# Geochemistry of late Caledonian minettes from Northern Britain: implications for the Caledonian sub-continental lithospheric mantle

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## Abstract

The geochemistry of late Caledonian minettes from across the orogenic belt is compared in order to constrain the composition of the Caledonian sub-continental lithospheric mantle (SCLM). All the minettes are similar petrographically and chemically and several samples have characteristics typical of near primary mantle melts. Samples from the Northern Highlands and the Caledonian foreland show enrichment in many trace elements (notably LILE and *LREE*) relative to those from the Grampians, the Southern Uplands and northern England, coupled with distinct Nd and Sr isotope characteristics. Processes such as fractional crystallization, crustal assimilation, and partial melting played a negligible role in creating the differences between the two groups which reflect long-term, time-integrated differences in the compositions of their SCLM sources. The Great Glen Fault appears to represent the boundary between these two lithospheric mantle domains. Other currently exposed Caledonian tectonic dislocations cannot be correlated directly with compositional changes within the SCLM. The chemical provinciality displayed by the minettes shows some resemblance to that within other late Caledonian igneous suites, including the newer granites, suggesting that the minettes may represent the lithospheric mantle contributions to these rocks.

KEYWORDS: Caledonian, continental lithospheric mantle, minette, newer granites, Great Glen fault.

### Introduction

POST OROGENIC, late Caledonian calc-alkaline lamprophyres crop out as dykes across the whole of the Caledonian orogen, from the North West Highlands of Scotland to the English Lake District. They are widely distributed, but volumetrically minor, only forming significant dyke swarms in local instances. Previous work has concentrated on the petrogenesis of individual dykes or groups of dykes in discrete geographical areas (Macdonald *et al.*, 1985, 1986; Rock *et al.*, 1986*a,b*; Henney, 1991) and on the possible relation of the lamprophyres to Caledonian granitoids and sygenites (Thompson and Fowler,

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1986; Rock and Hunter, 1987). Shand *et al.* (1994) related the chemistry of calc-alkaline lamprophyres from the eastern Southern Uplands to the local late-Caledonian tectono-magmatic regime, but the only pan-orogenic study is the preliminary work of Rock *et al.* (1988) who were unable to obtain data for comparable rock types, but instead used the sparse available analyses for calc-alkaline lamprophyres (*sensu lato*).

Throughout the Caledonian orogen all four principal types of calc-alkaline lamprophyre (minettes, kersantites, spessartites and vogesites) are present. Minettes are more abundant in the Northern Highlands and spessartites in the Southern Uplands.



FIG. 1. Map of Northern Britain showing the locations of the minettes discussed in the text, and major Caledonian tectonic boundaries.

Nevertheless, in each region the most mafic, primitive compositions found are minettes characterized by high MgO contents ( $\leq 15$  wt.%), high transition metal trace elements (Ni  $\leq 600$  ppm, Cr  $\leq 800$  ppm) and high Mg numbers (70-83). This indicates that these lamprophyres have undergone limited fractionation and retain compositions close to primary mantle melts. It is now widely accepted that such volatile-rich, mafic, potassic magmas are formed by small degree melting either, of metasomatized sub-continental lithospheric mantle (SCLM); or, of metasomatic veins within the SCLM (Luhr et al., 1989; McKenzie, 1989; Sheppard and Taylor, 1992; Gibson et al., 1993, 1995; Thompson and Gibson, 1994). Such melts are therefore either dominantly or wholly lithospheric in origin and preserve the best evidence for the composition of the SCLM. Production of the late Caledonian minettes was probably triggered by heating associated with post-orogenic extension and collapse (Watson, 1984; Thompson et al., 1989; Shand et al., 1994). Other attempts to investigate the role of the SCLM and its role in Caledonian magmatism have been restricted to interpolating data from the Siluro-Devonian volcanics (Thirlwall, 1981, 1982, 1986), and the extensive Newer Granite suite (Halliday, 1984; Halliday et al., 1985; Frost and O'Nions, 1985;

Clayburn, 1988). However, these rocks represent the end products of potentially multi-source, multi-stage processes in which the relative roles of the various crustal and mantle reservoirs involved, and interactions between them, are difficult to disentangle.

This paper presents new data for minettes from the Affric-Kintail and Creagan Rhambher areas of the Northern Highlands and the Onich area of the Grampian Highlands and compares them with others from across the Caledonides to investigate the relationship between chemistry and geographic or tectonic setting. Only minettes that satisfy the chemical and mineralogical screens of Rock (1984) have been used. The sample locations and their relationship to the Caledonian tectonic architecture are shown in Fig. 1. The samples used include dykes from areas of relatively low intrusion density, and from two regional swarms, the Affric-Kintail swarm in the Northern Highlands and the Criffell swarm from the western Southern Uplands (Henney, 1991). All the dykes in this study are undeformed, except for minor localized shearing, and are the products of a post-orogenic phase of magmatism dated at 415 to 395 Ma (Barnes et al., 1986; Macdonald et al., 1986; Rock and Rundle, 1986; Rock et al., 1986b, 1988; Thirlwall, 1989).

#### Analytical techniques.

Forty nine minettes from the Affric-Kintail swarm and two from the Onich area have been analyzed at the University of Birmingham for major and trace elements by X-ray fluorescence using a Philips PW1400 automated wavelength dispersive XRF and the methods of Morrison et al. (1987). Trace elements were determined on pressed powder pellets using a Rh anode X-ray tube for excitation. Major elements were determined on 46 mm diameter fusion beads from pre-ignited powders, with spectroflux 100B at a 1:5 ratio, using Sc or Rh anodes. Two samples from the Creagan Rhambher area were analysed using a combination of ICPAES at Oxford Brookes University, for major elements; and XRF methods at the British Geological Survey, for trace elements. Rare Earth Element determinations on the samples were obtained by ICPAES at Royal Holloway, University of London, using whole rock dissolution methods and cation-exchange preconcentration, following the methodology of Walsh et al. (1981). The Rb-Sr and Sm-Nd isotope determinations were carried out at the BGS Isotope facility, Grays Inn, London, using a VG 354 mass spectrometer (Henney, 1991). Mineral chemistry was determined at the University of Manchester on a Geoscan, energy dispersive, electron microprobe, using a 15 kV beam current and 100 s count time. Representative mineral data are given in Tables 1 and 2 and minette analyses

TABLE 1. Microprobe data for representative micas from Northern Highlands (DO 93/6, DO93/7) and Southern Uplands (1370) minettes. mg# = molar 100\*Mg/(Mg+Fe), (-: not analysed, b.d.: below detection limit). For sample 1370 the oxygen equivalent of fluorine calculated based on: O=F = wt% F(at. wt.O/2\*atm.wt.F), (Henney, 1991). Data from this study and Henney (1991)

Sample	DO 93/6	DO 93/6	DO 93/6	DO 93/6	DO 93/6	DO 93/7	DO 93/7	1370	1370	1370	1370
Analysis no.	18 core	22 core	30 core	107 core	107 rim	172 core	172 rim	core 1	rim 1	core 4	core 4
SiO <sub>2</sub>	37.39	38.12	36.22	38.74	38.13	38.85	37.08	38.56	35.06	38.63	37.89
TiO <sub>2</sub>	3.83	4.21	5.76	4.08	4.92	4.12	5.33	3.36	3.89	3.27	3.29
Cr <sub>2</sub> O <sub>3</sub>	b.d.	1.70	b.d.	1.56	b.d.	0.45	b.d.	0.13	0.02	0.03	0.03
Al <sub>2</sub> O <sub>3</sub>	13.60	14.26	12.53	14.63	13.22	13.73	12.75	14.76	15.30	14.37	14.37
FeO	15.76	5.95	16.03	5.90	9.39	6.48	13.53	5.56	14.74	6.63	6.97
MnO	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.07	0.27	0.06	0.05
MgO	15.03	20.17	13.46	20.53	19.05	20.04	15.47	20.99	15.68	20.40	20.78
CaO	0.20	0.20	0.25	0.26	0.24	b.d.	b.d.	b.d.	0.02	0.01	0.03
Na <sub>2</sub> O	0.94	0.56	1.28	0.64	0.95	0.35	0.66	0.34	0.57	0.41	0.40
K <sub>2</sub> O	8.69	9.38	8.02	9.54	8.57	9.48	8.26	9.52	7.65	9.01	8.90
F	—	-	_			-	_	1.52	1.06	1.36	1.16
Total	95.42	94.55	93.55	95.89	94.48	93.49	93.08	94.81	94.26	94.18	93.87
Si	5.60	5.53	5.56	5.54	5.59	5.68	5.63	5.45	5.22	5.48	5.42
Ti	0.43	0.46	0.66	0.44	0.54	0.45	0.61	0.36	0.44	0.35	0.35
Cr	0	0.19	0	0.18	0	0.05	0	0.01	0	0	0
Al	2.40	2.44	2.27	2.47	2.29	2.37	2.28	2.46	2.68	2.40	2.51
Fe	1.97	0.72	2.06	0.70	1.15	0.79	1.72	0.66	1.83	0.79	0.83
Mn	0	0	0	0	0	0	0	0.01	0.03	0.01	0.01
Mg	3.36	4.36	3.08	4.35	4.17	4.37	3.50	4.42	3.48	4.43	4.43
Ca	0.03	0.03	0.04	0.04	0.04	0	0	0	0	0	0
Na	0.27	0.16	0.38	0.18	0.27	0.10	0.19	0.09	0.16	0.11	0.11
Κ	1.66	1.74	1.57	1.74	1.61	1.77	1.60	1.71	1.45	1.63	1.62
0	22	22	22	22	22	22	22	22	22	22	22
Cation tot.	15.73	15.64	15.62	15.63	15.66	15.59	15.52	15.17	15.31	15.20	15.29
mg#	63.0	85.8	60.0	86.1	78.3	84.6	67.1	87.0	65.5	84.9	84.2

in Table 3. These have been selected to illustrate the compositional range available; a fuller data set is available from the authors on request.

# Petrography and mineral chemistry

Petrographically, the Northern Highlands and Onich minettes are porphyritic with varying amounts of biotite-phlogopite, clinopyroxene and olivine phenocrysts; but only mica is a ubiquitous phenocryst phase. Many are flow textured with strongly aligned micas. Felsic phases are restricted to the groundmass, where K-feldspar, often sanidine, dominates and is commonly spherulitic.

Mica phenocrysts are fresh and display skeletal form; often described as castellated (Rock, 1984).

These skeletal phenocrysts can reach up to 10 mm in diameter but are generally in the range of 2-5 mm. The micas display complex oscillatory zoning, but also show normal zoning overall, with generally phlogopitic cores surrounded by strongly pleochroic, biotite-rich rims. The olivines are altered, often entirely pseudomorphed by mixtures of serpentine and carbonate forming equidimensional patches 2-3 mm across, that appear to have replaced euhedral phenocrysts. The clinopyroxenes are also altered, but far less extensively, and form wellshaped euhedral crystals with dimensions generally in the range 3-5 mm. Probe analyses of unaltered pyroxenes show they have a narrow range covering diopside, endiopside, augite and salite compositions. Groundmass minerals are varying amounts of Kfeldspar, well-shaped apatites, some of which may be

TABLE 2. Microprobe data for representative clinopyroxenes from Northern Highlands (GA 93/1, UG 93/2, UG 93/6) and Southern Uplands (1329, 1312) minettes. mg# = molar 100\*Mg/(Mg+Fe), (-: not analysed, b.d.: below detection limit). Data sources as Table 1

Sample Analysis no.	GA 93/1 190 core	GA 93/1 192 core	GA 93/1 198 core	UG93/6 1 core	UG93/2 207 core	1329 core 6	1329 rim 6	1312 core 1	1312 rim 1
SiO <sub>2</sub>	54.32	52.24	54.02	52.50	51.52	51.87	52.05	52.75	53.09
TiO <sub>2</sub>	0.40	0.9	0.43	0.30	1.04	0.42	0.43	0.33	0.35
$Cr_2O_3$	0.81	b.d.	0.93	b.d.	0.23	0.16	0.15	0.35	0.36
$Al_2O_3$	1.23	2.91	1.37	1.27	3.08	2.48	2.5	1.86	1.98
FeO	4.26	6.95	4.12	8.79	8.02	5.53	5.33	4.9	4.74
MnO	b.d.	b.d.	b.d.	0.37	b.d.	0.17	0.11	0.16	0.15
MgO	17.21	15.24	17.09	13.01	14.32	16.4	16.97	18.47	18.26
CaO	22.39	21.88	22.11	21.25	21.88	21.93	21.31	19.38	19.91
Na <sub>2</sub> O	b.d.	0.34	0.41	1.50	0.29	0.39	0.36	0.42	0.43
K <sub>2</sub> O	b.d.	0.10	0.1	b.d.	0.12	b.d.	b.d.	b.d.	b.d.
Total	100.62	100.56	100.59	99.01	100.51	99.35	99.21	98.62	99.27
Si	1.969	1.919	1.946	1.982	1.906	1.914	1.916	1.938	1.939
Ti	0.011	0.025	0.012	0.009	0.029	0.012	0.012	0.009	0.01
Cr	0.023	0	0.027	0	0.007	0.005	0.004	0.01	0.011
Al	0.053	0.126	0.046	0.057	0.135	0.108	0.109	0.081	0.085
Fe	0.129	0.214	0.125	0.278	0.248	0.171	0.164	0.152	0.145
Mn	0	0	0	0.012	0	0.005	0.004	0.005	0.005
Mg	0.93	0.835	0.932	0.732	0.79	0.902	0.931	1.011	0.994
Ca	0.87	0.861	0.864	0.859	0.867	0.867	0.84	0.763	0.779
Na	0	0.024	0.029	0.11	0.021	0.028	0.026	0.03	0.031
K	0	0.005	0.005	0	0.006	0	0	0	0
0	6	6	6	6	6	6	6	6	6
Cation total	3.985	4.009	3.986	4.039	4.009	4.012	4.006	3.999	3.999
mg#	87.8	79.6	88.2	72.5	84.1	84.0	85.0	87.0	87.0

microphenocrysts; biotite-phlogopite micas, greenbrown amphibole, minor plagioclase, Fe-Ti oxides, secondary minerals such as carbonate and chlorite and in some cases, minor epidote.

Petrographically the minettes described here resemble those from elsewhere in the Caledonides (Rock, 1984; Henney, 1991; Shand et al., 1994). Representative data for clinopyroxene and mica phenocrysts in minettes from the Northern Highlands and the Southern Uplands are presented in Tables 1 and 2, and Figs 2 and 3. These clearly demonstrate that the phenocryst populations of both suites are essentially identical. They also resemble the micas and clinopyroxenes produced in the experimental studies of Esperança and Holloway (1987) on a mafic minette from the Navajo Volcanic Field of the Colorado Plateau. These pyroxene and mica compositions closely resemble those reported from other worldwide minette occurrences (Bachinski and Simpson, 1984; Rock, 1991).

The petrographic features of the minettes, in particular the presence of euhedral and skeletal phenocrysts, flow textures, and the common occurrence of spherulitic groundmass feldspars, all indicate that they probably formed from fairly rapidly chilled magmas. Much of the alteration displayed by the olivine and clinopyroxene phenocrysts could be autometasomatic and caused by exsolution of fluids during upward migration and emplacement of the dyke magmas. The zoning shown by the mica phenocrysts, from Mg-rich cores to more Fe-rich rims, and the absence of significant zoning in the pyroxene phenocrysts, fit the trends predicted by Esperança and Holloway (1987) for cooling and crystallization of a mafic minette magma rising from near- or sub-Moho depths. Such conditions would also have promoted the rapid growth of large, often skeletal micas. Some Northern Highland minettes also contain discrete xenoliths of probable cognate origin consisting of coarse-grained, (>5 mm), mixtures of phlogopite-

TABLE 3. Representative geochemical data for Caledonian minettes; (-: not analysed, b.d.: below detection limit). The Southern Uplands minettes major element data have been recalculated to 100% on a volatile free basis (Henney, 1991). mg# = molar Mg/(Mg+Fe), Fe normalized to Fe<sup>3</sup>/Fe<sub>t</sub> ratio of 0.3 in calculation. PJH208 and PHR29 are from Creagan Rhamber in the eastern section of the Northern Highlands, see Fig. 1. (Grid References: DO93/6 NG9398-2070; DO93/7 NG 9399-2071; GA93/1 NH 1752-2353; DO93/3 NG 8919-2280; PJH208 and PH29 from NH622-942, two localities 100m apart; Criffell samples are from the Western Southern Uplands (Henney, 1991)

Sample	DO 93/6	5 DO 93/7	Norther GA 93/1	n Highland DO 93/1	I Minettes DO 93/3	3 PJH 20	8 PHR 29	Criffel PFTO3	Minettes BBP22
SiO <sub>2</sub>	51.91	51.40	53.62	50.83	51.43	45.60	46.18	55.78	56.08
TiO2	1.39	1.41	1.04	1.40	0.55	0.81	0.80	1.12	1.25
Al <sub>2</sub> O <sub>3</sub>	12.65	12.07	12.79	12.14	10.00	10.28	9.77	14.06	15.29
Fe <sub>2</sub> O <sub>3</sub>	7.30	7.64	7.12	7.60	8.54	5.94	6.05	6.44	6.99
MnO	0.10	0.11	0.11	0.11	0.13	0.14	0.17	0.10	0.10
MgO	6.40	7.56	8.20	7.14	14.76	7.09	7.06	7.50	5.68
CaO	9.07	8.33	7.73	8.14	7.72	10.03	10.51	5.97	6.70
Na <sub>2</sub> O	2.81	2.48	3.14	2.55	1.49	1.19	1.00	2.33	2.83
K <sub>2</sub> O	5.41	5.24	3.58	5.61	3.99	4.93	5.03	5.88	4.48
$P_2O_5$	2.43	2.49	1.03	2.43	0.47	1.53	1.73	0.81	0.59
BaO	0.35	0.46	0.25	0.47	0.39	1.58	1.42	_	_
Cr <sub>2</sub> O <sub>3</sub>	0.05	0.05	0.06	0.05	0.02	—	—	_	_
NiO	0.02	0.02	0.03	0.02	0.05		_		_
SrO	0.21	0.19	0.20	0.64	0.27	0.34	0.51	—	
LOI	-	-	-	_	-	8.07	7.38	-	-
Total	100.09	99,44	98.90	99.14	99.80	97.53	97.60	100.00	100.00
mg#	72.33	74.68	77.44	73.69	83.75	54.41	53.85	76.71	74.69
K <sub>2</sub> O/Na <sub>2</sub> O	1.93	2.11	1.14	2.20	5.48	4.14	5.03	2.52	1.52
Cu	53	37	38	66	53	52	47	158	11/
Nh	28.4	383	14.8	28	30	17	16	1/1	14
Ni	140	200	250	159	127	150	123	209	197
Rb	87.1	51	69 5	85	88.2	101	103	148	111
Sr	1751	1610	1648	5433	2294	2881	4276	1230	1245
Th	hđ	39	11	2	12	38	36	21	13
Y	18.4	35.9	27.8	21.9	21.6	31	30	16	18
Zn	97	75	83	103	97	82	71	91	70
Zr	341	205	261	395	377	424	319	288	214
Ba	3109	10021	2194	4241	3331	14150	12671	2638	2021
Cr	401	612	378	427	322	445	423	289	320
v	126	138	108	138	130	95	86	205	230
La	170	173.6	138.5	178.7	160	208	192	111	43
Ce	-	398.7	305.4	410		417	449	231	98
Pr	_	43.3	33.7	48.7		_	-		_
Nd		147.1	118.6	152.3	_	216	226	95.4	7.38
Sm	_	19.7	17.5	20.1	_	32.6	33.6	14.7	48.8
Eu		4.5	4	4.5	_			3.15	1.88
Gd	_	10.9	10.4	11		_	-	-	-
Dy	_	4.7	4.8	4.6	-	_	-	-	_
Ho	_	1.29	1.48	1.18	-	_	_	_	_
Yb	_	1.15	1.29	1.09		_	_	1.25	1.39
Lu	-	0.16	0.18	0.16			-	0.19	0.23
ε <sub>Nd</sub>	-			_	-	-6.9	-7.2	-1.7	-1
Sr <sub>i</sub>	-	-	-	-	_	0.707	0.70768	0.705	93 0.70540



Fig. 2. Mol.% Mg-Fe-Al for mica phenocrysts from minettes of the Affric-Kintail lamprophyre dyke swarm (closed circles) and the Criffell area of the Southern Uplands (open circles). Data from this study and Henney (1991).

biotite and clinopyroxene, with variable amounts of hornblende, apatite and rare interstitial K-feldspar. They resemble cognate xenoliths reported from other mafic minettes (Thompson *et al.*, 1989) and probably formed as side wall precipitates in the feeder dykes. Taken together, the textural features also indicate that mica was a common liquidus phase in the minettes.

# Minette geochemistry

The major and transitional trace element compositions of all the late Caledonian minettes are similar. No significant differences could be detected between samples from areas of relatively high or relatively low intrusion density, or between dykes from the



FIG. 3. Mol.% Ca-Mg-Fe for clinopyroxene phenocrysts. Symbols, data sources as in Fig. 2.



FIG. 4 Ni and K<sub>2</sub>O/Na<sub>2</sub>O vs. MgO in late Caledonian minettes. Symbols as follows:  $\blacksquare$  — Summer Isles;  $\blacklozenge$  — Affric-Kintail and Creagan Rhambher in the Northern Highlands;  $\Box$  — Onich area;  $\triangle$  — western and eastern Southern Uplands;  $\bigcirc$  — Sedbergh. See Fig. 1 for localities. Data sources: this study and our unpublished data, Thompson *et al.* (1984); Henney, (1991); Shand *et al.*, (1994).



FIG. 5. Chondrite-normalized (Thompson *et al.*, 1984) spidergrams for representative minettes from the NHL (A) and SL (B), respectively. Data sources as for Fig. 4.

western and eastern regions of either the Northern Highlands or the Southern Uplands respectively. There is a considerable compositional range within the dykes as a whole, for example  $K_2O/Na_2O$  varies from ~7 to ~1, MgO from 5 to 15%, Ni from 120 to 600 ppm and Cr 156 to 866 ppm, although relatively mafic samples with MgO >6% and correspondingly high Mg numbers predominate (Fig. 4). This similarity in both mineral and whole-rock chemistries (Figs 2 to 4) is considered to be evidence that the various groups of minettes have formed under broadly similar petrogenetic conditions. General aspects of these have been reviewed elsewhere (Shand *et al.*, 1994) so this section focuses on those aspects most relevant to the themes of this paper.

Figure 5 shows chondrite-normalized plots illustrating the range of incompatible element abundances in the minettes. There is considerable sample-tosample variability in trace element ratios such as Ba/ Rb, Th/K and Ce/Sr, which probably reflects generation by melting of an heterogenously-veined mantle, rather than a source where metasomatic products are evenly distributed (Thompson *et al.*,

1993). Nevertheless, the patterns are very similar overall. Typically, they show high absolute abundances of the LILE (Ba, Rb, Th, K, Sr) and LREE, and unlike alkaline lamprophyres, usually show little or no depletion of the LILE relative to the LREE. There are depletions in some of the HFSE, most notably Nb and Ti, relative to the other incompatible elements, and also low abundances overall for the *HREE*, (Yb $\leq 2$  ppm, Lu $\leq 1$  ppm; Table 3). These trace element characteristics are distinctive and similar to those of various worldwide occurrences of mafic potassic magmas, as well as those for subduction-related magmas, except that the absolute element concentrations and ratios are far higher than those in any reported volcanic arc magmas (Thompson et al., 1984; Luhr et al., 1989, Thompson et al., 1989; Sheppard and Taylor, 1992; Gibson et al., 1993).

Figure 5 also shows that there are distinct differences in incompatible trace element abundances and ratios between the minettes discussed here, which can be used to divide them into two main groups. Figure 5A shows patterns for dykes from the



FIG. 6. Nb vs. Y for late Caledonian minettes, symbols and locations as for Fig 4.

Northern Highlands and the Summer Isles on the Caledonian foreland (NHL), and Fig. 5B patterns for dykes from locations south of the Great Glen fault (SL). The main difference between the two groups is that, relative to the SL, the NHL minettes are enriched in the more incompatible elements, namely P and all the elements plotted to the left of this, although the two groups have overlapping abundances of the less incompatible elements such as Ti and Y. The differences are greatest for the most incompatible elements and some NHL minettes exhibit extreme values of the *LILE* (Ba~14000

ppm, Sr ~ 19000 ppm) far in excess of any found in the SL. Nevertheless, the contrasts between the two minette groups are not restricted to any particular element group but include the *LILE*, the *LREE* and the *HFSE*. This is shown by Fig. 6, a plot of Nb vs. Y; and also Fig. 7, which shows rare earth element patterns for the minettes. The NHL are enriched in the *LREE*, (La and Ce 400–600 times chondrites, average Ce<sub>N</sub>/Yb<sub>N</sub> ratios of 65) relative to the SL, (La and Ce 300 times chondrites, average Ce<sub>N</sub>/Yb<sub>N</sub> of 22) but the *HREE* abundances for both groups are identical (Lu 4 to 7 times chondrites).

Figure 8 shows Sr and Nd isotope data for the NHL and SL minettes (Henney, 1991; Shand *et al.*, 1994) together with the ranges and average values for various crustal materials (Frost and O'Nions, 1985; van Breemen and Hawkesworth, 1980; Halliday, 1984). It is clear from this that the two groups are also isotopically distinct. The SL data display slightly negative  $\varepsilon_{Nd}$  values of -1 to -2 coupled with a much wider spread of Sr<sub>i</sub> of 0.70510 to 0.70700. The NHL minettes have distinctly lower  $\varepsilon_{Nd}$ , around -7, and higher Sr<sub>i</sub> of 0.70726 to 0.70768.

# Discussion

The compositional range in the minettes described here (Fig. 4) clearly indicates that fractionation has occurred, whilst the position of the NHL samples on Fig. 8, lying between the values for the SL minettes and crustal materials, could be interpreted as evidence



FIG. 7. Chondrite-normalized (Nakamura, 1974) *REE* plots for: (A) NHL minettes; (B) SL minettes; (C) a comparison with *REE* patterns for minettes from the Elkheads mountains, Colorado, W. USA. Data sources as for Fig. 4 plus Thompson *et al.*, (1989).



FIG. 8. ε<sub>Nd</sub>-Sr<sub>i</sub> plot for NHL (closed symbols) and SL minettes (open symbols) and relevant crustal rocks calculated at 400 Ma. ALG, ALA and M refer to the average granulite-facies Lewisian, average amphibolite-facies Lewisian and average Moine values used in the mixing calculations, respectively. Circled numbers refer to mixtures of PFT03 with ALG (1), ALA (2) and M (3), respectively. Data from Frost and O'Nions (1985); van Breemen and Hawkesworth (1980); Halliday (1984); Henney (1991); Shand *et al.* (1994).

for crustal assimilation. Hence the possibility arises that the geochemical differences between the NHL and SL might be attributed, at least in part, to various combinations of these processes. A major difficulty with this can be seen from the data plotted in Fig. 4 which demonstrate that the NHL and SL minette groups have similar MgO ranges, and show coupled decreases in MgO, K<sub>2</sub>O/Na<sub>2</sub>O and compatible trace elements such as Ni, reflecting the early appearance of phlogopite and olivine on the liquidus. This means that elements such as K, Ba and Rb will not have been behaving incompatibly during the evolution of these magmas. The data for these particular elements, may if anything, underestimate the contrast between the two groups for all except the most mafic variants. Similar trends have been recorded in other minette suites (Thompson et al., 1989).

The minettes all occur as minor intrusions. No petrographic evidence of assimilation or partial melting of metasedimentary xenoliths is seen in the NHL. Esperança and Holloway (1987) suggested, on experimental grounds, that minettes containing the assemblage olivine + clinopyroxene + phlogopite  $\pm$  oxide could not have been significantly reequilibrated at low pressures and temperatures, which supports our interpretation that the textures of the minette dykes reflect those of rapidly emplaced and chilled liquids. There are thus no geological grounds for invoking AFC-type processes within large, high level magma chambers.

Figure 8 shows the results of simple mixing calculations between possible crustal contaminant reservoirs and the most mafic SL minette sample (PFT03, Table 2) for which we have isotopic data. To



FiG. 9. Chondrite-normalized spidergrams (Thompson *et al.*, 1984) documenting the effects of adding representative fusible crustal rock types in the amounts required by the isotopic calculations shown in Fig. 8 to a mafic minette (PFT03) from the Southern Uplands. Samples used: 7H, a microcline-bearing, acid, Lewsian granulite-facies gneiss; 5322, an evolved, Lewsian amphibolite-facies gneiss; and MS324a Moine pelite (Weaver and Tarney, 1980, 1981; Thompson *et al.*, 1986). NHL minette, DO93/7 is shown for comparison.

change the values of  $\varepsilon_{Nd}$  in SL minettes to those found in the NHL minettes, would have required the addition of up to 50% Moine metasediments, or else up to 40% granulite facies or 20% amphibolite facies Lewisian gneisses. We have calculated simple mixtures of sample PFT03 and possible crustal contaminants, in the amounts required by the isotopic data. Since there are considerable thermomechanical problems in assimilating material across the walls of rapidly ascending minette magmas, we used, not average crustal compositions, but the more acid components with relatively low solidus and liquidus temperatures. These samples represent not only the most easily fused but also the most incompatible, trace element-rich portions of these crustal rock suites. The results are shown in Fig. 9, along with a mafic NHL minette, DO93/7, for comparison. This clearly demonstrates that the effect of incorporating sialic material into minette magmas is to cause a considerable dilution in most of the incompatible trace elements in the resultant liquids. The main exceptions are Rb and Y, which increased in the mix with Moine pelite. Fowler (1988) has carried out extensive modelling of the effects of Moine assimilation by the Glen Dessary melasyenite, which has many chemical similarities to the minettes. One of the features of his calculations is the ubiquitous presence of Eu anomalies, something which is notably lacking in all the minette data (Fig. 7). We thus conclude that crustal contamination (aided or unaided by fractional crystallization processes) played no significant part in generating the trace element and isotopic differences between the two main groups of minettes discussed here.

The progressive enrichment shown by the NHL minettes in the more incompatible elements, relative to the SL, implies the parental magmas of the two groups could have been generated by variable degrees of partial melting of a similar mantle source composition. Some limits can be put on the melt fractions involved. Two patterns that illustrate the REE range in Upper-Miocene minettes from the Elkheads region of NW Colorado (Thompson et al., 1989) are plotted along with the Scottish samples in Fig. 7C. The overall similarities of the REE patterns for the Colorado and SL minettes are striking. McKenzie and O'Nions (1991) have applied REE inversion modelling to the Elkheads minettes. Their results suggest that they formed by 0.5 to 1.0% partial melting of an amphibole-bearing, previously metasomatized, mantle source. The LREE enrichment factor for this source, relative to a depleted MORB-type source, was calculated to be  $\sim 2$ . The REE inversion scheme can constrain processes that generate the bulk of the magmas, but not those that lead to enrichment in the very incompatible elements, such as K, which can be affected by melt fractions of 0.3% or less, partly because of the lack of precise and reliable distribution coefficients (Mckenzie and O'Nions, 1991). Nevertheless, these results imply that the NHL magmas were either the products of markedly <0.5% melting, or the products of similar degrees of melting of an even more LREE-enriched source. The latter scenario better fits the isotope data. The greater LREE enrichment in the NHL minettes coupled with their more negative  $\varepsilon_{Nd}$  values, relative to the SL minettes, requires quite distinct, timeintegrated, LREE-enrichments of the source regions of the two groups.

#### Caledonian geochemical provinciality

The minette data indicate that two principal Caledonian SCLM domains occurred below northern Britain and that their chemical features were established at quite separate periods of geological time. Future isotopic studies may distinguish subdomains within these two broad groups. The NHL group includes the Summer Isles minette and the dykes from the western and the eastern Northern Highlands. The SL minette group appears to extend from the Grampian region as far as the English Lake District. These domains thus straddle most of the Caledonian tectonic features (Fig. 1). Discrepancies between the positions of the surface expressions of major tectonic boundaries and the positions of compositional boundaries in the underlying SCLM have also been noted from other provinces, such as the Rio Grande rift in the Western USA (Gibson *et al.*, 1992). Seismic reflection profiling has demonstrated that tectonic discontinuities can rarely be traced beyond the Moho, and that, in regions where thin skinned tectonics predominated, they often extend only into the upper 10 km or so of the crust (Klemperer and Peddy, 1992).

The exception to this is the Great Glen fault. The contrasting chemistry of the minettes on each side of this feature suggests that it forms a major compositional boundary in the SCLM, but that other transcurrent faults such as the Highland Boundary and Southern Uplands faults do not. The BIRPS seismic profiles show the Great Glen fault, and its continuation as the Walls Boundary fault, cut vertically all the way through the crust as a rather narrow zone of disruption (no more than a few kilometres wide), and may continue through the entire lithosphere (Klemperer and Hobbs, 1992). Whether the fault zone juxtaposed different lithospheric mantle domains or merely acted as a barrier to continued northwards underthrusting of SCLM from the south as discussed below, is not clear. The extent and timing of strike-slip movements in the British Caledonides is still a matter of considerable debate, although it is widely accepted that large scale transcurrent movement of the order of several hundred kilometres has occurred along the Great Glen fault (van der Voo and Scotese, 1981; Esang and Piper, 1984; Watson, 1984; Bluck, 1985; Hutton, 1987; Hutton, 1988; D. Rogers et al., 1989). G. Rogers and Dunning (1991) have shown that the period between 429 and 425 Ma was a time of major movements within the Northern Scottish Caledonides and that transcurrent faulting effectively ceased during Old Red Sandstone times.

The southern domain stretches across the inferred position of the lapetus suture into northern England. Freeman et al. (1988) have interpreted BIRPS deep seismic reflection profiles for the Iapetus Suture zone as demonstrating underthrusting of mantle from the southern (Lake District) continent so as to partly underlie the northern continent during the late stages of Caledonian collision. Shand (1989), Henney (1991) and Shand et al. (1994) suggested that this underthrust Lake District SCLM is the source of the Southern Uplands minettes and its northerly extent is delineated by their distribution. They thus implied that these minettes had a different mantle source to lamprophyres from further north in the Caledonian orogenic belt. The data discussed here imply that some of this underthrusting might have extended much further north, and carried SCLM material from the southern continent below the Grampian Highlands. The lack of evidence for this northwards extension on the BIRPS profiles may be partly due to the difficulties of identifying deeper reflection events (Freeman *et al.*, 1988) or simply because it was obliterated by later tectono-magmatic events in the Midland Valley region. The emplacement of this source would have post-dated subduction and docking of the southern continental mass with Scotland.

The geochemical and isotopic provinciality within the minettes shows some similarities to, but also some significant differences from, that within other late Caledonian igneous suites. Stephens and Halliday (1984) and Halliday (1984) have grouped the newer granites into three suites: the 'Argyll' and 'Grampian' suites both have  $\varepsilon_{Nd} < -6$ , high Ba and Sr contents, contain inherited zircons and occur north of a 'Mid-Grampian Line'. In contrast, granitoids from further south (and northern England), the 'South of Scotland suite', have relatively low LREE, Ba, and Sr and higher  $\epsilon_{Nd}$  of -4 to +1. This resembles features of the minette data except the boundary recognized between the granitoid suites lies further south. Halliday et al. (1985) relate the geographical changes in isotopic and chemical characteristics to changes in the compositions of both the crust and SCLM. As inherited zircons are unequivocally derived from continental crust, they concluded that the  $\varepsilon_{Nd}$  signature was also predominantly crustal in origin and that possibly only the high Ba and Sr signatures were of mantle derivation. Halliday (1984) interpreted the 'Mid-Grampian Line' as indicating a change (probably thrust bounded) in the nature of the basement material from ancient crust in the NW, to younger crust in the SE. Powell et al. (1988) proposed that the Loch Awe-Ossian steep belt represented a major tectonic boundary between crustal rocks with characteristics of the Northern Highlands and those of the Grampian Highlands. The different boundaries to the geochemical provinces may reflect the fact that the more evolved igneous rocks collected contrasting chemical signatures from the various mantle and crustal reservoirs involved in their petrogenesis. Our data support the suggestion that the mantle component in the late Caledonian granitoids is chemically and isotopically similar to a minette type magma, as proposed by Thompson and Fowler (1986) and Fowler (1988).

The Old Red Sandstone volcanics show an increase in Sr, Ba, K, P and *LREE/HREE* to the NW which Thirlwall (1981, 1982) related to increasing distance from a subduction zone somewhere to the south. Thirlwall (1988, 1989) still argues for a direct relationship to subduction for the volcanics north of the Southern Uplands fault, but not for the igneous rocks to the south of this feature.

Instead, he proposed that they may be related to melting of underthrust Lake District lithosphere, as Pb isotope data indicates they contain crustal material isotopically similar to the Skiddaw Group sediments. Support for this model is provided by BIRPS seismic reflection profiling (Freeman *et al.*, 1988).

Thirlwall (1989), using samples with up to 70% SiO<sub>2</sub>, noted an apparent decrease in Sr content from west to east in late Caledonian igneous rocks across the whole of northern Scotland. He also delineated a narrow,  $\sim 80$  km wide, 'high-Sr zone' extending down the western margin of Scotland and across the Great Glen fault, characterized by rocks with high Ba, Sr and La/Y, and relatively low Rb, Th, U and Nb. This 'high-Sr zone' contains the the granitoids and syenites of the NW Highlands, plus the SW Highlands lavas and granitoids (that is those from immediately south of the Great Glen fault, but north of the 'Mid-Grampian Line'). The NHL minettes have the highest Sr contents of all the Caledonian rocks in Northern Scotland, and all but the Summer Isles minette lie outside this 'high-Sr zone'. The incompatible element-rich SCLM domain extended below the whole of the Northern Highlands north of the Great Glen fault. The compositions of the lavas and plutons, especially the evolved rocks with high SiO<sub>2</sub> contents, almost certainly reflect the end products of a series of magmatic interactions involving material from crust and mantle reservoirs of various ages, (see also Frost and O'Nions, 1985), whereas the minettes carry an essentially unadulterated SCLM signature.

#### Conclusions

(1) Late Caledonian minette dykes from across the orogenic belt can be split into two broad compositional groups on the basic of their incompatible element chemistry and Sr-Nd isotope compositions. The Northern Highlands lamprophyres (NHL) have high abundances of the incompatible trace elements, notably the *LILE* and *LREE*, high <sup>87</sup>Sr/<sup>86</sup>Sr<sub>i</sub> ratios (0.70726–0.70768) and low  $\varepsilon_{Nd}$  of -7; the Southern lamprophyres (SL) have similar major element compositions to the NHL but lower incompatible element abundances, lower <sup>87</sup>Sr/<sup>86</sup>Sr<sub>i</sub> of 0.70510–0.70700, and  $\varepsilon_{Nd}$  values of -1 to -2.

(2) The geochemical differences between the two groups cannot be attributed to fractionation, assimilation or melting processes but instead reflect differences in the geochemistry of their subcontinental lithospheric mantle (SCLM) source regions.

(3) The SCLM below northern Britain contained two principal geochemical domains in late Caledonian times, the features of which were established by separate metasomatic events. (4) The boundary between the two SCLM domains appears to coincide with the Great Glen fault which indicates that it extends throughout the lithosphere. Other Caledonian tectonic dislocations do not appear to extend to sub-Moho depths.

(5) The source of SL minettes may be lithospheric mantle from the southern continent underthrust below the leading edge of the northern continent during the closing stages of collision.

(6) The minettes may represent the lithospheric mantle contributions to the newer granite magmas which show similar, but not identical, geochemical provinciality.

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