Trace Element Evidence for Mantle Heterogeneity Beneath the Scottish Midland Valley in the Carboniferous and Permian

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Trace element evidence for mantle heterogeneity beneath the Scottish Midland Valley in the Carboniferous and Permian

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The alkaline rocks of Carboniferous to Permian age in the Midland Valley province range in composition from hypersthene-normative, transitional basalts to strongly undersaturated basanitic and nephelinitic varieties. They were formed by varying degrees of equilibrium partial melting of a phlogopite peridotite mantle. Ba, Ce, Nb, P, Sr and Zr were strongly partitioned into the liquid during melting; K and Rb were retained by residual phlogopite for small degrees of melting only.

The composition of the mantle source is inferred to have been broadly similar to that from which oceanic alkaline basalts are currently being generated. It was, however, heterogeneous as regards distribution of the incompatible trace elements, with up to fourfold variations in elemental abundances and ratios. The mantle beneath the province may be divisible into several areas, of some hundreds of square kilometres each, which retained a characteristic incompatible element chemistry for up to 50 Ma and which imparted a distinctive chemistry to all the basic magmas generated within them.

INTRODUCTION

The main outcrops of Carboniferous and Permian igneous rocks in Scotland lie within the Midland Valley graben. Small outliers occur in the Highlands and Southern Uplands, while sequences of flows up to 120 m thick lie discontinuously along the Scottish borders. The border outcrops are not included in this report because of a lack of relevant chemical data.

The area of the Midland Valley province, defined as the rectangle enclosing the main outcrops, is some 30000 km^2, within which rather more than 12000 km^2 of lava currently crop out. The volume of alkaline lavas is about 6000 km^3, 80% of which is basaltic (Francis 1967), though the original volumes may have been nearer 10000 km^3. An estimated 1200–1500 km^3 of alkaline magma is also present as intrusions of various ages covering the range of the extrusive activity.

The rocks of the province range in age from earliest Carboniferous to Permian, a span of some 80 Ma being indicated by available age dates (Fitch *et al.* 1970). An estimated minimum of 80% of the total volume of igneous material was, however, emplaced during the Dinantian (Macdonald 1975), say a 25–30 Ma period, mainly as a series of individual lava piles showing partial overlap. The terminology and distribution of the main lava sequences are described by Francis (1967, 1968). Major element characteristics of each have been discussed by Macdonald (1975) and Macdonald *et al.* (1977). Macdonald (1975) concluded that the Dinantian lava successions represented several magmatic lineages, each differing in such parameters as the degree of silica undersaturation, Na_2O/K_2O and $FeO/(FeO+MgO)$ ratios and TiO_2 and P_2O_5 contents.

The Midland Valley alkaline basic rocks range in composition from hypersthene (hy.)-normative, transitional basalts to basanitic and nephelinitic varieties. For simplicity two

Table 1. Representative trace element (micrograms per gram) and major element (percentages by mass) analyses of alkali basalts (1–6) and basanites (7–11), and of a low-K tholeiite (12), from the Midland Valley province

	(1) ZP 423	(2) MV 501	(3) MV 400	(4) MV 222	(5) HS 36	(6) MV 27	(7) MV 520	(8) FM 476	(9) MV 105	(10) HS 94	(11) MV 703	(12) MV 261
trace elements												
Ba	170	505	665	480	810	960	740	1115	1115	1160	550	105
Ce	18	35	58	42	31	44	34	132	86	87	25	8
Nb	14	39	38	25	34	28	46	132	52	69	28	3
Rb	26	33	27	18	42	25	48	15	11	21	19	2
Sr	618	537	635	460	594	575	545	1716	1130	1283	690	140
Y	27	30	19	21	22	30	30	38	27	36	26	21
Zn	88	70	93	103	130	73	70	103	88	89	71	65
Zr	118	172	200	170	136	186	155	300	306	301	180	72
major elements												
K_2O	0.70	0.96	1.30	0.74	1.58	1.71	1.92	1.12	1.31	0.94	1.35	0.20
TiO_2	1.52	2.36	2.65	2.82	1.75	2.54	2.37	2.46	2.78	2.55	3.22	1.45
P_2O_5	0.27	0.42	0.55	0.36	0.31	0.47	0.83	1.01	0.73	0.81	0.37	0.11
Mg no.	69	61	63	62	61	65	63	63	66	66	62	60

Specimen localities. (Din., Dinantian; Nam., Namurian; Steph., Stephanian.) ZP 423: hy.-norm. ankaramitic basalt, sheet, Kilsyth Hills; Din; specimen courtesy of P. M. Craig. MV 501: hy.-norm. basalt, Passage Group lavas, Ayrshire; Nam. (Macdonald *et al.* 1977, no. 23). MV 400: hy.-norm. basalt, Burntisland lavas, Fife; Din. (Macdonald *et al.* 1977, no. 6). MV 222: ne.-norm. ankaramitic basalt, flow, Kintyre; Din. (Macdonald 1975, table 2, no. 4). HS 36: ne.-norm. basalt, Mauchline lavas, Ayrshire; Steph. (Macdonald *et al.* 1977, no. 33). MV 27: ne.-norm. basalt, Dalmeny; Din. (Guppy & Thomas 1931, no. 272). MV 520: essexite, intrusion, Crawfordjohn; late Carb.–Permian? (Scott 1915). FM 476: nepheline basanite, intrusion, Lomond Hills; Permian (Macdonald *et al.* 1977, no. 37). MV 105: ?nepheline basanite, Chapel Ness intrusion, Elie, Fife; late Carb.–Permian (Forsyth & Chisholm 1977, table 10, no. V). HS 94: basanite, Bathgate–Linlithgow lavas; Din.–Nam. (Macdonald *et al.* 1977, no. 17). MV 703: basanite, plug, Kersewell, Carnwath; age uncertain (Guppy & Thomas 1931, no. 290). MV 261: low-K tholeiite, Kintyre lavas; Din. (Macdonald 1975, table 2, no. 1).

groups are distinguished in this paper: an *alkali basalt* group, consisting of hy.-normative basalts and alkali olivine basalts with normative nepheline (ne.) $< 5\%$, and a *basanitic* group, consisting of those basic rocks with ne. $> 5\%$.

Major element compositions appear to have evolved rather systematically with time, such that two thermal cycles may be distinguished (Macdonald *et al.* 1977), each starting with hy.-normative magmatism and progressing towards increasingly silica-undersaturated types. Details of the magma types and their relations to extrusive and intrusive sequences may be found in MacGregor (1948), MacGregor & MacGregor (1948), Francis (1967, 1968), Macdonald (1975) and Macdonald *et al.* (1977).

Table 2. Ranges and averages of trace elements (micrograms per gram) and selected major elements (percentages by mass) in Midland Valley basic rocks (Mg no. $\geqslant$ 60)

	alkali basalts				basanites			
	hy.-norm.		ne. 0–5 %		ne. 5–10 %		ne. > 10 %	
	range	average	range	average	range	average	range	average
trace elements								
Ba	170–665	449	260–1230	686	550–2213	1046	740–1150	912
Ce	18–69	40	16–70	42	15–107	71	34–132	96
Nb	14–47	31	9–79	41	28–73	55	28–132	72
Rb	3–37	21	8–45	25	3–50	20	11–48	25
Sr	275–680	540	342–1636	708	555–1283	809	545–1716	939
Y	13–34	25	13–36	25	12–36	28	20–40	31
Zn	64–106	84	70–147	96	62–246	110	70–174	109
Zr	105–322	182	108–285	179	130–301	212	142–330	243
major elements								
K_2O	0.48–1.38	0.99	0.45–1.71	1.06	0.49–2.10	1.15	0.80–1.92	1.48
TiO_2	1.52–3.08	2.22	1.57–3.12	2.38	2.44–3.22	2.83	2.30–2.93	2.68
P_2O_5	0.27–0.55	0.39	0.25–0.79	0.45	0.37–1.10	0.69	0.58–1.92	1.09
n(max.)	17		25		11		11	

The majority of the basic rocks with Mg number $\geqslant$ 60 are either aphyric or carry phenocrysts of ol. + cpx. and rarely, plag. ± oxide. There is no evidence that a significant number of these rocks represent low-pressure accumulative types. Generalized petrographic descriptions of relevant rock types are provided by MacGregor & MacGregor (1948, pp. 54 and 65).

Ba, Ce, Nb, Rb, Sr, Y, Zn and Zr have been determined by analysis by X-ray fluorescence in 64 samples of basic alkaline rock (Mg number† $\geqslant$ 60) from the Midland Valley province. Representative analyses are presented in table 1. Estimated analytical precisions are: Sr and Zr 2%, other elements 5%.

K_2O, TiO_2 and P_2O_5 determinations given in table 1 are taken from the references cited in the table or are previously unpublished data (ZP 423).

Ranges and means for the same elements are given in table 2, the complete range of basic compositions being arbitrarily divided into four on the basis of normative composition. It is apparent that each element shows considerable variations in abundance, both within and between the normative groups.

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† Mg number = 100 Mg/(Mg + Fe^{2+}), atomic ratio; Fe_2O_3/FeO ratio taken to be 0.25 (Kesson 1973).

TRACE ELEMENT VARIATIONS

Four different processes may have acted to produce variations in trace element distribution in the Midland Valley basic rocks.

(i) *Deuteric alteration.* As Macdonald (1975, p. 270) has stressed, many of the Midland Valley alkaline rocks are remarkably fresh, despite their Upper Palaeozoic age. A large majority of the specimens used in this study have mineralogies unaltered, or only slightly altered, by deuteric processes. Olivine is commonly fresh or only partially serpentinized. Plagioclase and pyroxene are ubiquitously fresh. Certain specimens show minor amounts of secondary carbonate but there is no evidence of extensive zeolitization.

The elements most likely to have been mobilized by deuteric effects are Ba, K, Rb and Sr. The strong correlations (table 3), not only between these elements but between them and such reputedly immobile elements as Ce and Nb suggest, however, that any such mobilization must have been slight. It may be assumed that the observed trace element contents normally represent the primary magmatic abundances.

(ii) *Crustal contamination.* In the absence of relevant isotopic data, it is difficult to assess the possible importance of this process. Two lines of evidence suggest, however, that the basalts have not been significantly affected by crustal rocks.

(*a*) It will be shown later that the mantle sources of the alkaline rocks had values of Rb/Sr and K/Rb comparable to those inferred for the source areas of Recent alkaline basalts of oceanic islands. Since the trace element composition of the Midland Valley mantle was deduced from the basalts, the implication is that their K, Rb and Sr contents have not been substantially modified by crustal contamination.

(*b*) There is no significant correlation between K and Rb and the degree of silica-saturation of the alkali basalts of the Midland Valley. Such a correlation would seem to be a necessary result of the contamination of basic magma by significant amounts of sialic material.

(iii) *Fractional crystallization.* Polybaric fractional crystallization tends to obscure those chemical features of basic magmas derived from their mantle sources. Certain features of the trace element variations within certain Midland Valley sequences very probably result from high to moderate pressure fractionation of the parental magmas. To minimize these effects, the compositions of *primary* magmas only should be used to infer mantle compositions. Perversely, the assignment of a primary status to a magma depends on the composition chosen for its mantle source. A widely accepted criterion is that only basalts with Mg number > 66–67 are likely primary basalts, implying a mantle olivine of composition Fo > 87. However, Wilkinson & Binns (1977) have made a case for a more heterogeneous mantle, containing relatively Fe-rich lherzolitic areas capable of generating basic magmas with Mg numbers $\leqslant 50$.

In view of this uncertainty, attention here is largely restricted to basic rocks with Mg number $\geqslant 60$. These may be termed 'near-primary' magmas, i.e. they have suffered only modest (less than 20%) amounts of fractionation of ferromagnesian phases during ascent from their sources. This is in accord with the suggestion of Macdonald (1975), based on major element chemistry, that the majority of the Midland Valley Dinantian basalts had experienced a recognizable polybaric fractionation history, involving the removal of wehrlitic (ol. + cpx.) or clinopyroxenitic (Al-cpx.) assemblages at pressures greater than 10 kbar (1 MPa) and ol. + plag. + oxide assemblages at lower pressures.

While such fractionation will have affected the absolute abundances of the incompatible

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elements, it will not have seriously modified the ratios of two elements with similar, low, solid–liquid partition coefficients.

(iv) *Primary magmatic variations.* Trace element variations that persist *after* removal of possible fractionation events are taken to represent variable conditions of magma genesis. These are of two types: variations related to the degree of partial melting and those resulting from variations in mantle source composition.

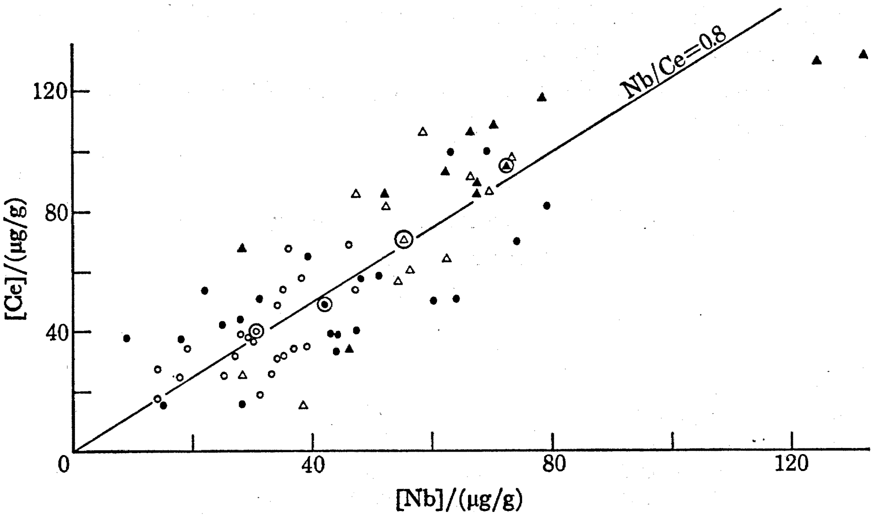

Figure 1. Ce–Nb graph for alkaline basic rocks with Mg number ⩾ 60. Open circles, hy.-normative basalts; closed circles, basalts with ne. 0–5 %; open triangles, basanites with ne. 5–10 %; closed triangles, basanites with ne. > 10 %. Circled symbols represent the averages for each group.

Petrogenetic model

The main groups of basic rocks may be taken, as a first approximation, to represent the products (or the derivatives thereof) of variable degrees of closed-system, partial melting of a fertile mantle source over a limited range of pressures. Thus the basanites resulted from the smallest degrees of melting (say not more than 7 %; Sun & Hanson 1975), the ne.-normative alkali basalts from intermediate degrees (7–15 % ?) and the hy.-normative alkali basalts the most extensive mantle fusion (15–20 % ?). This model is based on the following kinds of interpretation.

Figure 1 is a plot of Ce against Nb for all available analyses of Midland Valley basic rocks having Mg number ⩾ 60. Different symbols distinguish four groups of rocks on the basis of their degree of silica-undersaturation. Averages for each group are shown. The data form a collinear display extending through the origin and scattering about a Nb/Ce ratio of 0.8. The bulk distribution coefficients of Ce and Nb for the residual mantle mineralogies may be taken to be very low, i.e. these elements have been essentially incompatible during the melting process. The Nb/Ce ratio of 0.8 thus approximates that of the mantle source and the amounts of Ce and Nb are inversely proportional to the degrees of partial melting.

Graphical analysis of this sort, plus the correlation coefficients presented in table 3 suggest that Ba, P, Sr and Zr also behaved essentially as incompatible elements. If those elements were ever major constituents of an accessory phase in the source peridotites (e.g. P in apatite or Zr in zircon), then those phases melted or were reacted out during the first 1–2 % of melting and were not present in the residual mineralogies at any stage. Y apparently was retained by clinopyroxene ± garnet, though the partition coefficients can be shown to have been less than unity for both phases.

It appears, on the other hand, that K, Rb, Ti and Zn were not incompatible over the full melting range. A plot of Ce against TiO_2 (figure 2) reveals the following:

(i) The alkali basalts show a positive correlation between those elements, approximately collinear with the origin. As will be shown, the scatter is mainly due to minor differences in the source materials, though removal of Ti in clinopyroxene during high pressure fractionation may well have been a contributory factor.

(ii) The basanites generally have higher Ce contents and Ce/Ti ratios than the alkali basalts and are not collinear with them.

Table 3. Correlation matrix for trace and selected major elements

	Ba	Ce	Nb	Rb	Sr	Y	Zn	Zr	K_2O	TiO_2	P_2O_5	d.s.u.
Ba												
Ce	0.47											
Nb	0.43	0.83										
Rb	−0.06	−0.13	−0.04									
Sr	0.45	0.65	0.77	−0.28								
Y	0.34	0.48	0.53	−0.03	0.46							
Zn	0.15	0.18	0.12	0.09	−0.08	0.10						
Zr	0.46	0.83	0.69	−0.27	0.65	0.56	0.19					
K_2O	0.20	0.21	0.15	0.73	−0.11	0.16	0.19	0.09				
TiO_2	0.43	0.57	0.38	−0.41	0.37	0.32	0.25	0.67	−0.03			
P_2O_5	0.30	0.69	0.56	−0.07	0.49	0.37	0.15	0.71	0.30	0.47		
d.s.u.	0.21	0.63	0.58	0.15	0.39	0.47	0.15	0.53	0.46	0.39	0.56	

d.s.u., Degree of silica-undersaturation.

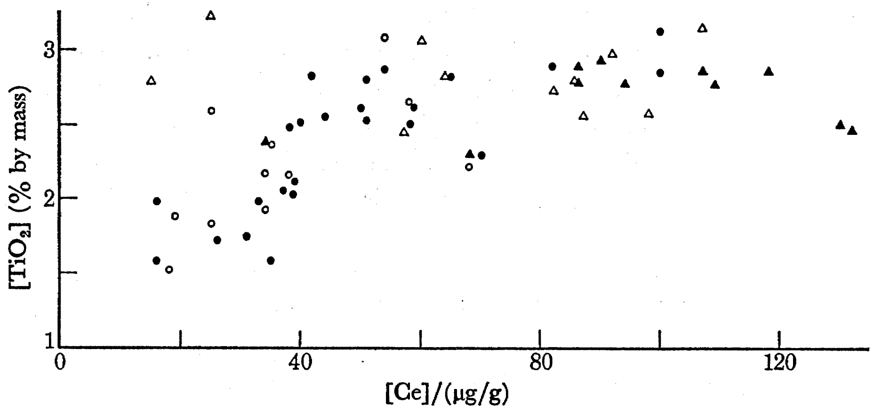

Figure 2. Ce–TiO_2 graph for alkaline basic rocks (Mg number ⩾ 60). Symbols as in figure 1.

The interpretation most consistent with the model used in this paper is that a mineral in which Ti is a major component was residual for the basanites but not for the alkali basalts.

By similar reasoning, residual phases concentrating K, Rb and Zn can be inferred to have remained in the mantle after generation of the basanites. The collinearity of these elements with each other and with the incompatible elements in the alkali basalts suggests, however, that the accessory minerals had disappeared from the residue by this stage of melting and that those elements remaining in the residual mantle (e.g. Y in clinopyroxene) had low bulk distribution coefficients.

Nature of accessory phases

The K/Rb ratios of the Midland Valley alkaline basic rocks (Mg number ⩾ 60) show a wide range, with a mode at about 350 (figure 3). The basanites have average K/Rb ratios rather higher than those of the alkali basalts. The pattern is similar to that described from oceanic alkali basalts by Sun & Hanson (1975), and following their line of argument and that of Arth (1976), it may be inferred that *phlogopite* was the residual phase concentrating K and Rb during the earliest stages of melting. The constraint of the present model is that phlogopite should have completely melted during the first 7 % of melting such that it was not a residual phase during formation of the alkali basalts (cf. Hofmann & Hart 1978).

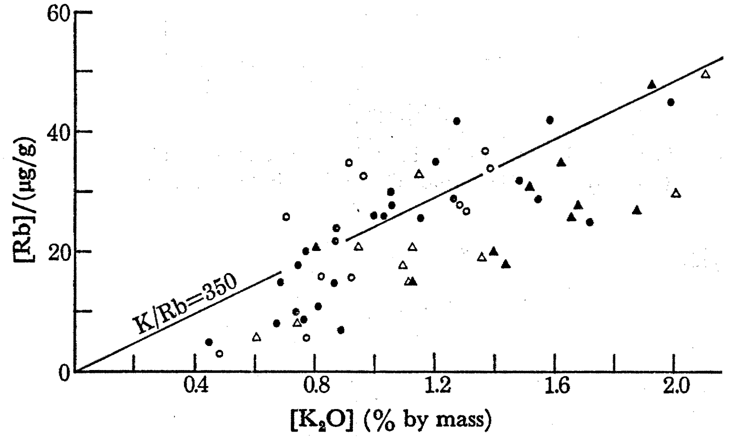

FIGURE 3. K_2O–Rb graph for alkaline basic rocks (Mg number ⩾ 60). Symbols as in figure 1.

It is tempting to suggest that the mica phase was in fact *titanphlogopite*, thereby finding a suitable residual phase to concentrate Ti. The lack of significant correlation between K and Ti (table 3) renders this doubtful, however. Neither is there any unequivocal evidence for another likely mantle host, e.g. titanclinohumite, ilmenite or Ti-rich clinopyroxene.

Zn shows only a restricted range of compositions though the strongly undersaturated varieties are on average richer in Zn. Zn is apparently partitioned into the melt though less strongly than Ba and the other incompatible elements and is possibly being retained by a sulphide phase ± clinopyroxene. This assumes closed-system fusion: alternatively, Zn contents were perhaps being buffered by a volatile phase.

The general model applied here is that the Midland Valley basic rocks or their parental magmas were formed by varying degrees of partial melting of a phlogopite-bearing peridotitic mantle. Phlogopite was completely consumed by the melt at about the point when the melt became critically undersaturated with respect to silica. Ba, Ce, Nb, P, Sr, Y and Zr were either incompatible or had very low bulk distribution coefficients for the relevant residual mineralogies. K and Rb concentrations were initially buffered by phlogopite. Zn may have been partially retained by a sulphide phase while the nature of the accessory Ti-mineral (if any) is uncertain.

Recognition of mantle heterogeneity

A good correlation between Ce and Nb in the alkaline rocks of the Midland Valley was noted in figure 1. In figure 4, Ce and Nb data are presented for two of the lava suites: the Mauchline and Thornhill lavas (Stephanian) and the North Ayrshire lavas of Dinantian age. The suites clearly have different Nb/Ce ratios.

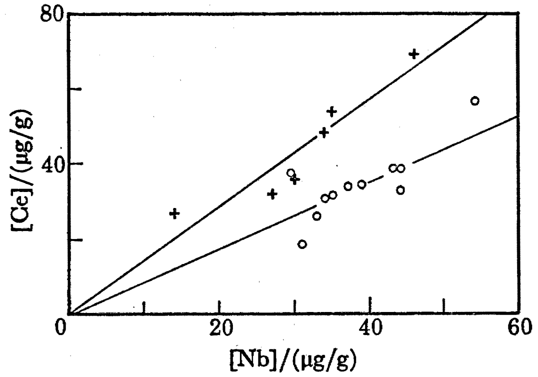

Figure 4. Ce plotted against Nb for basic rocks (Mg number ⩾60) of the N Ayrshire (crosses) and Mauchline–Thornhill (circles) sequences.

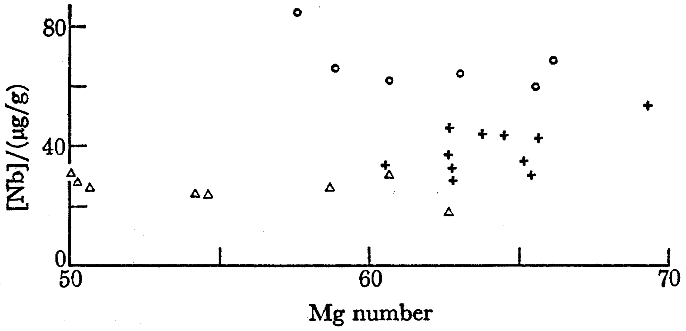

Figure 5. Mg number – Nb graph for lavas of the East Lothian (triangles), Bathgate–Linlithgow (circles) and Mauchline–Thornhill (crosses) sequences.

Table 4. Estimated abundances of incompatible trace elements at Mg number = 60 in various lava sequences

eruptive sequence	age	normative character	Ba	Ce	Nb	P	Sr	Zr	Σ (Ba→Zr)
Burntisland	Din.	hy.	650	60	40	2617	550	225	4142
East Lothian	Din.	hy.	600	30	24	1963	675	160	3452
N. Ayrshire	Din.	hy.	465	50	30	—	555	235	—
Arthur's Seat	Din.	c.u.	530	43	35	1701	700	170	3179
Campsie Block	Din.	c.u.	220	25	20	1527	500	140	2432
Kintyre	Din.	ne.	450	60	30	1527	550	210	2827
Bathgate–Linlithgow	Din.–Nam.	ne.	1000?	65	65	3053	900	250	5333
Passage Group, Ayrshire	Nam.–West.	hy.	400	15	30	1527	400	150	2522
Mauchline–Thornhill	Steph.	ne.	650	35	37	1876	600	150	3348
estimated maximum error	—	—	± 50	± 5	± 5	± 220	± 50	± 10	

c.u., Critically undersaturated with respect to silica. Din., Dinantian; Nam., Namurian; Steph., Stephanian; West., Westphalian.

The point may be stressed from a different viewpoint. Nb is plotted against Mg number for three volcanic sequences in figure 5. Clear differences exist between them at comparable Mg numbers.

The abundances of the incompatible elements at Mg number = 60 in several of the major lava sequences are given in table 4. These were estimated either directly, or by extrapolation, from incompatible element – Mg number graphs. Error estimates reflect the degree of scatter for each element.

The table clearly shows the wide range of elemental abundances and ratios which exists in rocks of identical Mg number. Nb, for example, varies by a factor of 3.3, Zr/Nb ratio by 1.8. The variations in the elemental *ratios* preclude the possibility that they were caused by varying degrees of fractional crystallization. The differences must have been derived at source.

It was noted earlier that, on a regional scale, the abundances of the incompatible elements, except K, Rb and Ti, correlated positively with the degree of silica-undersaturation. The lavas used in table 4 belong, with the exception of only three samples, to the alkali basalt group (normative ne. < 5%). Within this more restricted major element compositional range, there is little or no correlation between the incompatible elements and the degree of silica-saturation. Regional variations apparently override the effects of major element composition (cf. Kesson 1973). If basic rocks with comparable major element chemistry may be taken to have had comparable evolutionary histories, then the variations in trace element chemistry in the lava sequences reflect local variations in the source material, i.e. mantle heterogeneity. In the following sections, two scales of differences between individual lava sequences will be examined. The other is a less well defined, larger-scale variation, involving groups of lava suites and related intrusions.

Nature of the mantle heterogeneity

By totalling the incompatible elements at Mg number = 60 in the lava sequences, two types of suite may be arbitrarily distinguished: those with values of Σ (Ba + Ce + Nb + P + Sr + Zr) > 3400 μg/g and those with less than 3400 μg/g. These may be termed the 'high' and 'low' groups respectively.

Within each group, however, there is a wide range in abundances of the individual elements. For example, Nb in the 'high' group varies from 24 to 65 μg/g at Mg number 60; the P_2O_5/Ce ratio in the same group ranges from 100 to 150. Thus the observation that the basalts of a certain suite are relatively depleted in one incompatible trace element carries no implication that they are depleted in all such elements.

Neither can there be any implication that the basalts are reflecting their generation in areas of relatively *primitive* or *depleted* mantle. The ratios of Zr/Nb and K/Ba have been used by Erlank & Kable (1976) to define such areas in the suboceanic mantle. They suggest that tholeiitic basalts with low values of both ratios represent melts of relatively primitive, undepleted mantle, while basalts with high ratios have been generated in areas which had undergone previous mantle fusion events, depleting them in Ba relative to K and Nb relative to Zr.

In the Midland Valley alkali basalts, however, no such simple relation exists (figure 6). Figure 6 is a plot of Zr/Nb against K/Ba ratios. Only alkali basalts have been plotted, since it is likely that these elements were not being retained in substantial amounts by a residual phase in the mantle during generation of those basalts. The Bathgate–Linlithgow lavas, belonging to the 'high' group, have a low Zr/Nb ratio (a 'primitive' characteristic) and a high K/Ba ratio (a 'depleted' characteristic). The Passage Group lavas of Ayrshire, one of the 'low' incompatible element suites, have a very low Zr/Nb ratio and a low K/Ba ratio. If the lower elemental abundances of the 'low' group point to a lower incompatible element content of their mantle sources, then that depletion has not been caused by a previous melting event within an originally homogeneous mantle.

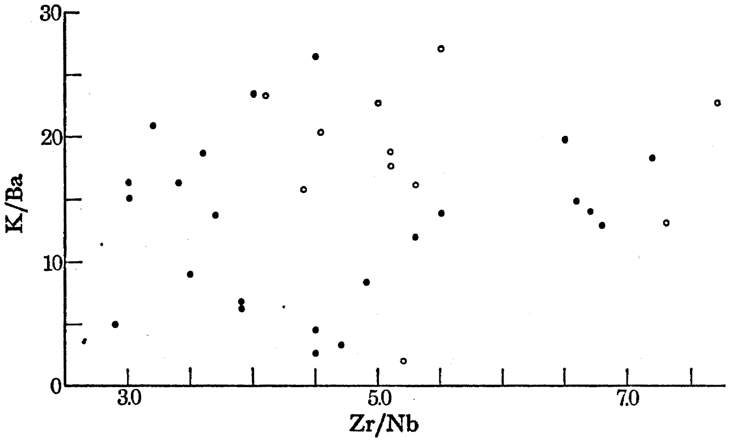

FIGURE 6. Zr/Nb ratio plotted against K/Ba ratio in alkali basalts (Mg number ⩾ 60) of the Midland Valley province. Open circles, hy.-norm. basalts; closed circles, basalts with ne. < 5 %.

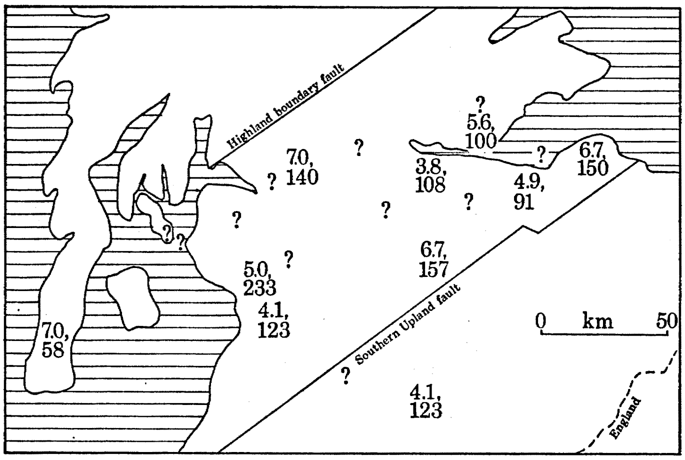

FIGURE 7. Inferred Zr/Nb (upper figures) and P_2O_5/Ce (lower figures) ratios of the mantle sources of the various Midland Valley lava suites. Question marks indicate sequences for which insufficient data are currently available.

These points are summarized in figure 7, where the average Zr/Nb and P_2O_5/Ce ratios at Mg number 60 for the main lava sequences and thus their inferred mantle sources are shown.

It appears, therefore, that the incompatible elements were not uniformly distributed in the Midland Valley mantle sources. They showed apparently non-systematic variations both in their absolute and relative concentrations.

Larger-scale heterogeneities

The inter-suite characteristics described above may, in some instances, be extended to cover geographical areas that include several phases of magmatism. In a K–Ti–2P diagram

(Schmincke & Flower 1974), the composition fields for basic rocks from East Lothian and Ayrshire show very little overlap (figure 8). Both fields contain data for rocks varying in age from Dinantian to late Carboniferous or early Permian and ranging in character from hy.-normative to strongly silica-undersaturated (ne. > 10%). The source volume of the Ayrshire rocks appears to have been rather different from that underlying East Lothian for a considerable period of time (more than 50 Ma?).

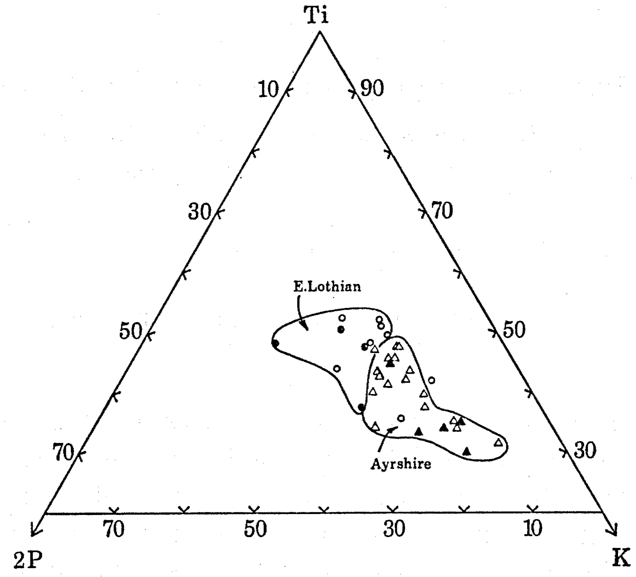

FIGURE 8. Ti–K–2P plot (atom percentages) for alkaline basic rocks (defined as having normative 100 An/(An + Ab) ⩾ 50) of Permo-Carboniferous age from Ayrshire (triangles) and East Lothian (circles). Open symbols, ne. < 5%; closed symbols, ne. ⩾ 5%.

It seems likely that several distinct areas of this type, each covering some hundreds of square kilometres, exist within the Midland Valley province but the lack of data currently precludes their clear definition. It follows from the preceding discussion, however, that within each of these larger areas, smaller-scale variations, involving different elements, also occur.

CAUSES OF MANTLE HETEROGENEITY

One consequence of the petrogenetic model used in this paper is that the ratios of the incompatible elements in the hy.-normative basalts reflect those of their mantle sources. Certain inferred ratios are presented in table 5 and compared with the estimated ratios in other sources of alkaline basalts, mainly based on data from oceanic islands. The Midland Valley ratios are, of course, modes; source heterogeneity provides variable ranges of these ratios.

The Permo-Carboniferous mantle beneath the Midland Valley appears to have been rather similar to the present sub-oceanic mantle in its relative abundances of K, Nb, P, Rb, Sr and Zr. It was apparently rather richer in Ba and poorer in Ce.

Sun & Hanson (1975) and Hanson (1977) have recently discussed the relations between oceanic island basalts and oceanic ridge basalts, outlining the need for a process or processes that can effectively enrich in the incompatible elements the sources of the alkaline basalts and/or deplete those of the low-K tholeiites. Enrichment of mantle by metasomatic fluids

(Lloyd & Bailey 1975) or by a network of basaltic to ultrabasic veins are possibilities cited by Hanson (1977).

Of some interest in this respect is the incompatible element chemistry of a low-K tholeiite from the base of the Dinantian lava succession in Kintyre (Macdonald 1975). Allowing that such rocks are formed by moderate (20–25%) degrees of melting of mantle peridotite, leaving a residue of harzburgitic composition, then the ratios of the incompatible elements should reflect the mantle source, perhaps even more accurately than those of the hy.-normative members of the alkaline suite.

TABLE 5. INFERRED ELEMENT RATIOS OF CERTAIN MANTLE SOURCE AREAS

	Rb/Sr	K/Sr	K/Rb	K/Ba	Ba/Nb	Zr/Nb	P_2O_5/Ce	K/Ce	references
sources of Midland Valley alkaline rocks	0.05	19	350	19	~9	5	90	219	this paper
sources of oceanic alkaline basic rocks	0.04	18	400	28	16	6.6	75	140	Sun & Hanson (1975), Langmuir *et al.* (1977)
low-K tholeiite, Kintyre	0.014	12	830	16	35	24	138	208	this paper

The Rb and Sr contents of the Kintyre low-K tholeiite are 2 and 140 μg/g respectively, with an Rb/Sr ratio of 0.0143. These data are consistent with the suggestion that the rock formed by 20% partial melting, with up to 20% subsequent fractional crystallization, of a mantle source containing 23–28 μg Sr/g and 0.3–0.4 μg Rb/g. These figures compare closely with those used by Hofmann & Hart (1978, p. 49) for the sub-oceanic mantle. The K content of the Kintyre source would be 266–332 μg/g and the K/Rb ratio 830, again consistent with Hofmann & Hart's estimates.

Certain other inferred geochemical parameters of the source of the Kintyre low-K tholeiite are given in table 5 and compared with those deduced for the volumetrically much more abundant Kintyre alkaline lavas. The tholeiite source was depleted in Ce, Nb and Rb relative to the source of the alkaline basalts. The situation thus mirrors that of the present day ocean basalts.

Several interesting possibilities are raised by this unique flow among the Midland Valley lavas.

(i) It was generated in a different pressure régime from the alkaline rocks. The mantle would then be vertically heterogeneous chemically.

(ii) It represents the products of fusion of an area of mantle not affected by the metasomatic event which effectively 'rejuvenated' the incompatible element chemistry of the mantle source.

(iii) It represents fusion of a mantle source, depletion of which had contributed at some earlier stage to the enrichment of the eventual sources of the alkaline basalts.

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