pm 20\%$ of the values given.

Alteration products of olivine (talc-tremolite and serpentine) are entered as olivine, but biotite magmatic reaction products are reckoned as biotite. Similarly, in all cases of hornblende alteration after augite (except in the picrites K38B and O11F), the hornblende is reckoned as augite. The hornblende in K38B and O11F apparently developed from augite during crystallisation rather than as the result of post-crystallisation alteration, and is therefore entered as hornblende in Table 15; remnant augite is included with hornblende in these rocks, since little survives the alteration process. Primary hornblende is present in C6A-E, and is entered as such in Table 15.

Table 15

MODAL MINERALOGY OF ANALYSED ROCKS

Rock No.	K1B & C	K1D	K2A	K2E	K3D	K8	K14C	K14E	K14G	K16B	K18D	K18E	K22A	K22D	K22F	K22G	K30A	K30B	K30C	K30D	K30E	K30F	K30G	K30H
Olivine	22	16	12	5	16	27	17	16	10	14	21	37	31	21	35	38	31	29	25	28	18	31	26	24
Augite	33	28	35	52	29	23	32	32	35	28	27	17	26	41	16	25	23	20	24	17	31	5	23	25
Hornblende																								
Biotite	17	21	24	18	13	9	13	11	10	17	10	10	12	14	17	10	11	11	13	12	12	27	13	14
Plagioclase	20	28	25	20	30	26	28	28	31	30	28	23	23	20	27	18	26	23	29	30	28	33	28	29
Orthoclase	8	7	4	5	12	15	10	13	23	11	14	13	8	4	5	9	9	7	9	13	11	4	10	8

Table 15 Cont.

Rock No.	K30I	K30J	K30K	K38A	K38B	D6	A2D	O4	O5I	O6B	O6E	O11A	O11B	O11C	O11D	O11E	O11F	I4	C5A	C5B	C5C	C5D	C5E	C5F	C5G	C5H
Olivine	31	14	24	21	15	27	6	28	26	24	31	38	26	34	25	34	25	20	38	19	19	16	22	18	24	11
Augite	17	24	38	43		19	42	28	40	38	32	20	32	15	36	29		30	26	23	19	29	23	24	38	41
Hornblende					54												59									
Biotite	16	19	7	6	31	13	5	14	14	16	19	10	7	7	5	15	16	13	8	10	11	13	14	10	9	12
Plagioclase	29	31	20	24		28	33	18	16	19	16	19	22	27	19	17		33	20	29	33	30	26	31	16	28
Orthoclase	7	12	11	6		13	14	12	4	3	2	13	13	17	15	7		4	8	19	18	12	15	17	13	8

Table 15 Cont.

Rock No.	C5I	C5J	C6A	C6B	C6D	C6E
Olivine	2	11				
Augite	30	23	5	30	15	36
Hornblende			60	26	73	23
Biotite	14	17		7	2	14
Plagioclase	30	32	16	22	6	18
Orthoclase	24	17	19	15	2	9

Table 16PETROGRAPHY OF ANALYSED ROCKS

This table sets out the main petrographic characters of the analysed rock specimens. A "+" in any column indicates that the rock in question exhibits a given texture, a blank that it is lacking or very subordinate. T and S in the line "Olivine Alteration" are explained below.

Lack of any entry in the major categories Olivine, Augite, Biotite, Plagioclase or Orthoclase implies only absence of the particular mineralogical feature concerned, not absence of the mineral itself; Table 15 should be consulted for modal data. However, the lines "Hypersthene - reaction product" and "hornblende - primary" indicate presence or absence of these minerals, and they have not been distinguished in Table 15.

Abbreviations used in Table 16

Rock No. letters are locality indicators

K = Kentallen	L = Balnahard, Colonsay
D = Duror	C5 = Scalasaig, Colonsay; main intrusion
A = Ardsheal Hill	C6 = Scalasaig, Colonsay; small appinitic diorite
O = Glen Orchy	

Rock types

K = Kentallenite
C = Chilled facies
D = Dioritic facies
P = Picritic facies

Olivine alteration

T = Alteration to Talc or Tremolite
S = Alteration to Serpentine

Table 16 (continued)

	04	05I	06B	06E	011A	011B	011C	011D	011E	011F	L4	C5A	C5B	C5C	C5D	C5E	C5F	C5G	C5H	C5I	C5J	C6A	C6B	C6D	C6E	
Rock type	K	K	K	K	K	K	K	K	K	P	K	K	K	C	K	K	C	K	D	D	D	D	D	D	D	
Exsolution of ore							+																			
olivine Coronas							+																			
Alteration	S	S	S	S	S		S	S	S	S		T	T		S	T		S	T	T	T					
Zoning	+	+	+				+	+	+	+	+				+	+	+	+	+							
agite Spongy	+						+	+					+		+	+	+	+								
Alt. to h'blende				+						+		+							+	+	+	+	+	+	+	
ypersthene Reaction product								+																		
ornblende Primary																							+	+	+	+
Brown	+	+	+	+	+	+	+	+	+	+	+	+			+	+	+	+	+	+	+		+	+	+	
iotite Green	+									+		+							+	+	+				+	+
Poikilitic	+	+	+	+	+		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+				+
Altered		+			+	+	+	+				+	+						+	+	+		+			
lagioclase Rims of o'clase		+				+		+				+	+						+	+	+	+				
Perthitic																							+	+		+
Orthoclase Monzonitic texture	+	+	+	+	+	+	+	+	+		+	+	+	+	+	+	+	+	+	+	+					

TABLE 17PRECISION OF ANALYTICAL DATA

	<u>s</u>	<u>C</u>
SiO ₂	0.32	0.64%
TiO ₂	0.019	0.82%
Al ₂ O ₃	0.097	1.07%
Fe ₂ O ₃ ^{T*}	0.21	1.83%
MnO	0.0034	2.36%
MgO	0.28	1.90%
CaO	0.078	1.07%

s - Standard deviation (uncertainty of a single observation).

C - Relative deviation (s as % of amount of element present).

* Fe₂O₃^T - Total iron as Fe₂O₃

TABLE 18

COMPOSITION OF STANDARD SAMPLES G-1 and W-1

	<u>G-1</u>		
	FS*	Edin.*	IS*
SiO ₂	72.8	72.7	72.5
TiO ₂	0.26	0.26	0.26
Al ₂ O ₃ _T	14.0	14.5	14.1
Fe ₂ O ₃	1.96	2.06	1.90
MnO	0.03	0.028	0.026
MgO	0.41	0.37	0.35
CaO	1.39	1.38	1.36

	<u>W-1</u>		
	FS	Edin.	IS
SiO ₂	52.6	52.7	52.6
TiO ₂	1.07	1.04	1.08
Al ₂ O ₃ _T	14.9	15.2	14.9
Fe ₂ O ₃	11.2	11.1	11.1
MnO	0.16	0.17	0.17
MgO	6.62	6.53	6.52
CaO	11.0	11.2	10.9

* FS - Preferred values, Fleischer and Stevens, 1962.

Edin. - Edinburgh analyses.

IS - Preferred values, Ingamells and Suhr, 1963.

APPENDIX DMETHODSX-ray Diffraction.

The method used for olivine composition determination by X-ray diffraction was that described by Yoder and Sahama (1957). It involves addition of pure Silicon to the ground sample, and measurement of the relative positions of the olivine (130) and Silicon (111) reflections of the resulting mixture. Calculation from these results gives a value for d_{130} of the olivine, which is converted to Forsterite molecular percent by use of the determinative curve presented by Yoder and Sahama.

X-ray Fluorescence.

Specimens selected for chemical analysis were generally of 1-2kg weight, and were scrubbed and rinsed with deionised water prior to crushing. A hydraulic rock splitter was used to break the rock into small pieces of less than 2cm minimum dimension, and a 300-500g grab-sample of these chips was reduced to 10 mesh by 'Manchester' rollers. A sixth of this material was further reduced to 100 mesh in an automatic agate mortar, and the rock powder was dried overnight at 110°C before analysis.

Samples were prepared for X-ray fluorescence major element analysis according to the method of Rose et al. (1962), using La_2O_3 as a heavy absorber and $\text{Li}_2\text{B}_4\text{O}_7$ as a flux and diluent. However, the ratio sample: La_2O_3 : $\text{Li}_2\text{B}_4\text{O}_7$ was 1:1:8 for kentallenites, not 1:1:4 as used by Rose et al. The 1:1:8 mixture was fused in a muffle furnace at 1000°C for 10 minutes, the resulting beads brought back to original weight by addition of boric acid to compensate for volatile loss, and cracked and ground in a tungsten carbide ball mill to pass 200 mesh. Some of the 200 mesh powder, after drying for 24 hours at 110°C, was pressed into a disc under 5 tons pressure, backed with boric acid,

and pressed under 15 tons pressure for one minute to form a semi-permanent mount, which was used for X-ray fluorescence analysis. "Peak only" counts were normally used. The discs were stored in a low humidity cabinet to avoid hydration of the working surface.

Minor element analysis was carried out on 100 mesh rock powder supported on a Mylar film, peak:background ratios being determined (after Andermann and Kemp, 1958).

Determinative curves for all elements were set up using a number of standard materials prepared in a manner similar to that of the unknown rock powders. The standards were:

U.S. Geol. Survey standards G-1 and W-1

(using the values of Fleischer and Stevens, 1962.)

U.S. National Bureau of Standards - Silica brick	102
Opal glass	91
Burnt refractories	76, 77.

C.A.A.S. standard Syenite Sy-1

(using the values of Webber, 1965.)

Karoo dolerites LM432 and LM593

(analysed in the University of Leeds Institute of African Studies.)

In all cases samples were analysed in batches of 4, one of which was an internal standard included to allow correction for drift. Table 19 is a compilation of the analytical conditions for the major and minor elements analysed by X-ray fluorescence.

Wet Chemistry

Alkalis were determined on an Eel Flame Photometer. The samples

TABLE 19a

OPERATING CONDITIONS OF X-RAY FLUORESCENCE SPECTROGRAPH

		<u>Major Elements</u>								
Element		SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	P ₂ O ₅	
kV		50	40	45	40	40	50	40	45	
mA		28	20	32	20	28	28	20	36	
Element Peak		Kα1	Kα1	Kα1	Kα1	Kα1	Kα1	Kα1	Kα1	
Analysing Crystal		P.E.	LiF.	P.E.	LiF.	LiF(110)	ADP	LiF	P.E.	
as 2θ	Peak (P)	79.70	56.09	115.90	57.38	94.66	107.25	82.55	59.50	
of crystal	Background (B)	-	-	-	-	99.5	-	-	58.50	
Count Type		P	P	P	P	P-B	P	P	P-B	
Count Time		60 sec	100 sec	100 sec	100 sec	100 sec	100 sec	100 sec	200 sec	
No. of Counts		1	1	2	1	1	4	2	1	
Preparation		Disc	Disc	Bisc	Disc	Disc	Disc	Disc	Disc	
Counter		Flow	Flow	Flow	Scint	Scint	Flow	Flow	Flow	
Counter E.H.T.		4.60	4.80	5.0	2.50	2.40	5.20	4.80	4.50	
Discrimination:		LL	16	20	8	4	6	16	13	15
		CW	18	16	14	26	32	16	15	15
		Att.	2 ²	2 ⁴	2 ⁴	2 ⁴	2 ²	2 ⁴	2 ⁴	2 ²
Vacuum		Yes	Yes	Yes	No	No	Yes	Yes	Yes	
Collimator		Coarse	Fine	Coarse	Fine	Fine	Coarse	Coarse	Fine	
X-ray Tube		Cr	Cr	Cr	W	W	Cr	Cr	W	

Table 19b

OPERATING CONDITIONS OF X-RAY FLUORESCENCE SPECTROGRAPH

Minor Elements

Element	Ni	Rb	Sr	Zr	Ba
kV	50	40	40	40	55
mA	20	20	20	24	20
Element Peak	K α 1	K α 1	K α 1	K α 1	K α 1
Analysing Crystal	LiF(110)	LiF	LiF	Topaz	Topaz
as 2θ Peak (P)	70.65	26.56	25.08	33.69	16.34
of crystal Background (B)	69.50	28.00	28.00	34.75	15.50
Count Type	$\frac{P}{B}$	$\frac{P}{B}$	$\frac{P}{B}$	$\frac{P}{B}$	$\frac{P}{B}$
Count Time	100 sec	100 sec	100 sec	100 sec	100 sec
No. of Counts	1	1	1	1	1
Preparation	Mylar	Mylar	Mylar	Mylar	Mylar
Counter	Scint	Scint	Scint	Scint	Scint
Counter E.H.T.	1.80	2.00	2.00	1.60	1.60
Discrimination LL	12	10	10	8	20
CW	28	16	16	15	20
Att.	2 ¹	2 ²	2 ²	2 ²	2 ²
Vacuum	No	No	No	No	No
Collimator	Coarse	Fine	Fine	Fine	Fine
X-ray Tube	W	W	W	W	W

were treated with HNO_3 and HF before determination of the alkalis in order to remove interfering elements, but it is thought (M.J. Saunders, pers. comm.) that some calcium and magnesium may remain in the solutions.

FeO was determined by the classical method (dichromate titration - see Peck, 1964) except in the olivines (Chapter 2), when a cold-solution method (Wilson, 1955) was adopted. H_2O was determined in a Pyrex test tube using a lead chromate flux.

Refractive Indices.

β refractive indices of the analysed minerals (Tables 1, 4 and 7; Chapter 2) were determined in sodium light, and a Leitz-Jelley Refractometer was used to determine the index of the final liquid.

2V.

Optic axial angles were determined on a Leitz 4-axis Universal Stage, using white light.

Mineral Separation.

Methods employed in mineral separation included electromagnetic, shaker table and heavy liquid techniques. In general, 'dry' methods were used before 'wet' ones.

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ACKNOWLEDGMENTS.

I should like to thank Professor F.H. Stewart for his interest, and for placing the facilities of the Grant Institute of Geology at my disposal.

I wish to express my gratitude to Dr. M.J. O'Hara, who suggested this research project, for his continual encouragement and interest in the work, his critical reading of the manuscript, and his helpful comments at all stages.

I am indebted to Dr. E.L.P. Mercy, Dr. N.B. Price and Mr. M.J. Saunders for their help, advice and discussion of analytical techniques, and to Dr. R.F. Cheeney for his assistance with the statistical treatment of data, including the writing of a Principal Component Analysis computer program.

I would like to acknowledge many stimulating discussions with, and the assistance of, Dr. K.R. Gill, Dr. S.W. Richardson, Mr. B.G. Jamieson, Mr. D.F. Strong and Mr. C.R. Bowdidge.

Thanks are also due to Mr. Colin Chaplin, Miss M. Hamilton and Miss J. Tarrant for their assistance with the photography of the plates and figures, to Mr. R.L. Bennett for help with mineral separation, and to Miss L. Kinghorn and Miss A. Lord for typing the manuscript.

Financial assistance during the course of this research was given by a grant from the Natural Environment Research Council (formerly D.S.I.R.), and by Robertson Research Company Limited, both of which are gratefully acknowledged.