# Nd AND Sr ISOTOPIC COMPOSITION OF THE LAMPROPHYRIC MALPEQUE BAY SILL, PRINCE EDWARD ISLAND

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### Abstract

The late Permian, primitive and alkaline (lamprophyric) Malpeque Bay sill, Prince Edward Island, shows  $\epsilon_{Nd}$  values of +5 and  $\epsilon_{Sr}$  of -19, similar to those noted for alkaline rocks from many continents and oceanic islands. These epsilon values indicate a source region showing long-term depletion in large ion lithophile (LIL) and high-field-strength (HFS) elements as a result of previous extraction of melt. Estimates of Rb/Sr and Nd/Sm ratios in the source region indicate enrichment in light-rare-earth elements (REE) and depletion of Rb relative to Sr a short time prior to magma segregation. With time, this source region would develop both Nd and Sr isotopic ratios below bulk earth values and epsilon values unlike those normally reported for mafic magmas. Numerous examples of metasomatized lherzolites show similar light REE enrichment and Rb depletion, indicating that the high concentrations of many incompatible elements (e.g., REE, U, Th and Nb) in the sill may have in part resulted from metasomatism of the source region. However, many or most metasomatized lherzolites show a negative Ti anomaly, a characteristic absent from trace-element patterns for the Malpeque Bay sill and most alkaline magmas. Although this does not eliminate the possibility of source-region metasomatism, it does suggest that many observed examples of metasomatized mantle cannot represent the source material for alkaline magmas such as the Malpeque Bay sill.

*Keywords:* late Permian, rifting, lamprophyre, primitive magma, Nd, Sr, isotopes, metasomatism, petrogenesis, Prince Edward Island.

#### SOMMAIRE

Le filon-couche qui affleure dans la baie de Malpèque, à l'Ile-du-Prince-Edouard, d'âge permien et de nature primitive et alcaline (lamprophyrique), montre un  $\epsilon_{Nd}$  de + 5 et un  $\epsilon_{Sr}$  de -19, valeurs semblables à celles qui caractérisent les roches alcalines de plusieurs centres volcaniques continentaux et océaniques. Ces valeurs témoignent d'une source longtemps appauvrie en éléments lithophiles à large rayon et à rapport élevé de valence à rayon, présumément à cause d'une extraction antérieure de magma. D'après une estimation des caractéristiques de la source de ce magma,

les rapports Rb/Sr et Nd/Sm semblent indiquer un enrichissement en terres rares légères peu de temps avant la séparation du magma. Avec le temps, une telle source pourrait développer des rapports isotopiques pour le Nd et le Sr inférieurs à la valeur pour la terre entière, et des valeurs "epsilon" qui diffèrent de celles qui caractérisent la plupart des magmas mafiques. Plusieurs exemples de lherzolites métasomatisées montrent de tels enrichissements en terres rares légères et un appauvrissement en Rb, par rapport au Sr, ce qui montre que les teneurs élevées en plusieurs éléments incompatibles (terres rares, U, Th et Nb) dans le filoncouche pourraient résulter d'une métasomatose à la source. Cependant, plusieurs nodules lherzolitiques possèdent une anomalie négative en Ti, absente dans les échantillons de Malpèque et dans plusieurs exemples de magmatisme alcalin, d'ailleurs. Quoique ce trait n'infirme pas l'hypothèse d'une métasomatose à la source, il souligne le fait que plusieurs exemples étudiés de xénolites métasomatisés ne pourraient représenter le manteau duquel sont issus les magmas alcalins, dont celui qui a été mis en place dans la baie de Malpèque.

#### (Traduit par la Rédaction)

Mots-clés: permien tardif, zones d'extension, lamprophyre, magma primitif, Nd, Sr, isotopes, métasomatose, pétrogenèse, Ile-du-Prince-Edouard.

### INTRODUCTION

The Late Permian Malpeque Bay sill (Greenough *et al.* 1988) contains the only igneous rocks in Prince Edward Island. These nepheline-normative mafic rocks have a high Mg' value [Mg' = Mg/(Mg +  $0.9Fe_{total}$ ) atomic] of 0.70, high Ni/MgO (ppm/wt.%) values (23-39), and Mg-rich olivine phenocrysts (Fo<sub>91</sub>), indicative of an extremely primitive magma. High Zr and Nb concentrations and high Nb/Zr ratios (~0.5) representative of lamprophyres from highly "enriched" sources attest to the alkaline nature of the sill. However, low Rb and K<sub>2</sub>O concentrations and low Rb/Sr ratios (~0.01) more typical of basaltic rocks appear at odds with the extreme concentrations of high-field-strength elements (*HFSE*).

Isotopic studies show that in many cases, alkaline magmas emplaced in both continental and oceanic settings are derived from a time-integrated

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incompatible-element-depleted source that must have been enriched (possibly by metasomatic processes) in large-ion-lithophile (*LIL*) and *HFS* elements close to the time of magma generation (*e.g.*, Menzies & Murty 1980a, Allègre *et al.* 1981, Bailey 1982). This follow-up study of the Malpeque Bay sill uses new  ${}^{87}$ Sr/ ${}^{86}$ Sr<sub>i</sub> and  ${}^{143}$ Nd/ ${}^{144}$ Nd<sub>i</sub> isotopic data to answer the following questions: 1) Was the unusual traceelement signature of the sill (*i.e.*, low alkali metals, high *HFSE*) a long-lived feature of its source region

TABLE 1. Sr AND Nd ISOTOFIC COMPOSITION OF THE MALPEQUE BAY SILL

	P83-43	P83-45	P83-47	P83-48
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Rb	5.79	9.39	7.50	14.93
Sr	1381	1144	1002	893
<sup>87</sup> Rb/ <sup>86</sup> Sr	0.0121	0.0238	0.0217	0.0484
87Sr/86Sr	0.704714	0.703719	0.703487	0.703442
20	0.00038	0.000048	0.000034	0.000028
87Sr/86Sr	0.704671	0.703636	0.703410	0.703272
eSr	0.41	~15.1	-18.3	-20.3
Sm	9.25	8.5	8.73	9.23
Nđ	44.5	41.0	42.6	44.2
147Sm/144Nd	0.12	0.125	0.12	0.126
143Na/144Na	0.512848		0.512766	0.512815
20	0.000024		0.000038	0.000034
143Na/144Na	0.512644		0.512565	0.512611
eNd	6.3		4.8	5.7

Rb, Sr, Sm and Nd concentrations in ppm. Subscripts m and i refer to measured and initial ratio calculated assuming an age of 247 Ma (Greenough <u>et al</u>. 1988).  $\varepsilon$  values calculated following DePaolo & Wasserburg (1976), and use uniform reservoir values of 0.7045 (Sr) and 0.512638 (Nd). or an artifact of processes that produced the magma itself? 2) Is mantle metasomatism a viable hypothesis to explain the *HFSE* enrichment and isotopic composition of the sill?

### SAMPLES

The 3-m-thick sill is exposed in only one 100-m outcrop. The four samples (and powders) used in the earlier project (Greenough et al. 1988) and in this study adequately describe its composition. In summary, these samples are fine grained (<0.02 mm) contain 5-15% euhedral and olivine microphenocrysts (average 0.2 mm) set in a matrix of augite (50%) and olivine (5%), with an intersertal mesostasis of high-Ti phlogopite (<5%) and finer-grained devitrified glass and felsic minerals (plagioclase? + nepheline?). The only obvious alteration minerals include minor iddingsite and serpentine on otherwise unaltered olivine grains.

# ANALYTICAL PROCEDURES

Rb, Sr, Nd, and Sm concentrations were determined using inductively coupled plasma – mass spectrometry (ICP-MS) techniques at Memorial University of Newfoundland (Longerich *et al.* 1990).



FIG. 1. Plot of  $\epsilon_{Nd}$  versus  $\epsilon_{Sr}$  for the Malpeque Bay sill and various oceanic and alkaline continental mafic rocks as reviewed by Halliday *et al.* (1988) and Roden (1987), respectively. Continental rocks are underlined. Epsilon values calculated after DePaolo & Wasserburg (1976), with UR and CHUR taken as 0.7050 and 0.51264, respectively. Sr and Nd data are normalized to NBS 987 (0.710250) and La Jolla (0.511850), respectively.

Precision and accuracy are 4% (Rb) and 3% (Sr, Sm, Nd), with interelement ratios  $\pm 1\%$  (based on replicate analyses of international standards).

Chemical separations of Sr and Nd followed standard two-column procedures. Details appear in Swinden *et al.* (1990). Mass spectrometric analyses of Sr and Nd were done on a VG Micromass 30B singlecollector mass spectrometer. Repeated analyses of La Jolla and NBS 987 standards gave 0.511889  $\pm$ 8 (n = 22) and 0.710310  $\pm$  20 (n = 12) during the period of analysis [errors quoted are  $2\sigma$  (mean)]. All values reported have been corrected to 0.511850 and 0.710250, respectively. Age corrections made to give initial isotopic ratios used interelement ratios measured by ICP-MS and a K-Ar age of 247 Ma for the sill (Greenough *et al.* 1988).

# DATA PRESENTATION

None of the  $2\sigma$  error bars on  ${}^{87}\text{Sr}/{}^{86}\text{Sr}_i$  values overlap (Table 1), but three samples (P83–85, 47, and 48) show similar ratios between 0.7036 and 0.7033 [ $\epsilon_{\text{Sr}}$  (DePaolo & Wasserburg 1976) -15 to -20%]. Initial Nd isotopic ratios range from 0.51256 to 0.51264, with  $\epsilon_{\text{Nd}}$  values of 4.8 to 6.3. Similar  $\epsilon_{\text{Nd}}$ and  $\epsilon_{\text{Sr}}$  values have been recorded, for example, from the Hawaiian Islands (O'Nions *et al.* 1977) and the Azores (Hawkesworth *et al.* 1979), as well as from the Dinantian volcanic suite from Britain (Smedley 1988) (Fig. 1).

### DISCUSSION

#### Variation in initial ratio

There are numerous possible explanations for the variations in  ${}^{87}\text{Sr}/{}^{86}\text{Sr}_i$  ratios. Given that three of the four samples show similar  ${}^{87}\text{Sr}/{}^{86}\text{Sr}_i$  ratios (~0.7035), whereas P83-43 is clearly anomalous (~0.7047), it appears most likely, considering the randomizing effect of alteration, that radiogenic Sr was added to P83-43. Rubidium loss from P83-43 *after* solidification can be discounted as the cause for the high (age-corrected)  ${}^{87}\text{Sr}/{}^{86}\text{Sr}_i$  ratio because even the measured values of  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  exceed all other samples. Further discussion assumes that samples P83-45, P83-47 and P83-48 provide estimates of  ${}^{87}\text{Sr}/{}^{86}\text{Sr}_i$  suitable for petrogenetic interpretation.

The initial Nd isotopic ratios for analyzed samples are similar; given suggestions that the *REE*, compared to Rb and Sr, are relatively immobile under conditions of very low grade metamorphism (*e.g.*,



FIG. 2. Plot of  $\epsilon_{Nd}$  versus  $\epsilon_{Sr}$  showing the Malpeque Bay sill and its source region if aged 1 Ga. Also shown for comparison is the mantle array and the field encompassing ~70% of samples representing metasomatized xenoliths "aged" 1 Ga, as reported in Roden (1987).

Herrmann *et al.* 1974, Floyd 1977), it seems likely that the mean initial ratio ( $\sim 0.51265$ ) is representative of the initial Nd isotopic ratio of the sill.

### Source-region composition

The Malpeque Bay sill shows trace- and major-

TABLE 2.	PARAMETERS	OF	MELTING	MODEL	AND	RESULTS	OF	CALCULATION	
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	01	Opx	Срх	Gar
Phase Prop.	55	25	10	10
Melt Prop.	5	5	45	45
D <sup>Rb</sup>	0.0002	0.003	0.003	0.01
D <sup>Sr</sup>	0.0002	0.02	0.12	0.08
D <sup>Sm</sup>	0.010	0.022	0.26	0.217
	0.007	0.013	0.17	0.087
	Source 1	s Sill		
	5%	10%	15%	Rocks
Rb/Sr	0.0077	0.0092	0.0098	0.0105
Sm/Nd	0.253	0.221	0.220	0.207

Sources of data: D values: Jacobsen & Wasserburg (1979). Melt proportions: Kay & Gast (1973). Modreski & Boattcher (1973). Phase proportions: Carswall (1980), Gurnay & Harte (1980). element characteristics commonly attributed to primary magmas (Greenough *et al.* 1988). Although numerous isotopic and trace-element studies have demonstrated that continental mafic magmas can be significantly contaminated by continental crust (*e.g.*, Carter *et al.* 1978, Dostal & Dupuy 1984), the primitive nature of the magma precludes significant crystallization, which must accompany crustal assimilation.

The sill is isotopically indistinguishable from some oceanic island basalts (OIB, *e.g.*, Hawaii, Fig. 1), lending support to the hypothesis that there may be little difference between source regions of continental and oceanic alkali basalts (*e.g.*, Allègre *et al.* 1981, Halliday *et al.* 1988, Smedley 1988). Rocks from both continental and oceanic areas define a correlation line (the "mantle array") on the  $\epsilon_{Nd} - \epsilon_{Sr}$  diagram, which shows a certain tendency for clustering in quadrant II. Source regions producing magmas that plot in quadrant II (*e.g.*, the Malpeque Bay sill) consist dominantly of the residual solids from previous extraction of a melt (DePaolo & Wasserburg 1976).



FIG. 3. Mantle-normalized diagrams showing trace-element concentrations in various primitive [0.68 < Mg' < 0.72] alkali basalts, basanites and nephelinites of continental or oceanic island origin. Normalization values are from Sun & Nesbitt (1977), Wood (1979) and Sun (1982), with REE 1.77 times chondritic values in Evensen et al. (1978). Data sources: Hawaii: Koloa nephelinite, Hawaii, sample 74Wa9 (Clague & Dalrymple 1988). Austral Islands (1): MacDonald seamount basanite, MCD-079 (Dupuy et al. 1988). Austral Islands (2): Tubuai Island alkali basalt, TBA-036 (Dupuy et al. 1988). Antarctica: Hut Point Peninsula basanite, 2-105-53 (Kyle 1981). Australia: Western Victoria basanites, average of 2128 and 2679 (Frey et al. 1978). Average Malpeque Bay sill from Greenough et al. (1988).</p>

The concentrations of trace elements in many alkali basalts are inconsistent with their isotopic compositions. For example, they contain too much Rb for their <sup>87</sup>Sr contents (e.g., Sun & Hanson 1975a, Bailey 1982). The isotopic composition of the Malpeque Bay sill is inconsistent with its trace element composition but, in the case of Rb, the inconsistency is the opposite of that normally observed (*i.e.*, too much radiogenic Sr for observed quantities of Rb). In order to demonstrate this as quantitatively as possible, the Rb/Sr and Sm/Nd ratios in the magma's source region were estimated, and the source "aged"  $1 \times 10^9$  years (Fig. 2). Shaw's (1970) non-modal batch melting equation was solved for Co (original concentration at the source) using average Rb, Sr, Sm and Nd concentrations (samples P83-45, 47 and 48: other parameters in Table 2). A garnet-bearing source region was assumed to account for low concentrations (~6 times chondrite) of the heavy REE (Kay & Gast 1973). The low K contents of the sill preclude an important role for phlogopite in the source region; therefore, residual phlogopite cannot be responsible for the low concentrations of Rb. Percentages of melting were varied between 5 and 15%, based on estimates (e.g., Sun & Hanson 1975b, Frey et al. 1978) that alkaline rocks represent less than 15% melting. Major-element-based equations developed by Chen (1988) indicate melting percentages between 8 and 14%. The estimated Rb/Sr and Sm/Nd ratios at the source appear in Table 2.

The source region of the sill must have been depleted in Rb, or enriched in Sr, just prior to magma genesis, because with time its Sr isotopic composition would rapidly deviate from the "mantle array" (Fig. 2). The source was probably enriched in *LREE* (Sm/Nd decreased) at the time of magma genesis because  $\epsilon_{Nd}$  values for the "aged" mantle are lower than those for the magma at the time of genesis.

The processes responsible for LIL and HFSE enrichment in alkaline magmas are not well understood. They include very small percentages of melting (Gast 1968, Kay & Gast 1973), high-pressure fractionation of an eclogitic assemblage (Mitchell & Bell 1976), chromatographic percolation of melt through the upper mantle (Navon & Stolper 1987), and mantle metasomatism (Bailey 1982, Fitton & Upton 1985). Although a role for small percentages of melting seems clear, the eclogite-fractionation hypothesis is not supported by the primitive composition of many alkaline magmas, given the large percentages of fractionation required. Chromatographic percolation of melt cannot by itself produce the extreme LIL and HFSE enrichments observed in many alkaline magmas (Greenough et al. 1988). The metasomatism hypothesis is testable using isotopic and trace-element data available for mantle xenoliths considered representative of metasomatized mantle (Menzies & Murty 1980b). Many of these xenoliths plot on the mantle array, but their isotopic compositions are inconsistent with their trace-element concentrations on a long-term basis. For example, many spinel lherzolite xenoliths are enriched in the light REE but depleted in Rb relative to Sr. With time, they would produce magmas plotting in quadrant III of the  $\epsilon_{Nd} - \epsilon_{Sr}$  diagram (Fig. 2) (Roden 1987). Thus based on Rb/Sr and Nd/Sm data, such LREEenriched but Rb-depleted xenoliths could be similar to the source material for the Malpeque Bay sill. However, they cannot represent the source for most alkaline magmas because such xenoliths are not enriched in Rb relative to Sr. Furthermore, they tend to show a negative Ti anomaly (O'Reilly & Griffin 1988, Salters & Shimizu 1988) conspicuously missing from the majority of alkaline magmas, including that which formed the Malpeque Bay sill (Fig. 3). Although some form of mantle metasomatism may be a prerequisite to alkaline magmatism, many metasomatized xenoliths in alkaline magmas appear to be a consequence of and not a precursor to alkaline magmatism (e.g., Roden et al. 1984, Wilshire 1987).

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