

## MINERALOGY, PETROLOGY AND GEOCHEMISTRY OF THE ALKALINE MALPEQUE BAY SILL, PRINCE EDWARD ISLAND

JOHN D. GREENOUGH\*

*Department of Earth Sciences, Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X5*

AKIO HAYATSU

*Department of Geophysics, University of Western Ontario, London, Ontario, N6A 5B7*

V. STEPHEN PAPEZIK<sup>+</sup>

*Department of Earth Sciences, Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X5*

### ABSTRACT

A lamprophyric sill exposed at Malpeque Bay, Prince Edward Island, formed *circa* 247 Ma ago (Late Permian) in response to early tectonism that preceded opening of the Atlantic Ocean. The high Ca and Ti contents of clinopyroxene and extremely high Ti concentrations in phlogopite attest to the sill's alkaline nature. Extremely low Rb and K concentrations suggest that phlogopite or other K-bearing mantle phases had only a minor effect on formation of the Malpeque Bay magma. Other elements such as Sr, Ba, and the REE show more substantial metasomatic enrichment but the concentrations of Hf, Ta, U, Th, Zr and Nb increased the most. The metasomatizing agent (fluid or magma) was probably CO<sub>2</sub>-rich and either incapable of transporting K and Rb or carried these elements through the source region leaving behind elements such as Zr and Nb. Whole-rock Fe-Mg-Ni relationships, the high Mg content of olivine phenocrysts, and the presence of spinel lherzolite nodules indicate a primary magma. The low equilibration temperatures of the xenoliths (~970°C) suggest that they cannot represent the magma source but are typical of the recrystallized and re-equilibrated xenoliths associated with alkali basalts and nephelinites.

**Keywords:** lamprophyre, olivine nephelinite, primary magma, spinel lherzolite, sill, Late Permian, rifting, Prince Edward Island, geochemistry, major elements, trace elements, rare-earth elements, metasomatism, petrogenesis.

### SOMMAIRE

Un filon-couche lamprophyrique a été mis en place près de la baie de Malpeque, sur l'île du Prince-Edouard, il y a environ 247 Ma (Permien tardif), suite aux contraintes tectoniques qui ont précédé l'ouverture de l'océan Atlantique. Les concentrations élevées de Ca et Ti dans le clinopyroxène et très élevées de Ti dans la phlogopite manifestent son caractère alcalin. Les teneurs très basses en Rb

et K font penser que phlogopite ou autre phase porteuse de potassium dans le manteau n'a pas exercé d'influence importante sur la formation du magma. Les éléments Sr, Ba et les terres rares montrent un enrichissement métasomatique plus important, mais ce sont les concentrations de Hf, Ta, U, Th, Zr et Nb qui ont le plus augmenté. L'agent du métasomatisme (fluide ou magma) était tout probablement enrichi en CO<sub>2</sub>, et soit incapable de transporter le K et le Rb, soit très efficace à le faire, laissant à la source une concentration relative des éléments tels le Zr et le Nb. Les relations Fe-Mg-Ni parmi les roches globale, le caractère magnésien des phénocristaux d'olivine, et la présence d'enclaves de lherzolite à spinelle seraient les indications d'un magma primaire. Une température d'équilibration des enclaves anormalement basse (environ 970°C) montrent qu'il ne s'agit pas d'échantillons représentatifs de la source du magma, mais plutôt des populations d'enclaves typiques des basaltes alcalins et des néphélinites.

(Traduit par la Rédaction)

**Mots-clés:** lamprophyre, néphélinite à olivine, magma primaire, lherzolite à spinelle, filon-couche, Permien tardif, tectonique d'extension, île du Prince-Edouard, chimisme, éléments traces, terres rares, métasomatisme, pétrogenèse.

### INTRODUCTION

The only igneous rocks exposed in the province of Prince Edward Island occur on George Island in Malpeque Bay (Fig. 1). Larochelle (1967) suggested that the unmetamorphosed mafic sill may be Upper Permian, but the importance of this age and the petrologic and tectonic significance of the intrusion have been recognized only recently. A compilation of dates for volcanic rocks in eastern North America, that are considered related to opening of the Atlantic Ocean, shows that most of the magmatic activity took place between 170 and 200 Ma, with a peak at 190 Ma (McHone & Butler 1984). Most of these continental basaltic rocks show a tholeiitic affinity, with many trace-element characteristics similar to those of ocean-floor basalts, but the continental basalts also exhibit the effects of crustal contami-

\*Present address, Department of Geology, Mount Allison University, Sackville, New Brunswick E0A 3C0

<sup>+</sup>Passed away summer 1984.

nation (e.g., Smith *et al.* 1975, Dostal & Dupuy 1984, Greenough & Papezik 1986a).

This study of the Malpeque Bay sill was undertaken to determine its petrologic and tectonic significance. We discuss (1) the age of the sill, (2) its mineralogical composition, (3) whole-rock geochemistry, (4) the composition of minerals in associated spinel lherzolite xenoliths, and (5) the sill's petrogenesis.

#### GENERAL GEOLOGY AND AGE OF THE SILL

The sill was first described by Milligan (1949) as a dyke approximately 3 m thick which cut red sandstones. Laroche (1967) pointed out that the unit is a sill and that it probably intruded unconsolidated (penecontemporaneous) sediments, as indicated by the convoluted nature of some of the contacts. Prest (1972) gave thorough field and petrographic descriptions of the rocks and also presented two chemical analyses indicating low SiO<sub>2</sub> contents (40 wt. %). Deposition of the Prince Edward Island red beds may have taken place as early as late Pennsylvanian or early Permian, but the age of the upper-

most beds, intruded by the sill, remains in doubt due to a lack of fossils (Langston 1963). Paleomagnetic data obtained by Laroche (1967) indicate that intrusion occurred during the late Permian.

Table 1 shows the results of K-Ar dating of four whole-rock samples. The conventional ages of three samples (P83-43, 45 and 47) agree with each other very well in spite of differences in their potassium contents, whereas the apparent age of P83-48 is 3% lower than the other three. The discrepancy in ages is probably due to either argon loss or low initial <sup>40</sup>Ar/<sup>39</sup>Ar ratio but not to analytical error because a second analysis on another specimen from P83-48 yielded the same result. Therefore, the most likely age of the sill, 247 Ma (average of samples P83-43, 45 and 47), confirms Laroche's (1967) late Permian estimate of the age of intrusion and resolves the discrepancy with K-Ar ages (207 ± 8 Ma) reported by Poole *et al.* (1968).

#### PETROGRAPHY AND SAMPLING LOCATIONS

In outcrop the sill varies from a vesicular brecciated rock containing baked sediment and lherzolite xenoliths to a dark fine-grained rock, with olivine phenocrysts, that also contains xenoliths. Sampling locations of the nonvesicular and nonbrecciated specimens appear in Figure 1. All samples contain 5-15% euhedral olivine microphenocrysts (average 0.2 mm) set in a very fine-grained (clinopyroxene grains <0.02 mm) matrix. The matrix contains clinopyroxene (50%) and olivine (5%) with an inter-

TABLE 1. RESULTS OF RADIOMETRIC DATING OF THE MALPEQUE BAY SILL

	K (%)	<sup>40</sup> Ar radiogenic (cm <sup>3</sup> )	Age (Ma)
P83-43	0.4072	4.189 × 10 <sup>-6</sup>	246.9
P83-45	0.8788	0.050 × 10 <sup>-6</sup>	247.1
P83-47	1.044	10.733 × 10 <sup>-6</sup>	246.7
P83-48A	0.4712	4.703 × 10 <sup>-6</sup>	240.0
P83-48B	0.4773	4.761 × 10 <sup>-6</sup>	239.9

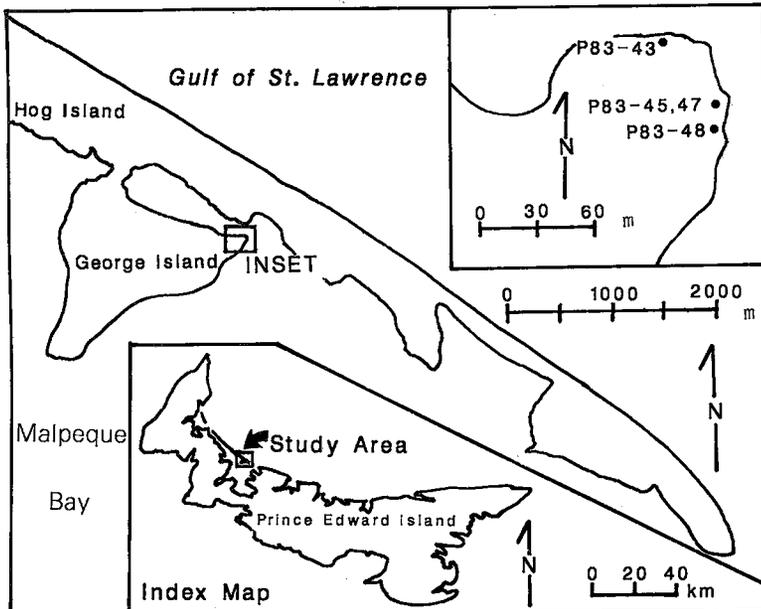


FIG. 1. Location map showing the study area on George Island, within the province of Prince Edward Island, and detailed sampling locations.

TABLE 2. REPRESENTATIVE COMPOSITIONS OF SILL CLINOPYROXENE, OLIVINE AND PHLOGOPITE

	P83-43 CPX	P83-45 CPX	P83-47 CPX	P83-48 CPX	P83-43 Ol	P83-45 Ol	P83-47 Ol	P83-41 Phl
SiO <sub>2</sub>	47.14	47.51	47.68	49.34	38.42	38.89	39.11	37.64
TiO <sub>2</sub>	3.26	3.13	2.81	2.51	0.07	0.04	0.03	8.63
Al <sub>2</sub> O <sub>3</sub>	5.87	5.45	6.48	4.75	0.04	0.13	0.03	11.41
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.05	0.18	0.52	0.00	0.02	0.04	-
FeO*	7.14	7.22	6.83	6.61	19.09	15.70	14.13	13.18
MnO	0.09	0.10	0.06	0.12	0.32	0.19	0.12	0.08
MgO	12.82	12.28	12.28	14.17	40.91	43.34	45.36	13.90
NiO	0.00	0.03	0.00	0.00	0.15	0.19	0.29	-
CaO	22.07	22.98	21.53	21.49	0.54	0.39	0.27	0.78
Na <sub>2</sub> O	0.68	0.53	0.72	0.45	-	-	-	0.69
K <sub>2</sub> O	0.00	0.00	0.05	0.00	-	-	-	7.63
TOTAL	99.09	99.28	98.62	99.96	99.54	98.89	99.38	93.94
Si	1.777	1.792	1.798	1.831	0.991	0.992	0.987	5.642
IVAl	0.223	0.208	0.202	0.169	0.000	0.003	0.000	2.015
VIAl	0.037	0.033	0.086	0.038	-	-	-	-
Ti	0.092	0.088	0.080	0.069	0.001	0.001	0.000	0.986
Cr	0.000	0.001	0.004	0.015	0.000	0.000	0.001	-
Fe	0.225	0.227	0.214	0.205	0.412	0.334	0.297	1.652
Mn	0.002	0.002	0.001	0.003	0.006	0.003	0.002	0.010
Mg	0.720	0.689	0.689	0.783	1.573	1.649	1.707	3.105
Ni	0.000	0.000	0.000	0.000	0.003	0.003	0.005	-
Ca	0.891	0.929	0.869	0.854	0.014	0.010	0.006	0.125
Na	0.050	0.038	0.052	0.031	-	-	-	0.200
K	0.000	0.000	0.002	0.000	-	-	-	1.459
Ca	48.5	50.3	49.0	46.3	-	-	-	-
Mg	39.2	37.3	38.9	42.4	-	-	-	-
Fe+Mn	12.4	12.4	12.1	11.3	-	-	-	-
Fo (mol. %)					79.2	83.2	85.2	

Major-element oxides in wt. %, with total Fe as FeO.

Number of ions on the basis of 6 oxygen atoms for clinopyroxene, 4 for olivine and 22 for phlogopite.

All Al shown as <sup>IV</sup>Al for olivine and phlogopite.

sertal mesostasis of orange-brown mica (< 5%) and finer-grained devitrified glass and felsic minerals (plagioclase? + nepheline?). Minor "iddingsite" and serpentine appear on otherwise unaltered olivine grains and constitute the only obvious alteration in the rocks.

Ultramafic xenoliths are associated with samples P83-47 and 48, but comprise less than 5% of the rocks; the xenoliths consist of equigranular, 1 mm olivine, orthopyroxene, and clinopyroxene, and 0.5 mm brown spinel grains in approximate proportions 60:23:12:5. The lherzolite nodules show no signs of shearing or deformation.

#### MINERAL CHEMISTRY

Chemical compositions of minerals from the sill and from an associated lherzolite xenolith appear in Tables 2 and 3. Analyses were carried out at the Memorial University of Newfoundland on a JEOL JXA-50A (wavelength-dispersion) electron-microprobe analyzer with Krisel software using minerals of known composition as standards.

#### Minerals in the sill

Clinopyroxene from the sill (Table 2, Fig. 2) contains more than 45% Wo and averages 48% Wo. In comparison with pyroxene from basaltic rocks, Ti (~ 2.8 wt.% TiO<sub>2</sub>), Al (~ 5.7 wt.% Al<sub>2</sub>O<sub>3</sub>) and Ca

(~ 22 wt.% CaO) show relatively high concentrations (Le Bas 1962) as well as a positive correlation with one another. Such characteristics are typical of

TABLE 3. REPRESENTATIVE COMPOSITIONS OF CLINOPYROXENE, ORTHOPYROXENE, SPINEL AND OLIVINE IN THE XENOLITHS

	CPX	CPX	OPX	OPX	SP	SP	Ol
SiO <sub>2</sub>	52.27	53.08	54.86	54.87	0.27	0.35	40.07
TiO <sub>2</sub>	0.39	0.40	0.08	0.10	0.09	0.06	0.02
Al <sub>2</sub> O <sub>3</sub>	5.23	4.80	3.25	3.50	58.25	58.34	0.01
Cr <sub>2</sub> O <sub>3</sub>	0.59	0.44	0.23	0.18	7.72	7.48	0.00
FeO*	2.74	2.66	6.89	7.14	12.73	12.87	10.84
MnO	0.04	0.12	0.13	0.20	0.07	0.09	0.13
MgO	14.96	16.82	33.37	33.49	19.68	19.77	48.05
NiO	0.08	0.04	0.00	0.07	-	-	0.33
CaO	21.41	20.43	0.45	0.41	-	-	0.04
Na <sub>2</sub> O	1.18	1.07	0.09	0.05	-	-	-
K <sub>2</sub> O	0.01	0.01	0.02	0.00	-	-	-
TOTAL	98.90	99.87	99.37	100.01	98.81	98.96	99.49
Si	1.914	1.917	1.913	1.904	0.056	0.066	0.993
IVAl	0.086	0.083	0.087	0.096	-	-	0.000
VIAl	0.140	0.120	0.046	0.046	14.372	14.368	-
Ti	0.011	0.010	0.002	0.002	0.012	0.008	0.000
Cr	0.022	0.016	0.008	0.006	1.276	1.216	0.000
Fe	0.083	0.079	0.200	0.207	2.224	2.224	0.225
Mn	0.001	0.003	0.003	0.005	0.012	0.012	0.002
Mg	0.816	0.905	1.735	1.732	6.136	6.158	1.775
Ni	0.002	0.001	0.000	0.001	-	-	0.006
Ca	0.839	0.790	0.016	0.015	-	-	0.000
Na	0.083	0.074	0.005	0.003	-	-	-
K	0.000	0.000	0.000	0.000	-	-	-
Ca	48.2	44.5	0.8	0.8	-	-	-
Mg	46.9	50.9	88.8	88.4	-	-	-
Fe+Mn	4.9	4.6	10.4	10.8	-	-	-
Cr/(Cr+Al)					0.082	0.078	
Fo (mol. %)							88.8

Major-element oxides in wt. %, with total Fe as FeO.

Number of ions on the basis of 6 oxygen atoms for pyroxene, 32 for spinel and 4 for olivine.

All Al shown as <sup>IV</sup>Al for olivine and <sup>VI</sup>Al for spinel.

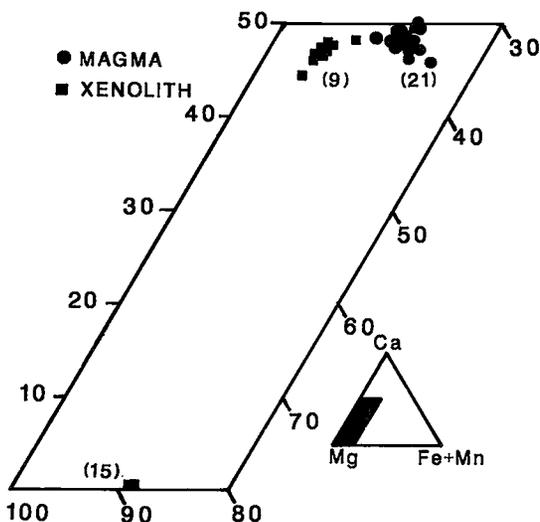


FIG. 2. Plot of the En (Mg), Wo (Ca) and Fs (Fe+Mn) contents of pyroxene from the lamprophyre and associated lherzolite xenolith.

pyroxene compositions from strongly undersaturated (nephelinitic) magmas.

Olivine compositions range from Fo<sub>78</sub> to Fo<sub>91</sub> with a mean of Fo<sub>84</sub> (Table 2, Fig. 3). Grains with less than 86 mol. % Fo have calcium contents greater than 0.25 wt. % CaO, typical of hypabyssal intrusions (Simkin & Smith 1970). The core of a few grains with higher Fo and lower Ca contents (0.02 wt. % CaO) may have crystallized at a greater depth and may have been carried along with the magma to crustal levels. These grains could represent xenolith debris; however, they are much finer grained than olivine grains in the associated lherzolite and display euhedral forms.

Titanium in phlogopite is considered "high" if it exceeds 4 wt. % TiO<sub>2</sub>, but grains from the Malpeque Bay sill contain 8–9 wt. % TiO<sub>2</sub>. Strong & Harris

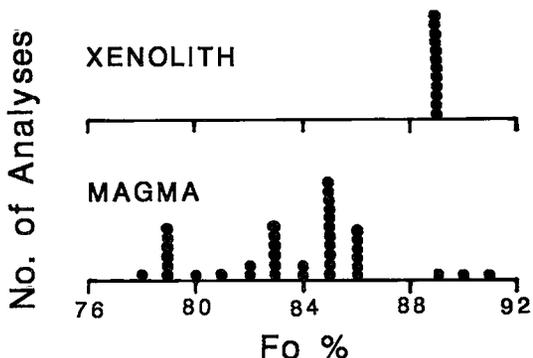


FIG. 3. Histogram showing the Fo contents of olivine from the lamprophyre and associated lherzolite xenolith.

(1974) noted relatively high TiO<sub>2</sub> concentrations (6.5–7.5 wt. %) in phlogopite from a lamprophyre in Newfoundland, and Wagner & Velde (1986) reported up to 11.2 wt. % TiO<sub>2</sub> in phlogopite from a lamproite.

#### Minerals in the xenoliths

The compositions of mineral grains in a xenolith associated with sample P83-48 appear in Table 3. Spinel in the xenolith is characterized by Cr/(Cr + Al) value less than 0.08, *i.e.*, it is Al-spinel according to Carswell (1980). Both olivine (Fig. 3) and orthopyroxene (Fig. 2) show constant compositions of Fo<sub>89</sub> and En<sub>90</sub>, respectively. These values fall toward the Fe-rich end of the narrow distribution of compositions normally observed in Al-spinel lherzolites (Carswell 1980). The clinopyroxene is typical of "Cr-diopside" found in spinel lherzolites. It displays a greater range of compositions (particularly CaO contents) than other minerals in the xenolith (Fig. 2) as is commonly reported for such xenoliths (*e.g.*, Varne 1977).

#### WHOLE-ROCK GEOCHEMISTRY

Samples were prepared for analysis by removing all weathered surfaces and ensuring the absence of xenolith material. Whole-rock chemical compositions (Table 4) were determined by G. Andrews (Memorial University of Newfoundland) using

TABLE 4. MAJOR-ELEMENT AND NORMATIVE COMPOSITION OF THE MALPEQUE BAY SILL

	P83-43	P83-45	P83-47	P83-48
SiO <sub>2</sub>	41.5	42.4	42.5	41.7
TiO <sub>2</sub>	2.74	2.67	2.77	2.77
Al <sub>2</sub> O <sub>3</sub>	9.60	9.08	9.24	9.42
Fe <sub>2</sub> O <sub>3</sub>	5.25	5.03	4.24	4.94
FeO	7.00	7.32	8.03	7.40
MnO	0.17	0.17	0.17	0.17
MgO	13.58	15.08	14.43	14.15
CaO	10.70	9.60	9.98	10.43
Na <sub>2</sub> O	3.37	3.36	3.53	3.66
K <sub>2</sub> O	0.55	1.07	1.06	0.65
P <sub>2</sub> O <sub>5</sub>	0.92	0.84	0.88	0.86
L.O.I.	3.56	2.36	2.57	3.41
TOTAL	98.94	98.98	99.40	99.56
Mg <sup>1</sup>	0.70	0.72	0.71	0.70

	BARTH NIGGLI MOLECULAR NORMS			
Q	-	-	-	-
Or	3.35	6.40	6.35	3.90
Ab	8.57	7.80	7.22	6.89
An	9.75	6.62	6.30	7.52
Ne	13.60	13.67	14.94	15.96
Di	31.08	28.68	30.36	31.64
Hy	-	-	-	-
Ol	25.70	29.21	27.06	26.30
Mt	2.01	2.00	2.00	2.01
Il	3.94	3.78	3.90	3.94
Ap	2.00	1.78	1.87	1.84

Major element concentrations in oxide wt. %.

Mg<sup>1</sup> = Mg/(Mg + 0.9 Fe) atomic.

Molecular norms calculated assuming Fe<sub>2</sub>O<sub>3</sub>/FeO = 0.185.

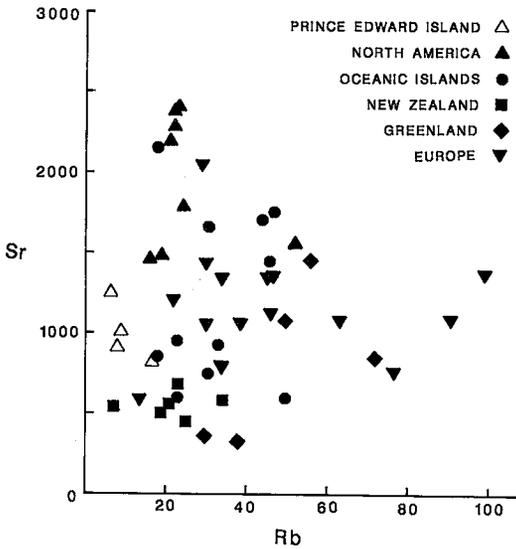


FIG. 4. Plot of Rb and Sr concentrations (ppm) in relatively unfractionated ( $Mg' > 0.65$ , or  $Ni > 200$  ppm) lamprophyres and related rocks. Sources of data: Prince Edward Island, this study; North America, Phelps *et al.* (1983), Luhr & Carmichael (1981); Oceanic Islands, Kay & Gast (1973), Greenough (1979), Wilkinson & Stolz (1983); New Zealand, Briggs & Goles (1984); Greenland, Hansen (1980, 1981), Clarke *et al.* (1983); Europe, Alibert *et al.* (1983), Downes (1984).

atomic-absorption spectrophotometry. Concentrations of trace elements determined by D. Press (also at M.U.N.) using X-ray fluorescence methods may be judged for precision and accuracy from replicate

TABLE 5. TRACE-ELEMENT CONCENTRATIONS IN THE MALPEQUE BAY SILL

	P83-43	P83-45	P83-47	P83-48	W-1 ( $\sigma$ ) n = 7	NBS1632a n = 4 ( $\sigma$ )
Rb	6	9	8	17	22.6 (2.1)	
Cs	1.6	0.8	0.6	1.8		2.7 (0.2)
Sr	1257	1017	917	822	172 (3)	
Ba	706	616	639	623	183 (10)	
Th	7.1	6.4	6.4	7.3		4.6 (0.1)
U	1.8	2.3	1.6	1.7		1.4 (0.1)
Zr	234	217	225	231	87.3 (1.7)	
Hf	5.5	5.0	5.8	5.9		1.9 (0.1)
Nb	101	94	95	102	7.3 (1.5)	
Ta	5.6	5.1	5.1	5.7		<0.5
Y	25	27	25	29	25.1 (3.1)	
La	52	48	48	54		15.3 (0.2)
Ce	90	85	88	101		29.3 (0.5)
Nd	40	39	40	46		12.0 (0.1)
Sm	9.0	8.5	8.9	9.6		2.5 (0.1)
Eu	2.7	2.6	2.8	2.8		0.49 (0.04)
Tb	0.9	1.0	1.0	1.0		0.34 (0.02)
Yb	1.5	1.4	1.3	1.6		1.13 (0.07)
Lu	0.20	0.19	0.19	0.21		0.18 (0.01)
Sc	23	22	22	24		6.6 (0.1)
V	276	259	268	271	263 (5)	
Cr	296	373	370	353	98.6 (2.5)	
Co	79	75	68	72		6.5 (0.5)
Ni	332	463	416	383	78.7 (2.8)	
Au*	23	45	36	36		<5
Mo	10	7	7	10		<2
Cu	68	70	67	68	99.0 (2.2)	
Zn	108	106	117	111	95.7 (1.7)	
Ga	15	15	16	18	16.2 (2.1)	
Se	4.5	5.4	6.5	4.8		3.0 (0.2)

\* Concentrations in ppm except for Au, in ppb. Elements determined by XRF were run with the standard W-1 and those by instrumental neutron-activation, with NBS 1632 a.

analyses of U.S.G.S. standard W-1 (Table 5). Trace elements determined by instrumental neutron-activation analysis at Nuclear Activation Services Ltd. were run with standard NBS 1632 A.

$Mg'$  values [ $Mg' = Mg/(Mg + 0.9Fe)$  atomic, where Fe = total iron] are very high ( $\sim 0.70$ ) indicating that the rocks are relatively primitive. They can be classified as olivine nephelinites as all samples are

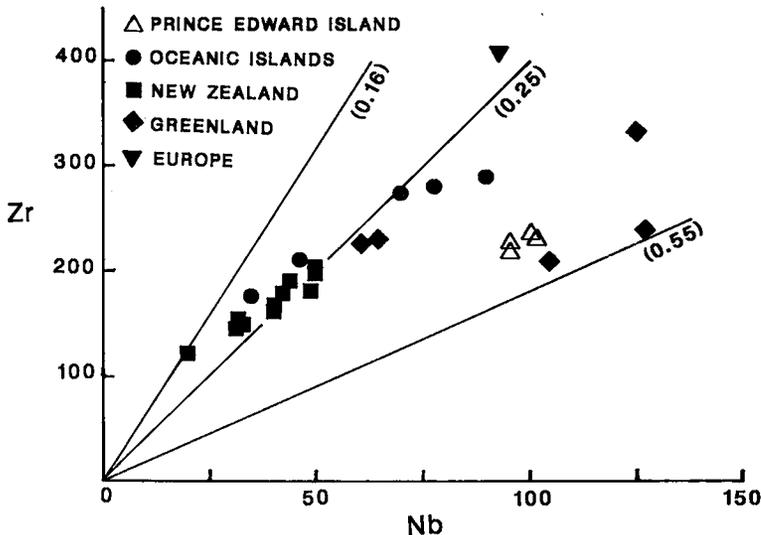


FIG. 5. Plot of Nb versus Zr (ppm) in relatively unfractionated ( $Mg' > 0.65$  or  $Ni > 200$  ppm) lamprophyres and related rocks. Lines denote constant Nb/Zr ratios. Sources as in Figure 4.

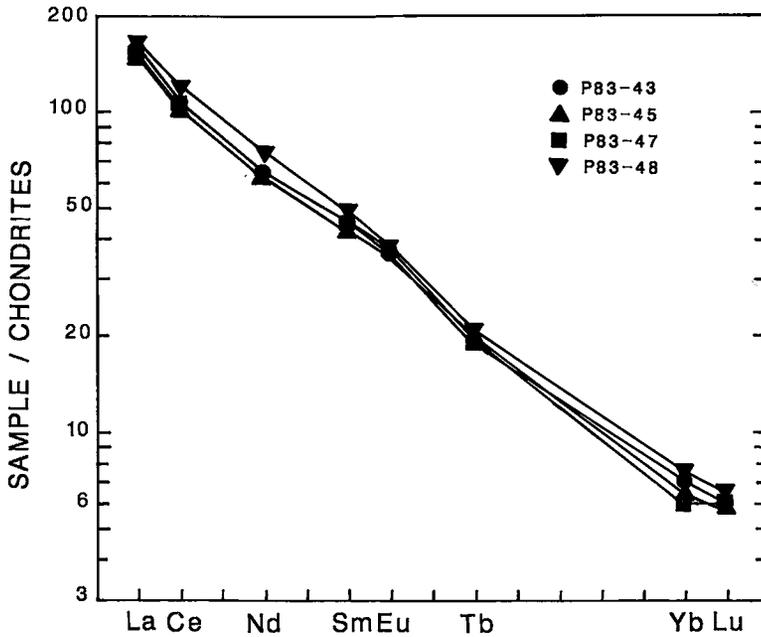


FIG. 6. Chondrite-normalized REE patterns for the Malpeque Bay lamprophyre. Values for normalization from Taylor & Gorton (1977).

highly nepheline-normative ( $\sim 14$  mol.% Ne, Table 4). They also show some basaltic characteristics in that Ti ( $\sim 2.7$  wt.%  $\text{TiO}_2$ , Fig. 4), Ca ( $\sim 10$  wt.% CaO), and K ( $\sim 0.8$  wt.%  $\text{K}_2\text{O}$ ) concentrations overlap with those found in primitive alkali basalts (*cf.* Kay & Gast 1973, Hansen 1980, 1981, Basaltic Volcanism Study Project (BVSP) 1981).

Concentrations of some large-ion lithophile (LIL) elements (*e.g.*, Rb  $\sim 10$  ppm, Sr  $\sim 1000$  ppm,

Ba  $\sim 650$  ppm) are high in comparison with most basalts (*cf.* BVSP 1981) but are low (especially Rb) in comparison with most unfractionated lamprophyres (Fig. 4). In contrast, the high-valency cations tend to show very high concentrations (*e.g.*, Nb  $\sim 100$  ppm, Zr  $\sim 225$  ppm) and values of ratios such as Nb/Y ( $\sim 3.7$ ) and Nb/Zr ( $\sim 0.5$ ) only compare with those in lamprophyres (Fig. 5).

Concentrations of the light rare-earth elements

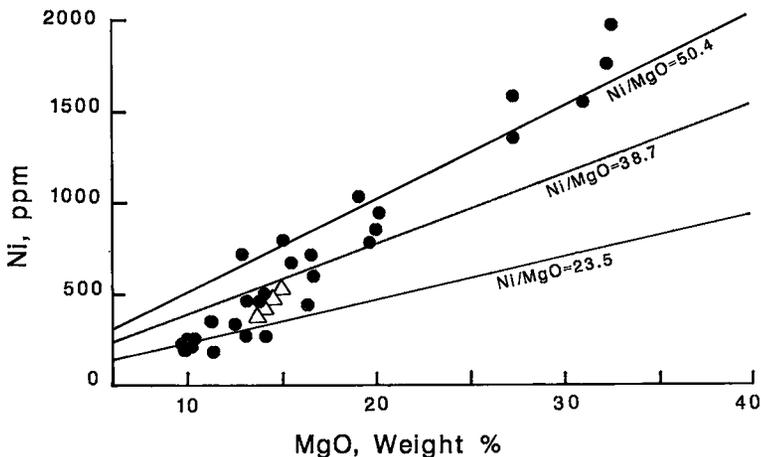


FIG. 7. Plot of Ni (ppm) versus MgO (wt. %) concentrations in potential primary magmas (solid dots, as reviewed in BVSP 1981, p. 424) and the Malpeque Bay lamprophyre (open triangles). Solid lines show constant values of the Ni/MgO ratio.

(*REE*) in the Malpeque Bay lamprophyre are higher than in most basaltic rocks but are similar to the lower concentrations recorded for some lamprophyres (*cf.*, Kay & Gast 1973, Moller *et al.* 1980, Alibert *et al.* 1983, Clarke *et al.* 1983). The heavy *REE* are only about 6 times chondritic levels (Fig. 6) but are comparable to those in the lamprophyres noted above as well as to unfractionated basaltic rocks from Hawaii (BVSP 1981, p. 172). The chondrite-normalized *REE* patterns define relatively straight lines with steep slopes typical of alkaline rocks (Fig. 6).

Relatively high Ni and Cr concentrations (~400 and 350 ppm, respectively) seem representative of unfractionated magmas (*e.g.*, BVSP 1981, pp. 422-424). Comparison of concentrations of Sc, V, Co, Mo, Cu and Zn with those in other unfractionated lamprophyres is hampered by the scarcity of data. Most of these elements, however, show only small variations (by much less than a factor of 10) in mafic magmas in general; the concentrations reported here fall within the ranges normally observed (*cf.* BVSP 1981). Gold concentrations in the lamprophyre are higher than those in early Mesozoic continental tholeiites from the Atlantic provinces (<20 ppb *versus* ~35 ppb, J.D.G. unpub. data).

## DISCUSSION

### Primary nature of the lamprophyre

Most of the evidence from lherzolites suggests that mantle olivine is approximately  $Fo_{90}$  in composition (Carswell 1980). The  $Mg'$  values of magmas formed in equilibrium with such olivine should be between 0.72 and 0.70 (Roeder & Emslie 1970, Green 1971). It follows that the Malpeque Bay lamprophyre with  $Mg'$  values between 0.70 and 0.72 qualifies as a primary magma. Estimates of values for the temperature-dependent partition coefficient  $K_D = (Ni/MgO)_{\text{olivine}} / (Ni/MgO)_{\text{melt}}$  also are useful in identifying primary magmas. Given that  $K_D$  values should fall between 1.65 and 2.72 for most mafic magmas (Hart & Davis 1978, Leeman & Lindstrom 1978) and assuming a lherzolite source with  $Fo_{90}$  olivine containing 3200 ppm Ni, primary magmas will have Ni/MgO values between 23 and 39 (reviewed in BVSP 1981, pp. 424-426). Figure 7 illustrates that the Malpeque Bay lamprophyre shows Ni/MgO values expected for a primary magma. Further, the composition of the most Mg-rich olivine phenocrysts ( $Fo_{91}$ ) indicates that fractionation has not taken place.

Concentrations of the heavy *REE* in the lamprophyre are as low as normally observed in mafic magmas devoid of substantial accumulations of phenocrysts. As removal of low-pressure phases such

TABLE 6. ESTIMATES OF EQUILIBRATION TEMPERATURE OF XENOLITHS BASED ON VARIOUS GEOTHERMOMETERS

Reference	Method	Range of Temperatures (°C)	Mean
Wells (1977)	Solvus	880-1009	994
Mori (1977)	Solvus	1002-1203	1103
Mori & Green (1978)	Solvus	911-1058	984
Mori (1977)	Cpx-01-Sp (Eq. 2)	980-994	987
Mori (1977)	Opx-01-Sp (Eq. 3)	924-943	934
Fabries (1979)	Sp-01	900	900
Mori & Green (1978)	Fe/Mg Opx-Cpx	820-992	904
Mori & Green (1978)	Fe/Mg 01-Cpx	886-1003	945
Roeder <i>et al.</i> (1979)	01-Sp	1030-1044	1032
Mysen (1976)	$V^{Al}/Cr$ Opx-Cpx	854-1076	960
Average Temperature			969

Range of temperatures calculated from all possible combinations of analyses shown in Table 3, the mean represents the average of these temperatures (usually 4).

as olivine, pyroxene or plagioclase would raise these concentrations (Frey *et al.* 1974), the *REE* are consistent with the proposal that the rocks are primitive.

Further evidence that the lamprophyre represents a primary magma comes from the fact that it contains lherzolite xenoliths. Estimates of the ascent velocities necessary to carry these nodules into the upper crust (1-50 cm/s) preclude substantial fractionation *en route* (Spera 1980).

### Spinel lherzolite as a source material

The  $Fo$  content of olivine in the spinel lherzolite xenoliths ( $Fo_{89}$ ) is similar to that expected in the mantle source for the magma itself (BVSP 1981, 424-426). High values of the Al/Cr ratio show that the spinel was not precipitated from a magma at depth, but the values are representative of mantle source-material (Carswell 1980). To test the hypothesis that the spinel lherzolite represents the source material for the lamprophyre, equilibration temperatures for the former were estimated using various geothermometers (Table 6).

Geothermometers using clinopyroxene yielded a wide range of temperatures, in part due to the variations in composition shown in Table 3. This is particularly true of methods based on the solvus. Nevertheless, averages of temperatures estimated from all possible combinations of mineral grains in Table 3 show similar results for all geothermometers except the solvus-based method of Mori (1977). Carswell (1980) noted that Mori's equation for the solvus yields higher temperatures than the solvus-based methods of Wells (1977) or Mori & Green (1978) but that temperatures from the Mori equation agree with results from methods not based on the solvus (*e.g.*, Mysen 1976). However, when applied to the Malpeque Bay pyroxene the Mysen equation based on the solvus gives higher temperatures than all other geothermometers (Table 6), whereas the Wells (1977) and Mori & Green (1978) methods tend to agree with other methods. The differences in results may be related to slightly lower

Al concentrations (Mori 1977) in the Malpeque Bay pyroxenes relative to the pyroxenes used in calculations by Carswell (1980). However, Al concentrations in the Malpeque Bay pyroxenes are high enough that the Lindsley & Andersen (1983) two-pyroxene geothermometer is not applicable. An average of the mean temperatures from all methods reported in Table 6 yields a temperature of 969°C. All temperatures fall within the range normally reported for spinel lherzolites (900–1150°C) and demonstrate that the lherzolite cannot represent the source for the lamprophyre (which must have been hotter) or phases precipitated from the magma at depth (Carswell 1980). The lherzolites apparently represent recrystallized and re-equilibrated mantle material overlying the magma's source area, and were included in the magma on its way to the surface.

### Petrogenesis

Any attempt to characterize the source for the Malpeque Bay lamprophyre must account for the following characteristics: 1) low Rb and Ti concentrations (for example) within the range of some alkali basalts, 2) light-*REE* concentrations at the lower end of the range shown by lamprophyres, and 3) high Zr and Nb concentrations and low Nb/Zr ratios characteristic of lamprophyres from highly "enriched" sources.

It has long been known that K and Rb concentrations in alkaline magmas are much more variable and irregular than (for example) Sr and *REE* concentrations. This variability has in some cases been attributed to the presence or absence of phlogopite during melting events (e.g., Kay & Gast 1973). More recent studies of mantle xenoliths have shown that the nodules best representing the sources for alkaline magmas (because of enrichment in incompatible elements) usually contain phlogopite (Jagoutz *et al.* 1979, Gurney & Harte 1980). Similarly, melting experiments bearing on the origin of alkaline magmas have consistently pointed to the importance of phlogopite in magma genesis (Modreski & Boettcher

1973, Arima & Edgar 1983, Llyod *et al.* 1985). The Malpeque Bay lamprophyre clearly shows anomalously low Rb (Fig. 4) and K, given its high Sr-concentrations (1000 ppm), indicating that phlogopite played a subordinate role in its genesis (in comparison with other nepheline-normative magmas).

Early students of alkaline magmas commonly suggested that small percentages of melting of a garnet-rich mantle source can explain their enrichment in incompatible elements (e.g., Gast 1968, Kay & Gast 1973). More recently it has been recognized that models using a primitive undepleted source, the lowest recorded distribution coefficients, and extremely small percentages of melting cannot duplicate observed incompatible-element concentrations (Sun & Hanson 1975, Cullers *et al.* 1985). This is true for the Malpeque Bay lamprophyre as well. To illustrate this, Shaw's (1970) non-modal batch-melting equation was used to model magmatic Sr concentrations. A garnet lherzolite source was assumed (to account for the low heavy-*REE* concentrations: Kay & Gast 1973) together with reasonable values for the partitioning coefficients (*D* values), modal percentages of minerals and melting proportions (Table 7). Assuming primitive to slightly elevated Sr values (e.g., 28 ppm: Jagoutz *et al.* 1979), the lowest Sr concentrations observed in the sill cannot be duplicated even when the percentages of melting approach zero (model predicts ~600 ppm). Furthermore, it is not clear how extremely small proportions of melt could be removed from the mantle. If minor phases (such as phlogopite) exist, then small percentages of melting make it more difficult to explain, for example, the high Rb concentrations common in many alkaline magmas because the minor phases make Rb a more compatible element ( $D^{Rb}$  in phlogopite = 3.1: Philpotts & Schnetzler 1970).

High-pressure fractionation of eclogite has been suggested as a means for elevating incompatible-element concentrations in alkaline magmas. However, as noted by Mitchell & Bell (1976), prohibitively high percentages are required. A fractionation model seems to be at odds with Fe–Mg–Ni relationships that support a primary origin for the Malpeque Bay lamprophyre.

Most petrologists have concluded that the source regions for alkaline rocks have been metasomatically enriched (Fitton & Upton 1985). Suggested compositions for the metasomatizing fluid vary from assorted combinations of H<sub>2</sub>O, CO<sub>2</sub>, F and Cl charged fluid (e.g., Bachinski & Scott 1979, Moller *et al.* 1980, Phelps *et al.* 1983, Cullers *et al.* 1985) to basanite magma itself (e.g., Alibert *et al.* 1983, Menzies 1985).

Unless partition coefficients are much lower than those given for Rb and Sr in Table 7, the "basanite melt" hypothesis would have to be a two-stage

TABLE 7. PARAMETERS FOR THE MELTING MODEL

	O1	Opx	Cpx	Gar	Phl
<u>Sr model</u>					
Modal prop.	55	25	10	10	
Melt prop.	5	5	45	45	
$D^{Sr}$	0.016	0.016	0.165	0.140	
<u>Rb model</u>					
Modal prop.	53	22	10	10	5
Melt prop.	1	3	12	17	67
$D^{Rb}$	0.01	0.01	0.05	0.02	3.1

### Sources:

*D* values: Frey *et al.* (1978), Philpotts & Schnetzler (1970).  
Melting proportions: Kay & Gast (1973), Modreski & Boettcher (1973).  
Phase proportions: Carswell (1980), Gurney & Harte (1980).

process where the metasomatized source is remelted in a second step. The maximum amount of incompatible-element enrichment possible is given by a single-pass zone-melting model (Kay 1979) in which the melt percolates through a large volume of depleted to primitive mantle-material. The final concentrations in this melt equal those given by the batch-melting equation (Shaw 1970) as the percentage of melting nears zero (Alibert *et al.* 1983). We already have suggested that such a model cannot explain the observed Sr concentrations unless  $D$  values are much lower than in Table 7. If phlogopite is assumed to be present in the mantle material traversed by the melt, then Rb concentrations would remain very low (approximately 2 ppm assuming 0.3 ppm Rb in the source, and melting parameters as in Table 7). To achieve higher concentrations of the incompatible elements, the liquid must be concentrated (pooled) and then undergo fractionation, or partial melting (after crystallization) at some later time.

The other possibilities, that the metasomatizing solution was a  $H_2O$ ,  $CO_2$ , F, or Cl rich fluid or magma (with lower  $D$  values for most incompatible elements), are difficult to test. Recent experimental data on the solubilities of various elements in proposed mantle metasomatizing fluids indicate that very large fluid/rock ratios are required, thus favoring a magma as the metasomatizing agent (Schneider & Eggler 1986). Nevertheless, the association of high volatile concentrations with alkaline magmas is well established (Bailey 1982).  $H_2O$ - and possibly F-rich fluids result in silica-saturated melts such as minettes and lamproites with very high K and Rb concentrations (Bachinski & Scott 1979, Jaques *et al.* 1984). More undersaturated melts such as kimberlites and carbonatites appear related to high  $CO_2$  and low  $H_2O$  metasomatizing fluids, which also result in enrichment of K and Rb as well as the REE and high-valency cations. Conflicting with these observations are experiments by McGetchin & Besancon (1973) showing that carbonate inclusions from mantle pyrope contain very low concentrations of K (also see Moller *et al.* 1980). However, Wendlandt & Harrison (1979) found that at upper-mantle pressures the light REE are strongly fractionated into a  $CO_2$ -rich vapor phase. If  $CO_2$ -rich metasomatizing fluids do result in only minimal K and Rb enrichment, but otherwise leave all of the other melt characteristics typical of kimberlites and carbonatites (*i.e.*, Si-undersaturated melts), then such fluids might produce source characteristics requisite of the Malpeque Bay lamprophyre. Menzies *et al.* (1985) proposed that chemical variations in a suite of spinel lherzolite xenoliths were due to metasomatic enrichment fronts in a contact-metamorphic aureole surrounding apophyses of basanitic melt. In a wet zone close to the interface of the magma and wallrock,

the precipitation of mica or amphibole (or both) results in enrichment of most incompatible elements. To explain lherzolites enriched only in the light REE and not in large-ion lithophile elements, they suggested a dry zone of metasomatism farther from the contact that was affected by  $CO_2$ -rich metasomatic fluids. Possibly this process, acting on a larger scale, created the source for the Malpeque Bay lamprophyre.

Greenough & Papezik (1986b) recently showed that movement of volatile complexes in a mafic sill can explain enrichment in elements such as K, Rb, Zr, and Nb. In some parts of the sill where volatiles were apparently incapable of escaping, all incompatible elements were enriched. In granophyric pegmatites in the upper half of the sill only Zr and Nb were enriched through the formation of minor phases, whereas K, Rb, Sr, and Ba were removed from the sill system by escaping volatiles. Such a scenario in the upper mantle could explain the origin of the low K and Rb but high Zr and Nb concentrations of the Malpeque Bay lamprophyre in the case where a  $CO_2$ -rich fluid was capable of carrying all elements. The source was not enriched in K and Rb because the metasomatizing fluids did not leave these elements behind.

A final hypothesis suggests that the  $CO_2$ -rich lamprophyre had very high concentrations of K and Rb, but the loss of volatiles during ascent and cooling removed these elements. This hypothesis does not explain why Zr and Nb remained enriched especially because the fine-grained lamprophyre (once emplaced) cooled rapidly, allowing little time for separative processes (such as envisaged for the Newfoundland sill of Greenough & Papezik 1986b) to occur.

#### *Tectonic implications*

The 247 Ma date on the Malpeque Bay sill sets it apart from most other postmetamorphic igneous rocks in the northern Appalachians. These show a frequency peak at around 190 Ma (McHone & Butler 1984) and are typically related to opening of the Atlantic Ocean. Rocks of similar age to the Malpeque Bay sill include those of the coastal New England igneous province (210–240 Ma syenites and alkali granite: McHone & Butler 1984, Foland & Faul 1977), the mildly alkaline Seabrook diabase dykes in New Hampshire (212–236 Ma: Bellini *et al.* 1982), and tholeiitic diabase dykes recovered in the Northumberland Strait, Canada (212–239 Ma: Pe-Piper & Jansa 1986). With the exception of the Northumberland Strait dykes, these rocks show alkaline compositions typical of early-rift igneous activity (*cf.* Le Pichon & Sibuet 1981). Their timing and composition relate them to an early cycle of North Atlantic crustal attenuation and magmatism. The next cycle of magmatism, 40 Ma later, is more closely associa-

ted with actual opening of the Atlantic Ocean (Pe-Piper & Jansa 1986).

## SUMMARY

The age (247 Ma) and alkaline geochemistry of the Malpeque Bay sill relate it to an early stage of crustal attenuation that preceded opening of the Atlantic Ocean. The lamprophyre has an olivine nephelinite composition and, in comparison with other lamprophyres, displays relatively low concentrations of some *LIL* elements (e.g., K and Rb) but elevated contents of high-valency cations (e.g., Zr and Nb). Constraints from trace-element modeling suggest that these characteristics can be related to mantle metasomatism. Analogy with other types of alkaline rocks indicates that the metasomatizing material was a CO<sub>2</sub>-rich fluid or magma that either was incapable of carrying substantial K and Rb, or that carried these elements through the source system leaving behind only the high-valency cations. Phlogopite or other K-bearing phases had little effect on the composition of the final magma. This is in marked contrast to the sources for many lamprophyres where larger amounts of these minerals probably help control Rb and K concentrations in the melt. Spinel lherzolites associated with the lamprophyre cannot represent its source as they show low temperatures of equilibration. Olivine compositions, major- and trace-element data, and the presence of lherzolite xenoliths indicate that the magma came to the surface rapidly and constitutes a primary melt.

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