Chemical and Isotopic Systematics of Basalts and Peridotite Xenoliths: Implications for the Composition and Evolution of the Earth's Mantle

by

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"If I have seen further it is by standing on the shoulders of giants."

Sir Isaac Newton

Statement

The analytical data, interpretations and conclusions presented in this thesis are my own unless otherwise acknowledged. Work carried out jointly with others is described in the Preface.

W. F. McDonough

W.F. McDonough

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First and foremost, I sincerely thank Malcolm McCulloch and Shen-su Sun for the time and effort which they have invested in me. Working with them has been both pleasurable and rewarding. I also thank Ted Ringwood for his many discussions and suggestions and his active support of my research.

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I thank Professor D.H. Green (U of T., Hobart) for generously providing several important geological samples for this study. I thank Les Kinsley, Elmer Kiss, Robin Maier, Derek Millar, Dave Nelson, Richard Rudowski, Norm Schram, Mike Shelley and Nick Ware for plenty of technical help throughout this study, which was always efficient, helpful and friendly. I thank my fellow graduate students, Roland Maas, Dave Nelson and Janet Hergt for their help and cooperation. I also thank Bruce Chappell for XRF analyses.

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ABSTRACT

A series of studies on basalts and peridotite xenoliths has been undertaken to understand the composition and evolution of the earth's mantle. Data gained from these studies are used together with literature data to constrain the initial composition of the earth's mantle and to characterize it's chemical and isotopic evolution.

Chemical and isotopic data for Tertiary-Recent intraplate basalts from southeastern Australia are used to identify the composition of their mantle source. Distinctions in the Sr and Nd isotopic compositions of alkalic and tholeiitic basalts from this area requires that they be derived from different source regions. A generalized model is proposed for the generation of intraplate basalts which involves mixtures of lithospheric mantle and plume-derived, asthenospheric mantle components.

Chemical and isotopic data for spinel-bearing harzburgite and lherzolite xenoliths which are carried in the southeastern Australian basalts are used to characterize the composition of the regional lithospheric mantle. Large variations in the Sr and Nd isotopic compositions (0.7025-0.7084 and ε_{Nd} =+13 to -6) of these xenoliths are in marked contrast with their host basalt (0.7038-0.7045 and ε_{Nd} =+4.2 to 1.7) and reflect the long-term, small scale heterogeneities in the continental lithospheric mantle. An early basalt depletion event identified in these xenoliths records the initial development and stabilization of the continental lithospheric mantle. Later growth of this mantle is envisaged as occurring in stages and involves the progressive underplating of refractory peridotite diapirs.

Evidence for a secular variation in the mantle's Rb/Cs ratio is presented, indicating that the compositions of modern mid-ocean ridge and ocean island basalts cannot be assumed to reflect the composition of the earth's primitive mantle. Combined chemical and isotopic data for terrestrial rocks and chondritic meteorites provide constraints on the absolute and relative abundances of refractory and non-refractory, lithophile, siderophile and chalcophile elements in the earth's primitive mantle. Using this information in combination with the chemical compositions of 30 fertile peridotite xenoliths from Europe, Asia, North and South America and Australia I have proposed an internally consistent compositional model of the earth's primitive mantle.

Preface

Here I state my contribution to each of the chapters and appendices of this PhD.

Chapter 1: I carried out the isotopic measurements and wrote the text of this paper, however this paper was greatly improved upon by my co-authors.

Chapter 2: I carried out the isotopic measurements and wrote the text of this paper. Malcolm McCulloch contributed to many of the ideas in this paper.

Chapter 3: Most of this paper was written by myself, however R.L. Rudnick wrote the section on the lower crust. My co-authors have contributed to the ideas presented in this paper and greatly improved on the style and presentation. The isotope data was collected by M. McCulloch, A. Haynes and H. Hensel.

Appendix I: This paper was written by R.L. Rudnick. I provided the isotopic analyses and was involved in the interpretation of the data, synthesis of ideas and review and revisions of the text.

Appendix II: This paper was written by D. Coombs. I wrote the last section of this paper, provided isotopic analyses and added comments on other parts of the paper.

Appendix III: This section contains geochemical and isotopic data which I obtained at the RSES, for basalts from Australia, New Zealand and the southwest Pacific, which have yet to be published.

Chapter 4: I wrote this paper with many ideas and suggestions from my co-authors. The data used in this study are from the literature.

Chapter 5: I wrote this chapter. The ideas presented are the result of collaborative research between Shen-su Sun and myself, however I am responsible for the interpretations and model presented.

Appendix IV: This paper was written by Shen-su Sun; the ideas in this paper are the result of our collaborative effort.

CONTENTS

PART II: SYNTHESIS

Thesis Outline

This thesis represents the findings of my research carried out during the course of my PhD. It has been divided into two parts, each having its own chapters and appendices. All chapters in this thesis represent papers of which I am the first author. The appendices represent papers for which I am a co-author, these have been mostly or wholly written by their first author. Part I of this thesis consists of several studies of basalts and peridotite xenoliths and Part II represents a synthesis of the findings of Part I and literature data. These data are used to document the composition and evolution of the earth's mantle. Below are brief descriptions of the contents of each of the chapters and appendices.

PART I

Chapter 1. Chemical and isotopic data for modern, intraplate basalts from southeastern Australia are used to identify the composition and nature of the different mantle sources and processes involved in their generation. The Sr and Nd isotopic compositions of tholeiitic and alkalic basalts are distinctive and require at least 2 different mantle sources.

Chapter 2. Chemical and isotopic data for spinel-bearing harzburgite and lherzolite xenoliths, which are carried in the above mentioned southeastern Australian basalts, are used to characterize the composition of the regional lithospheric mantle, the processes involved in its initial growth and stabilization and the evolution of this part of the mantle. Additionally, these data are used to evaluate the role of the lowermost lithosphere in intraplate volcanism.

Chapter 3. Chemical and isotopic data for basalts, lower crustal xenoliths and peridotite xenoliths from eastern Australia are used to create an integrated picture of the nature of the lower portion of the eastern Australian lithosphere. These data are used to present a model for the composition, growth and evolution of the lower crust and lithospheric mantle.

Appendix 1. Chemical and isotopic data for a suite of lower crustal xenoliths from northern Queensland were used to show that the members of this suite are genetically related and that they are the products of a basaltic magma which underwent simultaneous fractional crystallization and assimilation. These data also allowed us to suggest that basaltic underplating is an important process involved in the growth of the regional lower crust and has occurred throughout the Cenozoic.

Appendix 2. This is a regional study of Cenozoic basaltic magmatism in the southern part of the south island of New Zealand, which characterizes the field relationships, mineralogy and composition of lavas in this area and presents some ideas on the nature of their sources. A Gondwanaland reconstruction of Australia, New Zealand and Antarctica suggests that these continental blocks were contiguous and the similarities in the chemical and isotopic compositions of the Cenozoic basalts may reflect a lithospheric mantle source with a common history.

Appendix 3. This section presents chemical and isotopic data for intraplate basalts from Australia, New Zealand and the southwest Pacific.

PART II

Chapter 4. The Rb and Cs contents and the Rb/Cs ratios of Archean to modern crust and mantle rocks are used to constrain the earth's primitive mantle Rb/Cs ratio (20±10). These data are used to document a secular variation in the mantle's Rb/Cs ratio which is attributed to continent formation and mantle recycling. This has important implications for the present dynamic state of the earth's mantle and its overall evolution. The average Rb/Cs ratio for all lunar samples is 22±3. Similar Rb/Cs ratios for the earth's primitive mantle and the moon are consistent with models that invoke a terrestrial origin for the moon.

Chapter 5. Consistent elemental ratios for refractory lithophile elements in carbonaceous chondrites are presented and a revised estimate of the average composition of CI carbonaceous chondrites is given. These data are used, along with chemical and isotopic information on a variety of terrestrial rocks, to constrain the absolute and relative abundances of refractory and non-refractory, lithophile, siderophile and chalcophile elements in the earth's primitive mantle. A model is proposed whereby the composition of the earth's primitive mantle is derived from an analysis of chemical data for 30 fertile peridotite xenoliths from Europe, Asia, North and South America and Australia.

Appendix 4. Major and trace element data for mid-ocean ridge (MORB) and ocean island basalts (OIB) are used to formulate the chemical systematics of sub-oceanic mantle melting processes. The chemical and isotopic compositions of different types of OIB mantle reservoirs are shown to correlate and these data are used to unravel their genesis. Nb data indicate that the mantle sources of MORB and OIB are not conjugate reservoirs to the continental crust and suggest that other mantle reservoirs must play a role in the mass balance of Nb in the bulk earth. Negative Eu anomalies observed in some OIB, which are not attributed crystal fractionation processes, suggest the addition of subducted sediment into their mantle sources, however sediment recycling is not considered an important process over the last 2 Ga of mantle evolution.

PART 1

STUDIES OF BASALTS AND PERIDOTITE XENOLITHS

CHAPTER 1

Isotopic and Geochemical Systematics in Tertiary-Recent Basalts from Southeastern Australia and Implications for the Evolution of the Sub-continental Lithosphere

by W.F. McDonough, M.T. McCulloch and S.-s. Sun

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Isotopic and geochemical systematics in Tertiary-Recent basalts from southeastern Australia and implications for the evolution of the sub-continental lithosphere

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Abstract—Tertiary-Recent Tasmanian and Newer (Victoria/South Australia) basalts range from quartz tholeiite to olivine melilitite and show systematic increases in their incompatible element abundances with increasing degree of silica undersaturation. These two basalt provinces show similar relative abundances of rare earth elements (REE), differences in the relative concentrations of Rb, Ba, Th, K and Nb, and distinct, restricted isotopic compositions. The Tasmanian basalts have $^{87}Sr/^{86}Sr$ from 0.7026 to 0.7034, and ϵ_{Nd} from +7.5 to +5.8; the Newer basalts have higher $^{87}Sr/^{86}Sr$ from 0.7038 to 0.7045, and lower ϵ_{Nd} from +4.2 to +1.7. The range in Sr and Nd isotope compositions can be defined by primary magma compositions for both provinces, using Mg-values, Ni content and the presence of spinel lherzolite nodules. Major and trace element and Sr, Nd and Pb isotope compositions are uniform on a scale of up to 50 km for four separate Newer basanite centers. The chemical and isotopic data are consistent with a model whereby tholeiitic basalts are derived by large degrees of partial melting from a chemically uniform but isotopically variable source, and generation of undersaturated, alkaline basalts by smaller degrees of partial melting of the same source. No isotopic or geochemical evidence was found which would suggest that the more evolved basalts have been contaminated by continental crust.

In contrast to tholeiitic and alkalic basalts from Hawaii, there is a continuous spectrum of isotope compositions for the Newer tholeiitic to alkalic basalts. A model is proposed for the generation of these basalts involving mixtures of hotspot mantle plume-derived melt and lithospheric mantle-derived melt, where observed differences between ocean island and continental alkaline basalts are attributed to differences between the sub-oceanic and sub-continental lithospheric mantles. Isotopic differences between tholeiitic and alkalic basalts are interpreted to be due to varying degrees of exchange and mixing between the hotspot plume and lithospheric mantle melt components. The model is consistent with the generation of these basalts from a source which has been recently enriched in the LREE.

INTRODUCTION

INTEGRATED PETROLOGIC, major and trace element and isotopic studies of primitive basalts can provide much needed insight into the composition and evolution of their mantle source regions. In contrast to ocean island basalts (OIB) the study of continental intraplate basalts has been relatively neglected due to the possibility of contamination by the continental crust during their ascent and emplacement. However, ALLEGRE *et al.* (1981), in a study of continental intraplate basalts which showed minimal effects of crustal contamination, suggested that continental alkaline basalts are derived from source regions similar to that of OIB. Their work was reconnaissance in nature and there now exists a need for more detailed investigations into the similarities and potential differences between the source regions of continental alkaline basalts *versus* OIB. From detailed studies which integrate major and trace element and isotope data we may begin to evaluate the role played by the convective (asthenospheric) mantle and that of the non-convective lithospheric mantle in contributing their geochemical and isotopic signatures to tholeiitic and alkalic basalts from continental and oceanic intraplate settings. Ultimately we hope to resolve how differences between the sub-oceanic and sub-continental lithospheric mantles are manifested in the basalt types erupted from these regions. Finally, when modelling contamination processes, what role is played by the crust and by the lithospheric mantle?

Chemical and isotopic data are presented for southeastern Australian tholeiitic and alkalic basalts with primary, or near primary, major and trace element compositions. We have also analyzed more evolved basalts to determine if they have been contaminated by crustal rocks and to document such effects, if present. Comparisons are also made between the isotopic compositions of spinel lherzolite nodules and their host basalts in order to evaluate the possible role of lithospheric mantle contamination. Many samples have been previously analyzed for major (IRVING and GREEN, 1976) and trace element concentrations (FREY *et al.*, 1978). These earlier studies placed constraints on depth of melt separation and degree of partial melting involved in the generation of these basalts. In this study we present Sr and Nd isotopic data for all of these basalts and provide a broader major and trace element and isotopic data base by which to evaluate the conclusions of these earlier studies. Comparisons are also made between the chemical and isotopic composition of these continental, tholeiitic to alkalic basalts and similar basalts found in the Hawaiian islands.

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Geological background

The samples come from two Tertiary-Recent basalt provinces in southeastern Australia: the Tertiary basalts of Tasmania and the Pliocene-Recent Newer basalts of western Victoria and southeastern South Australia. Figure 1 shows the distribution and localities of the Newer basalt samples. The Newer basalt field is a monogenetic volcanic field covering some 25,000 Km^2, while the Tertiary Tasmanian basalts occur as scattered flows and plugs in eastern Tasmania. WELLMAN and MCDOUGALL (1974) and SUTHERLAND (1981) propose that the Tertiary-Recent volcanism along eastern Australia is related to the migration of mantle plumes beneath the continent. Basalts from southeastern Australia have erupted through predominantly Ordovician geosynclinal sediments of the Ballarat and Melbourne troughs and Silurian intrusives.

Thin section examination of the basalts shows little alteration apart from minor hematite, especially around the edges of olivine crystals. Detailed location and petrographic information for these samples can be found in IRVING and GREEN (1976) and FREY *et al.* (1978).

ANALYTICAL METHODS

Methods used for preparation of rock powders and determination of major element composition for these basalts is described in IRVING and GREEN (1976). Trace element concentrations and isotope ratios were determined on splits of whole rock powders used in the earlier studies of IRVING and GREEN (1976) and FREY *et al.* (1978). Trace element concentrations reported in Table 1, except for Nd, were determined by B. Chappell using the XRF technique of NORRISH and CHAPPELL (1977). Nd concentrations were determined by isotope dilution. Sr and Rb concentrations were determined by both XRF and isotope dilution; agreement between the two methods was within 2% absolute or better. Trace element concentrations reported in Table 2 were determined by spark-source mass spectrometry (TAYLOR and GORTON, 1977). There is generally good agreement with the Rb, Sr and Nd concentrations reported in FREY *et al.* (1978) and those redetermined in this study, except that isotope dilution yields 93 ppm Nd for sample 2860 compared to 77 ppm Nd reported in FREY *et al.* (1978).

Samples were totally spiked with ^{150}Nd and ^{147}Sm tracers and decomposed in open beakers using HF, HF-HClO$_4$ solutions and then converted to chlorides using 6 N HCl. The REE, Sr and Rb were initially separated on 5 gram cation exchange columns using 1 N, 2.5 N and 6 N HCl as the elutriants. Rb was purified on 2 gram columns using 1 N HCl, while Sr was purified on 2.5 gram columns using 1 N and 2.5 N HCl. Nd and Sm were separated from each other and the remaining REE on a separate column using 0.2 M 2-methyllactic acid with a pH of 4.6. During the analyses of these basalts the blank, using our stock solutions, was 0.5 ng for Nd and 3.5 ng for Sr. No blank corrections were necessary for any of the measured isotope ratios. Nd and Sr isotope ratios were measured as metal using a triple Re filament in the MSZ mass spectrometer (CLEMENT and COMPSTON, 1972). Sr isotope ratios were measured by peak switching ^{88}Sr-^{86}Sr and ^{86}Sr-^{87}Sr, and then normalized to ^{86}Sr/^{88}Sr = 0.1194. Nd isotope ratios were measured by peak switching between ^{142}Nd-^{144}Nd, ^{143}Nd-^{144}Nd and ^{146}Nd-^{144}Nd, and these ratios were normalized to ^{146}Nd/^{142}Nd = 0.636151 to correct for the effects of mass fractionation. Precision for isotopic measurements are reported as the $2\sigma_{\text{mean}}$ for the analysis. Rb, Sr, Sm and Nd concentrations (ppm) and ^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd isotopic ratios determined for BCR-1 during the measurement of the basalt samples are: Rb = 46.9 ± .1, Sr = 326 ± 3, Sm = 6.59 ± .01, and Nd = 28.74 ± 0.05, and BCR-1 isotope ratios are ^{87}Sr/^{86}Sr = .70494 ± 1 (n = 3) and ^{143}Nd/^{144}Nd = 0.511833 ± 10 (n = 7). This is $-0.2\epsilon_{\text{Nd}}$ units lower than the value previously reported in this laboratory (*e.g.*, MCCULLOCH and CHAPPELL, 1982) and is a result of the installation of a new electrometer and data acquisition system. The ratio obtained for Ndα (WASSERBURG *et al.*, 1981) during the same period is 0.511101 ± 8 (n = 8), which compares with WASSERBURG *et al.*'s (1981) reported value of 0.511121 ± 8. We measured ^{143}Nd/^{144}Nd = 0.511040 ± 7 (n = 4) for the La Jolla standard during the final stages of this study. There is excellent agreement in relative values of the ^{143}Nd/^{144}Nd ratio between our data and that reported in WASSERBURG *et al.* (1981) for these three Nd isotope standards (BCR-1, Ndα, and La Jolla). Finally, we measured ^{87}Sr/^{86}Sr = 0.71022 ± 1 (n = 7) for NBS − 987 during the course of this study, and ^{87}Sr/^{86}Sr = 0.70800 ± 3 (n = 2) for the E & A SrCO$_3$ standard during the final stages of this study.

A number of repeat Sr and Nd isotopic analyses were duplicated during the period of data collection. The duplicate analyses for samples 2177, 69-1006, 69-1018, 2679, 2128, 2854 and 2860 are reported in Table 3; all repeats fall within the reported $2\sigma_{\text{mean}}$ uncertainty limits.

RESULTS

The major and trace element compositions of Newer basalts are reported in Tables 1 and 2. Sr and Nd isotope compositions of these and other Newer basalts and Tasmanian basalts are given in Table 3. Major and trace element concentrations for samples reported in Table 3 and not found in Table 1 are given in FREY *et al.* (1978).

Major elements, Ni and Cr contents

The Pliocene-Recent Newer basalts consist of a broad compositional spectrum of tholeiitic and alkalic series basalts including quartz tholeiite, olivine tholeiite, hawaiite, nepheline hawaiite, nepheline mugearite, Fe-rich olivine basalt, olivine

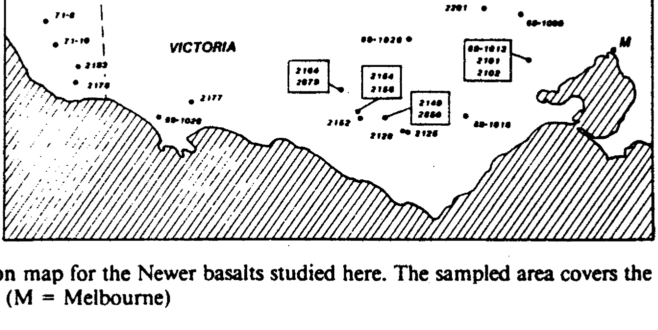

FIG. 1. Location map for the Newer basalts studied here. The sampled area covers the areal distribution of Newer basalts. (M = Melbourne)

TABLE 1. Major and Trace Element Data for Victorian Newer Basalts

	2125	69-1006	69-1020	69-1033	2201	2149	69-1013	2154	2183	2178
	Olivine Tholeiite	Fe-rich Basalt	Olivine Basalt		Alkali Ol Basalt		Hawaiite	Neph. Hawaiite		
SiO_2	50.11	49.09	49.23	49.58	47.37	46.79	48.74	46.26	48.34	47.46
TiO_2	2.06	3.40	1.88	2.65	2.43	2.62	2.36	2.72	2.35	3.11
Al_2O_3	13.89	17.20	14.37	13.86	14.80	13.60	14.59	13.15	13.41	14.43
Fe_2O_3	1.76	2.38	1.87	1.85	1.83	2.06	1.89	2.06	1.89	2.25
FeO	9.55	9.53	9.37	9.25	9.13	10.28	9.44	10.30	9.44	9.00
MnO	0.16	0.14	0.16	0.15	0.17	0.18	0.18	0.18	0.17	0.16
MgO	8.47	3.76	9.19	8.45	9.46	9.78	8.31	9.67	8.88	7.35
CaO	8.60	7.17	9.10	8.20	8.47	9.00	8.07	8.65	9.58	7.51
Na_2O	3.55	4.14	3.20	3.45	3.54	3.34	4.50	4.18	3.69	4.63
K_2O	1.17	2.32	1.26	1.88	1.96	1.60	1.20	1.83	1.68	3.02
P_2O_5	0.41	0.87	0.37	0.68	0.84	0.76	0.72	1.00	0.57	1.08
CO_2	0.06	0.03	0.03	0.05	0.08	0.07	0.06	0.06	0.18	0.09
H_2O^+	0.06	1.08	0.75	0.87	1.29	0.35	1.17	0.48	0.17	0.18
H_2O^-					0.70	0.23		0.18		
Mg#	62.3	41.3	63.6	62.0	64.9	62.9	61.1	62.6	62.6	59.3
V	140.	173.	144.	167.	143.	163.	130.	129.	173.	133.
Cr	240.	7.	253.	229.	222.	217.	346.	232.	249.	100.
Ni	163.	17.	174.	189.	189.	181.	313.	214.	185.	99.
Cu	29.	14.	42.	49.	44.	51.	39.	40.	56.	37.
Zn	103.	127.	103.	120.	125.	118.	116.	125.	115.	122.
Sr	467.	995.	482.	625.	890.	713.	775.	953.	642.	1090.
Rb	25.	39.	28.	39.	40.	32.	58.	39.	34.	62.
Ba	245.	485.	370.	395.	500.	400.	485.	550.	455.	820.
Pb	3.	3.	2.	4.	3.	4.	5.	6.	3.	4.
Y	20.	31.	20.	24.	24.	22.	22.	25.	21.	27.
Nb	27.	52.	28.	42.	59.	45.	58.	69.	44.	79.
Zr	168.	330.	144.	279.	287.	241.	294.	362.	202.	385.
La	22.	39.	20.	33.	44.	33.	44.	56.	34.	62.
Ce	48.	89.	41.	73.	94.	78.	97.	129.	70.	135.
Nd	23.7	44.9	21.2	35.9	40.5	--	40.3	54.0	32.6	57.2

	2101	2102	69-1031	2209	2156	71-17	71-26	2164	71-10	70-1174	71-8
	Neph. Mugearite				Basanite				Olivine Analcimites		
SiO_2	49.63	48.88	48.87	48.78	45.59	45.29	45.40	45.16	43.85	43.75	44.09
TiO_2	2.18	2.19	2.26	2.26	2.52	2.43	2.72	2.81	3.64	3.68	3.87
Al_2O_3	15.45	15.41	15.71	15.77	12.28	12.00	12.64	13.55	9.17	9.37	10.56
Fe_2O_3	3.47	3.45	3.64	3.66	1.85	1.94	2.01	1.99	2.39	2.50	2.42
FeO	6.94	6.90	7.28	7.32	10.00	9.70	10.04	9.97	9.57	10.00	9.69
MnO	0.16	0.16	0.16	0.16	0.18	0.17	0.17	0.18	0.17	0.18	0.18
MgO	6.41	7.20	6.48	6.55	12.65	13.76	11.59	10.53	15.54	15.18	12.03
CaO	6.78	6.52	6.82	6.84	8.14	7.96	8.33	8.96	10.33	10.66	11.88
Na_2O	5.43	5.72	5.01	4.90	3.86	3.95	4.13	3.79	4.14	3.40	3.89
K_2O	2.91	2.87	2.89	2.87	2.01	1.95	2.08	2.06	0.35	0.39	0.36
P_2O_5	0.64	0.64	0.88	0.89	0.91	0.85	0.90	0.99	0.84	0.88	1.02
CO_2	0.54	0.04	0.08	0.08	0.06	0.07	0.08	0.19	0.05	0.11	0.05
H_2O^+	0.39	0.08	1.30	1.19	0.11	0.20	0.21	0.86	1.33	1.85	1.75
H_2O^-	0.28			0.40	0.04			0.26	0.88	1.17	1.46
Mg#	62.2	65.1	61.3	61.4	69.3	71.7	67.3	65.3	74.3	73.0	68.9
V	101.	113.	104.	104.	133.	132.	142.	145.	264.	264.	263.
Cr	144.	170.	99.	103.	412.	471.	317.	203.	535.	540.	292.
Ni	131.	149.	94.	92.	388.	439.	298.	221.	460.	496.	250.
Cu	28.	33.	35.	33.	43.	43.	46.	64.	57.	53.	68.
Zn	144.	155.	147.	148.	140.	135.	132.	134.	107.	108.	102.
Sr	995.	825.	1140.	1141.	835.	835.	845.	925.	804.	1200.	1021.
Rb	67.	72.	68.	64.	40.	40.	40.	40.	40.	29.	10.
Ba	860.	870.	720.	725.	450.	440.	465.	490.	820.	875.	855.
Pb	5.	7.	3.	6.	4.	4.	3.	4.	5.	5.	5.
Y	21.	22.	24.	24.	24.	23.	23.	25.	22.	21.	24.
Nb	89.	93.	70.	71.	66.	64.	63.	72.	76.	76.	86.
Zr	480.	493.	364.	361.	331.	319.	318.	346.	327.	327.	354.
La	56.	55.	60.	54.	49.	60.	47.	58.	63.	65.	69.
Ce	117.	114.	109.	111.	105.	100.	105.	120.	138.	137.	153.
Nd	47.1	45.4	--	47.7	47.6	--	--	52.4	64.9	--	68.0

Mg# = 100[Mg/Mg+Fe^{2+}]. Sample localities are given in Table 3, except for 69-1031 (Mt. Franklin), 71-17 and 71-26 (Mt. Noorat), and 70-1174 (Mt. Watch). Major and minor elements in wt%, trace elements in ppm.

basalt, alkali olivine basalt, nepheline basanite and olivine analcimite. The Fe-rich olivine basalts are the most chemically evolved rocks of the Newer suite studied by IRVING and GREEN (1976). A comprehensive description of the general geology, petrography and major element geochemistry of the Newer basalts is presented by IRVING and GREEN (1976).

The Tertiary Tasmanian basalts are older than the Newer basalts and are composed of tholeiitic and alkalic series basalts. These basalts were erupted some 20 to 30 Ma ago and exhibit a compositional range similar to that of the Newer basalts. Tasmanian basalts measured for Sr and Nd isotopic composition include olivine tholeiite, basanite, olivine nephelinite and an olivine melilitite.

Both the Newer and Tasmanian basalts have normative mineralogical composition ranging from nepheline to olivine normative, and one Newer basalt is a quartz normative tholeiite. Most nepheline normative basalts reported here, together with a Newer olivine basalt and the Tasmanian Andover olivine tholeiite contain Cr-diopside spinel lherzolite nodules. Whole rock Mg-values for most of these basalts range from 59 to 74, with many between 68 and 75. Basalts with Mg-values > 68 are considered to be primary mantle liquids derived from a refractory upper mantle peridotite with a Mg-value of ≧88–89 (IRVING and GREEN, 1976; FREY *et al.*, 1978). The Newer Fe-rich olivine basalt (69-1006) with a Mg-value of 41 and the evolved Scottsdale, Tasmanian olivine nephelinite (2860) with a Mg-value of 54 are the most chemically evolved lavas in each suite. These two samples were analyzed in order to investigate the isotopic effects of crustal level fractionation.

Ni and Cr contents of most of these basalts vary from 92 ppm to 496 ppm and 99 ppm to 540 ppm respectively. The

TABLE 2. Trace Element Data for Newer Basalts (in ppm)

	2177 Quartz Tholeiite	2152 Olivine Tholeiite	69-1026 Olivine Basalt	69-1036 Alkali Ol. Basalt	71-10 Olivine Analcimite	71-8
Y	91.	49.	53.	23.	22.	28.
Zr	158.	172.	162.	173.	--	--
Nb	28.	32.	28.	38.	--	--
Ba	281.	477.	623.	309.	894.	893.
La	47.0	46.8	45.8	22.3	62.	68.
Ce	97.	103.	125.	47.	125.	127.
Pr	12.0	11.1	10.3	5.7	16.0	18.2
Nd	50.2	49.0	40.8	24.6	65.2	67.8
Sm	11.7	9.68	9.04	5.83	11.6	11.7
Eu	3.92	2.92	2.64	1.90	3.41	3.33
Gd	12.3	9.1	9.2	5.3	6.8	6.8
Tb	1.91	1.46	1.44	0.89	1.23	1.21
Dy	11.5	9.3	8.2	5.2	5.2	5.0
Ho	2.40	1.48	1.60	0.84	0.91	0.89
Er	5.88	3.52	3.91	2.18	2.14	1.91
Yb	4.03	2.62	2.89	1.61	1.79	1.62
Hf	3.08	3.69	3.37	3.63	6.44	6.71
Cs	0.39	0.20	0.06	0.43	1.12	1.15
Pb	2.52	2.45	2.50	2.27	4.55	5.82
Th	2.29	2.95	2.37	2.63	7.25	7.14
U	0.43	0.60	0.23	0.63	1.67	1.34

two most evolved lavas have low Ni and Cr contents: Fe-rich olivine basalt (69-1006) has 17 ppm Ni and 7 ppm Cr and olivine nephelinite (2860) has 64 ppm Ni and 11 ppm Cr. Primary basalts have a higher and more restricted range in Ni and Cr content, ranging from 298 to 496 ppm Ni and 310 to 540 ppm Cr. The high Mg-values and Ni and Cr concentrations, and the presence of Cr-diopside lherzolite nodules (implying rapid uninterrupted ascent through the crust) are consistent with the derivation of these basalts by partial melting of a peridotitic mantle with no subsequent chemical modification (*i.e.*, crystal fractionation, crustal contamination, etc.). With primary basalts as a focusing point we can look at the trace element and isotopic composition of these and other, more evolved, basalts from these fields.

Incompatible elements

Figures 2a and 2b show the incompatible element compositions for a variety of Newer basalt types normalized to values for the primitive mantle. There are progressive increases in the incompatible element concentrations with increasing degree of silica undersaturation (Fig. 2a). Incompatible element abundances in the nepheline mugearites are similar to those in an alkali olivine basalt (Fig. 2b), except that the nepheline mugearites have lower Ti contents relative to the alkali olivine basalt. This suggests that a Ti-bearing phase is involved in the evolution of these magmas. Relative abundances of the incompatible elements Nb through Lu (Fig. 2b) in the hawaiite and nepheline hawaiites are similar to those in the alkali olivine basalt, though significant differences exist in the relative abundances of the most incompatible elements (Rb, Ba, Th, K and Nb). These differences may reflect variations in the initial source composition, different degrees of partial melting, and/or differences in the composition and relative amounts of fractionating phases involved in their generation (*e.g.*, IRVING and PRICE, 1981).

The olivine analcimites display a large relative depletion in K, variable depletions in Rb, and a minor depletion in Sr compared to a Newer basanite (Fig. 2a). Less pronounced Sr depletions are evident in the many Newer basalts suggesting either Sr is behaving more compatibly during partial melting

TABLE 3: MEASURED Sr AND Nd ISOTOPE COMPOSITIONS OF SE AUSTRALIAN BASALTS

Sample	Locality	Rock Type	$^{87}Sr/^{86}Sr$	$^{143}Nd/^{144}Nd$	ϵ_{Nd}
		VICTORIAN AND SOUTH AUSTRALIAN NEWER BASALTS			
69-1013	Anakies (W)	hawaiite*	.70386	.512004 ± 20	+3.3
2154	Noorat	ne. hawaiite*	.70390	.512030 ± 20	+3.8
2183	Mt. Gambier	ne. hawaiite*	.70408	.511984 ± 14	+2.9
2178	Mt. Schank	K-rich ne. hawaiite	.70413	.512007 ± 26	+3.3
2101	Anakies (E)	ne. mugearite*	.70384	.512006 ± 24	+3.3
2102	Anakies (E)	ne. mugearite*	.70384	.512004 ± 24	+3.3
2209	Mt. Franklin	ne. mugearite*	.70377	.512053 ± 18	+4.2
				.512049 ± 29	+4.2
2177	Mt. Eckersley	qz. tholeiite	.70491	.511765 ± 24	-1.4
			.70489		
2125	Stonyford	ol. tholeiite	.70427	.511945 ± 22	+2.1
69-1018	Mt. Gellibrand	ol. tholeiite	.70412	.511990 ± 23	+3.0
				.511970 ± 20	+2.6
2152	Marida Yallock	ol. tholeiite	.70442	.511865 ± 24	+0.6
69-1006	Mt. Gorong	Fe-rich ol. basalt	.70426	.512008 ± 22	+3.4
			.70423	.512016 ± 18	+3.6
69-1026	Mt. Widderin	ol. basalt	.70436	.511775 ± 31	-1.2
69-1020	Mt. Kincaid	ol. basalt	.70446	.511925 ± 26	+1.7
69-1033	Green Hill	ol. basalt*	.70407	.511970 ± 24	+2.6
2201	Mt. Warrenheip	alkali ol. basalt*	.70398	.512018 ± 18	+3.6
2149	Camperdown	alkali ol. basalt*	.70404	.512025 ± 18	+3.7
69-1036	Mt. Frazer	alkali ol. basalt*	.70384	.511992 ± 26	+3.0
2156	Mt. Noorat	basanite*	.70379	.512007 ± 22	+3.3
2164	Mt. Shadwell	basanite*	.70389	.512021 ± 29	+3.6
2679	Mt. Shadwell	basanite*	.70381	.512031 ± 20	+3.8
				.512016 ± 27	+3.5
2128	Mt. Porndon	basanite*	.70386	.512000 ± 24	+3.2
			.70389	.512002 ± 14	+3.2
2650	Mt. Leura	basanite*	.70381	.511997 ± 18	+3.1
71-10	Mt. Watch	ol. analcimite*	.70450	.511930 ± 21	+1.8
71-10		(residue[1])	.70434		
71-8	Mt. McIntyre	ol. analcimite	.70434	.511971 ± 18	+2.6
		TASMANIAN BASALTS			
T-14	Andover	ol. tholeiite*	.70324	.512162 ± 22	+6.4
2896	Lughrata	basanite*	.70310	.512200 ± 28	+7.1
2854	Scottsdale	ol. nephelinite*	.70265	.512212 ± 24	+7.3
			.70268	.512224 ± 16	+7.6
2860	Scottsdale	ol. nephelinite	.70260	.512215 ± 24	+7.4
			.70263		
2927	L. J. Marsh	ol. melilitite*	.70335	.512134 ± 22	+5.8

*Basalts containing Cr-diopside spinel lherzolite xenoliths. ol. = olivine ne = nepheline. All $^{87}Sr/^{86}Sr$ values have an uncertainty of $\leq \pm 0.00005$.

[1] leach experiment with 6N HCl, see text for details.

$$\epsilon_{Nd} = \left[\frac{(^{143}Nd/^{144}Nd)_{Sample}}{(^{143}Nd/^{144}Nd)_{Chur}} - 1\right] 10^4, \quad \text{where } (^{143}Nd/^{144}Nd)_{Chur} = 0.511836$$

than predicted by its relative position in Fig. 2, or the source region for these basalts is heterogeneous and relatively more depleted in Sr compared to the LREE. Depletions in K and Rb in the olivine analcimites are suggested to be relatively recent, since these basalts have the lowest Rb/Sr ratios but high $^{87}Sr/^{86}Sr$ ratios (0.7043) compared to most Newer basalts. This depletion K and Rb suggests that a residual K and Rb-rich phase is involved in the generation of the olivine analcimites.

IRVING and GREEN (1976) noted the dominant groundmass mineral of the olivine analcimites is analcime and argued that the analcime is not a replacement of leucite. In particular they pointed out that this would not be in accord with the low K_2O content (0.4%) and high Na_2O contents (3.4% to 3.9%) of these lavas. In thin section the olivine analcimites show some secondary alteration, characterized by hematite rims on phenocrystic olivines. The chemical composition of these basalts is unlikely to have been significantly affected by surface alteration since they do not show depletions in Ba, Th, Cs, U, or the LREE (Fig. 2a, Table 2), and have Th/U ratios of 4.3 and 5.3, similar to other Newer basalts (FREY *et al.*, 1978; and this study, Table 2). A leaching experiment was carried out on one olivine analcimite (71-10) where 100 mg of sample was leached for 18 hours in 6 N HCl in 170°C. After rinsing several times with cold 6 N HCl the residue was dissolved in HF and $HClO_4$. The leached residue has a slightly lower $^{87}Sr/^{86}Sr$ ratio (0.70434 ± 4) than the unleached sample (0.70450 ± 4), although these ratios overlap at their 3σ uncertainty. This indicates that surface alteration has at most only minor effects on the Sr isotope composition. The Mt. Watch olivine analcimite contains Cr-diopside bearing, spinel lherzolite nodules, and both analcimites have Mg-values and Ni contents characteristic of primary mantle derived magmas, implying that their chemical and isotopic compositions are inherited from their mantle source regions.

FREY *et al.* (1978) reported anomalously high REE and Y contents for three Newer basalts (see their Figs. 7 and 9). We have redetermined the trace element contents of these samples and confirm the anomalous enrichments (Table 2). The absolute concentrations of REE and Y are increased 2 to 3 fold compared to other tholeiitic and transitional Newer basalts, while the remaining incompatible element concentrations are similar to those in other Newer basalts (Fig. 3). Identified REE and Y-enriched Newer basalts include a quartz tholeiite, an olivine tholeiite and an olivine basalt. The REE and Y-enriched basalts have the lowest ϵ_{Nd} values (+0.6 and −1.4) and the highest $^{87}Sr/^{86}Sr$ ratios (0.7044 to 0.7049) compared to all other Newer basalts (Fig. 5a). Apart from the REE and Y-enriched Newer basalts, two other localities, both ocean islands (Hawaii and Norfolk Island, Tasman Sea), have been reported with basalts having similar REE and Y enrichments (GREEN, 1978; RODEN, M. F. *et al.*, 1984). A Hawaiian Koolau tholeiite (69TAN-2), with a similar REE and Y enrichment, has a higher $^{87}Sr/^{86}Sr$ ratio and a lower ϵ_{Nd} value compared to other Koolau tholeiites (Fig. 5a) (RODEN, M. F. *et al.*, 1984); this difference in Sr and Nd isotope composition is similar to that found in the Newer REE and Y-enriched basalts. The characteristic offset in Sr and Nd isotopic compositions reflects a time-integrated enrichment in these two source regions, and documents that this process can operate in both the sub-oceanic and sub-continental mantle. At present no adequate geochemical or physical model has been proposed which can explain the observed features in the REE-Y enriched lavas (FREY *et al.*, 1978; GREEN, 1978; RODEN, M. F. *et al.*, 1984). A geochemical and isotopic study of normal and REE and Y-enriched Norfolk Island basalts is underway, and a more detailed discussion of this feature will be presented elsewhere (MCDONOUGH *et al.*, in prep.).

The Tasmanian basalts (Fig. 2c) have incompatible element characteristics similar to those of the Newer basalts; there are progressive increases in incompatible element concentrations with increasing degree of silica undersaturation. Compared with a typical Newer primary basanite (*e.g.*, 2679), Tasmanian primary basalts (Fig. 2c) have a more fractionated pattern (steeper slope) for Rb, Ba and Th; in addition K contents are more depleted with respect to Th and Nb. These features reflect compositional differences between the source regions of the Newer basalts and Tasmanian basalts.

P_2O_5 versus Nd

P_2O_5 abundances strongly correlate with Nd concentrations for the Newer and Tasmanian basalts (insert, Fig. 4). Most of the Newer basalts show a constant P_2O_5/Nd ratio of 189; ± 6 ($2\sigma_{mean}$ uncertainty). Three groups of Newer basalts show deviations from this ratio: (1) the olivine analcimites (P_2O_5/Nd = 129 and 150) which also has significant depletions in K and Rb, (2) the Anakies (east) nepheline mugearites (136 and 141), and (3) the REE and Y-enriched basalts (62, 74 and 83). Differences in the P_2O_5/Nd ratio of the olivine analcimites and the REE and Y-enriched basalts may reflect compositional heterogeneities in their source regions. Apatite megacrysts are common in the Anakies nepheline mugearites (IRVING, 1974) and small amounts of these megacrysts will significantly change this ratio. The P_2O_5/Nd ratio for the Tasmanian basalts is 201 ± 16 and overlaps with that of the Newer basalts. There is no difference in the P_2O_5/Nd ratio between tholeiitic and alkalic basalts from either province indicating that the magma source region beneath southeastern Australia has a P_2O_2/Nd of 190 to 200. The P_2O_2/Nd ratio for continental alkaline basalts and OIB shows considerable overlap, with a total range from 140 to 200, suggesting that an average P_2O_5/Nd for the mantle source regions for hotspot magmatism is about 170 ± 30 (P/Nd = 74 ± 13). This value agrees with SUN's (1982) primitive mantle estimate for P_2O_5/Nd = 155 (P/Nd = 67), but is 35% greater than the primitive earth mantle estimate of 110 (P/Nd = 50) proposed by WECKWERTH *et al.*, (1983). The positive correlation between P and Nd is similar to that previously observed for P and Ce (SUN and HANSON, 1975; FREY *et al.*, 1978).

Sr and Nd isotopic compositions

The $^{87}Sr/^{86}Sr$ values of the Newer basalts are distinctly higher and ϵ_{Nd} values lower than those of the Tasmanian basalts (Fig. 5a). Excluding the anomalous REE and Y-enriched basalts, the Newer basalts have a range of $^{87}Sr/^{86}Sr$ ratios from 0.7038 to 0.7045, and ϵ_{Nd} values from +3.8 to +1.7. The $^{87}Sr/^{86}Sr$ ratios for Tasmanian basalts range from 0.7026 to 0.7034, and ϵ_{Nd} varies from +5.8 to +7.6. The range in $^{87}Sr/^{86}Sr$ for the Newer basalts is similar to that previously reported (DASCH and GREEN, 1975; STUCKLESS and IRVING, 1976). There are some significant discrepancies between the isotopic composition of whole rock powder splits of the same samples measured in the earlier studies and those reported here. For example, we determined $^{87}Sr/^{86}Sr$ ratios of 0.70386 and 0.70389 for the Mt. Porndon basanite (2128), whereas STUCKLESS and IRVING (1976) report a value of 0.7044 and DASCH and GREEN (1975) report a value of 0.7045. We obtained ϵ_{Nd} values of +3.2 and +3.3 for samples 2128 and 2102, whereas, DEPAOLO (1978) reports values of +4.0 ± 0.4 and +4.5 ± 0.3 respectively, for these same samples (DEPAOLO (1978) mislabelled sample 2101 and 2120). DEPAOLO's (1978) ϵ_{Nd} values are higher, but allowing for laboratory bias these values agree at the limit of analytical uncertainties.

Victorian hawaiites, nepheline hawaiites, nepheline mugearites, alkali olivine basalts and basanites have a mean Sr and Nd isotopic composition of 0.70385 and +3.3, with relatively minor variation (Fig. 5a). Primary magmas, as defined above, cover the measured range in Sr and Nd isotope compositions for the Newer basalts. The Mt. Shadwell basanite has a ϵ_{Nd} value of +3.7 and a $^{87}Sr/^{86}Sr$ ratio of 0.7038 and the Mt. Watch olivine analcimite (from South Australia) has a ϵ_{Nd} value of +1.8 and a $^{87}Sr/^{86}Sr$ ratio of 0.7043; both of these basalts satisfy the criteria for primary magmas. Two exceptions to this are the Mt. Franklin nepheline mugearite which has a

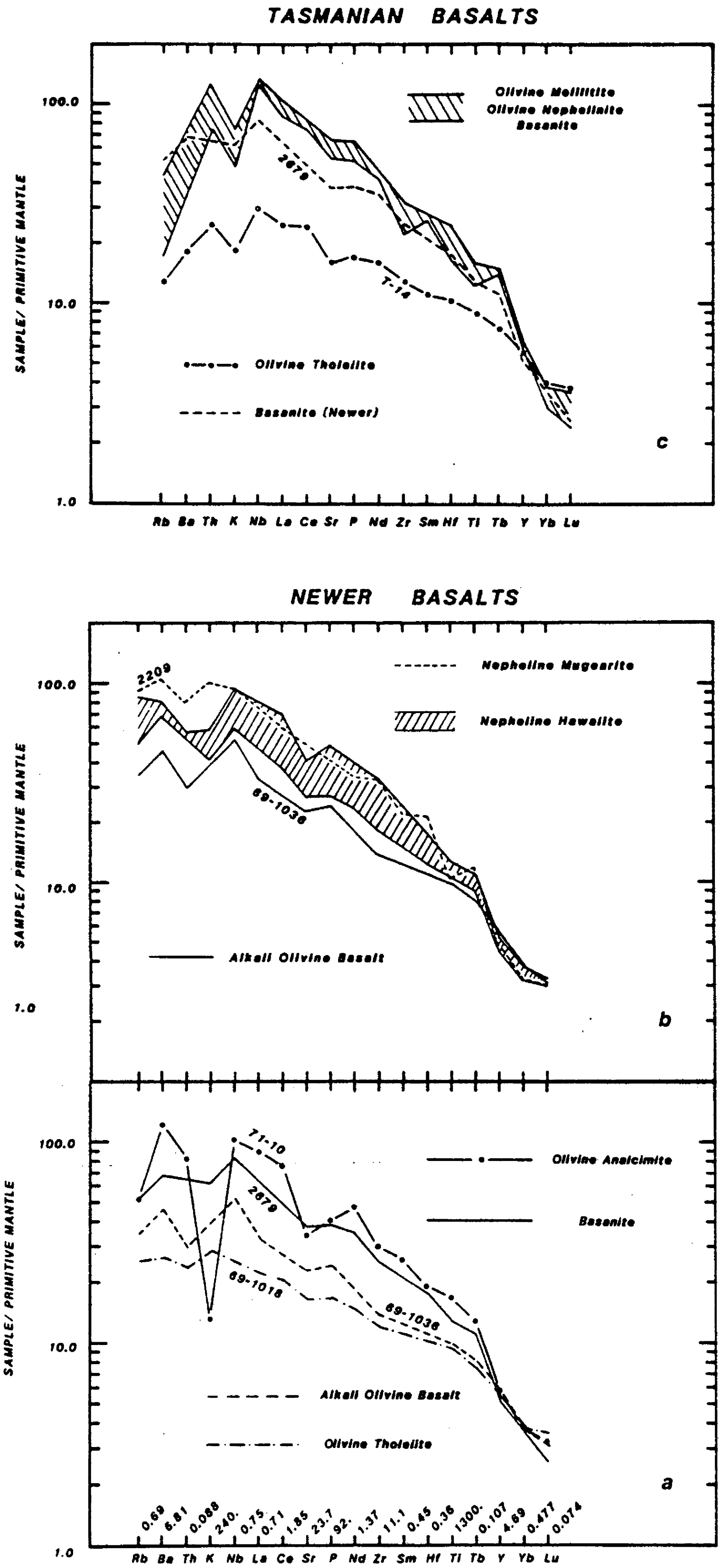

FIG. 2. Primitive mantle normalized diagrams for the Newer and Tasmanian basalts. (a) Representative Newer basalts showing increasing incompatible element concentration with increasing degree of silica undersaturation from olivine tholeiite through alkali olivine basalt to basanite and to olivine analcimite. (b) Newer nepheline mugearite and nepheline hawaiites compared to a Newer alkali olivine basalt which is considered to be a primary magma. (c) Tasmanian alkalic basalts and a Tasmanian tholeiite compared to

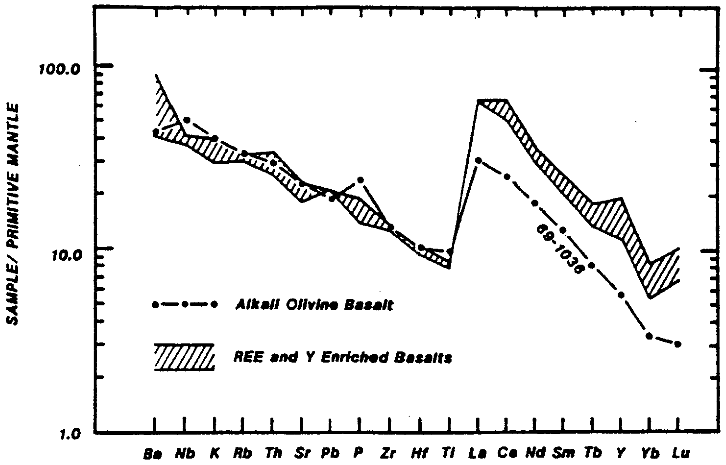

FIG. 3. Primitive mantle normalized incompatible element abundances of Newer REE and Y-enriched basalts compared to a typical Newer alkali olivine basalt. Normalizing values are as reported in Fig. 2, except for Pb which is 0.12. Trace element data from Table 2 and FREY *et al.* (1978).

slightly higher ϵ_{Nd} value of +4.2 and a similar ^{87}Sr/^{86}Sr ratio of 0.7038 and the REE-Y enriched Newer basalts which have much lower ϵ_{Nd} values and generally higher ^{87}Sr/^{86}Sr ratios. Victorian tholeiites and olivine basalts show a greater range in their Sr and Nd isotope compositions than that found in the Victorian alkaline basalts, with all but the Fe-rich olivine basalt plotting at higher ^{87}Sr/^{86}Sr and lower ϵ_{Nd} values (Fig. 5a inset). The four South Australian Newer basalts, a nepheline mugearite, a nepheline hawaiite and two olivine analcimites, have a large spread in isotope compositions from ϵ_{Nd} of +3.3 to +1.8 and ^{87}Sr/^{86}Sr from 0.7039 to 0.7045. This data indicate lower ϵ_{Nd} values and higher ^{87}Sr/^{86}Sr ratios in the source region beneath the far western part of the field (South Australia) and are in contrast with those measured for the Victorian Newer alkaline basalts. Finally, the transitional to tholeiitic Victorian basalts plot in an array projecting away from the field of the alkaline Victorian basalts.

Parent/daughter ratios for the Sr and Nd isotope systems in both the Newer and Tasmanian basalts show different patterns. The Sm/Nd ratios of the Tasmanian basalts vary from 0.19 to 0.23 and overlap with Sm/Nd ratios for the Newer basalts (0.17 to 0.26), whereas, Rb/Sr ratios for the two region are distinctly different. Tasmanian basalts have Rb/Sr ratios of 0.010 to 0.029; Newer basalts have Rb/Sr ratios of 0.039 to 0.087, except for the two olivine analcimites with ratios of 0.009 and 0.050. Although the Rb-Sr systematics of the two regions can be accounted for by a single stage fractionation event, this is not consistent with the Sm-Nd isotope systematics.

The Newer basalts have higher ^{87}Sr/^{86}Sr ratios and relatively flat normalized patterns for the most incompatible elements (Rb, Ba, Th, K and Nb) (Fig. 2a and 2c). In comparison, the Tasmanian basalts have lower ^{87}Sr/^{86}Sr ratios and a more fractionated, depleted pattern for these elements (*cf.*, the pattern of 2679 in Fig. 2c). The low ^{87}Sr/^{86}Sr ratios and the concave downward pattern for these elements in the Tasmanian basalts suggests that their mantle source region has had a long-term depleted character in contrast to that for the Newer basalts. Depletions in incompatible elements and low ^{87}Sr/^{86}Sr ratios are also features which characterize the MORB source region.

The entire eastern Australian borderland is peppered with large Cenozoic subalkaline to alkaline basalt provinces; Sr and Nd isotope compositions have been measured in only the Southern Highlands and nearby Mesozoic Kiama alkaline basalts (MENZIES and WASS, 1983). The Sr and Nd isotopic fields of the Tasmanian, Newer and REE-Y enriched Newer basalts are more restricted compared to the field for the Southern Highland basalts (Fig. 5b); collectively these regions exhibit a large range in Sr and Nd isotope compositions for the whole of the eastern Australian Cenozoic basalt province. This range in Sr and Nd isotope compositions is similar to that observed in other Cenozoic continental intraplate basalt provinces, including west Antarctica (FUTA and LE MASURIER, 1983), Kenya (NORRY *et al.*, 1980), the Basin and Range, and Colorado Plateau, (MENZIES *et al.*, 1983; ALIBERT and ALBARÈDE, 1984), western Europe (ALIBERT *et al.*, 1983; CHAUVEL and JAHN, 1984), China (ZHOU and CARLSON, 1982) and New Zealand (BARREIRO, 1983; MCDONOUGH and MCCULLOCH, unpublished data). All of these Cenozoic continental intraplate basalt provinces have Sr and Nd isotope compositions that generally plot on the lower left side of the oceanic mantle array, with ϵ_{Nd} values ranging from greater than +8.0 to about −1.0.

Pb isotopic compositions

Pb isotope data for 5 South Australian and Victorian Newer basalts have been previously reported (COOPER and GREEN, 1969), and we have recently measured the Pb isotopic composition of the Mt. Porndon basanite (2128) which has a value of 18.58 ± 0.02 ^{206}Pb/^{204}Pb, 15.57 ± 0.02 ^{207}Pb/^{204}Pb and 38.55 ± 0.04 ^{208}Pb/^{204}Pb (analytical methods reported in NELSON *et al.*, 1985). There is reasonably good agreement between the two data sets. The Pb isotope compositions for the 4 Newer basanites are similar, consistent with their similar Sr and Nd isotopic and major and trace element compositions. The ^{206}Pb/^{204}Pb compositions of the South Australian basalts are slightly lower than those of the Victorian basalts. There are distinct differences in the Sr, Nd and Pb isotopic compositions of the South Australian Newer alkaline basalts when compared to the Victorian Newer alkaline basalts, indicating a compositional source difference from east to west across the

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a Newer basanite which is considered to be a primary magma. Primitive mantle normalizing values (in ppm) are given above the element labels and are from SUN (1982), modified to the C1 abundances reported by ANDERS and EBIHARA (1982). In order to obtain a smooth pattern the positions of Sm and Hf have been reversed. A Zr/Hf ratio of 31.0 (value for C1 chondrite Orgueil) was used for normalization, whereas a Zr/Hf ratio of 38 ± 2 for the upper mantle and Bulk Earth may be more appropriate.

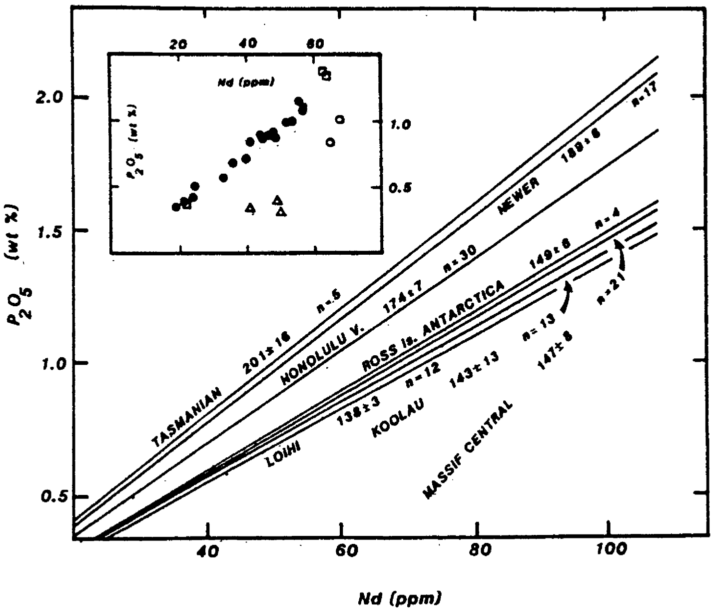

FIG. 4. P_2O_5 (wt%) *versus* Nd (ppm) for continental alkaline basalts and OIB. The location and P_2O_5/Nd ratio for different areas are given with a reported $2\sigma_{mean}$ uncertainty and n = the number of analyses used in determining the ratio. Data sources for the different localities are SUN and HANSON (1975), FREY *et al.* (1978), CLAGUE and FREY (1982), FREY and CLAGUE (1983), RODEN, M. F. *et al.* (1984) and CHAUVEL and JAHN (1984). Inset diagram shows a detailed P_2O_5 (wt%) *versus* Nd (ppm) plot for Newer (filled circles) and Tasmanian basalts (open squares). The REE and Y enriched basalts (open triangles) and olivine analcimites (open circles) are shown separately, the Anakies (east) nepheline mugearites samples are not plotted.

Newer volcanic field. On a $^{207}Pb/^{204}Pb$ *versus* $^{206}Pb/^{204}Pb$ and a $^{208}Pb/^{204}Pb$ *versus* $^{206}Pb/^{204}Pb$ diagram (Fig. 6) the data for the Newer basalts plot in a broad vertical array between the fields of Gough Island and Hawaiian Islands (SUN, 1980; COHEN and O'NIONS, 1982b), indicating their Pb isotopic compositions are similar to those observed in OIB.

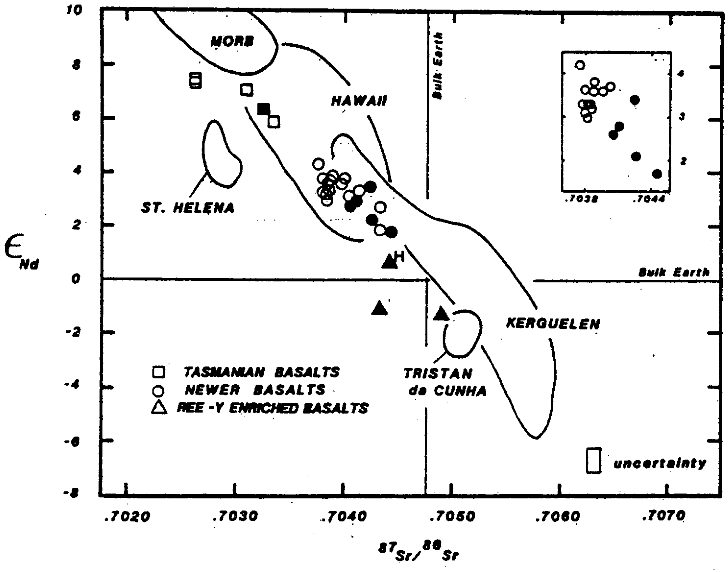

FIG. 5a. $^{87}Sr/^{86}Sr$ *versus* ϵ_{Nd} variation for the Tasmanian, Newer and REE and Y enriched Newer basalts. Filled symbols indicate the tholeiitic basalts. Also shown are the Sr-Nd isotope fields for MORB, and the ocean islands of St. Helena, Hawaii, Kerguelen and Tristan da Cunha (DEPAOLO and WASSERBURG, 1976; O'NIONS *et al.*, 1977; DOSSO and MURTHY, 1980; WHITE and HOFMANN, 1982; COHEN and O'NIONS, 1982a,b; STILLE *et al.*, 1983; RODEN, M. F. *et al.*, 1984; STAUDIGEL *et al.*, 1984). The 'H' data point is for the REE and Y enriched Koolau tholeiite, Ohau from RODEN, M. F. *et al.* (1984). Inset diagram shows the $^{87}Sr/^{86}Sr$ *versus* ϵ_{Nd} variation for only the Victorian tholeiitic (filled circles) and alkalic Newer basalts (open circles), and does not include the REE and Y-enriched, and South Australian, Newer basalts.

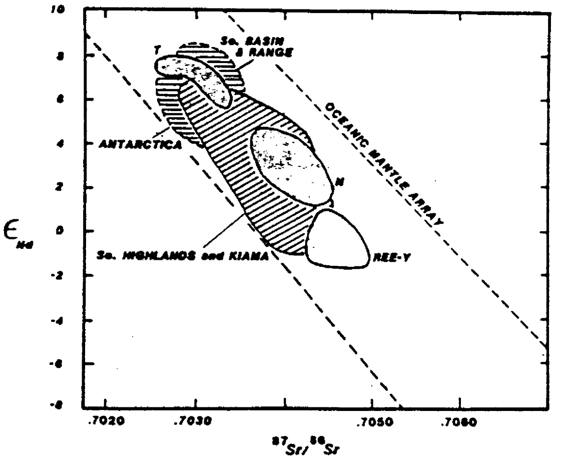

FIG. 5b. $^{87}Sr/^{86}Sr$ *versus* ϵ_{Nd} variation for the Tasmanian basalts (T), Newer basalts (N) and REE and Y enriched Newer basalts (REE − Y). Also shown are the Sr-Nd isotope fields for continental alkaline basalt provinces: South Basin and Range (MENZIES *et al.*, 1984), Antartica (FUTA and LE MASURIER, 1983), Southern Highlands and Kiama (MENZIES and WASS, 1983). It should be noted that many other continental alkaline basalt provinces plot in this same region and have been omitted for the sake of clarity and legibility; these include: Kenya (NORRY *et al.*, 1980), Colorado Plateau (ALIBERT and ALBARÈDE, 1984), western Europe (ALIBERT *et al.*, 1983; CHAUVEL and JAHN, 1984), China (ZHOU and CARLSON, 1982) and New Zealand (BARREIRO, 1983; MCDONOUGH and MCCULLOCH, unpublished data). The Oceanic Mantle Array has been drawn to encompass the data for MORB and the ocean islands including St. Helena, the Austral islands and the Comores islands.

DISCUSSION

1) Evaluating lithospheric contamination

CARLSON *et al.* (1981) and MAHONEY *et al.* (1982) have suggested that some continental basalts with greater than 5 wt% MgO have been contaminated by continental crust. They proposed that the observed spread in Sr and Nd isotope compositions are in part due to a crustal contamination process. MAHONEY *et al.* (1982) considered that one of the contaminating components may be enriched mantle. Others have argued that the observed chemical and isotopic variations found in continental intraplate basalts may reflect heterogeneities in the mantle or varying amounts of mixing between two or more mantle components, and there is no need to call upon crustal contamination (*e.g.*, DEPAOLO, 1983; MENZIES *et al.*, 1984). It is therefore necessary to evaluate whether the southeastern Australian basalts have had their chemical and isotopic composition affected by crustal contamination. In addition it is necessary to consider separately the roles of the crustal lithosphere and the lithospheric mantle when evaluating the effects of contamination. We define the crust as that portion of lithosphere above the Moho, and the lithospheric mantle is sandwiched between the Moho and the low velocity zone (LVZ). In the absence of a seismically defined LVZ we consider the base of the lithosphere to be the lowermost portion of the lithospheric mantle that is mechanically coupled to the continental crust.

i) crustal contamination—The southeastern Australian primary basalts and many slightly more evolved (Mg-values > 59) lavas carry spinel lherzolite nodules and a limited number of felsic granulite facies nodules. The lherzolite xenoliths are angular to subrounded and range up to 25 cm in diameter. The composition, angularity and size of these lherzolite xenoliths attest to 1) lithospheric fracturing during ascent of these magmas, 2) the rapid uninterrupted ascent (hours to days) of these magmas through the lithosphere, and 3) the mantle origin of these magmas. The high magma volatility (most are erupted as cinder cones) indicates a positive volatile pressure for these magmas during ascent, and suggests that these magmas would principally contaminate the surrounding environment without any (or very limited) uptake of crustal derived components.

The primitive nature of the samples chosen (*i.e.*, high Mg-value > 67, Ni > 280 ppm, Cr > 300 ppm, and presence of Cr-diopside lherzolite nodules) should mean that they had little opportunity to be contaminated by crustal rocks. The primary basalts cover the total range in Sr and Nd isotope composition for the Newer and Tasmanian fields. Evolved basalts, analyzed to specifically evaluate the possible role of crustal contamination, have relatively low Mg-values (59 to 41) which are attributed to crystal fractionation at crustal pressures (IRVING and GREEN, 1976; FREY *et al.*, 1978). These basalts are the most likely candidates to show

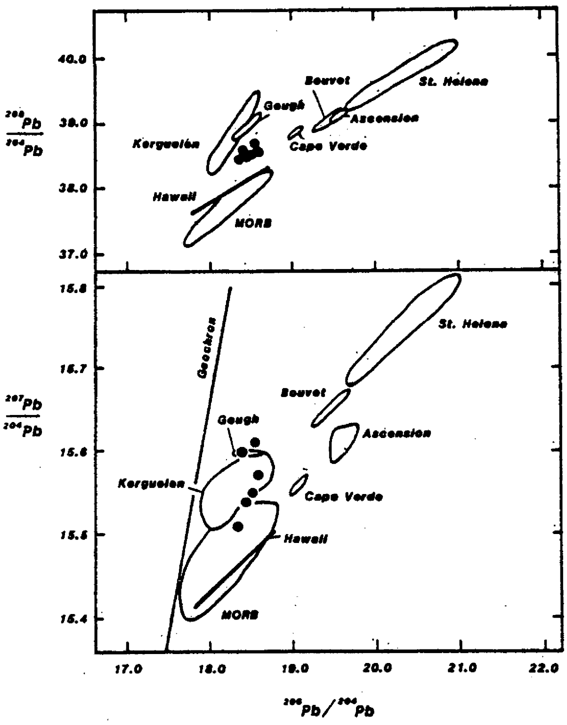

FIG. 6. $^{207}Pb/^{204}Pb$ *versus* $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ *versus* $^{206}Pb/^{204}Pb$ for Newer basalts (solid circles) (COOPER and GREEN, 1969; and this study) and OIB and MORB (data from SUN, 1980; COHEN and O'NIONS, 1982a,b).

any effects of crustal contamination. The isotopic compositions of the evolved basalts are not distinctive from the primary basalts, implying crustal contamination is not significant. In addition, the Fe-rich olivine basalt (69-1006) with the lowest Mg-value plots on the high ϵ_{Nd} side of the Sr-Nd isotopic array. This feature is opposite to what would be expected if a fractionated lava was contaminated by crust similar to that exposed in the region. From these observations we conclude that the Tasmanian and Newer basalts have not been contaminated by the crust, or at least not to any detectable extent.

Internal melts in the few felsic, granulite facies xenoliths that were found may be derived from the melting of these xenoliths, or they may represent the infiltration of host basalt melt, or some combination of these two processes. Preliminary microprobe analyses of some internal melt pockets suggests that they are derived by decompression melting of the felsic xenolith. Some internal melts in felsic granulite xenoliths from the Snake River Plains basalts are derived from the melting of the xenolith (LEEMAN *et al.*, 1985). The lherzolite nodules show only limited interaction with the host basaltic melt at the margins of the xenoliths with a few showing limited invasion of basaltic melt several millimeters into the xenolith. Such relationships demonstrate the limited ability of the basaltic magmas to infiltrate and contaminate their xenoliths, and presumably their surrounding conduit system, throughout the entire lithosphere. This process could conceivably result in some minor crustal contamination which would be most pronounced in the fractionated lavas, but as stated, there is no evidence for this.

There is no evidence to suggest that the REE and Y-enriched Newer basalts inherited their unusual chemical and isotopic characteristics as a result of crustal contamination. Because the relative concentrations of the non-REE trace elements in these basalts are similar to those in other Newer basalts (Fig. 3) this restricts the composition of the enriched phase, or processes which may have generated this signature. Also, since this 2 to 3 fold enrichment in the REE and Y has been identified in ocean island basalts, this suggests that the source of this enrichment is in the mantle. This chemical signature may be a result of hotspot magmatism.

ii) lithospheric mantle contamination—The extent to which Cr-diopside lherzolite nodules, presumably fragments of the lithospheric mantle, might have modified the Sr and Nd isotope compositions of Newer and Tasmanian basalts must also be considered. Sr and Nd isotope compositions of spinel lherzolites from a number of Newer volcanic centers show a wide variation in composition from $^{87}Sr/^{86}Sr$ 0.7037 to 0.7085 and $\epsilon_{Nd} = +11.4$ to -7.5 (CHEN and FREY, 1981; MCDONOUGH *et al.*, unpublished data). This is in contrast with the limited range in isotopic composition for their host basalts, most particularly the four lherzolite nodule-bearing basanites with identical Sr, Nd and Pb isotope compositions (Mt. Shadwell, Mt. Leura, Mt. Noorat and Mt. Porndon). There is no means of constraining the average isotopic composition of this part of the sub-continental lithospheric mantle, but the uniform isotopic compositions of these basalts would not be anticipated if lherzolite nodules with such a diversity of isotopic compositions had contaminated these lavas. Also there is no textural evidence for the melting of lherzolite nodules by their host basalt. This suggests that the basalts have not been significantly contaminated by the entrained lherzolite nodules.

While the spinel lherzolite xenoliths are unlikely to have modified their host basaltic magmas, partial melts derived from similar lherzolitic material at greater depths may be important in modifying the compositions of these basalts. Partial melts derived from garnet lherzolites in the lower parts of the sub-continental lithospheric mantle may be added to basaltic magmas prior to xenolith entrainment and eruption. Such material may represent a mantle component which is common to continental intraplate basalts. Since the Newer basalts are isotopically relatively uniform, and the southeastern Australian sub-continental lithospheric mantle is isotopically diverse (as inferred from Victorian spinel lherzolites), then an added lithospheric-mantle melt component must be homogenized with an ascending mantle diapir or its basaltic magmas prior to eruption. In a later section we consider possible mechanisms by which melt material derived from the lithospheric mantle may be added to these basaltic magmas.

2) Scales of isotopic homogeneity in the mantle beneath SE Australia

Several studies have identified different scales of isotopic homogeneity in the mantle. Sr and Nd isotope studies of MORB have shown that some ridge segments possess a uniform isotopic composition on a scale of 10 to 50 kilometers (*e.g.*, DUPRÉ *et al.*, 1981), and in an extreme example MACDOUGALL and LUGMAIR (1985) found uniform Sr and Nd isotopic compositions for MORBs along a 550 kilometer section of the East Pacific Rise. On a much larger scale HART (1984) recently suggested the existence of a distinctive globe-encircling Sr and Pb isotope signature in the southern hemisphere region of the mantle. Hart suggested that this portion of the mantle has had a long term history which is in general compositionally different from other parts of the mantle.

Chemical and isotopic homogeneity over a relatively small scale has been identified in the Newer volcanic field. Four different basanite centers (Mt. Shadwell, Mt. Leura, Mt. Noorat and Mt. Porndon), separated by more than 50 km, have uniform chemical and isotopic compositions (FREY *et al.*, 1978; and this study). Abundant upper mantle nodules and very few crustal nodules are found at these localities. Mt. Shadwell, Mt. Noorat and Mt. Porndon basanites are primary, mantle-derived magmas. The isotopic compositions of these basanites are all within analytical uncertainties: $^{87}Sr/^{86}Sr$ of .70385, ϵ_{Nd} of +3.4, and $^{206}Pb/^{204}Pb$ of 18.5,

$^{207}Pb/^{204}Pb$ of 15.55 and $^{208}Pb/^{204}Pb$ of 38.5. These data indicate that there possibly exist regions in the upper mantle beneath southeastern Australia which are isotopically homogeneous over a scale of about 50 kilometers.

On a larger scale, the variation in Sr and Nd isotope composition for the Newer basalts is about half of that found for tholeiitic and alkalic basalts from Oahu, Hawaii (Stille *et al.*, 1983; Roden, M. F. *et al.*, 1984), which covers most of the known variation in Sr and Nd isotope compositions for Hawaiian basalts (Fig. 5a). The range in Sr and Nd isotope data for the Tasmanian basalts is similar to that of the Newer basalts, but because of the limited sampling this data may not adequately represent the total range for these basalts.

The presence of low $^{87}Sr/^{86}Sr$ ratios (<0.7040) in the Newer and Tasmanian basalts (see also Compston *et al.*, 1968), and for basalts from the Austral islands (Vidal *et al.*, 1984; McDonough *et al.*, unpublished data), Rodrigues island (Baxter *et al.*, 1985), and Comores islands (White and Dupré, 1984), all of which are southern hemisphere localities centered on the conjectured DUPALL anomaly (Hart, 1984), is not consistent with the proposed large scale mantle anomaly in this region.

3) Geochemical characteristics of the mantle source region

Both the Newer and Tasmanian basalts show progressive increases in their incompatible element concentrations with increasing degree of silica undersaturation at a relatively constant Mg-value (Figs. 2a–c). This suggests that different degrees of partial melting of relatively similar mantle sources could possibly explain the chemical variation found in the olivine tholeiite to olivine nephelinite/melilitite spectrum in both regions.

A detailed major and trace element melting model has been presented by Frey *et al.* (1978) for many of the basalts reported here. Frey *et al.* (1978) used the REE to test an equilibrium melting model to explain variations in melt composition from olivine tholeiite to olivine basalt to alkali olivine basalt to basanite to olivine nephelinite/melilitite. Their model requires decreasing degrees of partial melting of a garnet lherzolite source to account for this spectrum of basalt compositions. They argued that the source could possess either a LREE-enriched or chondritic REE pattern. Their model calculations showed that to derive this spectrum of basalts from a LREE-enriched (LREE = 7 to 9× chondrites, HREE = 2.5 to 3× chondrites) source requires a range in the degree of partial melting from 20–25% for the tholeiites to 4–6% for the nephelinite/melilitite. Using a chondritic source ($LREE_N/HREE_N$ = 1.0), with about 2 to 3 times chondrite REE abundances, requires varying the degrees of partial melting from about 5% to about 0.5% to generate this spectrum. This type of chemical argument can be carried a step further by attempting to derive this range of basalt compositions from a LREE-depleted source region, since all but the high Y-REE bearing basalts have positive ϵ_{Nd} values, requiring the source region(s) for these basalts to have a time intergrated LREE-depleted (Sm/Nd > 0.31) character. To derive the olivine tholeiites in a single stage melting process requires less than 1% partial melting, and considerably less for the olivine nephelinites/melilitites. Although geophysical models cannot place strict lower limits on the percentage of partial melt which can be extracted from the upper mantle (Stolper *et al.*, 1981; McKenzie, 1984), to generate tholeiitic basalts by about 1% partial melting, or less, is unlikely, as this would require a source that is very depleted chemically and mineralogically. We consider that about 5 to 25% partial melting of an upper mantle peridotite is needed for the generation of tholeiitic basalts (Jaques and Green, 1980), with the absolute degree of partial melting depending on the proportion of fertile components (*i.e.*, garnet and clinopyroxene). Therefore, we suggest that in agreement with earlier findings (Frey *et al.*, 1978), the Newer and Tasmanian olivine tholeiites were generated by up to 20 to 25% partial melting and the olivine nephelinites/melilitites by 3 to 6% partial melting of a LREE-enriched garnet lherzolitic upper mantle *or* by about 5% partial melting for the tholeiites down to about 0.5% partial melting for the olivine nephelinites/melilitites for a garnet lherzolitic upper mantle with a chondritic REE pattern. In addition to the melting models tested by Frey *et al.* (1978), there are other more sophisticated melting models which may more accurately describe melting and magma extraction processes (Langmuir *et al.*, 1977; O'Hara, 1985). Although we have not tested such models, the application of these models are important to our understanding of source composition and melt volumes involved.

Though it is suggested that the calculated REE source patterns for these two regions are similar, the Newer and Tasmanian basalts come from isotopically distinct sources (Fig. 5a). Additionally, there are significant differences between the relative concentrations of K, Th, Ba and Rb in the two regions (Figs. 2a–c), which reflects differences in their upper mantle source compositions. Finally, the upper mantle source region for the Newer and Tasmanian basalts has a time integrated Sm/Nd ratio greater than its present Sm/Nd ratio, as indicated by the positive ϵ_{Nd} values of these basalts.

Relatively recent enrichment events can produce a basaltic source region which possesses a Sm/Nd ratio that is less than the time integrated Sm/Nd ratio. For example, Roden, M. K. *et al.* (1984) found that the St. Paul's Rocks ultramafics have a LREE-enriched pattern and a positive ϵ_{Nd} value. They suggested that these ultramafic rocks inherited this LREE-enrichment about 155 m.y. ago, and found that a LREE-enriched alkali basalt from the massif possessed a similar ϵ_{Nd} value, suggesting that the ultramafic material of the massif is an ideal mantle source from which the alkali basalts from the flanks of the massif can be derived by partial melting. There exists similar ultramafic material derived from the sub-continental lithospheric mantle beneath this part of southeastern Australia (*i.e.*, Cr-diopside bearing spinel lherzolite xenoliths) which have both chondritic and LREE-enriched patterns and positive ϵ_{Nd} values (FREY and GREEN, 1974; CHEN and FREY, 1981; MCDONOUGH *et al.*, unpublished data). By analogy with the model of RODEN, M. K. *et al.* (1984) it might be possible to derive the Newer basalts from such lherzolitic material. It is also possible that partial melts derived from such material are added to plume-derived melts in order to generate the range in Sr and Nd isotope compositions in the Newer basalts. In the following section we discuss these possibilities.

4) The nature of the source region and its components

It has been proposed that the Tertiary basalts along the entire eastern Australian borderland resulted from several hotspot traces (WELLMAN and MCDOUGALL, 1974; SUTHERLAND, 1981). It is not known whether the initiator of basaltic volcanism in the region is a deep seated mantle plume, physically similar to that envisioned for Hawaii, or results from a shallower thermal perturbation of unknown origin. In either case both would provide upwelling plumes of hot mantle material which ultimately supply the region with basaltic volcanism. Thus, there remains the question of the nature and origin of the different mantle components which lead to the range in Sr and Nd isotope compositions. To generate the observed spectrum of isotope compositions we consider a model involving mixing of two components: a plume component and a lithospheric mantle component.

A variety of mixing models have recently been proposed to explain systematic trends in chemical and isotopic data for basalts. CHEN and FREY (1983) have presented one such mixing model, in which there is mixing between two mantle components, one, the plume and the other, the surrounding mantle through which the plume is ascending. This model involves wall rock reaction between an ascending hot mantle plume and its surrounding, relatively cooler upper mantle peridotite. Chen and Frey's model involves mixing of very small degrees (<1.0%) of partial melt extracted from a cooler, depleted MORB-like source material (wall rock) with larger degrees of partial melt (1% to 5%) from a hotter mantle plume-derived material. Melt from the MORB-like source material would therefore possess alkaline affinities, a LREE-enriched pattern and a more positive ϵ_{Nd} value than melt derived from the plume component. The plume-derived melt would have a composition that could vary from alkalic to tholeiitic depending on the degree of partial melting involved and the amount of clinopyroxene and garnet in the plume component, and its REE pattern would be determined by the source pattern and phases in the residuum.

The Chen and Frey model provides a good working model and has considerable merit, but there are some significant questions that must be resolved. (1) Can the major element variations be explained by mixing varying proportions of these two components? (2) Can both chemical and isotopic endmember compositions be realistically constrained? It must be again stressed (as noted by these authors) that there is no *a priori* reason to call upon one endmember with a bulk earth Sr and Nd isotopic composition (*i.e.*, $\epsilon_{Nd} = 0$ and $^{87}Sr/^{86}Sr = 0.7047 \pm 5$). (3) Is their model wholly applicable to both the continental and oceanic environment? (4) What happens when a hot mantle plume intrudes the base of the lithosphere? Many of these questions cannot be rigorously answered and we do not intend to attempt this, but they must be considered when applying a model such as theirs. An important consideration of the Chen and Frey model which must be accounted for however are the consequences of a plume physically intersecting the base of the lithosphere. We predict that this will result in significant partial melting of the lithospheric mantle. With this in mind a lithospheric mantle-derived melt must be considered as an added component to any plume-derived melt and should be incorporated into any model invoking component mixing and mantle plumes, as is commonly done for intraplate volcanism.

We propose a model whereby the lithospheric mantle interacts with plume-derived melts during intrusion of an ascending mantle plume into the base of the lithosphere. The mixing model proposed here involves mixing a low degree of partial melt (alkalic in character) with a larger degree of partial melt (tholeiitic in character), as put forth in the Chen and Frey model, but that the larger degree of partial melt can represent melts of up to 20% melting. Also, in contrast to their model where the plume component mixes only with depleted mantle during the ascent of the plume, we propose that the plume component also mixes with a lithospheric mantle component, which in some cases may be a zone of partial melt (*e.g.*, LVZ?), as a result of the intersection of the hot plume with the base of the lithosphere. These mixtures of partial melts together contribute to the chemical and isotopic composition of the southeastern Australian basalts.

Figure 7 illustrates the model which we propose. An ascending mantle plume would intersect the base of the lithosphere. The base of the lithosphere is defined as the LVZ, and in the absence of a well defined LVZ we consider it to be the lowermost portion of the lithospheric mantle that is mechanically coupled to the continental crust. Intrusion of a mantle plume into this region would raise the temperature above the mantle solidus and initiate partial melting of the lithospheric mantle. Partial melting of lithospheric mantle may occur over a wide region. Lithospheric mantle-derived melts would mix with plume-derived melts and generate a spectrum of chemical and isotopic compositions as found in the southeastern Australian basalts. The mixing zone region is envisaged as the area where the plume intrudes the base of the lithosphere.

The range in plume Sr and Nd isotopic compositions

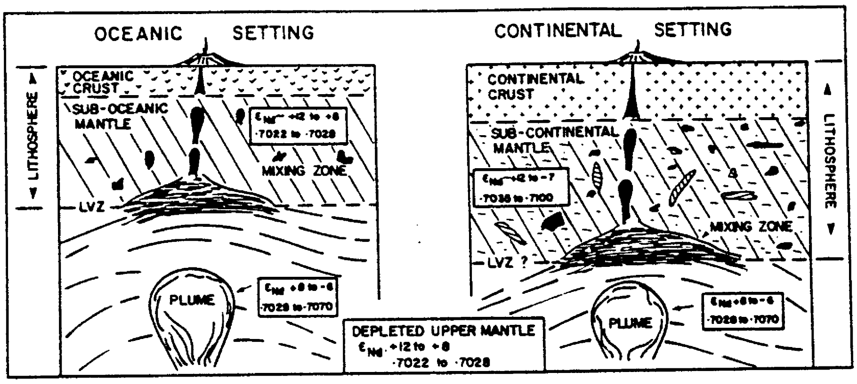

FIG. 7. A mantle model depicting the relative isotopic composition of the mixing components involved in oceanic and continental intraplate magmatism. A hot ascending mantle plume intrudes the base of the lithosphere and initiates melting of the lithosphere, magmas are mixtures of a plume derived component and a lithospheric mantle derived component. For simplicity, the Sr and Nd isotopic composition of the sub-oceanic lithospheric mantle and the depleted upper mantle is assumed to be equal to that of MORB, though we envision small, chemical and isotopic heterogeneities in these mantle reservoirs. The plume's isotopic composition is constrained by the range in Sr and Nd isotope ratios found in OIBs. The Sr and Nd isotopic composition of the sub-continental lithospheric mantle is estimated from the range in isotope ratios measured for lherzolite nodules found in the Newer basalts (CHEN and FREY, 1981; MCDONOUGH *et al.*, unpublished data). The values assumed here are considered applicable for the Newer basalts *only*, and other continental regions would have differing isotopic compositions depending on their age and geologic history. The sub-oceanic and the sub-continental lithospheric mantles contain small scale heterogeneous regions (black, angular fragments), with the sub-continental lithospheric mantle containing more ancient chemical and isotopic heterogeneities (lined, angular fragments).

is based on the observed variation in ϵ_{Nd} values and $^{87}Sr/^{86}Sr$ ratios found in OIB (*e.g.*, St. Helena, Iceland, Kerguelen, Society) and outside of normal MORB isotope compositions: this includes ϵ_{Nd} values of +8 to −6 and a $^{87}Sr/^{86}Sr$ ratios of 0.7028 to 0.7070. The Sr and Nd isotopic composition of the sub-oceanic lithospheric mantle is based on the variation found in normal MORB, and this is the same range assigned to the depleted upper mantle. Although an over-simplification of the nature of the depleted upper mantle and sub-oceanic lithospheric mantle, such a model is justified by our present knowledge. It is recognized that the depleted upper mantle may contain small scale heterogeneities in a matrix of more uniform peridotite. Support for this model is found in the variable isotopic compositions of seamounts (ZINDLER *et al.*, 1984) and MORBs (COHEN and O'NIONS, 1982a). The sub-oceanic lithospheric mantle could possess small scale heterogeneities incorporated during lithosphere forming processes at spreading centers (SLEEP, 1984). The range in Sr and Nd isotopic compositions assumed for sub-continental lithospheric mantle is based on the variation observed in spinel lherzolites from southeastern Australia (CHEN and FREY, 1981; MCDONOUGH *et al.*, unpublished data). This range in isotope compositions is specific to this region and may well be considerably larger as the number of analyzed samples increase. The Sr and Nd isotopic composition of other regions of sub-continental lithospheric mantle would differ depending on formation age and its history of depletion and enrichment events. The range in isotopic composition for the sub-continental lithospheric mantle is larger than for any of the other mantle reservoirs, which is to be expected, considering the variety and complexity of magmatic and tectonic processes leading to the formation of this part of the mantle. We have represented the sub-continental lithospheric mantle as possessing various heterogeneous fragments of different ages and parent/daughter isotope ratios to depict the variable chemical and isotopic nature of this region (Fig. 7).

This model predicts that for OIBs the lithospheric component possesses an isotopic character that is, in general, indistinguishable from present day MORB, while for continental intraplate basalt, such as in southeastern Australia, the lithospheric component possesses a heterogeneous isotopic character. The melt component derived from the lithospheric mantle could either be from a LVZ-derived melt, or from partial melting of the lower lithospheric mantle during the intrusion of a mantle plume into this region of the lithosphere, and/or some combination of these two sources. Thus, this model incorporates features from both the SUN (1980) and the CHEN and FREY (1983) models. NIXON *et al.* (1981) have presented a similar model for kimberlite genesis, where magmas from a deeper, ascending diapir mix with, or are contaminated by, incompatible element-rich melts derived from the base of the lithosphere.

One of our primary concerns is the chemical and isotopic characterization of the different mantle components involved in the generation of intraplate basalts. The model presented here involves at least two components: the plume and the lithospheric mantle. Clearly there is no *a priori* reason to assume that either of these components are homogeneous and, in fact, there is chemical and isotopic evidence which demonstrates the heterogenous nature of the sub-continental lithospheric mantle. If we turn our attention to ocean islands, where the lithospheric mantle component is chemically and isotopically less complex than beneath the continents, then it might be possible to gain an understanding of the chemical and isotopic nature of the plume component.

The chemical and isotopic composition of tholeiitic basalts from ocean islands probably provides the most direct information on the nature of the plume component. This is a consequence of tholeiitic basalts requiring higher melting temperatures than alkalic basalts, and hence are generated by larger degrees of partial melting. This suggests that large volume tholeiitic basalts are, in general, dominated by the plume component. For example, in the Hawaiian islands, Kauai, Ohau and Maui, there is a consistent trend whereby the shield-building tholeiitic lavas possess higher $^{87}Sr/^{86}Sr$ ratios and lower ϵ_{Nd} values than the post caldera collapse alkalic lavas whose compositions overlap with the field of MORBs (FEIGENSON, 1984; RODEN M. F. *et al.*, 1984; CHEN and FREY, 1983). This is consistent with the inference that the tholeiitic lavas are dominated by the plume component, whereas, the post caldera collapse alkalic lavas are dominantly derived from the sub-oceanic lithosphere. There are also examples where tholeiitic basalts have overlapping Sr and Nd isotopic compositions with the associated alkalic basalts (*e.g.*, Loihi, STAUDIGEL *et al.*, 1984), and other less common examples where tholeiitic basalts have lower $^{87}Sr/^{86}Sr$ ratios and higher ϵ_{Nd} values (*e.g.*, Pacific seamounts, ZINDLER *et al.*, 1984), which could be due to selective melting of a heterogeneous mantle source, either in the plume or lithospheric mantle. These examples indicate the potential problem with any single interpretive model but, we believe do not exclude the general applicability of the model presented here.

For continental intraplate basalts (*e.g.*, Newer basalts) it is more difficult to characterize the plume component because of the heterogeneous nature of the sub-continental lithospheric mantle. Development of the sub-continental lithospheric mantle involves many varied and complex geological processes which result in compositional diversity in this part of the mantle. RINGWOOD (1982) pointed out that ascending megalith diapirs (*i.e.*, plume material) of refractory peridotite are intrinsically less dense than the surrounding mantle and would rise buoyantly. Megaliths which rise beneath continents are thus permanently trapped within the sub-continental lithosphere, whereas those that rise beneath oceans are emplaced within the sub-oceanic lithosphere and later subjected to further episodes of subduction. Also, the sub-continental lithosphere evolves over relatively longer time periods and through the addition of many complex processes (*e.g.*, subduction along the continental margin) compared to the sub-oceanic lithosphere. Thus, it is anticipated that the sub-continental lithospheric mantle would be inherently more complex (isotopically and chemically) than the sub-oceanic lithospheric mantle.

5) Mantle sources for tholeiitic and alkali basalts

A final point for consideration is the difference in isotopic compositions sometimes observed between tholeiitic and alkalic basalts in both ocean island and continental settings. This is evident in the central portion of the Newer volcanic field where there is a slight tendency for the tholeiitic basalts to have higher $^{87}Sr/^{86}Sr$ ratios and lower ϵ_{Nd} values in comparison to the alkaline basalts (Fig. 5a inset). Though this feature is only discernible where the data is restricted to a limited geographical sampling within the field, its presence may be indicating the general nature of the plume component, whereas, the isotope composition of the alkalic Newer basalts may indicate the averaged isotopic composition of the regional sub-continental lithospheric mantle component. Several Hawaiian volcanoes have tholeiitic basalts which have distinctly different isotopic compositions compared to associated alkalic basalts. Therefore, for OIBs and continental intraplate basalts the isotopic composition of the tholeiitic basalts more directly reflects the nature of the plume component, whereas the alkaline basalts indicate the nature of the underlying lithospheric mantle. An alternative model is that the plume is a heterogeneous mixture (*e.g.*, a plum pudding model) where the late-stage, post-erosional alkalic basalts (*e.g.*, Honolulu volcanics) represent the low melting temperature peridotite material in the plume and the shield-building, tholeiitic basalts represent the more refractory peridotite. This latter model may be applicable to seamounts (*e.g.*, ZINDLER *et al.*, 1984), but would not be consistent for ocean islands (*e.g.*, Hawaii), because one would expect that such low melting temperature peridotite brought up in the plume would not survive the tholeiite shield-building stage.

CONCLUDING REMARKS

Two Tertiary-Recent volcanic provinces of southeastern Australia contain primary and evolved tholeiitic and alkalic basalts which have been derived by partial melting of a peridotitic mantle. No evidence of crustal contamination was found in the basalts studied here. Differences are found in the relative abundances of incompatible elements and isotope composition between the two basalt provinces. Local regions within these provinces show extreme compositional homogeneity. Slight differences in Sr and Nd isotope compositions exist between tholeiitic and alkalic basalts but, unlike the tholeiitic and alkalic basalt series from Hawaii (CHEN and FREY, 1983; STILLE *et al.*, 1983; RODEN, M. F. *et al.*, 1984) the differences are not large and the compositions overlap.

Melting models involving mixtures of mantle plume-derived melt and lithospheric mantle-derived melt components are proposed for the generation of these basalts. Lithospheric mantle-derived melts may be ponded in the low velocity zones at the base of the lithosphere. Mixing of plume-derived and lithospheric mantle-derived melt components (± other mantle components) occur during the intrusion of hotspot mantle plumes into the base of the lithosphere. This model may also be applicable to the generation of OIB with geochemical differences between oceanic and continental basalts resulting from compositional differences in their underlying lithospheric mantle.

From this model we predict some general features of hotspot volcanism. Firstly, one of the components involved in OIB generation is derived from the suboceanic lithospheric mantle and, because of the young age of the oldest exposed oceanic crust, it possesses a Sr and Nd isotopic composition that is, in general, similar to that of MORB's. Secondly, for OIBs the Sr and Nd isotopic composition of the plume component can be estimated to be equal to or greater than the most radiogenic Sr and unradiogenic Nd isotope composition in the series, and these isotopic compositions will most likely (but not always) be found in the tholeiitic basalts. In continental regions the isotopic composition of the sub-continental lithospheric mantle component may not necessarily be equivalent to that of MORB's. Finally, in general, the larger the spread in Sr and Nd isotope compositions of both continental and oceanic basalts the greater the difference in isotopic compositions between the lithospheric mantle- and mantle plume-derived melt components.

The combined isotope data for late Tertiary basalts from the Newer and Tasmanian provinces (COMPSTON *et al.*, 1968; and this study), and from the Austral islands, (VIDAL *et al.*, 1984; MCDONOUGH *et al.*, unpublished data), Rodrigues island (BAXTER *et al.*, 1985), and the Comores islands (WHITE and DUPRÉ, 1984) shows that a number of regions in southern latitude between 15°S and 45°S have ^{87}Sr/^{86}Sr less than 0.7040, with some as low as 0.7026 to 0.7029 (Tasmanian, and the Austral islands). HART (1984) proposed a DUPALL isotopic anomaly for this region of the southern hemisphere based upon ^{87}Sr/^{86}Sr ratios greater than 0.7040. These low ^{87}Sr/^{86}Sr values within the DUPALL anomaly area and occurrence of high ^{87}Sr/^{86}Sr (>0.7040) outside of the DUPALL belt (*e.g.*, Koolau tholeiites, Oahu, Hawaii, 0.7042, and Sao Miguel, Azores, 0.7047) is not consistent with the proposed DUPALL anomaly.

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CHAPTER 2

The Southeast Australian Lithospheric Mantle: Implications for its Growth and Evolution

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ABSTRACT

Trace element and isotopic compositions of whole rocks and mineral separates are reported for 15 spinel-bearing harzburgite and lherzolite xenoliths from southeast Australia. These samples have an exceedingly large range in isotopic compositions, with $^{87}Sr/^{86}Sr$ ranging from 0.7024 to 0.7084 and ε_{Nd} values ranging from +13.0 to -7.5. This range in isotopic compositions can be found in xenoliths from a single locality.

The isotopic compositions of clinopyroxene separates and their whole rocks were found to be different in some xenoliths. Samples containing small glass pockets, which replace preexisting hydrous minerals, generally show only small differences in isotopic composition between clinopyroxene and whole rock. A substantial difference in the Sr isotopic compositions of a coexisting phlogopite - clinopyroxene pair was found for a modally metasomatized peridotite. Coexisting clinopyroxenes and orthopyroxenes from an anhydrous lherzolite (T°C ~1030) were strongly leached; their Sr isotopic compositions are significantly different (0.7025 versus 0.7031), however their Nd isotopic compositions are identical. Dasch and Green [11] suggested that this sample (2905) preserved a Sr isochron age of about 700 Ma. Interestingly, the Nd isotope data yield a zero Ma age, whereas the Sr isotope data yield a 625 Ma age. The apparent Sr age can be attributed to either (1) the $^{87}Sr/^{86}Sr$ composition of the orthopyroxene having been affected by Rb on the grain boundaries, (2) preferential uptake of ^{87}Sr in orthopyroxene versus clinopyroxene, or (3) possibly impure minerals and/or contamination.

Sr and Nd concentrations in the whole rocks and clinopyroxenes show excellent positive correlation, and have an average Sr/Nd ratio of 15. This ratio is similar to the primitive mantle value, as well as that found in primitive MORBs and OIBs, but is much lower than that measured in island arc basalts and what might be predicted for a subduction zone derived fluid. A significant proportion of the Sr and Nd in these peridotites is contributed by a later incompatible element enrichment event. This introduced component is a basaltic melt with intraplate chemical characteristics and may be unrelated to the recent intraplate magmatic event.

The isotopic compositions of the peridotites reflect long-term, small-scale heterogeneities in the continental lithospheric mantle, and are in marked contrast to the near uniform isotopic compositions of the host alkali basalts ($^{87}Sr/^{86}Sr$ = 0.7038 to 0.7041 and ε_{Nd} = +3.6 to +2.9). A minimum of three evolutionary stages are identified in the growth of the continental lithospheric mantle: an early basalt depletion event, recording the initial development and stabilization of the lithospheric mantle, and subsequent enrichment episodes, documenting later reactivation events. There is no evidence for a chemically or isotopically zoned continental lithospheric mantle in southeast Australia. Observations are consistent with continental lithospheric mantle growth involving underplating by refractory peridotite diapirs.

1. INTRODUCTION

The continental lithospheric mantle is that part of the upper mantle below the Mohorovicic discontinuity which is mechanically coupled to the overlying crust. Spinel-bearing lherzolite and harzburgite xenoliths brought to the earth's surface by intraplate alkaline basalts provide direct information on the nature of the continental lithosphere. These rocks equilibrated at pressures of about 10 to 25 kbars and probably represent the major constituent of the continental lithospheric mantle. These xenoliths have been used to identify processes involved in the growth of the continental lithosphere [1,2], constrain the tectonic setting of its formation and provide an estimate of the primitive mantle composition [3]. Additionally, recent studies have proposed that the lithospheric mantle is involved in intraplate basalt genesis [4,5]. Therefore, geochemical and isotopic studies of these samples may provide insights into the composition of a lithospheric mantle derived melt component.

There is a basic need for more data which can be used to constrain competing models that describe the formation and growth of the continental lithospheric mantle. The models proposed generally involve either underplating of intrinsically buoyant, refractory peridotite diapirs onto the base of the lithosphere during plate-margin and intraplate volcanism [6,8] or lithospheric thickening due to post-tectonic, conductive cooling [7,9,10]. Combined petrological, geochemical and isotopic data gained from detailed studies of these peridotite fragments can therefore offer important constraints for these models.

Chemical and Sr and Nd isotopic results are presented here for a suite of spinel-bearing lherzolite and harzburgite xenoliths from southeast Australia. The data are combined with previous major and trace element studies [1,2] on these and related peridotite samples. We put forth a self-consistent, multistage evolutionary model for the growth and development of the continental lithospheric mantle in southeast Australia and evaluate the role of the lowermost lithosphere in basalt genesis.

2. THE SAMPLES AND PREVIOUS WORK

The fifteen peridotite xenoliths analyzed for this study come from 7 separate alkaline basalt centers in the Pliocene to Recent, Newer volcanics from southeast Australia. The samplesare representative of the dominant ultramafic lithology found in the xenolith suites from nearly all of the localities in the field. An effort was made to investigate the most common lithology, the spinel-bearing harzburgite and lherzolite xenoliths, including two amphibole-bearing and three phlogopite-bearing samples and several samples which contain melt patches that Frey and Green [1] suggested were replacing amphibole and phlogopite. Six of these xenoliths are the samples from the classic peridotite study of Frey and Green [1]. Four other samples are from Dasch and Green [11], one sample is from Nickel and Green [2], and the remaining four samples were recently collected. These lherzolite and harzburgite xenoliths all contain, in decreasing order of abundance, olivine, orthopyroxene, clinopyroxene and spinel, and some also contain amphibole, phlogopite or apatite. A Mt Leura specimen (2642) contains ~2% amphibole, whereas the Bullenmerri sample contains 4.7% amphibole [2]. Three samples are phlogopite-bearing with modal abundances varying from a trace constituent (2640) to a major component (about 9% in 84438 and 16% in 84413). Apatite has only been identified in one sample (2700) [1]. Small areas of glass, that contain recrystallized olivine and pyroxene, are common to all of the peridotites studied, although abundances of the glass pockets vary from rare to about 0.5% in some samples. Samples are coarse to medium grained, with porphyroclastic textures. Four samples (2730, 2736, BM134 and 85168) are strongly foliated. More detailed petrographic descriptions are given in references [1,2,11]; details of the whole rock and mineral major and trace element chemistry for seven of the xenoliths have been described elsewhere [1,2].

3. EXPERIMENTAL PROCEDURES

Whole rock analyses were performed on powders, some of which were used in an earlier study [1,11]. Analyses were performed on 100 to 250 mg of rock powder. Enclosing basaltic material was removed from the xenolith using a water cooled saw; powders were prepared by extracting centimeter size fragments from coarsely crushed interior material. Up to 40 grams of rock fragments were ground in an agate ringmill for 1 minute. In an attempt to keep sample contamination to a minimum, no additional grinding was performed. Clinopyroxene and phlogopite concentrates were separated from the remaining coarsely crushed fragments. Pure (>99%) mineral separates were obtained by hand picking, and 50 to 100 mg aliquots of these separates were used for isotope analyses. An additional experiment was carried out on 4 of these clinopyroxene separates (13 to 17 mg each) and an orthopyroxene separate (260 mg). Following the technique of Jagoutz [12], the mineral separates were washed in warm 5%HF, then warm 2.5N HCl, repeatedly rinsed in cold distilled water, and then each mineral grain was examined (using horizontal illumination and a binocular microscope) and those without visible inclusions were selected for analyses. These samples were then leached in a warm (~60°C) ultrasonic bath of 10% HF - 2.5N HCl for 10 minutes and afterwards rinsed several times in distilled water. All samples were dissolved in teflon bombs; experimental procedures are documented in [5,13].

The isotopic analyses of the leached clinopyroxene and orthopyroxene separates were carried out on a recently acquired MAT 261 mass spectrometer in a static data collection mode. Nd isotope analyses involved simultaneous data collection of masses 142, 143, 144, 145, 146 and 150, monitoring mass 149, in order to avoid Sm interferences, and correcting for mass fractionation by normalizing $^{146}Nd/^{142}Nd$ = 0.72190. Sr isotope analyses involved simultaneous data collection of masses 84, 86, 87 and 88, monitoring mass 85, in order to avoid Rb interferences, and correcting for mass fractionation by normalizing $^{88}Sr/^{86}Sr = 8.37520$. Table 1 presents the Sr and Nd isotopic compositions of different standards as measured on the 2 mass spectrometers used in this study. Differences in the measured Sr and Nd isotopic compositions of these standards (expressed as Δ) for the 2 machines are relatively constant. The isotopic compositions of the xenoliths and mineral separates have not been normalized to an assumed value of $^{87}Sr/^{86}Sr$ or $^{143}Nd/^{144}Nd$.

Total chemical blank measured during the analysis period for Nd is ≤ 30 pg, Sm is ≤ 10 pg, Sr is ≤ 60 pg, and Rb is ≤ 20 pg. No correction for procedural blank has been applied. Replicate analyses were performed to evaluate chemical and isotopic variations between separate aliquots of rock powder and to document experimental procedures on samples with low concentrations. Finally, there are significant differences in the $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios reported in this study and those reported in Dasch and Green [11] for splits of the same sample powders (2730, 2736 and 2769) and the mineral separates (2905).

4. RESULTS

4.1 Whole rock data

Chemical and isotopic results for whole rock samples are reported in Table 2. The whole rock data shows the largest known variation in Sr and Nd isotopic compositions for spinel-bearing lherzolite and harzburgite xenoliths from a given basalt field (Fig. 1). Three samples from Mt Gambier alone display nearly as large a range in isotopic compositions as found in all of the xenoliths. Combined with earlier isotope data [14] the Mt Leura peridotites show an enormous variation in Nd isotope composition from $\varepsilon_{Nd} = +10.6$ to -7.5. These observations reflect large isotopic heterogeneities in the continental lithospheric mantle beneath southeast Australia. Moreover, these heterogeneous regions occur even within xenoliths from a single vent and document compositional diversity over a restricted vertical section (e.g., the spinel lherzolite field, ~40 to 70 kms depth).

The Sr and Nd isotopic compositions of these peridotites generally plot along the oceanic mantle array (Fig. 1). The large variation in their Sr and Nd isotope compositions is in marked contrast to the limited range in isotope composition of the host alkalic basalts [5]. The spread in isotopic compositions of these peridotites is therefore a feature that cannot be attributed to host basalt contamination. If present, contamination by the host basalts would only reduce the total isotopic variation and thus, the present spread would represent a minimum for the xenolith source region. The two amphibole-bearing and three phlogopite-bearing peridotites have, in general, higher $^{87}Sr/^{86}Sr$ ratios for a given ε_{Nd} value compared to the other samples, whereas, the single apatite-bearing lherzolite plots on the lower left side of the oceanic mantle array.

There is no simple correlation between the Sr and Nd isotopic composition and the presence of a foliated fabric, although two foliated specimens from Mt Gambier have the highest $^{87}Sr/^{86}Sr$ ratios. The high $^{87}Sr/^{86}Sr$ ratios in these two samples are not attributed to secondary surface alteration effects. These samples have high $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ and low $^{147}Sm/^{144}Nd$ and negative ε_{Nd} values, thus reflecting a long term history of Rb and LREE-enrichment. Both peridotites contain heterogeneously distributed melt pockets which have been interpreted as replacing pre-existing hydrous phases [1]; this interpretation is consistent with their incompatible element enriched character. The Sr and Nd isotopic composition of the foliated Mt Leura lherzolite, 85168, is not distinct from those of other Mt Leura peridotites, and is similar to the host alkali basalt isotopic composition. However, it is unlikely that this peridotite has been affected by host basalt contamination since it has very low concentrations of Rb, Sr and the REE compared with the host and has significantly different Rb/Sr and Sm/Nd ratios.

Nine out of the fourteen whole rocks studied have positive ε_{Nd} values, consistent with a long-term LREE-depleted history (Fig. 2b). However, seven of these nine are LREE-enriched (samples in the upper left quadrant Fig. 2b). This feature has been observed in other peridotite xenolith suites [15-17]. The long-term, LREE-depleted Nd isotopic character is consistent with the peridotite's major and trace element geochemistry which reflects a previous basaltic melt depletion event. Such depleted peridotites were referred to as component A by Frey and Green [1]. Peridotites with LREE-enriched patterns and positive ε_{Nd} values must have experienced a recent LREE-enrichment event, although depleted mantle model ages allow this enrichment event to have occurred up to 800 Ma ago (Table 2). This added, LREE-enriched component was called component B by Frey and Green [1] and is present in only some of the depleted peridotites. For example, the Mt Gambier peridotite (2728) has a near-chondritic REE pattern and a large, positive ε_{Nd} value, requiring that at sometime in the past this sample possessed a LREE-depleted pattern. In contrast, the Mt Leura peridotite (2642) has a LREE-depleted pattern and a positive ε_{Nd} value. This sample may have experienced basalt melt extraction at about 1.5 Ga (its T_{CHUR} age), without subsequent LREE-enrichment. It is possible that the amphibole in this sample may be the result of H_2O addition which occurred without significantly changing the bulk rock REE pattern and major element composition.

Figure 2 gives Rb-Sr (a) and Sm-Nd (b) isochron diagrams for the peridotites. The data plot along highly scattered, positive trends in both diagrams. The Rb-Sr data for the 4 Mt. Leura samples define a horizontal line with a very large uncertainty. A reference isochron for the Rb-Sr system for the Mt. Gambier peridotites is shown in Fig. 2a and was derived by using the 3 Mt. Gambier samples. These data suggested an age of 1117 ± 69 Ma and an initial $^{87}Sr/^{86}Sr$ of 0.7032. Reference isochrons for the Sm-Nd system are shown for the Mt. Leura and Mt. Gambier peridotites (Fig. 2b). These were generated from a regression for the 4 Mt. Leura peridotites which yielded a 613 ± 96 Ma age with an initial ε_{Nd} value of +6.5 and the 3 Mt. Gambier peridotites which yielded a 1510 ± 525 Ma age with an initial ε_{Nd} value of +7.4. The different ages determined from the Sr and Nd isotope systems and the large uncertainties suggest these ages are not significant.

Differences in absolute concentrations of Sr, Sm and Nd of up to 15% were measured during replicate whole rock analyses. These differences are attributed to the heterogeneous distribution of clinopyroxene, phlogopite or glass in each aliquot of powder dissolved, considering that clinopyroxene, the dominant host for Sr and the

REE, commonly constitutes less than 10% by volume of the total rock powder. The $^{147}Sm/^{144}Nd$ ratios agree at or within ±0.002 for replicate analyses, although the absolute concentrations differ between each dissolution. Variations in Rb concentrations between replicate analyses may be due to an irregular distribution of Rb along grain boundaries and/or in fluid inclusions [12,18], except in the phlogopite-bearing samples where Rb concentrations will be a function of the amount of phlogopite present in each powder aliquot. Evidence for a grain boundary distribution of Rb can be found by comparing unleached and HF-HCL leached clinopyroxene separates (Table 3). These data show a substantial reduction in the Rb contents and $^{87}Rb/^{86}Sr$ ratios, but no difference in the Sm/Nd ratios or the Sr and Nd isotopic compositions. Chen and Frey [19] also demonstrated that the alkalis are readily removed from acid washed clinopyroxenes in a suite of Mt. Leura peridotite xenoliths, but that the REE and Sr abundances and $^{87}Sr/^{86}Sr$ ratios were unaffected by acid washing. Similarly, in a study of peridotite xenoliths from the southwest United States, Menzies et al. [17] showed that the Sr and Nd isotopic compositions of clinopyroxene separates were within analytical uncertainties before and after HCl leaching experiments.

4.2 Mineral Data

The Sr and Nd isotopic compositions of clinopyroxene, orthopyroxene and phlogopite separates are reported in Table 3. This table reports data for leached and unleached mineral separates. In general, the leached and unleached clinopyroxene separates have identical Sr and Nd isotopic compositions, considering uncertainties and differences in machine bias (see Table 1 and discussion in Section 3), although in both phlogopite-bearing xenoliths there are relatively small differences in the Sr isotopic compositions which are beyond analytical uncertainties. Thus, $^{87}Sr/^{86}Sr$ ratios of the leached samples better reflect the 'true' clinopyroxene value.

There are slight differences in the Sr and Nd isotopic compositions between clinopyroxene and whole rock analyses for peridotite 2730, which contains small glass pockets (Fig. 3, [11]). Since no evidence was found for host basalt infiltration

[1] we attribute these differences to the influence of the glass phase. These glass pockets are interpreted to be the breakdown products of hydrous phases during decompression in the volcanic pipe [1,11]. Thus, in samples that do not have modal hydrous phases, but do have melt pockets that replace preexisting hydrous phases, the isotopic analyses of clinopyroxene separates alone cannot fully characterize the peridotite xenoliths.

The mineral phases in the phlogopite lherzolite 84413 are in Sr isotopic disequilibrium. The $^{87}Rb/^{86}Sr$ of the phlogopite is much higher than that of the clinopyroxene (and whole rock), yet the clinopyroxene has a higher $^{87}Sr/^{86}Sr$ (0.70710-unleached versus 0.70721-leached) than the phlogopite (0.70498). The whole rock has an intermediate $^{87}Sr/^{86}Sr$ value (0.70553). The low $^{87}Sr/^{86}Sr$ of the phlogopite indicates a recent addition of a low $^{87}Sr/^{86}Sr$ component to this rock. It is possible that this recently added component is associated with the Pliocene to Recent basaltic magmatism in the region. As will be argued later, the addition of such a low $^{87}Sr/^{86}Sr$ component into this rock is evidence for a very recent magmatic enrichment event in the southeast Australian lithospheric mantle.

In both phlogopite-bearing samples, the clinopyroxenes have higher $^{87}Sr/^{86}Sr$ ratios than the whole rocks. The balance of the Sr is contained in the phlogopite, which has low $^{87}Sr/^{86}Sr$, thus explaining the differences between clinopyroxene and whole rock values. Phlogopite-bearing peridotites from south Africa have similar isotopic characteristics [20]. Clinopyroxenes in both phlogopite-bearing samples have lower ε_{Nd} values than the whole rock, which, in contrast with the Sr system, cannot be totally explained by the presence of phlogopite since it has low REE concentrations (less than 0.2 ppm Nd, Table 2). These differences must be due to another component which remains as yet unidentified. Differences in both the Nd and Sr systems between hydrous and anhydrous phases is evidence for isotopic disequilibrium and suggests recent introduction of a component (e.g., component B of Frey and Green [1]). Additional examples of isotopic disequilibrium have been reported [e.g., 15-21].

The clinopyroxene and orthopyroxene separates in sample 2905 have identical Nd isotopic compositions despite differences in ^{147}Sm/^{144}Nd ratios, suggesting that this peridotite was in Nd isotopic equilibrium. However, considering analytical uncertainties, the maximum age at which this peridotite could have closed to diffusive exchange is 38 Ma ago. This peridotite has a two pyroxene equilibration temperature of about 1030°C, in agreement with other anhydrous peridotites from the region [2], suggesting it resided at temperatures above Nd closure temperature [see further discussion in 12 and 22]. In contrast, the Sr isotopic compositions of these coexisting minerals are not the same; the orthopyroxene has a higher ^{87}Sr/^{86}Sr ratio (0.7031) than the clinopyroxene (0.7025). This discrepancy between the Sr and Nd isotope systems have been observed before [12, 22] and has been attributed to contamination. Dasch and Green [11] suggested that this sample (2905) preserved a Sr isochron age of about 700 Ma. Interestingly, the Sr isotope data for the clinopyroxene - orthopyroxene pair yields a 625 Ma age, although this age is not considered significant in the light of the Nd results. We suggest that the apparent Sr age can be attributed to either (1) the ^{87}Sr/^{86}Sr composition of the orthopyroxene having been affected by Rb on the grain boundaries, (2) preferential uptake of ^{87}Sr in orthopyroxene versus clinopyroxene, or (3) possibly incomplete purification of mineral separates and/or chemical processing blanks as previously suggested [12,22]. Further studies are necessary in order to better understand the effective grain size of these minerals under mantle conditions and the relative diffusion coefficients of Sr and Nd in natural orthopyroxenes and clinopyroxenes.

5. DISCUSSION

5.1 The nature of the LREE-enriched added component

Frey and Green [1] and Nickel and Green [2] suggested that the major and compatible minor element characteristics of these peridotites (their component A) resulted from the extraction of a basaltic melt. This melting event produced residual peridotites which possessed variable depletions in incompatible elements, depending upon the degree of melt extracted. They further suggested that the incompatible minor and trace element compositions of these residual peridotites were increased by the subsequent addition of an added component (their component B), which was enriched in these elements. They argued that component B is genetically unrelated to component A, and represents a liquid derived by a small degree (<5%) of melting in equilibrium with garnet [1]. This melt was possibly derived from the low velocity zone (LVZ) and interacted with the overlying lithosphere [1]. The nature and origin of this added component has been of considerable interest in recent years [17,28,29] and is commonly referred to as a metasomatic component. The data presented here allow us to place further constraints on the nature and origin of this component.

The Sr and Nd concentrations in these peridotites are positively correlated (Fig. 4); for n = 14, this correlation (r=0.985) corresponds to a >99.99% level of significance, with an average whole rock Sr/Nd ratio of 14.9±4.0 (1σ). A similar well defined Sr-Nd correlation and relatively constant Sr/Nd ratio (14.5±5.0) is found in clinopyroxene separates from these peridotites (Fig. 4). In marked contrast, the Sr/Nd ratio of a phlogopite separate is nearly 1800 (Fig. 4), although the Sr/Nd ratios in the phlogopite-bearing peridotites are 17.3. The agreement between the Sr/Nd ratios in clinopyroxene and whole rock is expected, given that only small differences in isotopic composition exist. These data indicate an overall control by clinopyroxene on the whole rock Sr and Nd chemistry, even in the presence of other phases.

The average Sr/Nd ratio of these peridotites is similar to the bulk earth Sr/Nd ratio of 17.1 (based on the value for C1 chondrites [23]). In contrast, the Sr/Nd ratio of primitive basalts is dependent upon their tectonic setting. A compilation of Sr and Nd data for relatively unfractionated basalts (e.g., Ni and Cr > 100 ppm, with no evidence of plagioclase fractionation) shows that, in general, MORBs have a low Sr/Nd ratio of 10 to 15, oceanic and continental intraplate basalts have intermediate Sr/Nd ratios of 15 to 20 and island arc basalts have much higher Sr/Nd ratios of 30 to 35 [23-25]. The host Newer basalts have a typical intraplate Sr/Nd ratio of 19.5 [5].

We suggest that, because of the correlation between Sr and Nd concentrations and degree of incompatible element enrichment (noted above), a significant proportion of the Sr and Nd in the Victorian peridotites was contributed during the enrichment event. If this is true, the Sr/Nd ratios in these peridotites reflect that of the added component, since none of the modal minerals (except phlogopite) have fractionated Nd from Sr, as evidenced by the similar Sr/Nd ratios between whole rocks and clinopyroxene separates. Thus this enriched component had a Sr/Nd ratio most similar to that of MORB and/or intraplate basalts and is unlike basalts from convergent plate margins or what might be predicted for a fluid flux associated with subduction zone magmatism. The overall incompatible element-enrichment produced by the addition of this component suggests it was of an intraplate, rather than MORB character, although a melt component derived by low degrees (<2%) of melting of the MORB source (i.e., Frey and Green's [1] LVZ source) would have the necessary chemical characteristics. Finally, because the isotopic composition of these peridotites are distinct from their host basalts, the introduced melt component is probably unrelated to this recent intraplate magmatic event.

The above inferences on the tectonic setting and nature of peridotite modification provides an interesting contrast with the tectonic history recorded in the overlying crustal rocks. In this part of southeast Australia there has been an extensive amount of granite genesis in the Paleozoic (~400 Ma ago [26]), and a greenstone belt, containing boninites and low-Ti andesites [27], was formed during the Cambrian. Nevertheless, the presence of a subduction zone environment in this region is not recorded in these peridotites.

5.2 Timing of the LREE-enrichment events

The chemical and isotopic compositions of these spinel-bearing lherzolite and harzburgite xenoliths allow formulation of the following model of lithosphere formation and modification. An initially primitive or pyrolitic mantle source underwent partial melting, giving rise to a basaltic melt, and a LREE-depleted residuum. This first stage is envisaged as the initial stabilization of a lithospheric mantle, in conjunction with crust formation. Following this depletion event the Nd isotopic composition of the residuum evolved over some time interval (though not well constrained) to positive ε_{Nd} values (or a more positive ε_{Nd} value if a depleted mantle model is assumed). Later, a LREE-enriched component was introduced into the residuum resulting in a significant decrease in the $^{147}Sm/^{144}Nd$ ratio (< 0.197), and the Nd isotopic composition began evolving to lower ε_{Nd} values; in some cases ultimately evolving to negative ε_{Nd} values. Using major and trace element data it was shown [1,2] that each of these peridotites experienced different degrees of depletion and enrichment. The broad range of isotopic compositions found in these peridotites provides additional support for this conclusion.

The considerable scatter of the data on the Sm-Nd and Rb-Sr isochron diagrams (Fig. 2) suggests these peridotites are mixtures of at least three components. This interpretation is consistent with the data presented here and in previous studies [1,2]. Therefore, these whole rock samples, and other peridotite samples which show similar geochemical characteristics, will not yield meaningful age information from traditional isochron diagrams. Thus, a previously reported mantle Sr isochron age of 650 Ma for peridotite xenoliths from Mt Leura [28] probably has no age significance, especially in light of the fact that these same samples do not fall on a Sm-Nd isochron.

There is no simple method for determining the $^{147}Sm/^{144}Nd$ or the $^{143}Nd/^{144}Nd$ of the whole rock prior to the enrichment event, nor can we determine the amount and isotopic composition of the enriched component added to the residual peridotite. Therefore, the precise timing of the depletion or enrichment events cannot be obtained, but age estimates for the LREE-enrichment can be made. Assuming a simple two stage model, whereby the peridotites experienced one depletion from a chondritic parent, and a latter enrichment event, an age estimate for this LREE-enrichment event can be calculated using a T_{DM} model [29]. Such a calculation is justified since these peridotites experienced LREE-depletion as a result of basaltic melt extraction. Although the degree of LREE-depletion associated with the first event is unknown, it is assumed to be greater than (for small amounts of melt extracted) or equal to that (for larger amounts of melt extracted) of the MORB source. Model ages are given in Table 1 and vary from 600 to 1370 Ma. These models provide only a gross age estimate for the timing of the enrichment event, as they assume only a single stage enrichment event. These estimates can be significantly in error if the rocks experienced multiple enrichment (or depletion) events. In addition, if the assumed depleted mantle model does not reflect the depletion history of the peridotite, then the uncertainties of these age estimates increase. Alternatively, if these peridotites have experienced multiple enrichment events, then T_{DM} model ages for the most LREE-enriched samples (e.g., 2604 and 2669) represent an upper age limit for the most recent LREE-enrichment event. However, for samples 2604 and 2669, this would imply that the last LREE-enrichment events were no later than 600 and 970 Ma, respectively.

Like the other samples, the phlogopite-bearing peridotites possess geochemical and isotopic compositions indicating an initial melt depletion and a later incompatible element enrichment (with model ages of ~800 Ma). In addition, the low $^{87}Sr/^{86}Sr$ measured for the phlogopite in 84413 suggests that it is a recent addition, post-dating the earlier depletion and enrichment event(s). It is unlikely that partial equilibration occurred between the phlogopite and the host basalt, because there is no evidence for basalt infiltration [1, and this study]. It would take about 60 Ma for the phlogopite to evolve to its present $^{87}Sr/^{86}Sr$ value if it was introduced from a depleted mantle source (i.e., $^{87}Sr/^{86}Sr = 0.7025$). If the component was derived from a less depleted mantle having a higher $^{87}Sr/^{86}Sr$ ratio, then the age of the phlogopite would be less than 60 Ma. Therefore, phlogopite generation occurred sometime during the Cenozoic, consistent with the observation that intraplate magmatism occurred throughout this period [30].

5.3 EVOLUTION OF THE CONTINENTAL LITHOSPHERIC MANTLE

Considerable controversy exists concerning the growth and evolution of continental lithosphere. Growth processes include: magmatic and tectonic accretion during ocean plate subduction, additions to the continental lithosphere during the intracratonic volcanism, and thirdly, additions of lithospheric mantle resulting from the conductive cooling of the lithosphere. A conductive cooling growth model is envisaged as a relatively passive process involving the underplating and thickening of the lithosphere from below as it cools; this growth model has been successfully applied to the oceanic lithosphere and is consistent with geophysical data [9,10,31]. The first two growth processes are envisaged to be active processes involving significant additions to the lower lithosphere directly from interplate or intraplate magmatism.

The subcrustal lithosphere added to the continents during magmatic events is predicted to be petrologically and chemically distinct from lithospheric mantle added during conductive cooling of the lithosphere. Mantle accreted onto the base of the lithosphere via conductive cooling would presumably have the petrologic, chemical and isotopic characteristics of the convective upper mantle (i.e., the asthenospheric mantle). This mantle would still be capable of producing basaltic melts, possibly with MORB-type compositions. In contrast, mantle accreted during interplate and intraplate magmatism would most likely be depleted peridotite, having a petrologic and chemical composition similar to component A as characterized by Frey and Green [1]. This material would be a Mg-rich, refractory residuum, less dense than the ambient mantle and thus, intrinsically buoyant [7,8,32,33]. The greater the basaltic component (an Fe-rich component) extracted from the peridotite source, the more buoyant the residuum with respect to the surrounding mantle. Such residual peridotite bodies produced during continental magmatism would become permanently trapped beneath the continents and incorporated into the lithosphere. In contrast, undepleted or less-depleted peridotite accreted directly onto the lithosphere from the asthenosphere would, because of its higher density, be gravitationally unstable and may sink back into the asthenosphere upon cooling [34, 35].

The data gained from the study of these xenoliths providesclues as to the processes involved in the growth and evolution of the continental lithosphere in southeast Australia. The early partial melting event recorded in these peridotite xenoliths documents the initial development and stabilization of the continental lithosphere. This event left the peridotites depleted with respect to a basaltic component and intrinsically buoyant. Thus, the initial growth of the continental lithospheric mantle occurred during interplate or intraplate magmatism in this region. This resulted in the underplating of refractory peridotite diapirs, from which fragments have been torn away by the recent volcanism and brought to the surface as these xenoliths.

Determining the tectonic environment of the initial lithospheric growth stage as being either at a convergent plate margin, intraplate setting or spreading plate boundary is not straightforward. Initial lithospheric development has been envisaged to be in an oceanic spreading ridge environment [1,2 and references therein], although the evidence used to support this is inconclusive. The constant Sr/Nd ratio in these peridotite xenoliths is significant. If these peridotite bodies were initially emplaced during convergent plate magmatism, then the Sr/Nd ratios in these rocks would reflect such an environment. The constant Sr/Nd ratio possibly reflects the residuum Sr/Nd ratio, and reflects initial lithospheric development in a mid-ocean ridge spreading center [e.g., 1,2] or an intraplate (possibly rift-type) environment.

Available petrologic, geochemical, isotopic and geophysical data [6-8] support a model in which the continental lithospheric mantle grows through the underplating of buoyancy driven refractory diapirs onto its base. This process leads to the stabilization and development of the continental lithosphere. Other growth processes, such as thermal accretion due to lithospheric cooling, are inferred to be subordinate, and are not supported by petrologic, seismological, thermal, and gravity data [6-8,34,35]. The many constraints provided by these varied approaches indicate that the continental lithospheric mantle is chemically, mechanically and thermally distinct from the underlying convecting upper mantle. Much of the oceanic lithospheric mantle is suggested to grow by conductive cooling and the passive underplating of asthenosphere, whereas we suggest that the continental lithospheric mantle grows by the active underplating of depleted peridotite. Consequently, one might expect significant petrologic, geochemical and isotopic differences between the oceanic and continental lithospheric mantles.

Finally, the chemical and isotopic compositions of these peridotite xenoliths show no evidence for a chemically zoned continental lithosphere, contrasting with earlier views [36,37]. Comparisons of chemical and isotopic data for spinel-bearing lherzolite and harzburgite xenoliths with garnet-bearing peridotite xenoliths reveals that both regions of the continental lithosphere are heterogeneous, but there is much overlap in their range of compositions [1,2,16,21,38,39]. The fertile, or high temperature, deformed (sheared), garnet peridotites do show chemical and isotopic characteristics which are not found in spinel-bearing peridotite suites, but these samples may be asthenospheric in origin [21,38,39].

5.4 ROLE OF THE LOWERMOST LITHOSPHERE IN INTRAPLATE VOLCANISM

In recent years, many workers have considered the continental lithospheric mantle as playing an important role in influencing the chemical and isotopic composition of continental basalts. The lithospheric mantle has been suggested to be the source of continental flood basalts [37,40-44], especially in cases where basalts have enriched isotopic characteristics and fairly primitive chemical characteristics. Additionally, recent studies of hotspot related, intraplate oceanic and continental basalts have proposed that melts derived from the lithospheric mantle contribute to hotspot plume-derived melts during basalt genesis [4,5]. In this respect, the chemical and isotopic data gained from the study of peridotite xenolith suites from continental and oceanic environments are applicable to studies of intraplate basalts.

We have recently put forth a model for hotspot related intraplate basalt genesis involving the interaction of the lowermost lithosphere and an upwelling hotspot mantle plume [5]. Figure 5 illustrates the major points of this model for a continental setting. A first order consideration in this model is the physical consequences resulting from the intrusion of a hot plume of peridotite into the base of the lithosphere. We predict that the basalt portion of the lithosphere would undergo melting, and that the degree of partial melting would vary considerably over the region of the lithosphere involved. Ultimately, the intraplate basalts which are produced would represent mixtures of plume-derived and lithosphere-derived melt components. We have previously argued [5] that the lithosphere-derived melt component would dominate the isotopic composition of the alkali basalts, whereas the isotopic composition of the associated tholeiitic basalts would be controlled by the plume-derived melt component.

The broad range of isotopic compositions in the southeast Australian peridotites contrasts with the narrow range found in the host basalts [5] indicating that either the source of the alkali basalts is isotopically unlike that of these spinel peridotites or that these basalts are a homogeneous mixture of a similar isotopically diverse lithosphere-derived component. Using the spinel peridotites as a guide, we predict that the deeper portion (i.e., the garnet stability field) of the southeast Australian lithosphere has similar isotopic heterogeneity, and suggest that the alkali basalts represent homogeneous mixtures of dominantly lithosphere-derived melt and asthenosphere derived melt components. The homogeneous character of the alkali basalt component is exemplified by four of the host basanite centers, which are separated by more than 50 kms, yet have identical Sr, Nd and Pb isotopic compositions [5]. Accordingly, the Sr and Nd isotopic composition of the alkali basalts dominantly reflect an average composition for the continental lithospheric mantle of the region, assuming the melt components are completely homogenized prior to eruption. Thus, we predict that the averaged isotopic composition of the lowermost lithosphere in the central portion of the Newer basalt field has a $^{87}Sr/^{86}Sr$ of about 0.7038 and an ε_{Nd} value of about +3. This approach provides only a gross compositional estimate, given its assumptions. The estimated isotopic composition of this portion of the continental lithosphere lies within the mantle array between the bulk earth and MORB composition, consistent with a long-term history of constant Sr/Nd ratios and multiple episodes of depletion and enrichment events.

Finally, we turn our attention to the possible continental lithospheric mantle sources of continental flood basalts. The large reported range of Sr and Nd isotopic compositions for garnet- and spinel-bearing peridotites allows for the possibility that isotopically enriched fragments of the lithospheric mantle may be the source of continental flood basalts. However, the physical processes involved in tapping solely the lithospheric mantle for continental flood basaltic magmatism are particularly difficult to envisage. To raise the lithospheric mantle above its solidus requires a change in pressure and/or temperature, though commonly a thermal input from below is invoked. Second, continental flood basaltic magmatism is dominantly tholeiitic, involving large degrees of partial melting and picritic basalts are common. Many of these lithospheric peridotite fragments have a depleted major element character that is incapable of producing these basalts and the difficulties are magnified given the high percentages of partial melting that are commonly needed. Additionally, these basalts require much high temperatures for their genesis than required for alkali basalt genesis indicating that their source is restricted to the hotter regions of the thermal anomaly. Given the need for an external source for the thermal anomaly and that refractory peridotites are common in the continental lithosphere, it is concluded that the dominant source of continental flood basalts is melt generated from the sublithospheric mantle.

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FIGURE CAPTIONS

Figure 1. $^{87}Sr/^{86}Sr$ versus ε_{Nd} values for whole rock spinel peridotite xenoliths from southeast Australia. Open symbols identify peridotites with a well defined foliated fabric. The limits of the oceanic mantle array include ocean islands and MORB [45]. The uncertainty estimate represents a typical $2\sigma m$ value. The field of Sr and Nd isotopic compositions for the Newer basalts includes tholeiitic and alkalic basalts [5].

Figure 2. (a) $^{87}Sr/^{86}Sr$ versus $^{87}Rb/^{86}Sr$ whole rock variation for southeast Australian peridotites. The 1100 Ma reference isochron is shown for the three Mt Gambier peridotites. Symbols as in Fig. 1. (b) $^{143}Nd/^{144}Nd$ versus $^{147}Sm/^{144}Nd$ whole rock variation for southeast Australian peridotites. The 1500 Ma reference isochron is shown for the three Mt Gambier peridotites, and the 610 Ma reference isochron is shown for the four Mt Leura peridotites, however these ages have no geological significance, see text. The diagram is divided in quadrants based on LREE-depleted versus LREE-enriched patterns and $+\varepsilon_{Nd}$ values versus $-\varepsilon_{Nd}$ values using primitive mantle values. Symbols as in Fig. 1.

Figure 3. $^{87}Sr/^{86}Sr$ versus ε_{Nd} values for whole rock and clinopyroxene mineral separates for peridotite xenoliths from southeast Australia. The $^{87}Sr/^{86}Sr$ ratio of a phlogopite mineral separate from peridotite 84-413 is represented by a vertical bar with an arrow projecting from the $^{87}Sr/^{86}Sr$ and ε_{Nd} value measured for the whole rock sample. The field shown for the 5 host basalts is from McDonough et al., [5]. The error bar indicates the typical $2\sigma m$ uncertainty.

Figure 4. Sr (ppm) versus Nd (ppm) concentrations for whole rock and their clinopyroxene mineral separates for peridotite xenoliths from southeast Australia. A single phlogopite mineral separate clearly shows a markedly different Sr/Nd ratio.

Figure 5. A mantle model depicting the relative role of the continental lithospheric mantle and an ascending mantle plume during hotspot related intraplate basalt genesis. Diagram is modified from McDonough et al., [5]. In this model a hot ascending mantle plume intrudes the base of the continental lithosphere and initiates melting of the lithospheric mantle; tapped magmas are mixtures of plume-derived and continental lithosphere-derived melt components. Alkalic basalts are considered to be dominated by a continental lithospheric

mantle-derived component. As depicted the continental lithospheric mantle contains a diversity of components, possibly of various ages, which are represented by different shadings. Griffin et al., [46] have identified a variety of ultramafic lithologies derived from presumed upper mantle depth from the Bullenmerri and Gnotuk centers in the region.

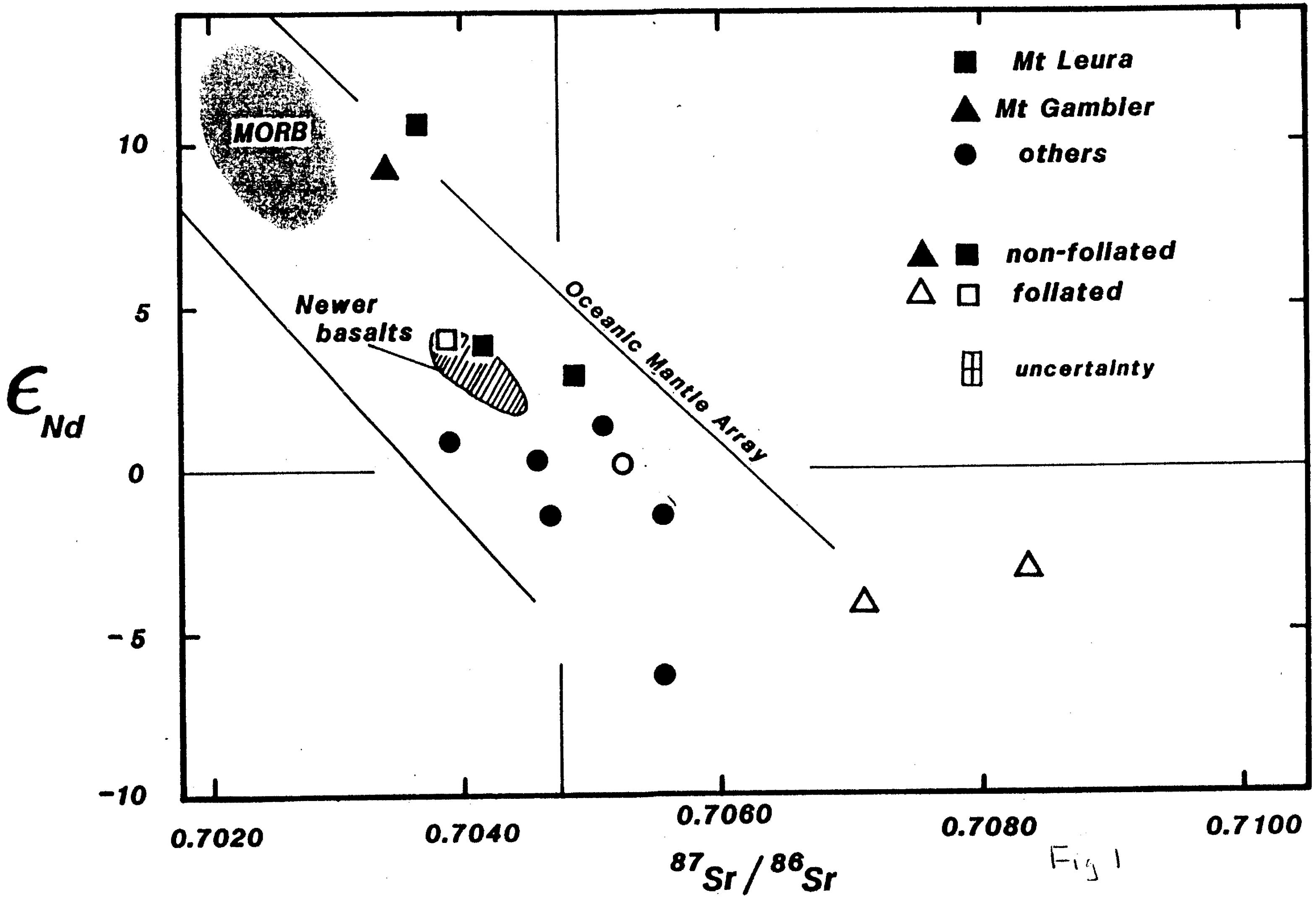

■ Mt Leura
▲ Mt Gambler
● others
▲ ■ non-foliated
△ □ foliated
⊞ uncertainty
MORB
Newer basalts
Oceanic Mantle Array
ϵ_{Nd}
10
5
0
-5
-10
0.7020
0.7040
0.7060
0.7080
0.7100
$^{87}Sr/^{86}Sr$

Fig 1

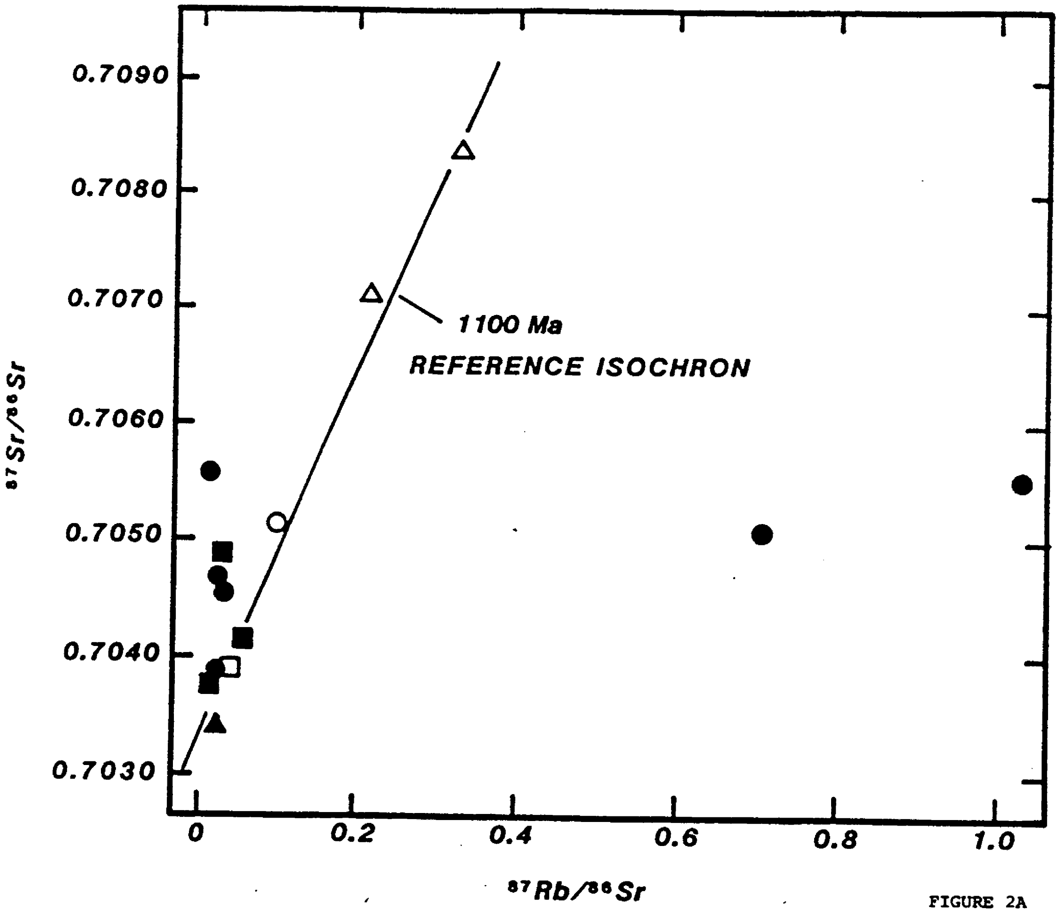
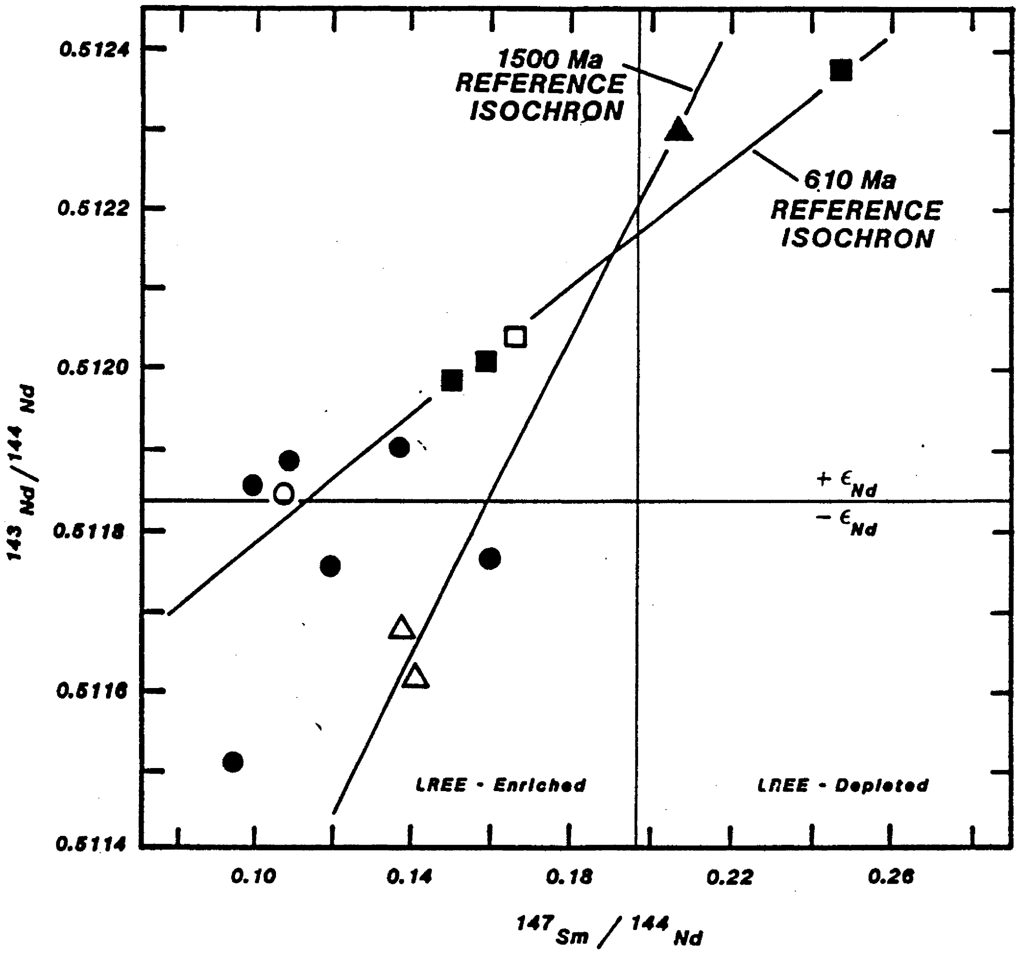

0.7090
0.7080
0.7070
0.7060
0.7050
0.7040
0.7030
$^{87}Sr/^{86}Sr$
0
0.2
0.4
0.6
0.8
1.0
$^{87}Rb/^{86}Sr$
1100 Ma
REFERENCE ISOCHRON

FIGURE 2A


0.5124
0.5122
0.5120
0.5118
0.5116
0.5114
$^{143}Nd/^{144}Nd$
0.10
0.14
0.18
0.22
0.26
$^{147}Sm/^{144}Nd$
1500 Ma
REFERENCE
ISOCHRON
610 Ma
REFERENCE
ISOCHRON
$+\epsilon_{Nd}$
$-\epsilon_{Nd}$
LREE - Enriched
LREE - Depleted

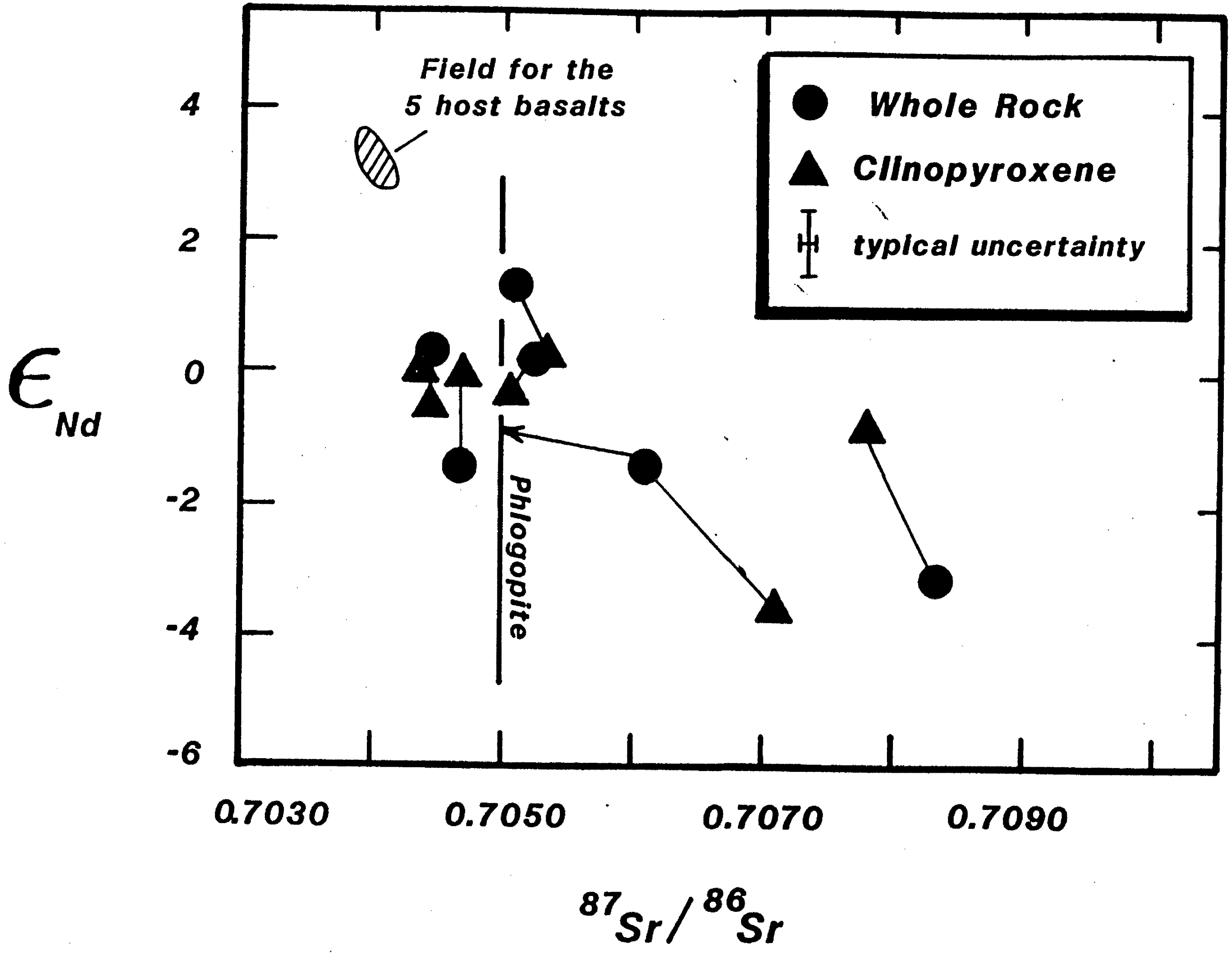

Field for the
5 host basalts
Whole Rock
Clinopyroxene
typical uncertainty
Phlogopite
ϵ_{Nd}
4
2
0
-2
-4
-6
0.7030
0.7050
0.7070
0.7090
$^{87}Sr/^{86}Sr$

FIGURE 3

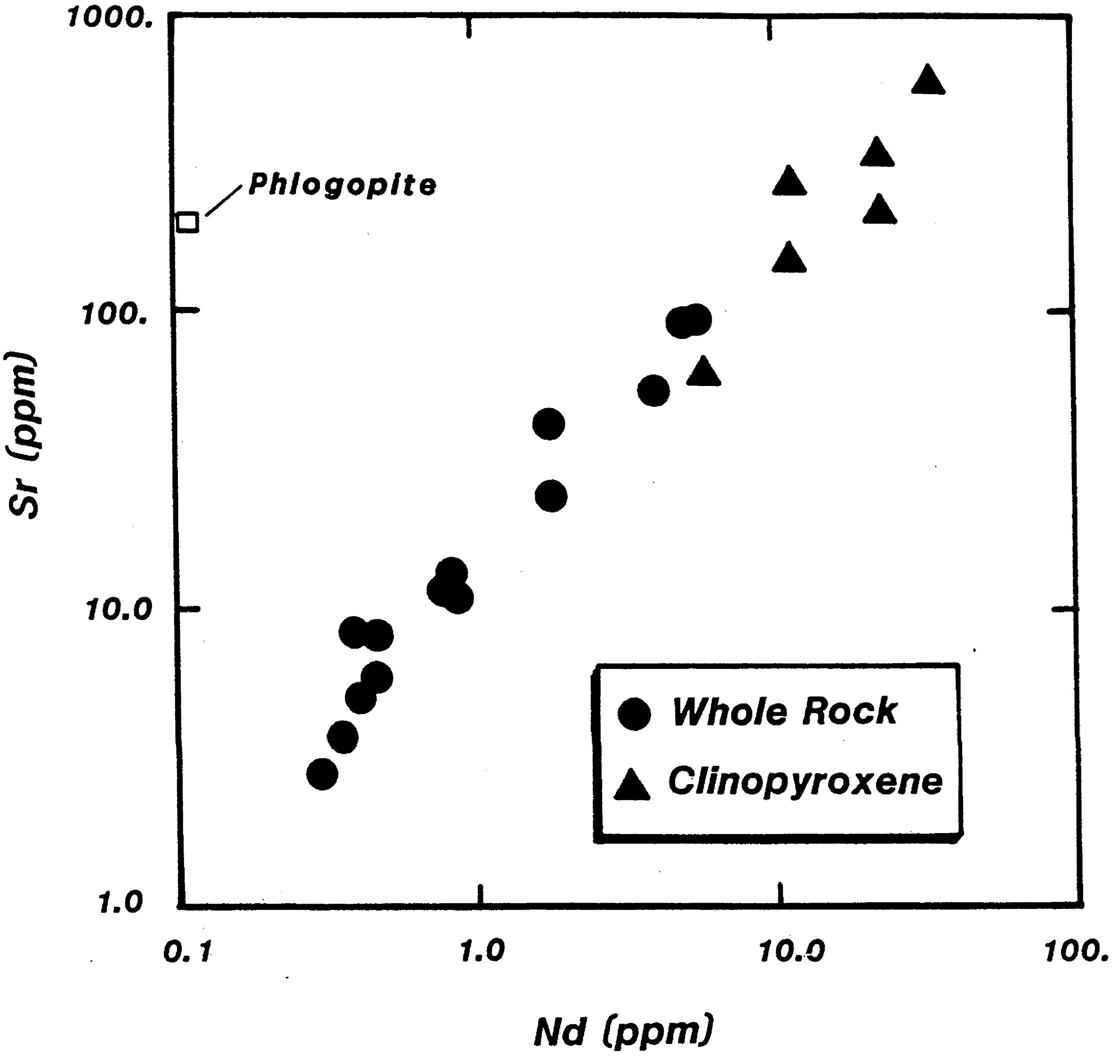

1000.
100.
10.0
1.0
Sr (ppm)
0.1
1.0
10.0
100.
Nd (ppm)
Phlogopite
● Whole Rock
▲ Clinopyroxene

Fig 4

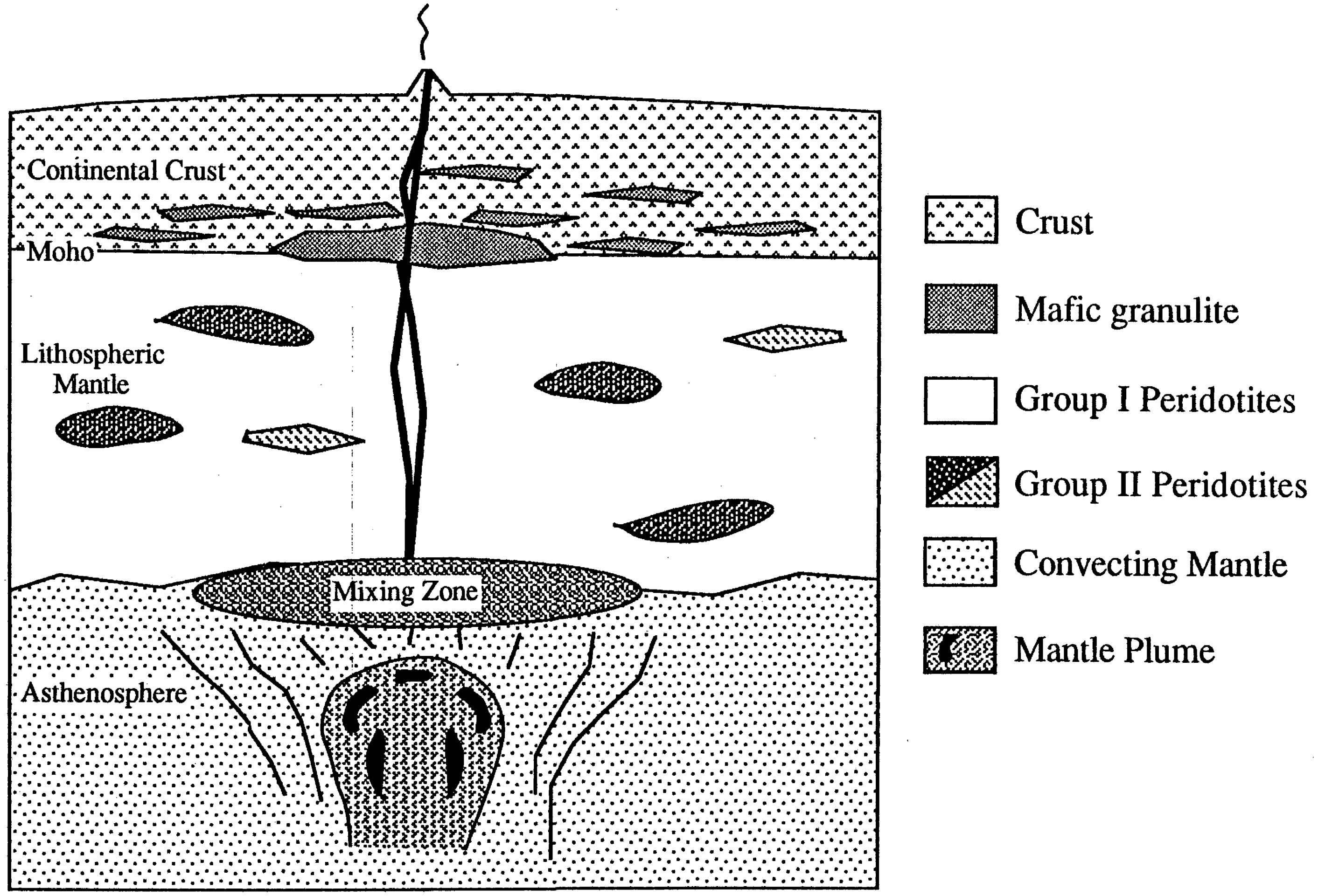

Continental Crust
Moho
Lithospheric Mantle
Mixing Zone
Asthenosphere
Crust
Mafic granulite
Group I Peridotites
Group II Peridotites
Convecting Mantle
Mantle Plume

Figure 5.

Table 1. Sr and Nd Isotopic Compositions of standards: A Comparion between 2 mass spectrometers at the ANU

	MAT mass spectrometer		MSZ mass spectrometer		Δ
Nd Standards	*$^{143}Nd/^{144}Nd$*	*n*	*$^{143}Nd/^{144}Nd$*	*n*	
BCR-1	0.512653 ± 5	6	0.512608 ±10	7	+45
BHVO-1	0.512999 ± 5	1	0.512967 ±17	7	+32
La Jolla	0.511873 ± 5	17	0.511841 ± 7	4	+32
Sr Standards	*$^{87}Sr/^{86}Sr$*	*n*	*$^{87}Sr/^{86}Sr$*	*n*	
BCR-1	0.704960 ± 10	3	0.704988 ± 40	6	-28
E & A $SrCO_3$	0.707966 ± 15	6	0.708001 ± 12	14	-34
NBS 987*	0.710197 ± 4	67	0.710253 ± 25	35	-56

$\Delta = [(\text{Isotope ratio})_{MAT} - (\text{Isotope ratio})_{MSZ}]10^6$ Uncertainties reported are ±2σm of the ratios, where *n* = number of analyses. * the ratio reported for the MAT mass spectrometer includes 11 analyses of 0.5 to 2.0 nanograms Sr on the filament with an average ratio equal to that given.

Table 2. Chemical and Isotopic Composition of Southeast Australian Peridotite Xenoliths

Locality	Sample	Rb	Sr	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	Sm	Nd	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	ε_{Nd}	T_{DM}
Anakies	2604	0.144	12.75	0.033	0.70457 ±7	0.139	0.848	0.099	0.512654 ±26	0.3	661
Porndon	84402	0.063	6.298	0.029	0.70468 ±5	0.119	0.455	0.158	0.512569 ±62	-1.3	1584
"		0.045	5.762	0.023	0.70467 ±4	0.125	0.467	0.162	0.512568 ±24	-1.4	1708
Leura	2640	0.053	5.054	0.030	0.70486 ±4	0.104	0.420	0.150	0.512788 ±40	2.9	867
Leura	2642	0.042	8.588	0.014	0.70370 ±20	0.175	0.425	0.249	0.513187 ±34	10.7	
"		0.051	8.348	0.018	0.70360 ±5	0.156	0.386	0.245	0.513176 ±28	10.5	
Leura	2769	0.232	11.58	0.058	0.70416 ±5	0.203	0.774	0.159	0.512831 ±18	3.8	890
Leura	85168	0.156	10.73	0.042	0.70387 ±3	0.239	0.870	0.166	0.512844 ±22	4.0	978
Bullenm'	BM134	1.854	53.46	0.100	0.70524 ±3	0.701	3.959	0.107	0.512649 ±20	0.2	717
Noorat	2700	0.371	41.86	0.026	0.70388 ±7	0.339	1.805	0.114	0.512686 ±24	0.9	711
Noorat	84413	36.32	88.61	1.183	0.70550 ±3	1.011	5.321	0.119	0.512558 ±26	-1.6	953
"		28.17	90.20	0.903	0.70557 ±5	0.975	4.992	0.118	0.512588 ±24	-1.0	896
"		31.84	88.88	1.034	0.70554 ±4	1.069	5.493	0.118	0.512560 ±26	-1.5	940
Shadwell	2669	0.110	23.90	0.013	0.70558 ±4	0.282	1.823	0.094	0.512314 ±24	-6.3	1063
Shadwell	84438	22.46	92.30	0.703	0.70509 ±3	1.211	5.364	0.137	0.512704 ±24	1.3	887
Gambier	2728	0.071	7.877	0.026	0.70357 ±10	0.152	0.441	0.209	0.513118 ±40	9.4	
"			8.189		0.70338 ±4		0.544		0.513099 ±64	9.0	
"		0.066	7.652	0.025	0.70342 ±4	0.143	0.424	0.204	0.513108 ±50	9.2	
Gambier	2730	0.393	3.373	0.336	0.70838 ±4	0.087	0.385	0.136	0.512473 ±38	-3.2	1325
"		0.385	3.366	0.330	0.70834 ±4	0.072	0.313	0.140	0.512482 ±32	-3.0	1378
Gambier	2736	0.201	2.810	0.207	0.70713 ±9	0.076	0.331	0.139	0.512426 ±44	-4.1	1473
"		0.205	2.836	0.218	0.70708 ±4	0.070	0.296	0.143	0.512418 ±24	-4.3	1573

Elemental concentrations are given in ppm and have analytical uncertainties of ≤ ± 0.5%. Uncertainties in isotope ratios are ± 2σm and represent intra-run statistics. All measurements were done on the MSZ mass spectrometer, see Table 1 for information on isotopic standards analyses. ε_{Nd} notation as reported in [5]. T_{DM}, the depleted mantle model ages, were calculated as in [47]. Bullenm' = Bullenmerri

Table 3. Chemical and Isotopic Compositions of Pyroxene and Phlogopite Separates

Sample	Mineral	Rb	Sr	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	Sm	Nd	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	ε_{Nd}
2604	CPX	0.248	498.5	0.0014	0.70452 ±3	5.406	33.13	0.099	0.512612 ±20	-0.5
"	CPX-r	0.299	514.4	0.0017	0.70448 ±3	6.100	38.00	0.097	0.512644 ±22	0.1
84402	CPX	0.087	159.0	0.0016	0.70468 ±5	3.098	11.36	0.165	0.512639 ±14	0.0
"	CPX-L	0.059	147.3	0.0012	0.70460 ±2	2.356	8.620	0.165	0.512688 ± 7	1.0
BM-134	CPX	0.116	272.0	0.0012	0.70505 ±4	1.853	11.55	0.097	0.512625 ±16	-0.3
84413	CPX	1.019	336.1	0.0086	0.70710 ±4	6.672	32.37	0.125	0.512450 ±20	-3.7
"	CPX-L	0.018	269.5	0.00019	0.70721 ±2	4.900	24.03	0.123	0.512443 ± 5	-3.8
"	Phologpite	200.8	197.3	2.9381	0.70498 ±4	0.018	0.111	0.096		
84438	CPX	0.855	214.0	0.0115	0.70534 ±5	5.418	22.70	0.144	0.512654 ±20	0.3
"	CPX-L	0.127	194.6	0.0019	0.70506 ±2	4.502	18.82	0.145	0.512691 ± 7	1.0
2730	CPX	0.348	61.2	0.0164	0.70779 ±3	1.364	5.813	0.142	0.512598 ±34	-0.8
2905	CPX-L	0.099	79.72	0.0036	0.70248 ±1	2.460	5.896	0.252	0.513303 ± 6	13.0
"	OPX-L	0.0064	0.2383	0.0777	0.70314 ±1	0.01567	0.02643	0.357	0.513303 ±20	13.0

CPX = clinopyroxene, OPX = orthopyroxene, r = repeat dissolution, L = opticallly pure and HF-HCl washed separates. CPX-L and OPX-L isotopic measurements were done on the MAT mass spectrometer, all others were done on the MSZ mass spectrometer; see Table 1 for comparison of isotopic standards analyses. Element concentrations are in ppm. See Table 2 for additional details.

CHAPTER 3

The Chemical and Isotopic Composition of the Lower Eastern Australian Lithosphere

by W.F. McDonough, R.L. Rudnick and M.T. McCulloch

In (Drummond, B., ed.) The Eastern Australian Lithosphere
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ABSTRACT

Petrological, chemical and isotopic data for granulite facies xenoliths entrained in Mesozoic and Cenozoic basalts from eastern Australia indicate that the lower crust is generally mafic, though intermediate to felsic compositions are observed and may represent common lithologies in restricted zones. The majority of the mafic xenoliths are cumulates from mafic magmas or restite material left after the extraction of granitic melts from mafic-intermediate precursors; others represent crystallized basaltic melts. Isotopic data suggest that crustal underplating by mafic magmas occurred during the Palaeozoic and Cenozoic. Seismic data for eastern Australia indicate that the depth to the Moho is variable (35-55 Km) and that in some regions the Moho is transitional. Similarly, integrated petrological, geochemical and isotopic data for spinel-bearing lherzolite and harzburgite xenoliths allow development of an internally consistent, multistage evolutionary model for the stabilisation and growth of the eastern Australian lithospheric mantle. The bulk of this region consists of refractory peridotite which has experienced multiple episodes of melt extraction and incompatible element enrichment, which produced significant chemical and isotopic heterogeneities. Growth of the eastern Australia lithospheric mantle is believed to have occurred by the accretion of intrinsically buoyant, refractory peridotite diapirs. Later tectono-magmatic reactivation episodes are recorded in the xenoliths, these events occurred in an intraplate and/or divergent plate tectonic environment. The presently available Sr and Nd isotopic data for upper mantle xenoliths from eastern Australia do not provide age constraints on lithosphere formation.

1. INTRODUCTION

Petrological, chemical and isotopic studies of upper crustal rocks have led to a self consistent model for the bulk composition and growth of the upper continental crust through time (McCulloch and Wasserburg, 1978; Taylor and McLennan, 1985). In contrast, the lower crust and subadjacent lithospheric mantle are isotopically, geochemically and geophysically less well known. Samples of deep crust are limited to xenolith fragments entrained in basalts and kimberlites, and rocks of tectonically emplaced high-grade metamorphic terrains. In eastern Australia numerous Cenozoic alkali basalts contain a variety of granulitic, eclogitic and peridotitic xenoliths which provide crucial information on the composition and origin of the lower crust and lithospheric mantle. In addition, the basalts themselves can provide information about the averaged regional composition of the lowermost lithospheric mantle (Chen and Frey, 1985; McDonough et al., 1985).

Lower crustal xenoliths throughout the world are characterised by dominantly mafic lithologies (Kay and Kay, 1981), although felsic and metasedimentary lithologies are locally abundant (Padovani and Carter, 1977; Leyreloup et al., 1977). This is in marked contrast to the typical lithologies of granulite facies terrains, which tend to be dominated by intermediate to felsic rocks (Kay and Kay, 1981). Whereas granulite xenoliths are demonstrably fragments of present-day lower crust (as evidenced by their high pressure mineralogies and decompression features), the relationship of granulite terrains to the lower crust is uncertain. If granulite terrains form primarily in continental collision zones (Newton and Perkins, 1982), they simply represent supracrustal rocks which have been transiently buried to great depths. Therefore, the study of granulite facies xenoliths may provide the most important constraints on lower crustal composition.

Studies of upper mantle xenolith suites worldwide show that the subcontinental lithospheric mantle is composed of ultramafic rocks, dominated by lherzolites and harzburgites, although other rock types, mainly pyroxene-rich and of cumulate origin, are found (Frey and Green, 1974; Wilshire and Shervais, 1975; Frey and Prinz, 1978; Irving, 1980; Nixon et al, 1981). Direct sampling of the subcontinental lithospheric mantle is usually restricted to xenoliths in alkali basalts and kimberlites; the only other source of this material being alpine peridotites which are dominantly composed of lherzolite and harzburgite with lesser amounts of dunite and pyroxenite (Frey, 1984). These bodies are more probably fragments of the suboceanic or continental margin lithospheric mantle. Studies on eastern Australian ultramafic xenolith suites have been fundamental in establishing models on the growth and composition of the subcontinental lithospheric mantle (e.g., Frey and Green, 1974; Irving, 1980; Nickel and Green, 1984).

Through systematic studies combining petrographic, chemical and isotopic data on these fragments of the eastern Australian deep lithosphere, we can develop models for the composition, structure and growth history of this region. This contribution examines the available data on lower crustal and upper mantle xenoliths in eastern Australia and their host basalts and develops a framework for understanding this region. New data are presented from several ongoing studies of lower crustal and upper mantle xenoliths and their host basalts.

2. The Lower Crust

Xenoliths with granulite facies mineralogies occur in a variety of young basaltic scoria cones, maars and tuff rings and older kimberlitic diatremes that intrude rocks of variable crustal ages throughout eastern Australia (Table 1; see summaries by Ferguson et al, 1979; Sutherland and Hollis, 1982; Griffin and O'Reilly, 1986). Thermobarometry for coexisting phases in these xenoliths yields high pressures and temperatures (in the range of 0.7 to 1.2 GPa and 600-1100°C, see Table 1 for references), which, coupled with the commonly observed decompression features, suggest a deep crustal origin for these rocks. Most of the xenolith-bearing basaltic and kimberlitic occurrences were emplaced through rocks of the Tasman fold belt, which have Palaeozoic depositional and crystallisation ages, but Proterozoic mantle extraction ages (McCulloch and Chappell, 1982; Hensel et al., 1985). Several xenolith localities lie in regions of older crust: the Calcutteroo and Kayrunnera kimberlitic pipes in South Australia and New South Wales, respectively, were emplaced through Proterozoic sediments; and xenolith-bearing basalts from the McBride province, N. Queensland, were erupted through metamorphic rocks of the Proterozoic Georgetown Inlier.

Lithologies of the granulite xenoliths are predominantly mafic, but intermediate to felsic granulite xenoliths have been observed at Delegate, N.S.W. (Lovering and White, 1969), Calcutteroo and White Cliffs, S.A. (Ferguson et al., 1979; McCulloch et al., 1982; Arculus et al., 1987), McBride province, north Queensland (Rudnick and Taylor, this volume) and the Newer volcanic province (Rudnick, unpubl.). Felsic xenoliths are abundant only in the case of the Newer volcanic province, where they are the only crustal xenoliths observed in several vents (e.g., Mt. Leura, Mt. Noorat). The felsic xenoliths generally show more severe decompression effects (for example, sillimanite and garnet-bearing felsic xenoliths from the Newer volcanics have pumiceous textures due to melting) and they have therefore generally not been included in geochemical studies.

Table 1 summarises published petrologic studies on lower crustal xenoliths from eastern Australia and the following paragraphs summarise the chemical and isotopic data available on these suites. The major conclusion reached by more recent petrologic studies are that the eastern Australian lower crust is mafic, and interleaving of this material with mantle lherzolite creates a transitional Moho, which extends over approximately 30 km depth range (Ferguson et al., 1979; Wass and Hollis, 1983; O'Reilly and Griffin, 1985). Debate continues as to the depth at which spinel lherzolites become dominant lithologies (see below).

A mafic lower crust may be the result of two genetically distinct processes: (1) the crystallisation of, and/or crystal accumulation from, mafic magmas intruded into the deep crust, or (2) removal of partial melts from mafic to intermediate rocks in the deep crust, leaving a mafic residue. In the absence of obvious igneous textures, distinguishing between these two origins for mafic xenoliths is only possible by detailed geochemical and petrologic studies, and to date few of these have been completed.

Wilkinson (1975) and Wilkinson and Taylor (1980) reported on the petrology and composition of a suite of ultramafic to mafic granulite xenoliths from Boomi Creek, New South Wales (NSW). Additionally, Stolz (1984) reported similar information on comparable xenoliths from Walcha, NSW. These studies showed coherent geochemical correlations for both compatible and incompatible trace elements in each xenolith suite, and concluded that the xenolith suites represent cogenetic cumulates which crystallised from a tholeiitic melt in the deep crust; no cumulate textures were preserved.

Arculus et al. (1987) summarise petrologic and geochemical data for a variety of mafic granulite and eclogite xenoliths from 7 widespread localities in South Australia, Victoria and New South Wales. They note most of the xenoliths have basaltic compositions, and display a wide range in silica saturation from nepheline-normative to quartz-normative. Trace element compositions of the lower crustal xenoliths are highly variable; some have apparent basaltic characteristics whereas others show enrichments in certain trace elements (e.g., Ba, Sr, Pb and Nb), which are not attributable to igneous processes such as crystal accumulation alone. Arculus et al. (1987) conclude that these xenoliths represent basaltic melts, some locally enriched in cumulus phases or contaminated by interactions with pre-existing crust, that were later metamorphosed at higher pressures than the original fractionation events. Additional processes, as yet uncharacterised, are needed to explain the peculiar enrichments of alkaline earth elements.

In contrast with the highly variable major and trace element compositions of the xenoliths studied by Arculus et al., mafic lower crustal xenoliths from the Chudleigh volcanic province, north Queensland show coherent chemical and isotopic correlations. These correlations were interpreted as reflecting variations produced by simultaneous assimilation and fractionation of basaltic magmas within the deep crust (Rudnick et al., 1986a). In addition, the good correlations between isotope ratios and major and trace element concentrations degrades as the isotopic ratios are back-calculated to earlier times, suggesting the xenoliths are less than 100 Ma old, and are probably related to the Tertiary volcanic activity. The mineral assemblages and corona textures of the Chudleigh province xenoliths were interpreted to reflect a relatively simple P-T history: intrusion and fractional crystallisation of the basaltic magma between 20 to 40 km depth with subsequent isobaric cooling (Rudnick and Taylor, this volume). Therefore, this section of the lower crust seems to be dominated by young basaltic cumulates.

The geochemistry of lower crustal xenoliths from Hill 32 in the McBride province of north Queensland points to diverse origins for these rocks (Rudnick and Taylor, 1987a). The majority of the xenoliths are mafic, but they formed by a variety of processes including crystallisation of mafic magmas, crystal accumulation from mafic and felsic magmas and partial melt extraction from intermediate source rocks. Intermediate and felsic granulite facies xenoliths make up about 25% of the observed rock types and come from sedimentary and felsic igneous protoliths. Ion microprobe U-Pb zircon ages show that all these xenoliths experienced high-grade metamorphism in the late Palaeozoic, which coincides with the eruption of extensive felsic ash flows and emplacement of high-level felsic intrusives. Most of the xenoliths formed during this orogeny, although several originally crystallised in the Proterozoic (Rudnick and Williams, 1987). It is noteworthy that the two zircon-bearing mafic xenoliths with melt-like compositions appear to have formed during the Palaeozoic granite-forming events. They may thus represent mantle-derived heat sources which may have caused the crustal melting.

Figure 1 shows the available Nd and Sr isotopic compositions of eastern Australian lower crustal granulite xenoliths. Several eclogitic xenoliths (e.g., cpx-gt and no plagioclase) are also included, although they may represent upper mantle material. The two intermediate to felsic granulites plot far into the lower right quadrant, reflecting long term Rb and LREE enrichments and their supracrustal origin. The mafic granulite xenoliths fall along, and to the right of, the present-day mantle array. For the Chudleigh province mafic granulites the divergence to the right of the mantle array can be explained by assimilation of crustal materials with high $^{87}Sr/^{86}Sr$ and negative ε_{Nd} (Rudnick et al., 1986a). The isotopic compositions of mafic granulites from the Delegate breccia pipe, N.S.W. are given in Table 2, along with the composition of the host nephelinite. These samples have LREE-enriched patterns and plot along an extension of the mantle array, albeit many at negative ε_{Nd} values. It has been postulated that these xenoliths formed as basaltic melts which intruded the base of the crust and contain variable proportions of cumulate phases (Arculus et al., 1987). Therefore, the spread of these data on the isotope diagram (Fig. 1) may reflect their derivation from isotopically distinct mantle source regions, variable residence times within the deep crust and/or mixing with a crustal component. One eclogite from Delegate (69-27) has a very high present-day ε_{Nd} value of +15.7. This sample is strongly LREE-depleted ($^{147}Sm/^{144}Nd = 0.337$), and had an ε_{Nd} of +14.0 at 170 Ma (the age of the Delegate pipe (Compston and Lovering, 1969)). If this sample originally plotted along the mantle array at the time of its crystallisation, it has a minimum age of 395 Ma. Interestingly, this model age is similar to the crystallisation age of granites in this region of the Tasman fold belt (Williams et al., 1983), suggesting that igneous activity which formed the eclogite may have provided a heat source for crustal melting. The Calcutteroo mafic granulites generally fall in a scattered field to the right of the mantle array, with about half of the samples plotting in the upper right quadrant. The REE patterns of these xenoliths are quite variable, only one or two show geochemical characteristics of cumulates (McCulloch et al., 1982) and their low Rb contents are unlikely to reflect the original concentrations. If the isotopic ratios of these xenoliths are back-calculated to earlier times, the data still fall far to the right of the mantle array, suggesting that these samples originally had higher Rb/Sr ratios and that they have experienced a long-term Rb depletion.

In summary, the highly variable Sr and Nd isotopic compositions of lower crustal xenoliths from eastern Australia reflects the source regions of the rocks (i.e., mantle-derived melts and/or cumulates versus supracrustal rock types), and the processes which affected them during and after their original crystallisation. Some xenoliths have relatively primitive isotopic compositions and appear to represent mantle-derived melts or cumulates, whereas others, with more evolved isotopic compositions, represent mixtures of mantle-derived melts and supracrustal material. Still other xenoliths are high-grade supracrustal material. Many of the eastern Australian granulite facies xenoliths can be shown to have experienced Rb depletion after crystallisation, probably at lower crustal pressures and temperatures. The age of crystallisation for one suite of mafic xenoliths (Chudleigh province) is inferred to be relatively young (<100 Ma), whereas depleted mantle Nd model ages (Table 2) for other xenoliths are older (400 Ma for the eclogite from Delegate and 2170 Ma for a felsic granulite from Calcutteroo).

Until more detailed geochemical and isotopic studies are performed on spatially associated suites of lower crustal xenoliths, it is impossible to determine whether the mafic lower crust prevalent throughout eastern Australia is primarily the result of cumulate processes, or whether a significant proportion of the xenoliths represent restite material left after extraction of granitic melts. The abundant granites throughout the Tasman fold belt require mafic residual rocks to be present in the deep crust

(Compston and Chappell, 1979; Chappell, 1984), so it appears likely that some of this residual material would be sampled as xenoliths by the Tertiary basalts.

3. The Subcontinental Lithospheric Mantle

The most common type of ultramafic xenolith found in eastern Australia are the spinel-bearing lherzolite and harzburgite xenoliths, which are presumed to represent the bulk of the lithospheric mantle. Other upper mantle materials, which are considered to comprise only a minor volume of this region, are the ultramafic cumulate suites (e.g., Al-Ti-rich pyroxenites and related rocks) and megacrysts. The major and trace element compositions of ultramafic cumulate suites and megacrysts have provided data on the local passage of basaltic magmas through the lithospheric mantle. The chemical compositions of spinel-bearing lherzolite and harzburgite xenoliths (and the deeper, garnet-bearing varieties) have been used to characterize the overall nature and composition of the eastern Australian lithospheric mantle. Also, new laboratory seismic measurements are consistent with a dominantly peridotitic lithospheric mantle in eastern Australia (Bezant, 1986).

Ultramafic xenoliths were subdivided into 2 broad groups based on their composition and presumed origin by Wilshire and Shervais (1975). Frey and Prinz (1978) suggested an alternative classification which does not emphasize the xenolith origin, and avoids characterising a suite of xenoliths by a single lithologic name. The Cr-diopside group (Wilshire and Shervais, 1975) (or type I of Frey and Prinz, 1978) is dominated by lherzolite and harzburgite xenoliths, although less abundant Cr and Mg-rich dunites, wehrlites, olivine websterites, orthopyroxenites and clinopyroxenites are also included in this group. The second group, the Al-augite group (Wilshire and Shervais, 1975) (or type II of Frey and Prinz, 1978), includes Al-Ti-Fe-rich xenoliths: pyroxenites, wehrlites, websterites and the like. It is commonly suggested that these type II xenoliths are products of the passage of basalts through the lithospheric mantle, either in association with the present igneous activity or related to earlier events. Composite xenoliths of type I and II lithologies generally show type II assemblages crosscutting type I lithologies, suggesting an intrusive relationship (Wilshire et al., 1980; Irving, 1980).

The following sections summarise published and ongoing geochemical and isotopic studies of eastern Australian ultramafic xenoliths based on these subdivisions.

3.1. *Lherzolites and harzburgites (type I lithologies)*

Throughout eastern Australia Cenozoic basalts carry lherzolite and harzburgite xenoliths, which have been the focus of numerous petrological and geochemical studies (Wilshire and Binns, 1961; Frey and Green, 1974; Wilkinson, 1975; Wilkinson and Binns, 1977; Ferguson et al, 1977; Varne, 1977; MacRae, 1979; Ferguson and Sheraton, 1979; Irving, 1980; BVSP, 1981; Mitchell and Keays, 1981; Dal Negro et al, 1984; Nickel and Green, 1984; Sutherland et al, 1984; Griffin et al, 1984). Many of these studies have characterised the spectrum of petrographic and mineral/whole rock compositions for these xenoliths. These xenoliths show a restricted range in mineralogies and major element compositions.

Eastern Australian lherzolite and harzburgite xenoliths usually have a 4 phase mineralogy of olivine (~50 to ~85%), orthopyroxene (~35 to ~5%), clinopyroxene (~20 to ~2%) and spinel (<5%). Some also have limited quantities (<5%) of amphibole, which is pargasitic in composition, or phlogopitic mica. A variety of textures are found in these xenoliths, although coarse and porphyroclastic varieties (Harte, 1977) are most common (e.g., Frey and Green, 1974; Dasch and Green, 1975; Nickel and Green, 1984). Rare foliated peridotites, in which the planar fabrics are defined by tabular olivine and/or elongate grains of spinel and clinopyroxenes, are found throughout eastern Australia. The mineral chemistry of the lherzolite and harzburgite xenoliths is similar to that of other such xenoliths worldwide: olivines display a limited range of Mg/(Mg + Fe) values, usually Fo_{88-92}, and pyroxenes show only minor compositional variations, mostly in their Al_2O_3 and Cr_2O_3 contents. The whole rock major element compositions of these xenoliths reflect a residual peridotite which formed through extraction of variable amounts of a basaltic melt, and trace element compositions reflect a later, variable addition of an incompatible element enriched component (Frey and Green, 1974).

The estimated equilibration pressures and temperatures for these xenoliths indicate their upper mantle origin. Most equilibrated between 900° and 1100° C, based upon two pyroxene thermometry (Frey and Green, 1974; Nickel and Green, 1984; Griffin et al., 1984), with the anhydrous lherzolite and harzburgite xenoliths generally having higher temperatures (≥ 1000°C) than the hydrous bearing xenoliths (≤1000°C); see also Figure 1 of Nickel and Green (1984). Fewer studies on the deeper origin, garnet-bearing lherzolite and harzburgite xenoliths from eastern Australia show them to have equilibration temperatures of 980-1300°C, based on garnet-clinopyroxene thermometry (Sutherland et al., 1984).

Estimates of the depths of origin of the spinel-bearing lherzolite and harzburgite xenoliths has been mainly based on mineral stability studies. There is no mineral pair in the spinel-bearing xenoliths which can provide well constrained pressure estimates for these rocks, excepting the olivine - clinopyroxene geobarometer which requires high quality Ca data, and such data are not available for most of these xenoliths (Nickel and Green, 1984). The experimental study of O'Neill (1981), and related earlier studies, suggest that spinel peridotite xenoliths are stable above 50 to 65 kms depth (1.6 to 2.0 GPa), below which lherzolites are in the garnet stability field. The garnet-orthopyroxene geobarometer (Harley and Green, 1982), when applied to eastern Australian garnet-bearing lherzolite and harzburgite xenoliths using clinopyroxene-garnet temperatures, yields pressures of between 1.5 to 2.4 GPa (50-80 km) (Ferguson et al., 1977; Ferguson and Sheraton, 1979; Sutherland et al., 1984).

Recently Griffin et al. (1984) and O'Reilly and Griffin (1985) calculated a geotherm based upon thermobarometric estimates of garnet pyroxenite xenoliths from Bullenmerri and Gnotuk maars, Victoria. By projecting the 2 pyroxene temperatures of spinel lherzolites on to this geotherm, they estimated the depth of origin for these rocks to be between 25-50 km depth (0.8-1.6 GPa) in the upper mantle. They then compare these results with seismic refraction profiles from the Lachlan Fold Belt, N.S.W., and suggest that throughout eastern Australia the crust is only 25-30 km thick and that it is underlain by a mixture of peridotite, pyroxenite and granulite, which, when combined with the very hot temperatures inferred from their geotherm, explainsthe relatively low V_p (6.5-7.4 km/sec) observed at 25-40 km depths. They also suggest that the previously defined seismic Moho at 55 km represents the transition from spinel lherzolite to garnet lherzolite. This contrasts with previous crustal models (Ferguson et al., 1979; Finlayson et al., 1979) primarily by assigning a shallow depth to spinel lherzolites. Because of the implications of this model, and the pit falls which are often associated with derivation of regional geotherms from xenolith suites, the assumptions used in their model bear examination.

Firstly, although Griffin et al. (1984) used primary mineral assemblages of garnet pyroxenites to define their geotherm, they presented evidence that about 1/4 of these pyroxenites contain secondary mineral assemblages, often in the form of symplectic coronas surrounding garnets. These secondary assemblages yield different (both higher and lower) equilibration temperatures by 15 to 40°C, using the Wood and Banno (1973) 2 pyroxene thermometer, or 25 to 77°C using the Wells thermometer (Table 7 of Griffin et al., 1984). These features suggest disequilibrium and cast doubt on the assumption of mineralogical equilibrium which must be made to construct a geotherm.

Secondly, it is necessary to consider the precision with which geothermometers can be applied. The two pyroxene and garnet-clinopyroxene thermometers have uncertainties of ±5-7%, or about ±50°-70°C at 1000° C, based just on the thermodynamic calibrations (Wells, 1977; Ellis and Green, 1979). Because of the extreme temperature dependence of the geobarometer used by Griffin et al. (0.4 GPa per 100°C, Harley and Green (1982)), a temperature uncertainty of ±50-70°C leads to pressure uncertainties of ±0.2-0.3 GPa. Due to the steepness of the postulated geotherm, if the temperatures are lowered by only 50°C, then the corresponding pressures for spinel lherzolite xenoliths increase from 0.8-1.6 GPa (25-50 km) to 1.1 to 1.9 GPa (35 to 60 km). These uncertainties *must* be considered when comparing xenolith data with refraction profiles.

Thirdly, agreement of equilibration temperatures between lherzolite and pyroxenite portions of composite xenoliths was used by Griffin et al. (1984) to justify plotting lherzolite xenoliths on their pyroxenite-derived geotherm. However, numerous studies of such composite xenoliths have shown that lherzolites adjacent to pyroxenite dykes are chemically zoned in their bulk rock and mineral compositions (see below; Wilshire and Shervais, 1975; Wilshire et. al., 1980; Irving, 1980). The Fe-rich nature of the composite lherzolites described by Griffin et al. (Fo_{82} versus Fo_{86-91} for most type I spinel lherzolites) attests that similar effects occurred in these lherzolites. Therefore, it is likely that the composite lherzolite xenoliths were equilibrated by the very events(s) that formed them and should not be used as evidence of pervasive equilibration of spinel lherzolite to the calculated geotherm.

Finally, the depth of the spinel-garnet transition for lherzolites is not clear cut. Griffin et al. place this transition at 55 km depth, based on the experimental data of O'Neill (1981) (note that the spinel-garnet phase boundary of O'Neill is not plotted correctly in Fig. 8 of Griffin et al. -- the boundary is steeper than shown, but it crosses their geotherm at the same position). However, if one uses thermobarometry of xenoliths, a much deeper phase boundary is suggested. A spinel-garnet lherzolite xenolith from Jugiong, N.S.W., is a sample from this transition zone (Ferguson et al., 1975; Ferguson and Sheraton, 1979). Using the same thermobarometers employed by Griffin et al. to generate their geotherm, this xenolith yields equilibration conditions of 2.2 GPa (75 km) and 1150°C, 20 km deeper than postulated by Griffin et al. for this phase boundary. Nickel and Green (1985), who have recently improved the Harley and Green geobarometer, concluded that this xenolith was equilibrated at about 2.0 GPa (65 Km) and 1050°C. Regardless of which of these estimates are used, the equilibration temperature and pressure of this spinel-garnet lherzolite does not agree with data from experimental studies. This implies either the spinel-garnet transition is deeper than predicted by experimental data and so the observed increased Vp at 55 km depth does not coincide with this phase change or, the garnet-orthopyroxene barometer gives systematically high pressures (which may be due to overestimated temperatures). In either case these data cast doubt on the accuracy of the geotherm.

We conclude that the Griffin et al. (1984) geotherm is probably representative of crustal areas in which active volcanism occurs and is equivalent to the alkaline province geotherm of Jones et al. (1983). However such high temperatures are transient phenomena (Irving, 1976; Harte et al., 1981) and not representative for all of present-day eastern Australia. In addition, the inferences on crust-mantle structure derived from this geotherm are not steadfast. In particular, there is no thermobarometric or geophysical evidence that spinel lherzolites occur as shallow as 25 km depth. Finally, in agreement with earlier studies (Ferguson et al., 1979; Finlayson et al., 1981), we suggest that the seismic velocity profile of this region reflects a dominantly mafic lower crust (see below).

Major element compositions of the spinel-bearing lherzolite and harzburgite xenoliths from eastern Australia (e.g., BVSP, 1981; Nickel and Green, 1984) are similar to those of spinel lherzolites worldwide (see Frey, 1984 for a review). The refractory elements (e.g., MgO, Cr and Ni) define positive correlations with one another and the readily fusible major and minor elements (e.g., CaO, FeO, Al_2O_3, TiO_2, Na_2O) displaying negative correlations with MgO. The trace element compositions of some of these xenoliths have been characterized in detail (e.g., Frey and Green, 1974; Irving, 1980; BVSP, 1981; Mitchell and Keays, 1981). The peridotite xenoliths from eastern Australia display a range of REE patterns from LREE-enriched to LREE-depleted (Fig. 2). The relative abundances of Ir, Os and Pd in these xenoliths are close to the chondritic values, whereas Re and Au contents are more variable (BVSP, 1981; Mitchell and Keays, 1981). These siderophile element abundances are typical for many garnet- and spinel-bearing lherzolite and harzburgite xenoliths from other localities around the world (BVSP, 1981).

From the various studies on spinel-bearing lherzolite and harzburgite xenoliths from eastern Australia, internally consistent geochemical and petrological models have been developed for the origin and evolution of the lithospheric mantle. Foremost among these is the classic study by Frey and Green (1974) on the mineralogy and geochemistry of a representative spectrum of lherzolites and harzburgites from Victoria and South Australia. A later study (Nickel and Green, 1984), using a larger number of samples, has confirmed these earlier observations and interpretations. Major and trace element data from these studies showed that the underlying lithospheric mantle has experienced at least a two stage history. The first stage involved the extraction of basaltic melt from a homogeneous peridotite (commonly assumed to be pyrolite (Ringwood, 1966)), and the second stage consisted of an enrichment event, in which various incompatible elements were added back into the refractory peridotite. Support for this model comes from Sr and Nd isotope studies (discussed below).

The early removal of a basaltic melt component is reflected by low and variable amounts of clinopyroxene, and depletions in Ca, Al, Na, Fe, Sc, V, Cr and the heavy REE (elements that characterise the clinopyroxene component). This event also produced depletions in incompatible trace elements (elements which partition strongly into melts). Later, the residual peridotites were enriched by the addition of a volumetrically minor, incompatible element-rich component. This enrichment was found to affect all of the samples to varying degrees, but surprisingly, as noted by Frey and Green (1974), the most refractory inclusions in terms of depletion in Ca, Al, Fe, etc., contain the highest relative abundance of incompatible trace elements. This second stage enrichment event has been identified in many lherzolite and harzburgite xenolith suites worldwide (Frey, 1984) and is commonly referred to as a 'metasomatic' event. Frey and Green (1974) showed that the two evolutionary stages were not genetically related and suggested that there may be a significant time difference between them.

Data from Sr, Nd and Pb isotope studies of southeastern Australian lherzolite and harzburgite xenoliths also show that these rocks have developed through a complex, multstage evolution. The Pb isotopic compositions of some of these xenoliths requires a minimum of two stages (Cooper and Green, 1969). Many of the southeastern Australian lherzolites and harzburgites studied possess chondrite-normalized LREE enriched patterns and positive ε_{Nd} values. Since positive ε_{Nd} values reflect long-term LREE depletion (i.e., Sm/Nd > 0.31), these peridotites must have experienced a relatively recent LREE enrichment. Similar combined chemical and isotopic data on lherzolite xenoliths from the same region (Chen and Frey, 1980; 1981) has also been used to argue for an early melting event and at least 2 "metasomatic" events.

Sr and Nd isotopic compositions vary widely for southeastern Australian spinel-bearing lherzolite and harzburgite xenoliths (Fig. 3). This variation is greater than that previously reported for a single suite of spinel lherzolite xenoliths (Jagoutz et al, 1980; Menzies and Murthy, 1980; Stosch et al, 1980; Mengel et al, 1984; Roden, M.F. et al, 1984; Roden, M.K. et al, 1984; Betton and Civetta, 1984; Menzies et al, 1985). In addition, analyses of many samples from Mt Leura and Mt Gambier show that a wide range in isotopic compositions may be present at a single center (Burwell, 1975; Chen and Frey, 1981; McDonough and McCulloch, 1987). Enriched isotopic compositions are also found for clinopyroxene separates from Lake Bullenmerri garnet pyroxenite xenoliths (Fig.3, Table 2). These xenoliths have high $^{87}Sr/^{86}Sr$ ratios and negative ε_{Nd} values. The diversity of Sr and Nd isotopic compositions in the southeast Australian lithospheric mantle contrasts with the restricted isotopic compositions measured for the xenolith host, Newer basalts (McDonough et al., 1985).

Studies of sheared garnet lherzolites from south Africa showed these rocks to be fertile in terms of major element compositions, with chondritic REE patterns and depleted Nd and Sr isotopic compositions. In contrast, granular lherzolites have depleted major element compositions, LREE enriched patterns and evolved Nd and Sr isotopic compositions (Nixon et al., 1981; Richardson et al., 1986). Sheared lherzolites have not been reported from eastern Australia. Foliated peridotite xenoliths from eastern Australia have Sr and Nd isotopic compositions indistinguishable from those of the non-foliated equivalents. Interestingly however, foliated lherzolites from Mt Gambier (see samples 2730, and 2736 of Dasch and Green, 1975) possess the highest $^{87}Sr/^{86}Sr$ ratios measured for the upper mantle beneath southeastern Australia, although they do not possess the lowest ε_{Nd} values.

Good correlation (r = 0.99) between Sr and Nd concentrations in the peridotite xenoliths and their clinopyroxene separates gives a nearly constant Sr/Nd ratio of 15 (Fig. 4) (McDonough and McCulloch, 1987). Stosch and Lugmair (1986) reported a similar correlation for spinel peridotite xenoliths from Europe. The average Sr/Nd ratio of these peridotites is similar to the bulk earth value of 17 (Sun, 1982), and Sr/Nd ratios of primitive (i.e., unfractionated) basalts from mid-ocean ridges

(MORBs) (Sr/Nd = 10-15), and intraplate settings (ocean island basalts (OIBs) and continental intraplate basalts) (Sr/Nd = 15-20) (McDonough and McCulloch, 1987). In contrast, island arc basalts have much higher Sr/Nd ratios of >30. These higher ratios suggest either a high Sr/Nd ratio in the source of island arc basalts (if Sr is not fractionated from Nd during melting), or indicate that the residue would have a subchondritic Sr/Nd ratio (if Sr is fractionated from Nd during melting of a chondritic source). The Newer basalts, hosts for the southeastern Australian xenoliths, have a typical intraplate Sr/Nd ratio of 19.5 (McDonough et al., 1985). These data suggest that the constant Sr/Nd ratio in peridotite xenoliths reflects the added, incompatible element-enriched component, which is wholly associated with intraplate magmatism (McDonough and McCulloch, 1987); the data are not consistent with the signature expected for the mantle source of island arc magmas. However, this does not exclude the possibility of such a tectonic setting in this region at sometime in the past.

Early Rb-Sr isotopic studies on southeast Australian lherzolite and harzburgite xenoliths found correlations between $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios for whole rocks (Burwell, 1975) and mineral phases (Dasch and Green, 1975), and both studies speculated that these correlations had age significance. The proposed ages (600 to 700 Ma) were suggested to represent the time of the last melt extraction experienced by the peridotites, and were related to an early Cambrian orogenic event in the region (Dasch and Green, 1975; Burwell, 1975). Recently, combined Sr and Nd isotopic studies of lherzolite and harzburgite xenoliths (Chen and Frey, 1981; McDonough and McCulloch, 1986; 1987), in some cases for the same samples as the earlier studies, showed that the two isotope systems yield different ages, suggesting that these ages are not significant. These Sr and Nd isotope data have been used to support a model of recent mixing in the mantle and to suggest that these isotope systems do not record a precise timing of mantle events (McDonough and McCulloch, 1987).

As garnet-bearing lherzolites are relatively rare in eastern Australia (Ferguson et al., 1977; Ferguson and Sheraton, 1979; Sutherland et al, 1984) very little is known about the trace element and isotopic compositions of the deeper parts of the eastern Australian lithospheric mantle.

3.2. Al-rich Pyroxenites and related rocks (type II lithologies)

The Al-augite group, or type II ultramafic xenolith suites, are less abundant in eastern Australia. Most studies of these xenoliths have been restricted to descriptions of the relative abundance and variety of rock types found at given localities and aspects of their mineral compositions. Often these studies draw petrographic and chemical analogies with specimens described in more detailed petrological/geochemical studies (e.g., Frey and Prinz, 1978). Detailed petrogenetic studies of these type of xenoliths from eastern Australia include those of Irving (1974b), Knutson and Green (1975), Ellis (1976) and Irving (1980). These xenoliths are considered to represent cumulates which formed by dynamic flow crystallisation of basaltic magmas within the mantle (Irving, 1980) or minerals separated from basaltic magmas by filter pressing, or related processes, at mantle pressures (Wilshire et al, 1980).

Irving (1980) reported petrographic and geochemical data for a variety of composite xenoliths from Cenozoic basalts in northern Queensland and Victoria. These xenoliths consist of lherzolite or harzburgite veined by type II material (clinopyroxenite, wehrlite, websterite or orthopyroxenite). He interpreted these xenoliths as fragments of subcontinental lithospheric mantle intruded by pyroxene-rich cumulate material which separated from basaltic magmas during ascent. Similar composite xenoliths are reported from numerous other worldwide localities (Wilshire et al., 1980) and provide important information on the physical and chemical response of the lithospheric mantle to ascending basaltic magmas. Wilshire and Shervais (1975) and Irving (1980) suggested that pronounced compositional gradients across the contacts of type II veins and lherzolite wall rock reflect the thermal and chemical modification of the mantle produced by the passage of basaltic melts. Irving (1980) proposed that Fe-rich spinel lherzolite xenoliths, purported to be common in the subcontinental lithospheric mantle of eastern Australia (Wilkinson and Binns, 1977), are products of such wall rock-magma interaction. Though not conclusive, this model suggests that the fertile Fe-rich spinel lherzolite xenoliths are a small scale (on the order of tens of centimeters) localised reaction product, and therefore are of limited regional significance.

Wass and coworkers (Wass et al, 1980; Menzies and Wass, 1983) have documented the occurrence of a notable group of xenoliths which are rich in apatite and amphibole. They consider the apatite/amphibole xenolith suite to be distinct from type I and II xenoliths and analogous to pegmatite veins developed within the mantle under a relatively high partial pressure of CO_2 (Menzies and Wass, 1983). These volatile-rich xenoliths represent one end member of a spectrum of lithologies observed for mantle-derived xenoliths.

Sr and Nd isotopic studies on eastern Australian type II xenoliths, apatite/amphibole xenoliths and various megacrysts related to these, show that many have isotopic compositions similar to those of their host basalts or regionally related magmatism (Stuckless and Irving, 1978; Menzies, 1983; Menzies and Wass, 1983). This suggests that they are genetically related to the contemporaneous magmatism, though in some cases not specifically related to their host magma. This situation contrasts strongly with the lack of evidence for genetic links between most type I lherzolite and harzburgite xenoliths and their hosts. Finally, there are other type II xenoliths (e.g., the Lake Bullenmerri garnet pyroxenites) with rather evolved and high $^{87}Sr/^{86}Sr$ ratios and negative ε_{Nd} values (Table 2). These xenoliths have isotopic compositions that are markedly different from their host basalts (McDonough et al., 1985) and are interpreted as pyroxene-rich cumulates formed during earlier magmatic events, which are not related to the present basaltic magmatism.

4. Chemical and Isotopic Systematics of Intraplate Basalts

Basalts provide an additional source of information about the composition of the upper mantle. They are usually grouped by their mineralogy and composition as either tholeiitic, transitional or alkalic. Extensive efforts have been invested in trying to understand the origin of these different basalt types and to characterise their source regions. The combined data of experimental petrology and trace element geochemistry have given us greater insight into the differing origins of these basalt types and have shown that by varying the melting conditions (e.g., temperature, pressure, mantle volatile content and composition, degree of partial melting and source mineralogy) a variety of basalts can be produced (e.g., Ringwood, 1975; Frey et al., 1978; Takahashi and Kushiro, 1983).

Frey et al (1978) identified a series of relatively unfractionated, tholeiitic to alkalic basalts from southeast Australia and characterized the mineralogy and composition of their mantle source regions. More recently McDonough et al (1985) measured their Sr and Nd isotopic compositions and showed that the tholeiitic and alkalic basalts are from different sources.

The systematic chemical and isotopic differences observed in the tholeiitic to alkalic basalts from southeastern Australia has been attributed to mixing between plume-derived and lithospheric mantle-derived melt components (McDonough et al, 1985). In this model the isotopic compositions of tholeiitic basalts are considered to be plume-dominated, since tholeiitic basalts require higher melting temperatures and larger degrees of melting for their genesis. In contrast alkalic basalts require lower degrees of partial melting and may contain a dominantly lithospheric mantle-derived component. Therefore the isotopic composition of the primitive alkalic Newer basalts may represent an averaged isotopic composition of the regional subcontinental lithospheric mantle component (McDonough et al, 1985). More evolved basaltic compositions may have been affected by crustal assimilation. Identical systematic trends in the Sr and Nd isotopic compositions of alkalic and tholeiitic basalts have been recognized in Hawaiian basalts (Fig. 5). Chen and Frey (1985) have proposed a similar mixing model to explain the origin of these differing basalt types. In contrast, a recent study on French Polynesian basalts (Duncan et al., 1986) has identified a condition where the Sr and Nd isotopic compositions of spatially and temporally associated tholeiitic and alkalic basalts show a shift in isotopic composition from that observed in Hawaii and southeastern Australia (Fig. 5). Duncan et al (1986) suggested that the isotope data for French Polynesian basalts could be explained either by the above model, or as an alternative, they suggested a model involving a heterogeneous plume which mixes isotopically different components within the torus of the convecting plume. In either case all of these models are consistent with thermal and mechanical considerations of melts interacting with the base of the lithosphere. The intrusion of hot mantle plumes into the base of the lithosphere during intraplate magmatism would result in large scale melting of the lowermost lithospheric mantle.

Primary and near primary eastern Australian Cenozoic tholeiitic and alkalic basalts display a large range of Sr and Nd isotopic compositions, which falls within the 'oceanic mantle array' (Fig. 6). The NSW leucitites have $^{87}Sr/^{86}Sr$ ratios of 0.7050 to 0.7055 and ε_{Nd} values of 0 to -4 (Nelson et al, 1986), whereas Tasmanian (McDonough et al, 1985) and Norfolk Island alkalic basalts (unpublished data) have $^{87}Sr/^{86}Sr$ ratios of 0.7027 to 0.7033 and ε_{Nd} values of +8 to +5. If the isotopic composition of the alkalic basalts represents an averaged regional melt composition from the lowermost lithospheric mantle, then this range indicates significant isotopic heterogeneity in the lithospheric mantle throughout eastern Australia.

The NSW leucite-bearing lavas outcrop well to the west of the continental dividing range and are considerably further inland than any of the other Cenozoic eastern Australian basalts (Cundari, 1974). These lavas have more evolved Sr and Nd isotopic compositions than those of the Newer volcanics (Fig. 6). In contrast to the NSW leucite-bearing lavas, the Cosgrove olivine leucitite in northern Victoria (Birch, 1978) outcrops only about 100 kms from the nearest centers of the Newer volcanic field and is isotopically similar to the basalts of this province. It is conceivable that isotopic compositions of the NSW potassic lavas reflects a distinctive and possibly older composition of the lowermost lithospheric mantle beneath this region.

5. Origin and Growth of the Lower Portion of the Eastern Australian Lithosphere

Combining these petrological and geochemical data on eastern Australian xenoliths and basalts with geophysical information for the region we can construct a model for the origin and evolution of the lower portion of the eastern Australian lithosphere. This region of Australia is a relatively young part of the Australian continent (McCulloch, 1987) and may therefore have characteristics distinct from other regions of the continent which are part of the stable Australian craton.

Considerable controversy exists concerning the nature of continental growth through time. There appear to be several processes involved, including: lateral accretion via subduction-related magmatism (Taylor and White, 1965; Taylor, 1967), continental addition during intracratonic rifting, which is suggested to be an important Archean growth process (Kröner, 1981), and crustal underplating due to conductive cooling (Oxburgh and Parmentier, 1978). Of these three mechanisms, the underplating model involving mantle growth through conductive cooling may be the least likely to contribute to the long term stability of the lithospheric mantle. A lithosphere which has grown by passive underplating or thermal accretion is not consistent with various petrological, seismological, thermal, gravity and tectonic considerations (Clark and Ringwood, 1964; O'Hara, 1975; Oxburgh and Parmentier, 1978; Davies, 1979; Jordan, 1981; Ringwood, 1982). The material accreted during such a processes would be cooler, chemically unmodified asthenospheric mantle peridotite and once cooled, would be gravitationally unstable. Consequently, this denser portion of the lithospheric mantle would be negatively buoyant with respect to the underlying asthenosphere and likely to be detached from the lithospheric mantle and sink into the asthenosphere (Houseman et al., 1981).

There is strong evidence that the subcontinental lithospheric mantle grows dominantly by the accretion of thermally driven, intrinsically buoyant refractory peridotite diapirs (Clark and Ringwood, 1964; Oxburgh and Parmentier, 1978; Jordan, 1981; Ringwood, 1982). These peridotite diapirs are accreted onto the base of the lithospheric mantle during subduction zone and hotspot related magmatism, where they may be permanently trapped beneath continents. In contrast, in the oceanic lithosphere, they are recycled back into the mantle at subduction zones (Ringwood, 1982). It has been suggested that regions of the lithospheric mantle which have grown by the accretion of refractory peridotite are also susceptible to being detached from the lithospheric mantle and recycled back into the asthenosphere (McKenzie and O'Nions, 1983). However, the temperature gradients and density contrasts required (Houseman et al., 1981) are such that this would be a rare, possibly unlikely, fate for a chemically buoyant region of the subcontinental lithospheric mantle.

The early basaltic melt extraction event, so commonly identified in lherzolite and harzburgite xenoliths, may record the initial development and stabilisation of the subcontinental lithospheric mantle. A once fertile peridotite source region that undergoes partial melting would become less dense, due to extraction of a dense Fe-rich component, and buoyant with respect to the surrounding mantle. The second stage enrichment event, identified in the incompatible trace elements and Sr and Nd isotope compositions of these xenoliths (Frey and Green, 1974; Chen and Frey, 1981; McDonough and McCulloch, 1987), documents later tectono-magmatic reactivation events in the subcontinental lithospheric mantle. The chemical signature recorded in the lherzolites from these later events (in particular the Sr/Nd ratios) are similar to those expected in an intraplate or divergent plate tectonic setting.

Similarly, the composition and growth of the lower continental crust can be related to a series of tectonothermal events. The dominantly mafic lower crustal xenoliths formed through both basaltic underplating of the lower crust (some of which occurred during the Palaeozoic granite-forming orogenies) and partial melt extraction from pre-existing mafic to intermediate rock types. In addition, minor quantities of supracrustal rocks and felsic igneous rocks exist in the lower crust. The supracrustals presumably were tectonically emplaced during continental margin orogenic events. The felsic meta-igneous rocks may have been similarly derived, or may represent near *in situ* melts of intermediate to mafic rock types.

Seismic refraction profiles coupled with petrological/geochemical data for xenoliths in eastern Australia provide a picture of a heterogeneous deep lithosphere throughout the region (Fig. 7). Although still equivocal, the seismic data suggest that the Moho may vary considerably in depth and structure, from a distinct Moho at 35 km in Victoria to a transitional Moho between 50-55 kilometers in the Lachlan Fold Belt, N.S.W. (Finlayson et al, 1979; Finlayson, 1982; Wesson and Gibson, unpublished data). Laboratory measurements of ultrasonic velocities for typical spinel-bearing peridotite xenoliths from Mt. Porndon, Victoria (Bezant, 1986) and mafic lower crustal xenoliths from South Australia and north Queensland (Jackson and Arculus, 1984; Rudnick and Jackson, 1987) support a model of a thick, predominantly mafic granulite lower crust, with spinel lherzolite becoming a volumetrically significant rock type only at depths greater than about 40 km. Such data are consistent with the crustal profiles postulated by Ferguson et al. (1979), Finlayson et al. (1979) and Drummond and Collins (1986).

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Figure Captions

Figure 1. $^{87}Sr/^{86}Sr$ versus ε_{Nd} values of lower crustal xenoliths from eastern Australia. Data sources are from McCulloch et al (1982), Rudnick et al (1986a) and this paper (Table 2). Data fields defining the reference 'Oceanic Mantle Array' are given in McDonough et al (1985); ε_{Nd} are normalized to $^{143}Nd/^{144}Nd = 0.511836$ (CHUR). Open symbols are for garnet pyroxenites, filled symbols are for mafic granulites and half-filled symbols are for felsic to intermediate granulites.

Figure 2. REE pattern for spinel-bearing lherzolite and harzburgite xenoliths from eastern Australia. Data from Frey and Green (1974) and Irving (1980).

Figure 3. $^{87}Sr/^{86}Sr$ versus ε_{Nd} values for spinel-bearing lherzolite and harzburgite xenoliths from southeastern Australia and garnet and clinopyroxene separates from garnet pyroxenite xenoliths from Lake Bullenmerri. Data from McDonough and McCulloch (1987) and Table 2. Data field for the Newer basalts, the host basalts for all these xenoliths, is from McDonough et al (1985). Lherzolite and harzburgite localities include Mt. Porndon, Mt. Shadwell, Mt. Noorat and Anakies, western Victoria. Additional details see Figure 1. Sample with tie line represent analyses of coexisting garnet and clinopyroxene from a Lake Bullenmerri garnet pyroxenite xenolith.

Figure 4. Concentrations of Nd versus Sr for southeastern Australian spinel-bearing lherzolite and harzburgite xenoliths and some of their clinopyroxene mineral separates (McDonough and McCulloch, 1987).

Figure 5. $^{87}Sr/^{86}Sr$ versus ε_{Nd} values of Cenozoic, tholeiitic and alkalic basalts from Hawaii (Chen and Frey, 1985; Roden et al., 1985; Stille et al., 1984), French Polynesia (Duncan et al., 1986) and Newer volcanic province, southeastern Australian (McDonough et al., 1985).

Figure 6. $^{87}Sr/^{86}Sr$ versus ε_{Nd} values of Cenozoic, tholeiitic and alkalic basalts from eastern Australia. Data sources include Menzies and Wass (1983), McDonough et al (1985), Nelson et al (1986), Knutson et al (1986) and McDonough and McCulloch (unpublished). The inset diagram details the variation in $^{87}Sr/^{86}Sr$ versus ε_{Nd} values for tholeiitic and alkalic basalts from

the eastern 2/3 (Victoria region) of the Newer volcanic province; compare with Figure 5, which shows the total variation in $^{87}Sr/^{86}Sr$ versus ε_{Nd} value in the Newer basalts. For additional details see Figure 1.

Figure 7. A simplified continental lithosphere cartoon for eastern Australia emphasizing the chemically and isotopically heterogeneous nature of the crust and mantle and the variable depth of the Moho. The depth to the base of the lithosphere is not specified. The lithospheric mantle is defined as that portion of the lithosphere which is mechanically coupled to the continental crust. The transition from spinel lherzolite to garnet lherzolite (dashed line) is taken from O'Neill (1981). Compositional heterogeneities in the lithospheric mantle (discrete, textured areas) are idealise. These regions would have different chemical and isotopic compositions, which would reflect variations in the amount of melt extracted and the degree of secondary enrichment in incompatible elements. Regions in the lithospheric mantle with type II, Al-Fe-Ti-rich material are not depicted, but are considered to be distributed throughout the region as discrete vein-like bodies. The interaction of a hot mantle plume with the base of the lithospheric mantle is from the model presented in McDonough et al (1985). The considerable volumes of basaltic cumulate materials in the lower continental crust and uppermost lithospheric mantle is based on seismic data (Finlayson et al, 1979), thermobarometry data (Griffin et al, 1984; O'Reilly and Griffin, 1985; Rudnick and Taylor, this volume), and petrological data (Ewart et al, 1980; Kay and Kay, 1983; Wass and Hollis, 1983; Rudnick et al, 1986a).

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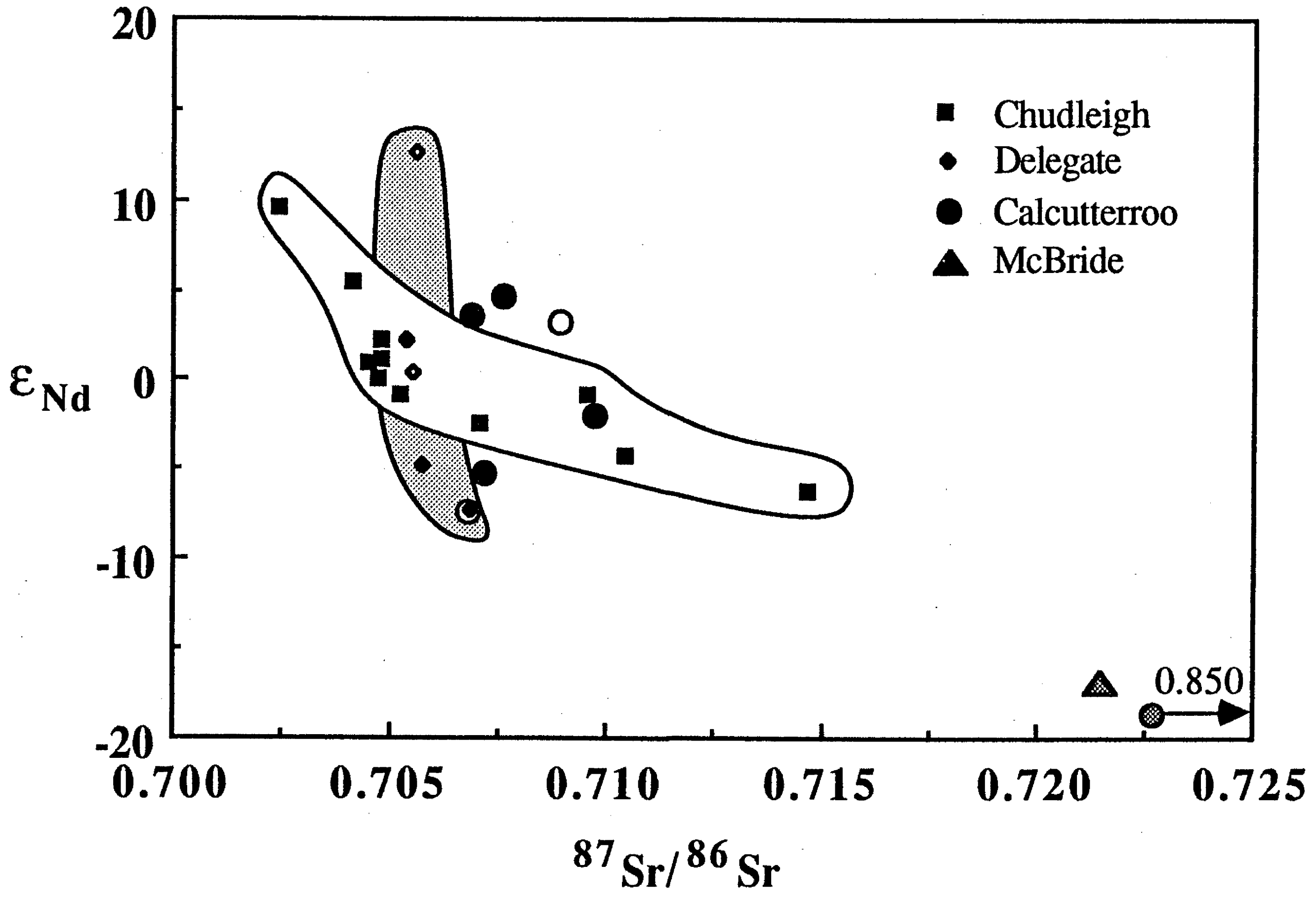
20
10
0
-10
-20
ε_{Nd}
0.700
0.705
0.710
0.715
0.720
0.725
$^{87}Sr/^{86}Sr$
■ Chudleigh
◆ Delegate
● Calcutterroo
▲ McBride
0.850

Figure 1

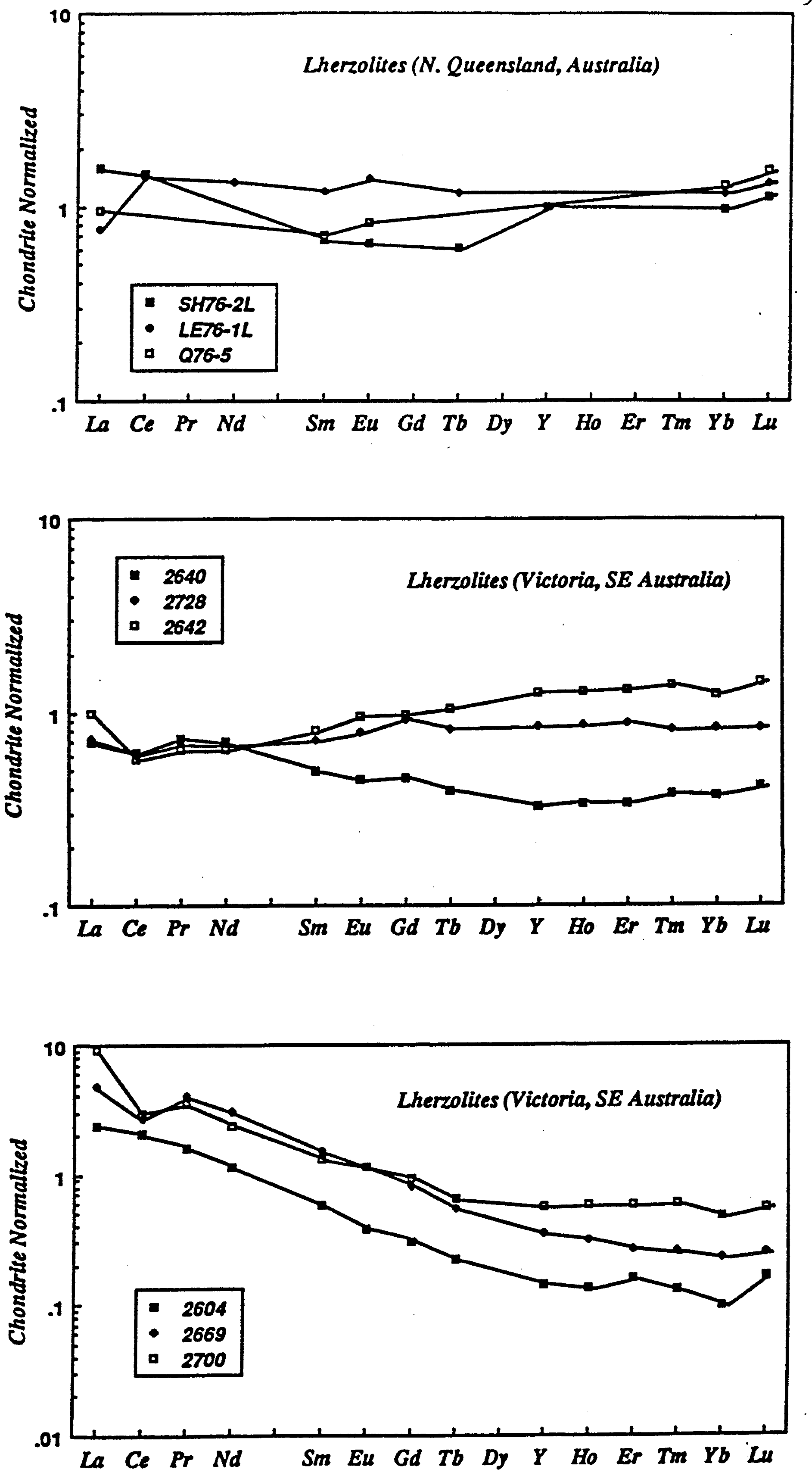
Lherzolites (N. Queensland, Australia)
SH76-2L
LE76-1L
Q76-5
Lherzolites (Victoria, SE Australia)
2640
2728
2642
Lherzolites (Victoria, SE Australia)
2604
2669
2700
Chondrite Normalized
10
1
.1
.01
La Ce Pr Nd Sm Eu Gd Tb Dy Y Ho Er Tm Yb Lu

Fig 2

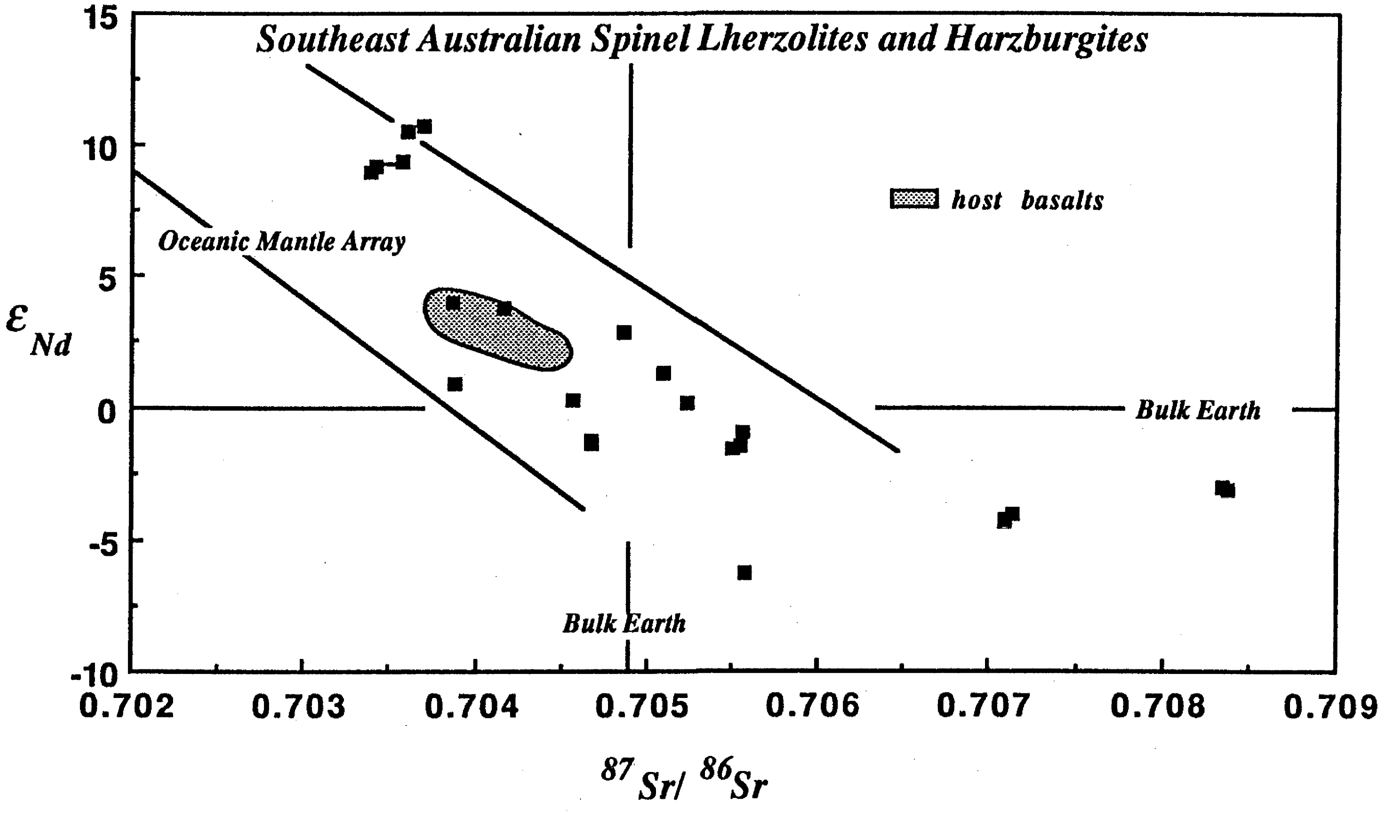
Southeast Australian Spinel Lherzolites and Harzburgites
host basalts
Oceanic Mantle Array
Bulk Earth
Bulk Earth
ε_{Nd}
15
10
5
0
-5
-10
0.702
0.703
0.704
0.705
0.706
0.707
0.708
0.709
$^{87}Sr/^{86}Sr$

Figure 3

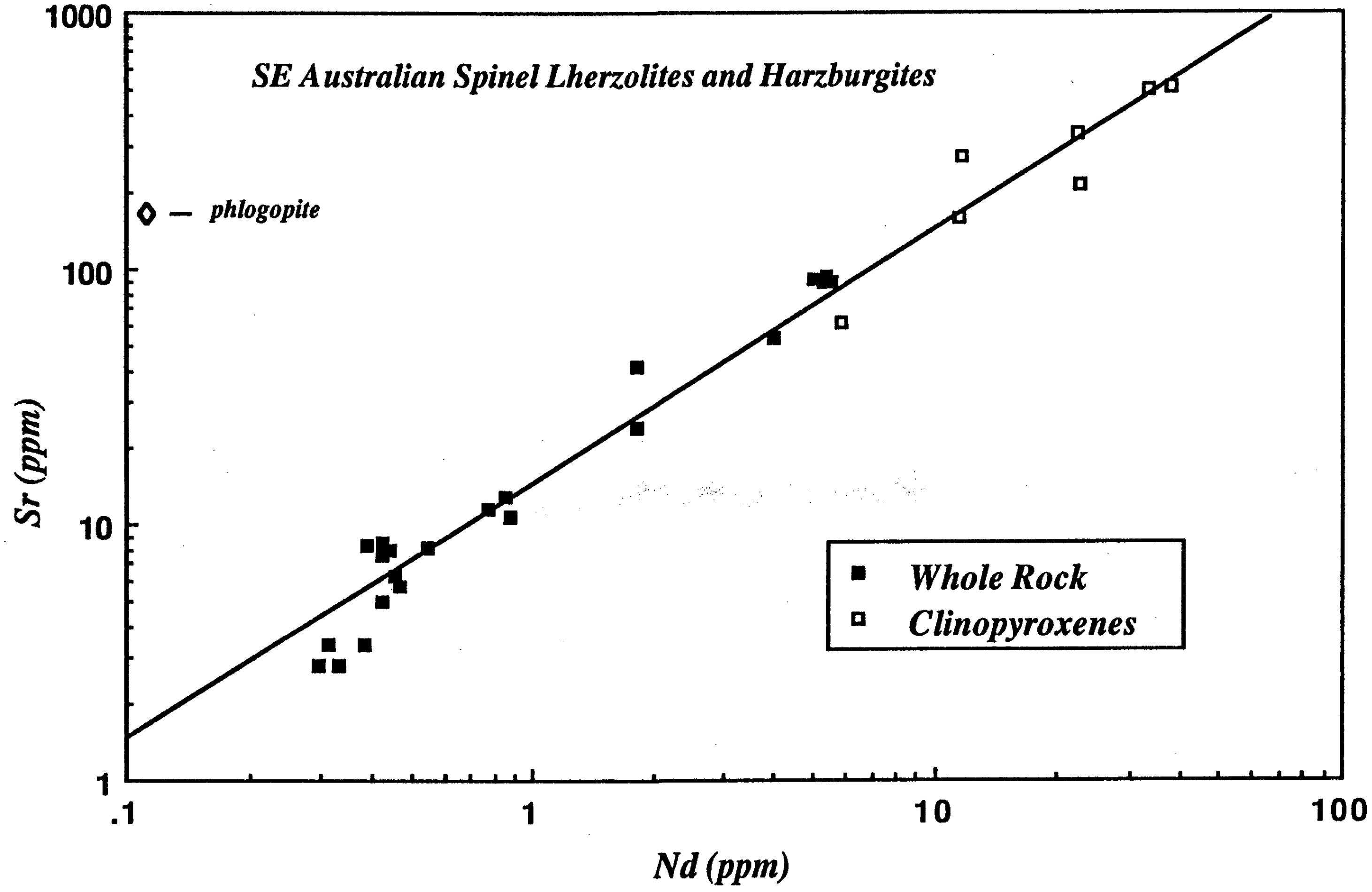
SE Australian Spinel Lherzolites and Harzburgites
◇ — phlogopite
■ Whole Rock
□ Clinopyroxenes
1000
100
10
1
Sr (ppm)
.1
1
10
100
Nd (ppm)

Figure 4

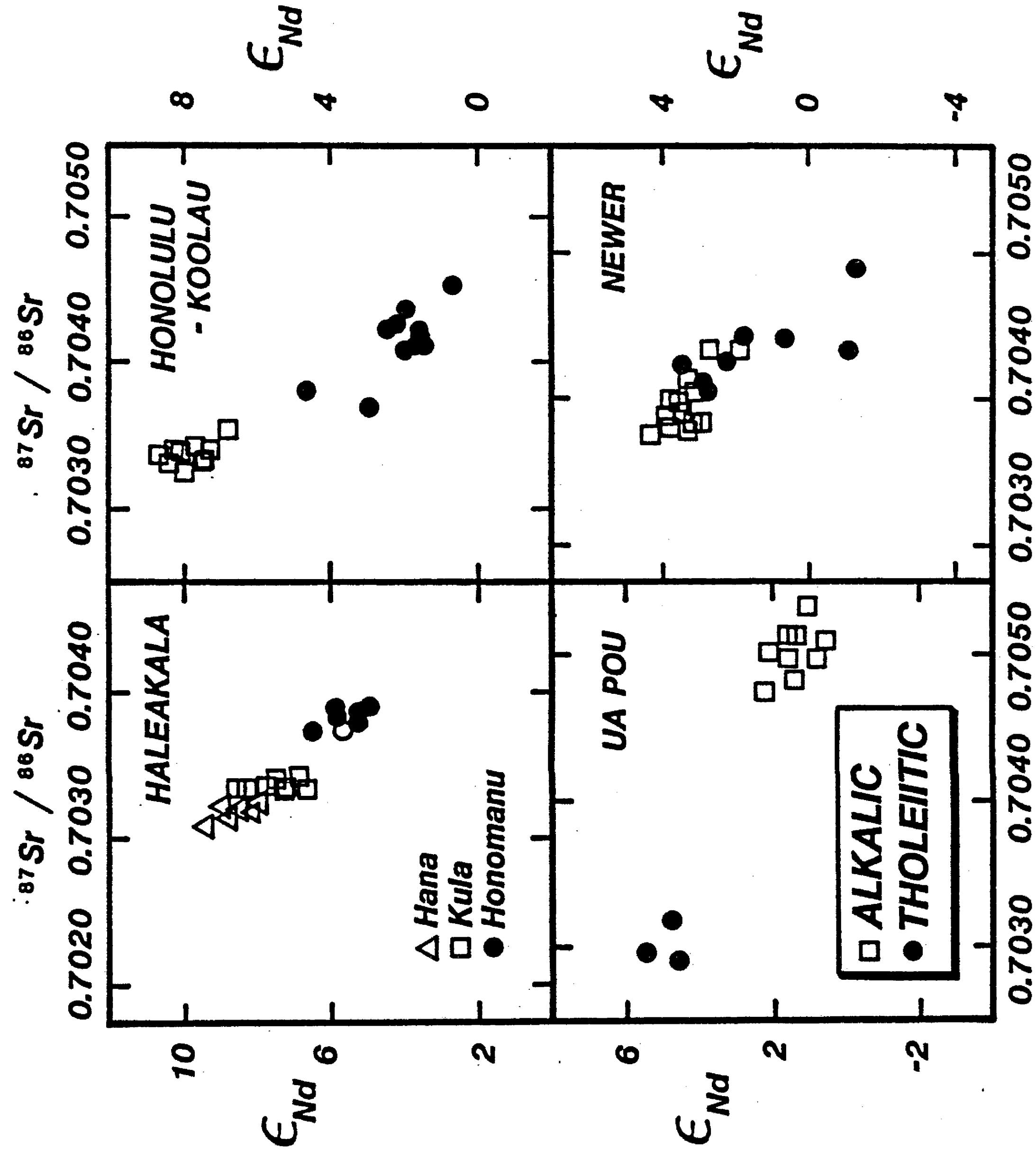
HALEAKALA
HONOLULU - KOOLAU
UA POU
NEWER
$^{87}Sr/^{86}Sr$
0.7020
0.7030
0.7040
0.7050
ϵ_{Nd}
10
6
2
8
4
0
-4
-2
△ Hana
□ Kula
● Honomanu
□ ALKALIC
● THOLEIITIC

FiG 5

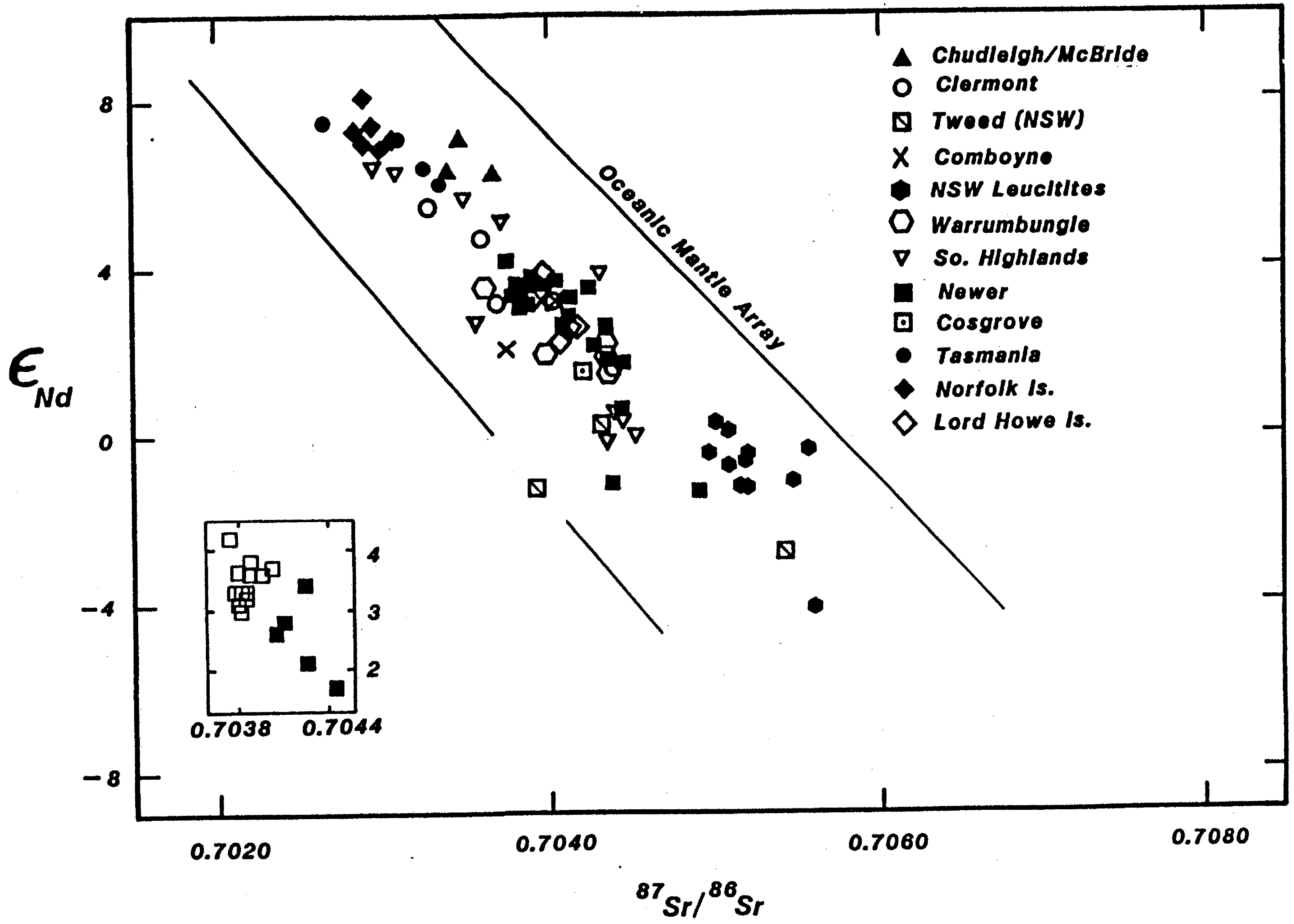
▲ Chudleigh/McBride
○ Clermont
▧ Tweed (NSW)
X Comboyne
⬢ NSW Leucitites
⬡ Warrumbungle
▽ So. Highlands
■ Newer
⊡ Cosgrove
● Tasmania
◆ Norfolk Is.
◇ Lord Howe Is.
Oceanic Mantle Array
ϵ_{Nd}
8
4
0
−4
−8
0.7020
0.7040
0.7060
0.7080
$^{87}Sr/^{86}Sr$
4
3
2
0.7038
0.7044

FiG. 6

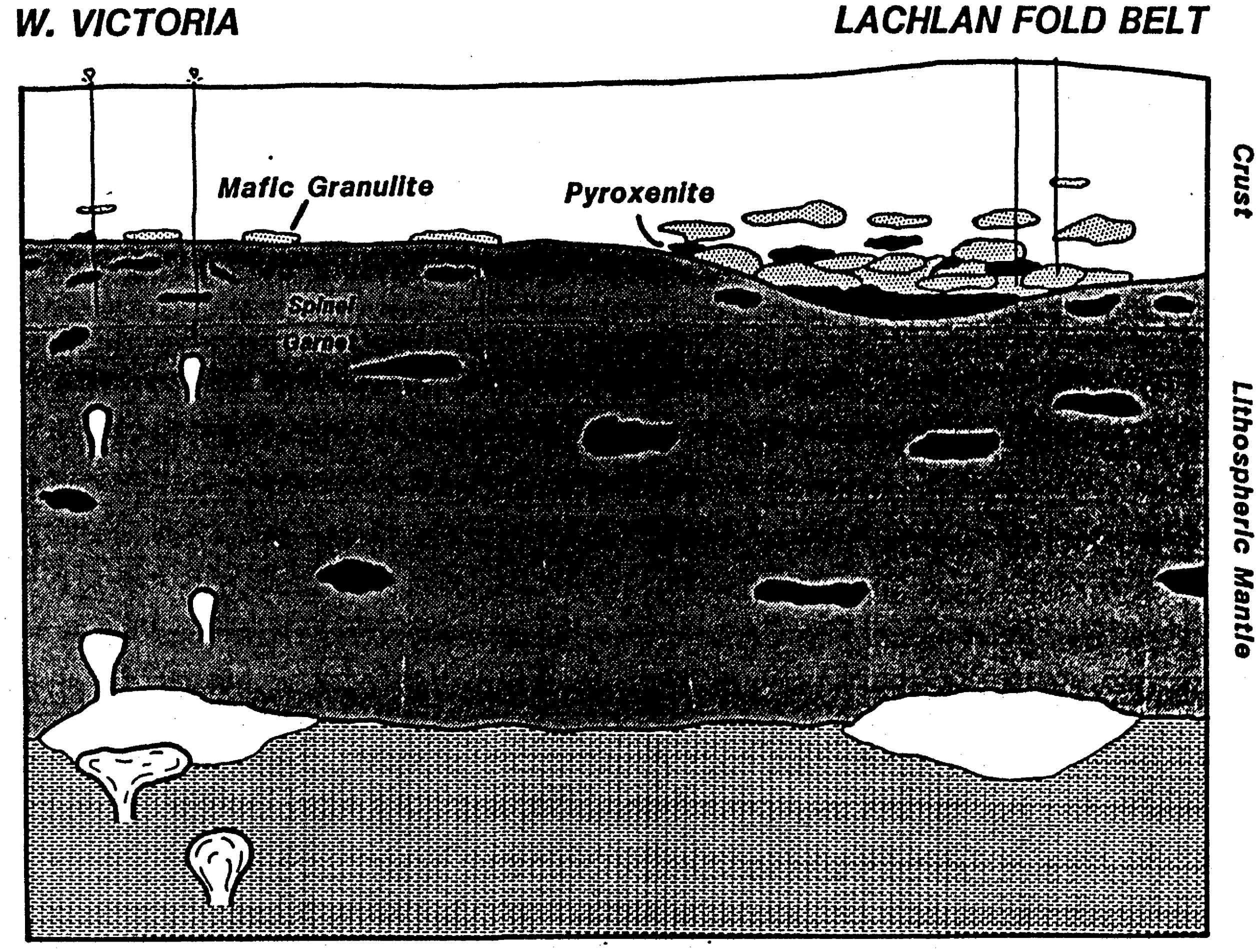
W. VICTORIA
LACHLAN FOLD BELT
Crust
Lithospheric Mantle
Mafic Granulite
Pyroxenite
Spinel
Garnet

FiG. 7

Table 1. Summary of Studies on Lower Crustal Xenoliths from Eastern Australia

Locality	Country Rocks	Age of Pipe	Xenolith Lithologies	T-P Conditions	Reference
SOUTH AUSTRALIA					
Calcutteroo	Prot. Marine Sediments	164-175 Ma	GG, 2 PxG Ky-Gar-Ksp G	600-900°C 1.1-1.6 GPa	McCulloch et al, 1982 Arculus et al., 1987
El Alamein	Prot. Marine Sediments	164-175 Ma	2 PxG, 2 PxGG	700-870°C	Arculus et al., 1987
VICTORIA					
Anakies	Cenozoic Basalts, Palaeozoic Seds.	Quaternary	2 PxG, 2PxGG	880-980°C	Wass and Hollis, 1983
NEW SOUTH WALES					
White Cliffs	Precambrian Chlorite Schists	260 Ma	GG	630°C 1.4 GPa	Arculus et al., 1987
Kayrunnera	Precambrian Chlorite Schists	260 Ma	GG	850-900°C 1.8-2.8 GPa	Edwards et al., 1979
Jugiong	Basalts	<17 Ma	2 PxG, 2 PxGG	850-960°C 1.6 GPa	Arculus et al., 1987
Delegate	Palaeozoic Sediments and Granites	170 Ma	2 PxG, 2 PxGG GG, Charn	850-950°C 0.6-1.8 GPa	Lovering and White, 1969 Irving, 1976 Arculus et al., 1987 Griffin and O'Reilly, 1986
Gloucester	Carboniferous Sediments	?	GG	1000°C 1.0-1.4 GPa	Wilkinson, 1974 Griffin and O'Reilly, 1986
Boomi Creek	Carboniferous Sediments	?	2 PxG	950°C 0.8-1.0 GPa	Wilkinson, 1975 Wilkinson and Taylor, 1980
Walcha	Tertiary Gravels	Tertiary	2 PxGG	1000°C 1.4 GPa	Stolz, 1984
QUEENSLAND					
McBride Province	Proterozoic Metamorphics	< 5 Ma	2 PxG, GG 2 PxGG, Charn Metasediments	700-1000°C 0.8-1.0 GPa	Kay and Kay, 1983 Rudnick and Taylor, this vol. Rudnick et al., 1986b Rudnick and Taylor, 1987
Chudleigh Province	Palaeozoic Sediments and Granites	< 2 Ma	2 PxG, 2 PxGG GG	700-1000°C 0.6-1.2 GPa	Kay and Kay, 1983 Rudnick et al., 1986a Rudnick and Taylor, this vol.

Where 2 PxG = two pyroxene granulite; 2 PxGG = two pyroxene garnet granulite; GG = garnet granulite, Charn = Charnockite. Ky = kyanite; Ksp = K-feldspar; Gar = garnet.

Table 2. The Sr and Nd isotopic compositions of Delegate and Lake Bullenmerri xenoliths.

	Rb (ppm)	Sr (ppm)	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	$\varepsilon_{Sr}(170Ma)$	Sm	Nd	$^{147}Sm/^{143}Nd$	$^{143}Nd/^{144}Nd$	$\varepsilon_{Nd}(0\ Ma)$	$\varepsilon_{Nd}(170Ma)$
Delegate xenoliths and host nephelinite (170 Ma)											
R 877 Host	15.2	1043	0.0742	0.70415	-8	9.8	50.4	0.1182	0.511948±14	+2.2	+3.9
69-27 GPx	2.53	226	0.0322	0.70563	+15	1.0	1.9	0.3367	0.512639±24	+15.7	+12.6
R698 2PxG	10.0	367	0.0788	0.70702	+32	4.2	13.7	0.1866	0.511447±14	-7.6	-7.3
R130 GG	25.6	798	0.0928	0.70561	+12	5.6	20.9	0.1614	0.511909±24	+1.4	+2.2
R960 GPx	4.30	165	0.0420	0.70566	+14	0.9	4.2	0.1297	0.511781±28	-1.1	+0.4
R967 GG	11.4	1008	0.0329	0.70584	+17	1.1	3.7	0.1700	0.511566±14	-5.3	-4.7
Lake Bullenmerri mineral separates (Quaternary)											
84-99 GPx-Gt	0.06	2.0	0.0956	0.70687±12		0.5	0.9	0.3653	0.511549±44	-5.6	
84-99 GPx-Cpx	0.20	181	0.0029	0.70654±4	---	1.9	12.9	0.0871	0.511607±16	-4.5	---
84-98 GPx-Cpx	0.14	220	0.0019	0.70648±4	---	3.5	20.8	0.1005	0.511501±26	-6.5	---

Uncertainties in the $^{87}Sr/^{86}Sr$ ratios are < 0.01%, and for Nd are reported at the 2 σ uncertainty level. $^{87}Sr/^{86}Sr$ ratios were normalized to $^{88}Sr/^{86}Sr = 8.37520$ and $^{143}Nd/^{144}Nd$ ratios were normalized to $^{146}Nd/^{142}Nd = 0.636151$. Sample dissolution methods are described in McDonough and McCulloch (1987) and mass spectrometry techniques are described in McDonough et al. (1985). Sample descriptions for the Delegate samples are given in Irving (1974); the garnet pyroxenite xenoliths from Lake Bullenmerri are similar to those described by Griffin et al. (1984). GPx = garnet pyroxenite, 2PxG = 2 pyroxene granulite, GG = garnet granulite, Host = nephelinite host rock. Episilon values were calculated using the following values: $^{87}Sr/^{86}Sr = 0.70475$, $^{87}Rb/^{86}Sr = 0.0867$, $^{143}Nd/^{144}Nd = 0.511836$, $^{147}Sm/^{144}Nd = 0.1967$. Decay constants used are $^{87}Rb = 1.42 \times 10^{-11}$ and $^{147}Sm = 6.54 \times 10^{-12}$.

APPENDIX 1

Lower Crustal Xenoliths from Queensland, Australia: Evidence for Deep Crustal Assimilation and Fractionation of Continental Basalts

by R.L. Rudnick, W.F. McDonough,
M.T. McCulloch and S.R. Taylor

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Lower crustal xenoliths from Queensland, Australia: Evidence for deep crustal assimilation and fractionation of continental basalts

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Abstract—A suite of mafic, granulite facies xenoliths from north Queensland possesses petrographic and geochemical features of basaltic cumulates crystallized at lower crustal pressures. Negative correlations between incompatible trace elements and Mg# and positive correlations between compatible trace elements and Mg# suggest the xenoliths are genetically related and crystallized from a continuously evolving melt. Zr, Hf, Y, HREE, Ti and V do not correlate with Mg#, but show excellent negative correlations with Al_2O_3 content, reflecting the proportion of cumulate plagioclase to clinopyroxene. These chemical trends also suggest the trace element concentrations have not been affected by subsolidus recrystallization. The xenoliths have a large range in Sr and Nd isotopic compositions ($^{87}Sr/^{86}Sr$ = 0.70239 to 0.71467, ϵ_{Nd} = +9.5 to −6.1) which cannot be produced by crystal fractionation alone, and excellent correlations between isotope ratios and Mg# suggest the variable isotope compositions are not due to mantle source heterogeneities.

These mafic xenoliths are proposed to be cumulate products from a melt undergoing simultaneous assimilation and fractional crystallization (AFC). The data illustrate that only a few percent AFC in lower crustal environments can dramatically change the Sr and Nd isotopic composition of a basaltic melt, and suggest the use of caution when inferring mantle source isotopic compositions from continental basalts. Additionally, the Nd isotopic data plot on a positive trend on an Sm-Nd isochron diagram with an age of ~570 Ma. However, if these xenoliths formed by AFC, the positive trend reflects mixing between two isotopic end members and has no age significance. The correlations between Sr and Nd isotopic compositions with Mg# degrade as the isotopic ratios are back-calculated to earlier times, suggesting the xenoliths are relatively young; the xenoliths may be related to the Cenozoic igneous activity which occurs throughout eastern Australia.

INTRODUCTION

INTEGRATED PETROGRAPHIC, geochemical and isotopic studies of lower crustal xenolith suites provide direct information on how and when portions of the lower crust formed. Moreover, xenoliths formed by cumulate processes can provide information on the origin and evolution of the melts from which they precipitate. We report the results of a combined petrographic, geochemical and isotopic study of mafic lower crustal xenoliths from north Queensland, Australia and show how trace element and isotopic analyses can be combined to define the dominant processes affecting lower crustal composition.

The xenoliths come from three Plio-Pleistocene (<2 Ma) alkali basalt vents in the Chudleigh volcanic province, north Queensland (STEPHENSON and GRIFFIN, 1976; STEPHENSON *et al.*, 1980): Batchelors Crater, Airstrip Crater and Sapphire Hill. These vents lie near the southern extension of the Burdekin fault zone, which is a steep, westward dipping thrust fault (WITHNALL, 1982) that separates Paleozoic volcanics and sediments of the Tasman fold belt on the east from Precambrian metamorphic rocks and granites of the Georgetown Inlier on the west (Fig. 1). The xenoliths are 5 to 50 cm in diameter; most with a blocky shape and coarse grain size (>2 mm) and all are mafic in composition ($SiO_2 \leqq 51\%$). There are three general classes of crustal xenoliths based on mineralogy and chemistry: (1) plagioclase-rich xenoliths, the most abundant type, (2) rarer, pyroxene-rich xenoliths and (3) xenoliths with mineralogy and major element compositions transitional between these two end members. The modal mineralogies and dominant textural features of the xenoliths are listed in Table 1 (petrographic descriptions are given in the Appendix). Here the xenoliths are grouped by mineralogy, with metamorphic grade increasing toward the bottom of the table. Because major element compositions of the plagioclase-rich xenoliths show little variation, their variable mineralogies are interpreted to reflect differing equilibration conditions. Hence, the olivine-bearing samples come from the shallowest levels and garnet, clinopyroxene-bearing samples come from the deepest levels (RUDNICK and TAYLOR, 1986). All of the xenoliths possess metamorphic textures, but relict cumulate textures (*i.e.*, orthopyroxene oikocrysts enclosing tabular plagioclase) are present in several of the plagioclase-rich samples. The xenolith mineral assemblages and cation exchange thermobarometry on coexisting mineral rims suggest equilibration conditions between 20–40 km and 700–1000°C (Fig. 2 and RUDNICK and TAYLOR, 1986). The presence of two coronal textures: (1) olivine rimmed by orthopyroxene and pyroxene-spinel symplectite and (2) spinel rimmed by garnets (Table 1), indicates these xenoliths crystallized at variable depths in the lower crust and cooled isobarically (KAY and KAY, 1983; RUDNICK and TAYLOR, 1986). Therefore, these xenoliths have not experienced a metamorphic "event", but rather, simply recrystallized to lower temperature mineralogies. Relict igneous textures are confined to the xenoliths which equili-

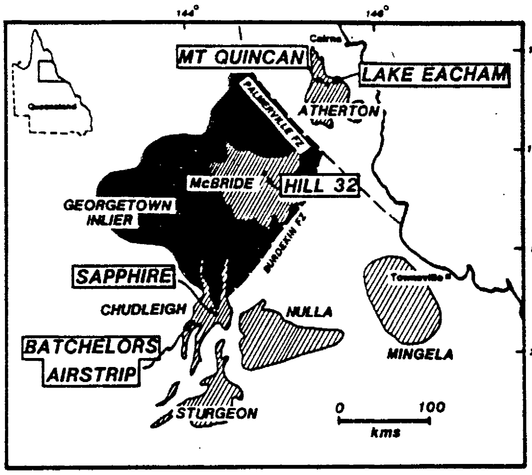

FIG. 1. Map of north Queensland Cenozoic volcanic provinces (hatched areas). Chudleigh province xenolith localities discussed here are Sapphire, Batchelors and Airstrip Craters. Shaded area is the Precambrian Georgetown Inlier, and the white areas to the east are Paleozoic volcanics, granites and sediments of the Tasman fold belt.

brated at the shallowest levels (Table 1). Deformation textures, present in some of the xenoliths (KAY and KAY, 1983; see Appendix), may reflect original igneous textures (*e.g.*, those in 83-107) or may have formed from reaction to localized stress fields associated with the nearby Burdekin fault zone.

Fourteen xenoliths were analyzed for major and trace elements; 11 of these were analyzed for their Sr and Nd isotopic compositions. The principal aims of this study were to (1) characterize the lower crust in this region of north Queensland; (2) identify the major lower crust-forming processes occurring there; (3) determine the age of this segment of lower crust; and (4) evaluate the significance of this data to continental magma evolution.

ANALYTICAL TECHNIQUES

Least altered xenoliths were chosen for chemical and isotopic analyses. The samples ranged from 260 to 1180 g, after removal of all weathered surfaces by sawing. The xenoliths were crushed in a steel jaw crusher, then the chips ground in an agate ring mill. No xenoliths showed invasion of the host basalt in thin section, although most suffered some decompression melting, manifested in kelyphite rims on the garnets (see KAY and KAY, 1983 and Appendix).

Major element analyses were obtained by wide-beam (15 kv) EDS microprobe analyses (REED and WARE, 1973) on glasses created in a positive Ar-pressure molybdenum strip heater. Each analysis represents the average of at least 10 spot analyses per sample. TiO_2 and P_2O_5 were measured for the same glasses using a Cameca, WDS, microprobe. Analytical uncertainty for all the major elements is less than 5%. V, Cr, Ni, Cu, Zn, Sr (and some Zr, Nb and Ba analyses—as indicated in Table 3) were obtained through XRF analyses (NORRISH and CHAPPELL, 1977). The remaining trace elements were measured *via* spark-source mass spectroscopy (TAYLOR and GORTON, 1977). Analytical uncertainty for most trace elements is less than 5%. Elements present in very low abun-

TABLE 1. Summary of Mineralogy and Textures in Chudleigh Province Xenoliths

Mineralogy	Samples	Textures
	Plagioclase-rich*	
Ol-Sp-Opx-Cpx-Pc	106 107 109	Relict igneous textures: poikilitic Px and lath-shaped Pc Coronas: Ol rimmed by Opx rimmed by Sp + Px. Pc composition: labradorite
Sp-Opx-Cpx-Pc	126 127 139 112	Relict igneous textures: large broken Pc? Coronas: Sp/Opx symplectites rimmed by Cpx. Pc comp: labradorite rimmed by andesine.
Sp-Gar-Opx-Cpx-Pc	114 131 138	Relict igneous textures: none? Coronas: Sp rimmed by Gar. Pc comp: labradorite or labradorite rimmed by andesine.
Gar-Opx-Cpx-Pc rare Sp cores	117 133 140	Relict igneous textures: none. Meta textures: polygonal crystals. Pc comp: andesine or labradorite rimmed by andesine.
Gar-Cpx-Pc rare Opx	125 BC	Relict Igneous Textues: none Meta textures: polygonal crystals; euhedral Gar. Pc comp: andesine.
	Pyroxene-rich	
Cpx-Opx-Pc-Rut±Ol	110 115	Relict igneous textures: possible cumulate layering. Meta. textures: polygonal Pc crystals. Pc comp.: labradorite.

Where Cpx = clinopyroxene, Opx = orthopyroxene, Ol = olivine, Pc = plagioclase, Sp = Spinel, Gar = garnet, Rut = rutile, Px = pyroxene.

*The two transitional xenoliths, 83-126 and BC, are grouped here with the plagioclase-rich xenoliths because of their high modal plagioclase content.

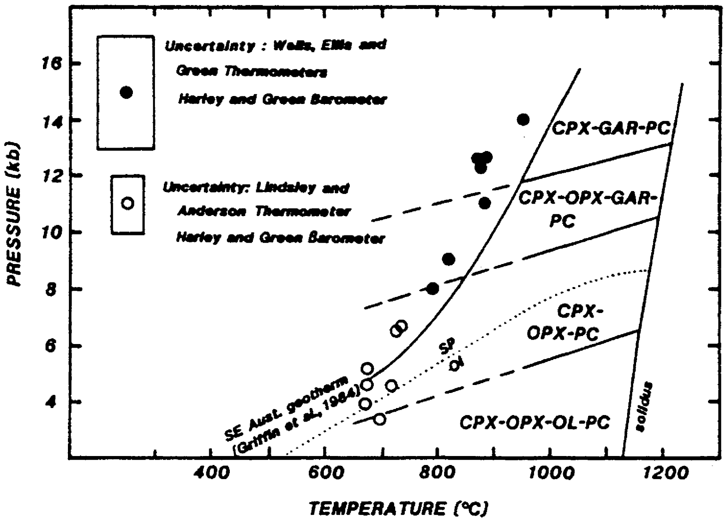

FIG. 2. Temperature and pressure estimates of garnet, two pyroxene plagioclase-rich xenoliths using the LINDSLEY and ANDERSON (1983) two pyroxene thermometer with the HARLEY and GREEN (1982) garnet-orthopyroxene barometer (open circles), or the WELLS (1977) two pyroxene or ELLIS and GREEN (1979) garnet-clinopyroxene thermometer with the HARLEY and GREEN (1982) barometer (closed circles). Points represent average of 5 analyses on adjacent mineral rims for each sample; boxes represent uncertainty. Experimentally determined stability fields are for a two pyroxene mafic xenolith from the Delegate breccia pipe which has major element composition similar to the Chudleigh plagioclase-rich xenoliths (IRVING, 1974). Dotted line represents spinel-olivine transition (HERZBERG, 1978). The plagioclase-rich xenoliths possess all the mineral assemblages shown here. Southeastern Australian geotherm of GRIFFIN *et al.* (1984) shown for reference.

dances, however, have higher uncertainties (10% for Th and U, 20% for Cs and Nb).

Dissolution procedures followed during this study are detailed in MCCULLOCH and CHAPPELL (1982). For each sample approximately 150 mg of powder was dissolved in teflon bombs. During the analyses of these samples the measured total chemical blank was 0.5 ng for Nd and 3.5 ng for Sr. No blank corrections were necessary for any of the isotope ratios. Mass spectrometry procedures and measured values for different isotopic standards are detailed in MCDONOUGH *et al.* (1985). Standard analyses performed concurrent with these analyses are listed at the bottom of Table 3.

RESULTS

Table 2 gives major element compositions and normative mineralogies for 10 plagioclase-rich, 2-pyroxene-rich and 2 transitional xenoliths. The plagioclase-rich xenoliths show little variation in SiO_2 (50 wt.%) and Al_2O_3 (20 wt.%), whereas Mg#s range from 41 to 76. Mg#s used here will be 100 (Mg/Mg + ΣFe), unless otherwise specified. Compared to the plagioclase-rich samples, the pyroxene-rich xenoliths have lower Al_2O_3 (9–10%), similar SiO_2 and higher Mg#s. Transitional xenoliths have major element compositions lying between the two end member types except that sample BC has the highest Mg# of the suite. All xenoliths are olivine-hypersthene normative, except plagioclase-rich xenolith 83-112, which has normative nepheline. This xenolith is also distinct from the rest of the plagioclase-rich xenoliths in that it is the only sample with large proportions of modal (and normative) ilmenite and magnetite, and because of this, it has the lowest Mg# of the suite.

Trace element concentrations are presented in Table 3. Chondrite normalized patterns (REE and Ba) are shown for the three xenolith types in Fig. 3. The plagioclase-rich xenoliths have low total REE concentrations (0.2 to 10 × chondrite), with LREE-enriched patterns and large positive Eu anomalies (Eu/Eu* = 1.5 to 4.3). These patterns mimic the REE partition coefficients for plagioclase in equilibrium with mafic to intermediate liquids (SCHNETZLER and PHILPOTTS, 1970; IRVING, 1978; FUJIMAKI *et al.*, 1984). The pyroxene-rich xenoliths have LREE-depleted patterns, with no Eu anomalies and slight negatively sloped HREE (Fig. 3b). Such REE patterns are similar to REE partition coefficient patterns for clinopyroxene in equilibrium with mafic to intermediate liquids (SCHNETZLER and PHILPOTTS, 1970; IRVING, 1978; FUJIMAKI *et al.*, 1984). These xenoliths are unlikely to be crystallized basaltic liquids because of their low Na_2O and Al_2O_3 contents at relatively high SiO_2 content. The lack of a positive Eu anomaly in these samples suggests that plagioclase was not a cumulate or restite phase and the modal plagioclase formed either through subsolidus re-equilibration or through crystallization of interstitial melt. The transitional xenoliths (Fig. 3c) are LREE depleted, but possess a positive Eu anomaly, thus they have features transitional to those of the plagioclase-rich and pyroxene-rich xenoliths.

Trace elements which are highly incompatible in plagioclase, olivine and pyroxenes (the inferred original phases in these xenoliths) are present in low abundances and negatively correlate with Mg# (Fig. 4a). The correlation of K, Th and U with Mg# suggest these

TABLE 2. Major Element Chemistry and CIPW Normative Mineralogies[1] of Chudleigh Province Mafic Granulite Xenoliths

	Plagioclase-rich										Pyroxene-rich		Transitional	
	83-107 AC	83-112 AC	83-114 BC	83-117 BC	83-125 SH	83-127 SH	83-131 SH	83-133 SH	83-138 SH	83-140 SH	83-110 AC	83-115 BC	83-126 SH	BC BC
SiO_2	49.58	50.97	50.45	49.75	50.74	50.09	50.51	49.98	49.68	51.18	50.83	50.88	51.10	49.72
TiO_2	0.12	1.99	0.36	0.17	0.30	0.18	0.27	0.22	0.24	0.36	0.86	0.82	0.62	0.35
Al_2O_3	20.69	19.02	18.16	20.22	19.42	20.56	20.02	20.02	19.81	19.04	10.07	9.90	18.11	17.98
FeO*	8.27	10.11	7.66	6.48	6.85	7.03	6.80	7.93	6.96	8.78	10.54	7.32	6.10	5.00
MnO	0.12	0.14	0.16	0.09	0.12	0.11	0.12	0.13	0.14	0.18	0.22	0.19	0.13	0.11
MgO	9.38	3.95	9.58	11.79	9.85	10.26	9.61	10.06	10.37	8.24	16.30	14.38	8.81	11.62
CaO	9.06	8.66	10.62	8.74	10.66	8.55	10.15	8.90	9.97	8.84	9.75	15.64	12.04	12.57
Na_2O	3.03	4.92	2.80	2.55	2.48	2.71	2.82	2.65	2.59	3.12	1.05	0.88	2.98	2.51
K_2O	0.23	0.43	0.16	0.15	0.25	0.22	0.19	0.23	0.15	0.28	0.08	0.06	0.27	0.07
P_2O_5	0.07	0.18	0.05	0.04	0.06	0.06	0.06	0.07	0.10	0.11	0.17	0.05	0.07	0.15
TOTAL	100.55	100.37	100.00	99.98	100.73	99.77	100.55	100.19	100.01	100.13	99.87	100.02	100.26	100.08
Mg #[2]	66.9	41.0	69.0	76.4	71.9	72.2	71.6	69.3	72.9	62.6	73.4	77.8	72.0	80.5
q	0	0	0	0	0	0	0	0	0	0	0	0	0	0
c	0	0	0	0.07	0	0.46	0	0	0	0	0	0	0	0
or	1.36	2.54	0.95	0.89	1.48	1.30	1.12	1.36	0.89	1.65	0.47	0.35	1.60	0.41
ab	25.64	38.06	23.69	21.58	20.98	22.93	23.86	22.42	21.91	26.40	8.88	7.45	25.21	21.24
an	42.17	28.54	36.51	43.10	41.12	42.02	41.41	42.05	41.98	37.12	22.53	22.89	35.24	37.59
ne	0	1.93	0	0	0	0	0	0	0	0	0	0	0	0
di	1.88	11.04	12.81	0	9.16	0	6.89	1.33	5.49	4.90	19.86	42.96	19.32	19.50
hy	8.30	0	10.67	16.85	15.39	19.03	11.79	17.37	12.95	17.99	39.78	18.24	4.50	1.59
ol	19.34	12.26	13.21	15.93	10.68	12.30	13.61	13.67	14.85	9.56	4.44	5.26	11.91	17.83
mt	1.58	1.94	1.47	1.24	1.31	1.35	1.30	1.52	1.33	1.68	2.02	1.40	1.17	0.96
il	0.23	3.78	0.68	0.32	0.57	0.34	0.51	0.42	0.46	0.68	1.63	1.29	1.23	1.06
ap	0.17	0.43	0.12	0.09	0.14	0.14	0.14	0.17	0.20	0.26	0.40	0.33	0.17	0.09

FeO* = total Fe as Fe^{2+}; BC = Batchelor's Crater; AC = Airstrip Crater; SH = Sapphire Hill; [1] CIPW Norms calculated assuming $Fe_2O_3/FeO = 0.15$;
[2] Mg # = 100 Mg/Mg + ΣFe
q = quartz, c = corundum, or = orthoclase, ab = albite, an = anorthite, ne = nepheline, di = diopside, hy = hypersthene, ol = olivine, mt = magnetite, il = ilmenite, ap = apatite

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TABLE 3. Trace Element Chemistry of Chudleigh Province Mafic Granulite Xenoliths

	Plagioclase-rich										Pyroxene-rich		Transitional	
	83-107	83-112	83-114	83-117	83-125	83-127	83-131	83-133	83-138	83-140	83-110	83-115	83-126	BC
V	31	283	77	24	64	14	43	30	43	34	253	302	109	142
Cr	40	9	206	82	322	22	211	81	234	85	755	1070	680	419
Ni	159	34	133	155	86	159	123	118	164	58	228	282	106	345
Cu	39	44	38	24	25	29	43	25	33	7	35	49	24	25
Zn	59	78	55	44	49	52	45	54	48	75	73	42	46	25
Rb	0.63[2]	1.56[2]	0.56[2]	0.39	2.02[2]	0.85[2]	0.96[2]	2.0[1]	1.0[1]	1.97[2]	0.22[2]	0.45[2]	1.06[2]	0.59[2]
Sr	420	590	375	397	535	505	441	412	423	540	214	39[2]	409	350[2]
Y	1.25	5.74	6.70	1.63	4.54	1.22	2.65	3[1]	3[1]	3.94	17[1]	23[1]	8.25	11.0
Zr	2.9	70	12.9	3.5	8.0	4.9	8	--	--	10.1	28[1]	36[1]	15	16.9
Nb	0.73	1.77	0.72	0.62	0.73	0.91	0.67	0.5[1]	<0.5[1]	0.80	0.48	0.74	0.56	0.45
Cs	0.27	0.07	0.16	0.26	0.11	0.16	0.22			0.10	0.11	0.24	0.02	0.09
Ba	161	575[1]	180	52	120	305[1]	53	66[1]	56[1]	420[1]	19	25	83	12
La	2.61	4.21	2.39	1.74	2.03	2.12	2.34			3.23	1.11	2.04	2.22	1.32
Ce	3.05	8.84	4.40	2.58	4.36	4.36	3.92			6.44	4.43	6.07	7.80	2.73
Pr	0.40	1.14	0.63	0.32	0.59	0.52	0.50			0.86	0.67	1.12	1.03	0.54
Nd	1.60	5.71	3.36	1.50	3.00	2.18	2.45			4.17	4.33	7.20	5.50	3.50
Sm	0.26	1.65	1.00	0.32	0.84	0.36	0.62			1.06	1.70	2.70	1.62	1.31
Eu	0.79	1.91	0.88	0.36	0.58	0.52	0.56			1.71	0.65	0.94	0.80	0.65
Gd	0.23	1.78	0.93	0.29	0.97	0.27	0.65			1.07	2.17	3.44	1.72	1.58
Tb	0.03	0.28	0.14	0.04	0.17	0.04	0.12			0.19	n.d.	n.d.	0.29	0.29
Dy	0.24	1.46	1.00	0.34	1.12	n.d.	0.94			0.87	2.85	4.35	n.d.	2.10
Ho	0.05	0.28	0.23	0.08	0.22	0.03	0.15			0.21	0.61	0.93	0.35	0.46
Er	0.10	0.68	0.55	0.22	0.56	0.08	0.37			0.52	1.68	2.44	0.92	1.23
Yb	0.08	0.80	0.54	0.16	0.54	0.06	0.36			0.51	1.52	2.09	0.60	1.03
Hf	0.07	1.84	0.45	0.15	0.32	0.09	0.30			0.33	0.71	1.07	0.49	0.63
Pb	1.04	1.21	1.15	0.87	2.05	0.47	2.05			1.15	0.59	0.76	1.78	0.28
Th	--	0.15	0.03	0.02	0.07	0.04	0.07			0.11	0.03	0.04	0.10	0.03
U	--	0.13	0.02	--	0.02	0.02	0.02			0.05	--	0.01	0.03	0.01
W	0.43	0.54	0.17	0.20	0.25	0.20	0.27			0.46	--	0.28	0.10	0.34
Sn	0.59	0.80	0.58	0.44	0.55	0.32	0.55			0.48	0.98	1.32	0.55	0.65
Mo	0.29	0.41	0.15	0.15	0.16	0.10	0.17			0.20	0.34	0.53	0.12	0.23
$(La/Yb)_N$	22.0	5.7	3.0	7.2	2.5	23.0	4.4			4.3	0.5	0.66	2.5	0.87
$(La/Sm)_N$	5.3	1.6	1.5	3.2	1.5	3.7	2.4			1.9	0.4	0.5	0.9	0.6
(Eu/Eu*)	4.2	3.4	2.9	3.8	2.0	5.1	2.8			4.9	1.0	1.0	1.5	1.3

[1] XRF values, [2] Isotope dilution values, -- means not detected, n.d. means not determined

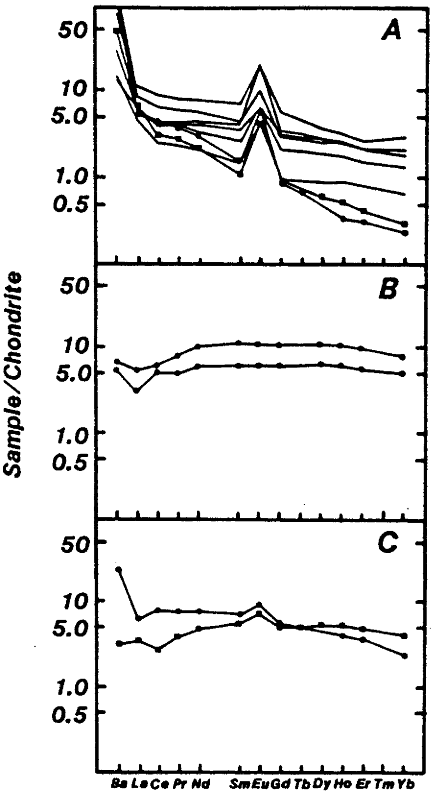

FIG. 3. Chondrite normalized REE and Ba concentrations for the three types of crustal xenoliths: (A) plagioclase-rich (pattern marked with squares is 83-107, pattern marked with circles is 83-127); (B) pyroxene-rich and (C) transitional xenoliths (pattern marked with squares is BC, pattern marked with circles is 83-126). Chondrite values from TAYLOR and MCLENNAN (1985).

elements have not suffered any depletion after crystallization in the deep crust. Compatible trace elements vary widely and positively correlate with Mg# (Fig. 4b).

Y, HREE, Zr, Hf, V and Ti are trace elements which, in basaltic systems, are moderately incompatible in clinopyroxene ($0.3 < D < 1.0$, where D = concentration of trace element in the crystal/concentration of element in the coexisting melt), but incompatible in plagioclase ($D < 0.05$ [IRVING, 1978; FUJIMAKI *et al.*, 1984]). These elements scatter when plotted against Mg#, but exhibit negative correlation with Al_2O_3 content (Fig. 5). (Note that 83-112 falls above the trends for V, Zr, Hf [and TiO_2], consistent with the presence of modal ilmenite and magnetite.) The size of the Eu anomaly (Eu/Eu*) exhibits a scattered, positive correlation with Al_2O_3. This suggests that these elements, and the Eu anomaly, are primarily controlled by the original proportions of pyroxene to plagioclase in the rocks. Sr, which is compatible in plagioclase (D = 1.0 to 2.5), less compatible in clinopyroxene (D = 0.1 to 0.2) and very incompatible in orthopyroxene and olivine ($D < 0.02$ [SCHNETZLER and PHILPOTTS, 1970; IRVING, 1978]), does not correlate with Al_2O_3, and produces a scattered, negative correlation with Mg# (Fig. 6a). Therefore, in the overall system Sr behaved incompatibly, and even though plagioclase-rich xenoliths form the majority of rock types in the suite, plagioclase was subordinate to ferromagnesian phases in the entire system. Rb shows a weak, negative correlation with Mg#, but exhibits a better correlation with Sr (Fig. 6b), suggesting that Rb has not been significantly affected by subsolidus recrystallization.

Table 4 presents Sr and Nd isotopic compositions for 10 of the xenoliths, chosen to span the range of chemical compositions present in the suite. In addition, $^{87}Sr/^{86}Sr$ ratios and ϵ_{Nd} for two of the host basalts are presented. $^{87}Sr/^{86}Sr$ ratios in the xenoliths vary widely from 0.70239 to 0.71467, and ϵ_{Nd} values range from +9.6 to −6.1. Most of the xenoliths plot along the mantle array, ranging from MORB-like values to values near bulk earth. Xenoliths with negative ϵ_{Nd} values fall to the right of the mantle array (Fig. 7). Except for sample 83-112, $^{87}Sr/^{86}Sr$ and ϵ_{Nd} correlate with Mg#, with correlation coefficients of −0.89 and 0.91, respectively (Fig. 8). For $n = 11$, this corresponds to a 99.99% level of significance.

The correlation between a wide variety of trace elements and isotopes with either Mg# or Al_2O_3 content indicates that these samples are genetically related, with the possible exception of 83-112. The petrologic, chemical and isotopic composition of sample 83-112 is distinct from the rest of the suite and implies a separate origin for this xenolith.

DISCUSSION

Significance of Mg# trends and trapped melt estimates

Before inferences about the xenoliths' origin can be made from the correlations between trace elements, isotopic ratios and Mg#, the principal parameters affecting the Mg# of the xenoliths must be delineated. Three parameters can affect Mg# in these xenoliths: (1) the original proportions of olivine, orthopyroxene and clinopyroxene, (2) the amount of trapped melt originally present, and (3) the composition of the coexisting melt (the term "coexisting melt" is used here as the melt with which the crystals were in contact with when they formed).

The large range in Mg#s is unlikely to be produced solely by varying the proportions of ferromagnesian minerals. The lowest whole-rock Mg# for the xenoliths is 63, and Mg# varies by 17 units for the entire suite (excluding 83-112, which has primary oxides). This variation is about twice that exhibited by coexisting olivines and pyroxenes in rocks with Mg#s > 60 from layered mafic intrusions (NWE, 1976; CAMPBELL, 1977; WILSON and LARSEN, 1985). Moreover, the concentrations of very incompatible trace elements (*e.g.*, U, Th, Ba, K, LREE) are not affected by the proportions of ferromagnesian phases. Thus the correlations between incompatible trace elements and Mg# (Fig. 4) suggests that factors other than phase proportions were important in establishing these trends.

Varying the proportions of trapped melt to ferromagnesian minerals could potentially yield the range

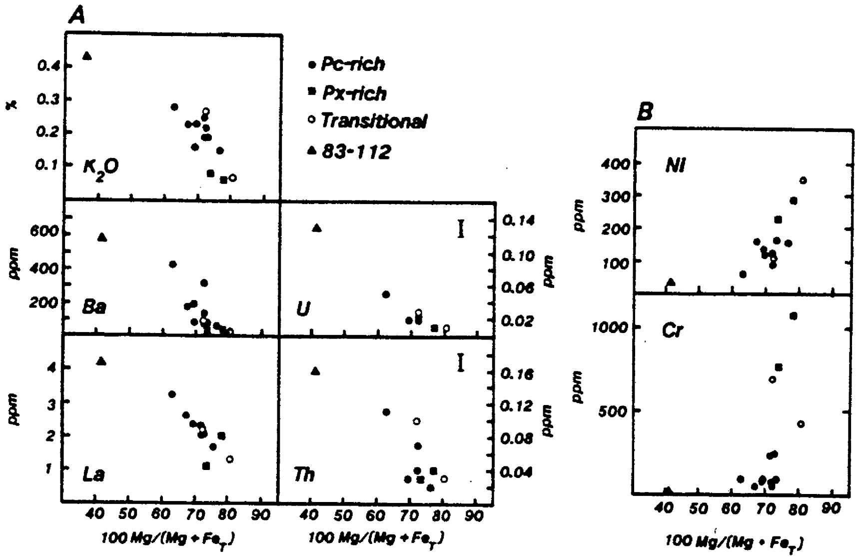

FIG. 4. (A) Incompatible trace elements plotted against Mg#. (B) Compatible trace elements plotted against Mg#. Symbols as in (A). Error bars provided for Th and U concentrations, uncertainties for other trace elements are close to the size of the data point. Pc = plagioclase, px = pyroxene.

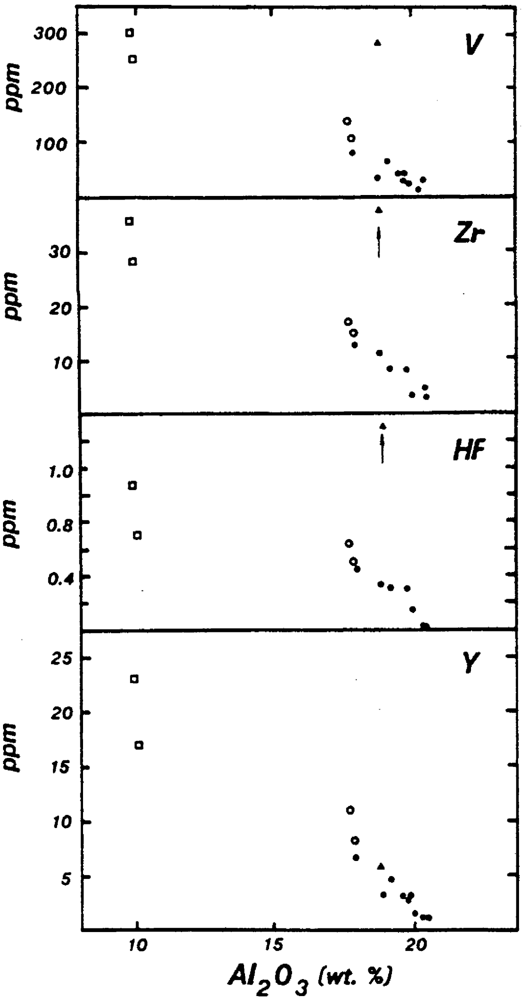

FIG. 5. V, Zr, Hf, Y plotted against Al_2O_3 content. TiO_2 and HREE show similar trends against Al_2O_3. Symbols as in Fig. 4. Note that 83-112 has elevated V, Zr and Hf, reflecting cumulate oxides.

of Mg#s and the correlations between Mg# and trace elements observed in the xenolith suite. However, if the trapped melt was in equilibrium with the crystals, the isotopic ratios would not change as a function of percentage of trapped liquid and the Mg#-isotope correlations could not be explained. Alternatively, the proportion of trapped melt could control the Mg#-isotope correlation if an evolved melt was percolated through the crystals (IRVINE, 1980; PALACZ and TAIT, 1985). In the Queensland xenoliths, metamorphic re-equilibration has completely obscured most igneous textures, so the proportion of trapped melt is not easily determined. However, the low incompatible trace element contents can be used to estimate the percentage of trapped melt in some samples. Sample 83-107 has one of the lower Mg#s of the suite (Mg# = 67). This sample also has extremely low HREE content (Yb < 0.4 times chondrite). If the trapped melt had a HREE content of 10 times chondrite (this is a minimum value since most eastern Australian basalts have higher HREE [FREY *et al.*, 1978; EWART, 1982; MCDONOUGH *et al.*, 1985]), only 4% trapped melt could have been present in this sample, if all of the HREE are contributed by the trapped melt. If half of the HREE are incorporated into the crystals, then only 2% trapped melt could have been present. This estimate is a maximum. Such a low proportion of trapped melt could not explain the low Mg#, higher incompatible trace element concentrations and more evolved isotopic compositions of this xenolith relative to the others.

The above observations suggest that the lower Mg#s in the xenoliths are not produced by greater proportions of trapped melt, but are primarily a function of the composition of the coexisting melt. That is, rocks with the lowest Mg# equilibrated with the most evolved melts, thus have the highest incompatible trace element concentrations, lowest compatible trace element concentrations and most radiogenic isotopic ratios.

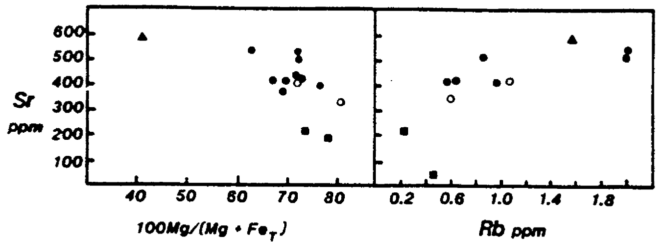

FIG. 6. (A) Sr plotted against Mg#. (B) Sr plotted against Rb. Symbols as in Fig. 4.

Origin of the xenoliths: cumulate or restite?

The systematic chemical and isotopic variations observed in these xenoliths suggests a genetic relationship with one another. These features are consistent with the xenoliths forming as crystals in equilibrium with a continuously evolving melt or melts. This can occur in two possible scenarios: the xenoliths could represent either crystal cumulates from an evolving melt, or restite left behind after variable degrees of partial melt extraction. Distinguishing between a cumulate or restite origin is difficult, however, several criteria may be used.

(1) Most of the xenoliths have metamorphic textures, however, relict cumulate textures are preserved in samples derived from shallower levels (Table 1).

(2) Cumulates often have simple mineralogies due to the separation and accumulation of phases and adcumulus growth. In contrast, residua would be expected to have polymineralic assemblages, provided that degree of partial melting is not large. The pyroxene-rich xenoliths, which originally contained pyroxenes and olivine, would therefore fit a cumulate origin.

(3) Trace element concentrations will vary markedly between cumulates and residua (FREY and PRINZ, 1978). Small amounts of crystal fractionation will cause large variations in the concentrations of compatible trace elements (*e.g.*, Cr, Ni), since they are strongly partitioned into the crystallizing phases, causing their concentrations in the melt to decrease rapidly. In contrast, small amounts of fractional crystallization will not significantly change incompatible trace element (*e.g.*, La, U, Th, K and Rb) concentrations in the melt, and the corresponding cumulates will have low, and relatively uniform, concentrations of these elements. In the Queensland xenoliths, the very incompatible trace elements are present in low concentrations with a total variation of a factor of 4, whereas compatible trace elements have highly variable concentrations (Ni varies by a factor of 10, Cr varies by a factor of 100). This is consistent with the xenoliths forming as crystal cumulates rather than residua.

(4) The good correlations between Sr and Nd isotopic compositions and Mg# (Fig. 8) are not expected to result from variable degrees of partial melting of either a chemically and isotopically heterogeneous or homogeneous source region. The Mg# is a sensitive

TABLE 4. Isotopic Composition of Chudliegh Province Lower Crustal Xenoliths and Host Basalts

Sample	Rb	Sr	^{87}Rb/^{86}Sr	^{87}Sr/^{86}Sr	Sm	Nd	^{147}Sm/^{144}Nd	^{143}Nd/^{144}Nd	$\epsilon_{Nd}(0)$	T(DM)	T(CHUR)
					XENOLITHS						
					Plagioclase-rich						
83-107	0.63	425.5	0.0042	0.71038 ± 3	0.31	1.59	0.1236	0.511621 ± 16	-4.2 ± 0.6	1095	449
83-112	1.56	589.9	0.0076	0.70950 ± 5	1.66	6.17	0.1627	0.511798 ± 26	-0.8 ± 0.3	1349	171
83-114	0.56	415.3	0.0039	0.70703 ± 6	1.10	3.59	0.1860	0.511707 ± 18	-2.5 ± 0.4	2500	1832
83-125	2.02	548.6	0.0106	0.70446 ± 3	0.94	3.26	0.1752	0.511881 ± 20	+0.9 ± 0.4	1433	---
83-127	0.85	516.6	0.0045	0.70468 ± 3	0.30	1.53	0.1201	0.511838 ± 32	0.0 ± 0.3	744	---
83-131	0.96	415.3	0.0059	0.70519 ± 3	0.62	2.26	0.1645	0.511794 ± 20	-0.8 ± 0.4	1399	199
83-140	1.98	513.4	0.0111	0.71467 ± 5	0.89	3.53	0.1528	0.511525 ± 32	-6.1 ± 0.6	1737	1079
					Pyroxene-rich						
83-110	0.22	214.7	0.0030	0.70410 ± 4	1.73	4.13	0.2541	0.512116 ± 36	+5.5 ± 0.7	---	---
83-115	0.45	39.3	0.0329	0.70473 ± 4	2.46	6.20	0.2396	0.511956 ± 14	+2.3 ± 0.3	---	---
					Transitional						
83-126	1.06	422.5	0.0072	0.70473 ± 5	1.66	5.52	0.1823	0.511893 ± 38	+1.1 ± 0.7	1627	---
BC	0.59	350.3	0.0048	0.70239 ± 3	1.29	3.38	0.2375	0.512326 ± 36	+9.6 ± 0.7	---	---
					HOST BASALTS						
83-124	Batchelors Crater			0.70340 ± 5				0.512162 ± 16	+6.4 ± 0.3		
83-150	Sapphire Hill			0.70347 ± 5				0.512197 ± 20	+7.1 ± 0.4		

Elemental abundances are given in ppm and have analytical uncertanties of ≤ ± 0.5%. ^{87}Sr/^{86}Sr ratios were normalized to ^{88}Sr/^{86}Sr = 8.37520 and ^{143}Nd/^{144}Nd ratios were normalized to ^{146}Nd/^{142}Nd = 0.636151. Uncertainties in isotope ratios are $2\sigma_m$ and represent intra-run statistics. The mean measured ^{87}Sr/^{86}Sr ratio for E & A $SrCO_3$ is 0.70800 and for NBS-987 is 0.71022, with inter-run $2\sigma_m$ uncertainties of ≤ ± 0.00005. The mean measured ^{143}Nd/^{144}Nd ratios are 0.511833 for BCR-1, 0.511121 for Nd α and 0.511040 for the La Jolla Nd standard (cf., Wasserburg et al., 1981), with inter-run $2\sigma_m$ uncertainties of ≤ ± 0.000020.

Parameters used in ϵ_{Nd} and model age calculations: $(^{147}Sm/^{144}Nd)_{CHUR}$ = 0.1967, $(^{143}Nd/^{144}Nd)_{CHUR}$ = 0.511836, $(^{147}Sm/^{144}Nd)_{DM}$ = 0.225, $(^{143}Nd/^{144}Nd)_{DM}$ = 0.51235.

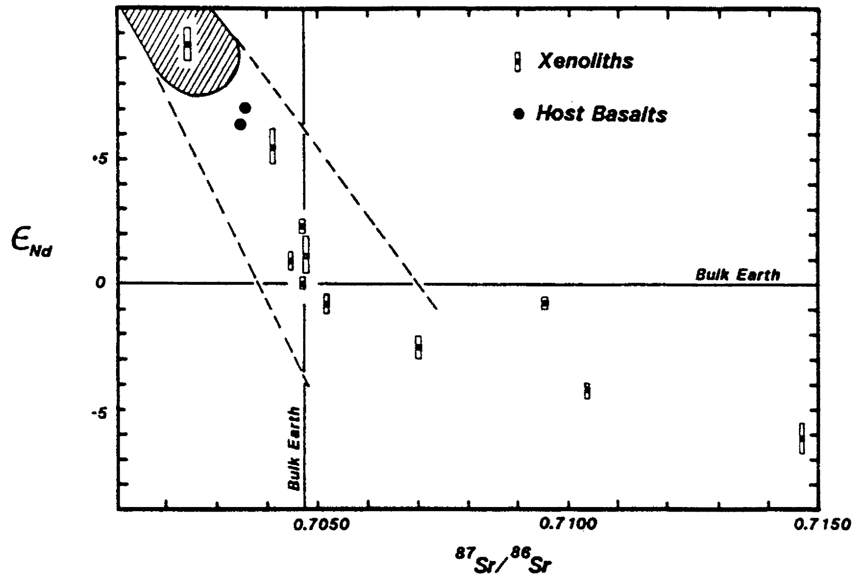

FIG. 7. Present day $^{87}Sr/^{86}Sr$ *versus* ϵ_{Nd} values for lower crustal xenoliths and host basalts. Symbols for xenoliths same as in Fig. 4. Hatched area is field of MORB. Dashed lines represent oceanic mantle array as defined by MORB and ocean island basalts, including St. Helena, Samoa, French Polynesia, Tristan da Cunha and Kerguelen (DEPAOLO and WASSERBURG, 1976; O'NIONS *et al.*, 1977; DOSSO and MURTHY, 1980; WHITE and HOFMANN, 1982; COHEN and O'NIONS, 1982).

indicator of the degree of partial melting, whereas Sr and Nd isotope ratios are insensitive to partial melting. Additionally, the Rb-Sr and Sm-Nd systems do not yield significant isochrons, thus suggesting the Mg#-isotope correlations reflect crystallization in an open system. Indeed, the range of $^{87}Sr/^{86}Sr$ ratios (0.7024 to 0.7147) is impossible to create through closed-system fractionation of a single melt. For example, if the xenoliths are derived from a melt with an initial $^{87}Sr/^{86}Sr$ ratio of 0.7024 (the lowest observed in the suite), then 83-140 (the sample with the highest $^{87}Sr/^{86}Sr$) would have initially needed 420 ppm Rb if it crystallized 300 Ma ago, or 62 ppm Rb if it crystallized 2500 Ma ago, in order to account for its high $^{87}Sr/^{86}Sr$ ratio. There are two major problems with this. First, if a plagioclase-rich cumulate like 83-140 has even 62 ppm Rb (a very high Rb content for a plagioclase cumulate, *cf.* MORSE, 1980), the Rb content of the coexisting liquid would be 520 to 1550 ppm Rb (using a bulk $D_{Rb} = 0.04$ to 0.12). These concentrations are unrealistically high. Secondly, this model would require the cumulate to have been depleted in Rb prior to or during entrainment in the host basalt. It is difficult to envision a Rb depletion which would preserve the correlation between Rb and Sr in the whole suite (Fig. 6b). Therefore, the high $^{87}Sr/^{86}Sr$ ratios observed in the more evolved rocks must be due to a process other than closed system crystal fractionation.

Given the xenoliths are cumulates, several observations rule against them being related to their host basalts. First, the $^{87}Sr/^{86}Sr$ ratios and ϵ_{Nd} value of the

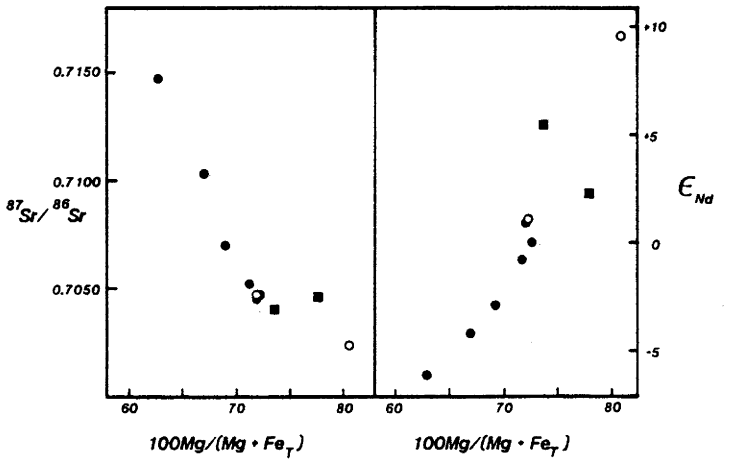

FIG. 8. $^{87}Sr/^{86}Sr$ and ϵ_{Nd} plotted against Mg#. 83-112, the one sample with primary Fe-oxides, is not plotted and would fall to the left of the diagrams. Symbols as in Fig. 4.

hosts are distinct from the isotopic compositions of the xenoliths (Table 4, Fig. 7). Secondly, as noted by FREY (1980) regarding the origin of Hawaiian pyroxenites, the ubiquitous metamorphic textures in these xenoliths suggest they are not direct cumulates from the host. Thirdly, the common occurrence of cumulate plagioclase in the xenoliths requires the coexisting liquid to have a negative Eu anomaly, yet the hosts have slight positive Eu anomalies (IRVING and FREY, 1984), as found in many other alkalic basalts (SUN and HANSON, 1975). Given these observations, it is concluded that the xenoliths are not precipitates from their host basalts.

Relative high $^{87}Sr/^{86}Sr$ ratios and low ϵ_{Nd} values are observed in some continental tholeiites and in some cases these features have been attributed to enriched mantle sources (MENZIES *et al.*, 1983; HAWKESWORTH *et al.*, 1983; KYLE *et al.*, 1983; MENZIES *et al.*, 1984; COX and HAWKESWORTH, 1985). Such an explanation for the range of $^{87}Sr/^{86}Sr$ ratios in the xenoliths is not consistent with the Mg#-isotope trends as it would require a very fortuitous relationship between the degree of melt fractionation and source composition.

AFC model

An alternative explanation for the observed trace element and isotopic correlations in the xenoliths is that the melt from which they crystallized was evolving through simultaneous assimilation and fractional crystallization (AFC). TAYLOR (1980), following BOWEN (1928), suggested that simple, two-component mixing is unlikely to describe the process of crustal assimilation because the heat required to melt crust must be derived from the latent heat of crystallization of the magma. Therefore, assimilation is likely to be accompanied by crystal fractionation and any assimilation models must include three components: magma, assimilate and cumulates. Most studies have applied AFC to explain compositional variations in lavas. The Queensland xenoliths provide an opportunity to examine the AFC process in mafic cumulates from the lower crust.

The isotopic and trace element variations produced through AFC can be described by a series of curves on isotope or trace element diagrams (TAYLOR, 1980; JAMES, 1981; DEPAOLO, 1981). The shape of the curves is primarily controlled by the elemental concentration ratios between the magma and assimilate and the chosen end member compositions. These curves reflect both melt and cumulate isotopic compositions at the time of crystallization, since cumulates will retain the isotope ratios of their coexisting melts. In the following arguments, we use Eqn. 15a of DEPAOLO (1981) to calculate the change in isotopic composition of the melt due to AFC. Both DEPAOLO (1981) and JAMES (1981) provide discussion of the effects of varying different input parameters on the shape of AFC curves.

The AFC model presented here is non-unique, given uncertainties in elemental concentrations and isotopic ratios in the parental melt and crustal assimilate(s). The following outlines the parameters chosen for our calculations and estimates of the uncertainty associated with each.

(1) r (the ratio of the mass of assimilate to the mass of crystals) is constant and equal to 0.85; such high values of r reflect the greater amount of assimilation possible in the warmer, lower crustal environment (JAMES, 1981). Changing r by 10% does not significantly change the shape of the curve but will move the position of the melt fraction. At higher r values the isotopic composition of the melt changes more dramatically at low percentages of AFC.

(2) the bulk D values ($\bar{D}$) are constant, with $\bar{D}_{Sr} = 0.8$ (reflecting Sr's incompatible behavior in the entire system (Fig. 6a)) and $\bar{D}_{Nd} = 0.1$. Changing the bulk D values by factors of 2 does not significantly change the shapes of the curves;

(3) Sr and Nd concentrations in the parental magma are 550 and 20 ppm, respectively. These concentrations are similar to those for primitive tholeiitic and alkalic basalts from southern Queensland (EWART *et al.*, 1980; EWART, 1982) and western Victoria (FREY *et al.*, 1978; MCDONOUGH *et al.*, 1985).

(4) Sr and Nd concentrations in the assimilate are 200 and 30 ppm, respectively. These values represent average concentrations for felsic rocks of the Tasman Fold Belt (BLACK, 1980; MCCULLOCH and CHAPPELL, 1982; HENSEL *et al.*, 1985), which are likely candidates for the contaminant. Note that terrigenous sedimentary rocks will have similar Nd contents (*e.g.*, TAYLOR and MCLENNAN, 1985), but can have highly variable Sr contents (Sr = 23 to 287 ppm for eastern Australian shales and graywackes [BLACK, 1980; MCCULLOCH and CHAPPELL, 1982; EWART, 1982]).

(5) the isotopic composition of the parental magma is equal to that of the most primitive xenolith (BC).

(6) the isotopic ratios of the cumulates have not changed significantly since crystallization (*i.e.*, the xenoliths are younger than ~100 Ma; see below).

Given these assumptions, the isotopic composition of the assimilate can be varied to produce curves which mimic the isotope variations observed in the xenoliths. The Queensland xenoliths crystallized and cooled in the lower 20 km of the crust within the Tasman fold belt, therefore the abundant granites and sediments in this region are likely candidates for the assimilate. Present day $^{87}Sr/^{86}Sr$ for Tasman Fold Belt granites in north Queensland range from 0.7123 to 0.9110 (BLACK, 1980). In more southerly parts of the Tasman fold belt, granites have present day $^{87}Sr/^{86}Sr$ ranging from 0.7046 to 0.8417 and $^{143}Nd/^{144}Nd$ from 0.51109 to 0.51204 (MCCULLOCH and CHAPPELL, 1982; HENSEL *et al.*, 1985). The model assimilates used here fall near the middle of these large isotopic ranges.

Figure 9 presents three curves which correspond to different crustal end members; two curves bracket the data, the central curve represents an "average" model. Because the data do not lie along a single curve, it is likely that more than one crustal end member was in-

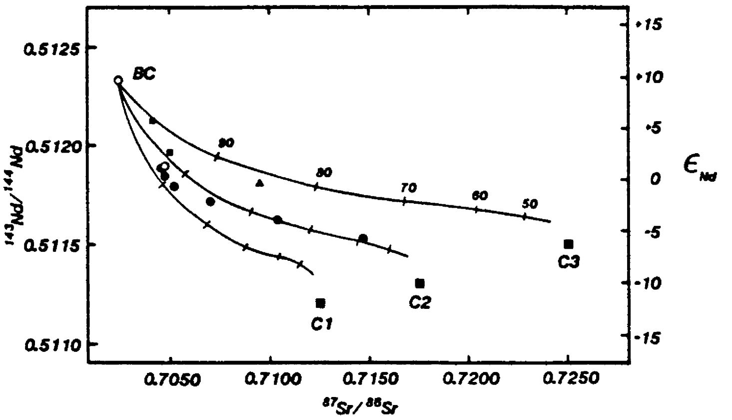

FIG. 9. AFC curves calculated using BC (the most primitive xenolith) as the starting composition and several crustal assimilates (C1, C2 and C3). Tick marks represent percentage of melt remaining.

volved. This is further supported by the range of depths from which the xenoliths were derived (20 to 40 km). In this context, it is interesting to note that there is a general correlation between depth of origin (as inferred from the mineralogies, Table 1) and isotopic composition: xenoliths derived from the deepest levels have more "primitive" isotopic ratios than xenoliths derived from shallow levels. However, this is not true for the most evolved sample (83-140), which is garnet-bearing. This may be evidence for more than one melt being involved.

The correlation between isotopic ratios and Mg# suggests a single isotopic composition for the parental melt. The mantle source region from which this melt was derived has the isotopic characteristics of MORB. However, this may not be true if the most primitive xenolith, BC, which is strongly LREE depleted, is actually older than the other xenoliths. Because BC falls along all the geochemical and isotopic trends, we consider it genetically related to the other xenoliths and thus include it in the model.

The $^{143}Nd/^{144}Nd$ ratio of the most evolved xenoliths can be used to place age constraints on the assimilate. Sample 83-107, the second most evolved xenolith, has a low $^{147}Sm/^{144}Nd$ ratio, thus is suitable for model age calculations (McCULLOCH and WASSERBURG, 1978). This sample has a model age of 390 Ma, if derived from a chondritic mantle (Table 4). Because the isotopic composition of this xenolith is a mixture between the original magma and the assimilate, this age represents a minimum model age for the assimilate, *i.e.*, the crustal assimilate must have been derived from the mantle before 390 Ma. The model age of the assimilate could be much older than this if 83-107 contains only a small proportion of assimilate and/or the assimilate was derived from a depleted mantle (T_{DM} = 1000 Ma; Table 4).

Nature of the coexisting liquid

The trace element and isotopic correlations exhibited by the xenoliths suggest they represent crystals that accumulated within the lower crust from a single melt or a series of related melts, which evolved through assimilation and fractional crystallization. The bulk composition of the coexisting melt is difficult to estimate accurately without knowing the proportion of cumulates to liquid in the system. Nevertheless, several indirect methods can be used to estimate bulk composition. First, given the limited amount of trapped melt originally present, the normative mineralogies of the xenoliths may be taken as a guide to the original cumulate phases (*cf.* ROGERS and HAWKESWORTH, 1982). The presence of olivine and Ca-rich plagioclase in the norms suggest the xenoliths crystallized from a mafic melt. Secondly, the Mg# of modal olivine can be used to calculate the Mg# of the coexisting liquid, assuming $D_{Fe/Mg}^{ol/melt} = 0.3$ (ROEDER and EMSLIE, 1970). Modal olivine is present in one of the analyzed samples (83-107), but is variably altered to iddingsite (see Appendix). Probe analyses for these olivines show that Fo contents negatively correlate with Al_2O_3 contents, consistent with a lowering of Fo content due to alteration (DEER *et al.*, 1982). The least altered olivines in this sample are Fo_{70} (with 0.33% Al_2O_3). If this is taken as an approximation of the igneous olivine's composition, then the coexisting melt had an Mg# of 41, using total Fe as $Fe+^2$. If one assumes an $Fe+^3/Fe+^2$ ratio of 0.15, then the coexisting melt had Mg# = 45. Sample 83-107 has one of the lower Mg#s of the suite, so this Mg# represents a lower estimate for the associated melts. This is consistent with the coexisting melt(s) being basaltic, with Mg#s generally >40.

Implications for continental lavas

In the AFC model presented above, the most contaminated xenolith is produced through 40% crystallization of the melt. If this melt were erupted, it would have chemical and Sr and Nd isotopic characteristics similar to those of other evolved continental basalts (*i.e.*, Mg# ≈ 40, negative Eu anomaly, low ϵ_{Nd} and high $^{87}Sr/^{86}Sr$). Unless the magma was tapped after only a few percent fractionation, the isotopically

MORB-like mantle source region for the xenolith's parental magmas would never be recognized. This illustrates the difficulty in inferring mantle compositional variations from continental lavas which have undergone any differentiation within the lower crust.

Oxygen isotopes are often used to delineate the amount of crustal assimilation that has occurred in basaltic melts, yet little is known about the effects of granulite facies metamorphism on $\delta^{18}O$ values. Some granulites exhibit slight decreases in $\delta^{18}O$ relative to their unmetamorphosed precursors (JAMES *et al.*, 1980; VALLEY and O'NEIL, 1984), whereas others exhibit significant $\delta^{18}O$ depletions as a result of metamorphism (SHIEH and SCHWARCZ, 1974; WILSON and BAKSI, 1983). Thus it is difficult to generalize about the $\delta^{18}O$ values of felsic granulites, which could be an important contaminant of basaltic magma in the lower crust. Preliminary oxygen isotope measurements of the Queensland xenoliths reveal that the most evolved xenolith in this suite (83-140) has a $\delta^{18}O$ value of +5.7‰ (RUDNICK and CHIVAS, unpubl. data). Oxygen isotopes will not be significantly fractionated during igneous crystallization. Therefore, if the oxygen isotopes of this rock have not exchanged with an external reservoir during isobaric cooling and development of the metamorphic mineralogy, then this $\delta^{18}O$ value reflects that of the coexisting melt. This, in turn, suggests that the assimilate may have had very low $\delta^{18}O$ yet high $^{87}Sr/^{86}Sr$ and low ϵ_{Nd}.

Age of the lower crust

The Queensland xenoliths plot along a scattered, positive trend on an $^{147}Sm/^{144}Nd$ *versus* $^{143}Nd/^{144}Nd$ isochron diagram (Fig. 10). If all the data points are considered, the regression yields an age of 570 ± 370 Ma with an initial $^{143}Nd/^{144}Nd$ ratio of 0.51118 ± 45 ($\epsilon_{Nd} = +1.6$) (using the model 4 regression technique of MCINTYRE *et al.*, 1966). However, if the above model of AFC is correct, then a positive trend would be produced on this diagram due to mixing between melt and assimilate. Since the xenoliths are cumulates, they would not be expected to plot along a straight mixing curve because their $^{147}Sm/^{144}Nd$ ratio is a function of both melt and assimilate compositions and cumulate mineralogy, whereas the $^{143}Nd/^{144}Nd$ ratio is a function of assimilation only. For example, assimilation will cause the data to fall along a line joining the original melt to the assimilate. Superimposed upon this are the effects of crystal accumulation. Pyroxene-rich xenoliths with LREE depletions will fall to the right of the mixing line, whereas LREE-enriched plagioclase-rich xenoliths will fall to the left of the mixing line (Fig. 10, inset). This explains the observed scatter in Fig. 10, and suggests that the positive trend is due to mixing between two end members and has no age significance.

The Queensland xenoliths possess geochemical features indicative of a common origin, and do not show the effects of element depletion often associated with granulite facies metamorphism. Yet for these xenoliths it is probably misleading to attach any age significance to the positive slope in Fig. 10. So is there any age information available from these data? The cumulate process creates highly variable whole rock Sm/Nd ratios, but generally very low Rb/Sr ratios. Consequently, the present $^{87}Sr/^{86}Sr$ ratios in the xenoliths are likely to reflect their initial values, whereas the $^{143}Nd/^{144}Nd$ ratios will change dramatically with time. The present correlation between ϵ_{Nd} and $^{87}Sr/^{86}Sr$ for the Queensland xenoliths becomes progressively weaker as the isotope ratios are back-calculated to earlier times. In addition, the good correlation of isotope ratios with

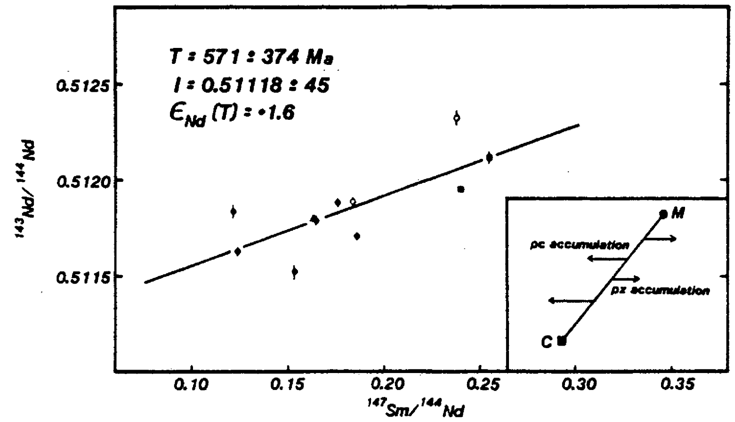

FIG. 10. Sm-Nd isochron diagram for lower crustal xenolith suite. Line represents regression yielding age of 571 ± 374 Ma. Symbols as in Fig. 4. Inset: schematic drawing showing predicted $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios for cumulates derived from melt (M) which is mixing with assimilate (C). Note that the line in the inset is not meant to coincide with the regression line shown in the main figure. It is assumed that the $^{147}Sm/^{144}Nd$ ratio of (M) is less than or equal to 0.197, in order to have a chondritic or LREE enriched melt. Accumulation of plagioclase (pc) causes $^{147}Sm/^{144}Nd$ to decrease, whereas accumulation of pyroxene (px) causes $^{147}Sm/^{144}Nd$ to increase relative to the melt. The melt composition continuously evolves between M and C.

Mg# (Fig. 8) becomes more scattered in the past. The correlation coefficient (r) for present day ϵ_{Nd} values *versus* Mg# is 0.91, at 400 Ma, $r = 0.79$ and at 1000 Ma, $r = -0.01$. Therefore, if we assume that the correlation of ϵ_{Nd} with Mg# is, like the trace element-Mg# correlations, due to AFC processes, then the time at which the greatest correlation exists may give the most reasonable age for the suite. This suggests the xenolith suite is relatively young (<100 Ma); and is probably not Paleozoic, as implied by the pseudoisochron.

Before any useful age information can be obtained from a suite of metamorphic rocks, it must first be shown that the rocks are genetically related (with the same initial ratio) and that their isotope ratios have not been affected by metamorphism. With a xenolith suite these problems are magnified due to lack of any field relationships. In addition, many investigators have plotted felsic xenoliths on the same isochrons as mafic xenoliths (ROGERS and HAWKESWORTH, 1982; MCCULLOCH *et al.*, 1982), but have not attempted to provide chemical evidence for their proposed genetic link.

If AFC was operating during the generation of other xenolith suites, it may be detectable by back-calculating isotope ratios to see if they lie along an AFC-type mixing curve at any time in the past. For example, the range of $^{87}Sr/^{86}Sr$ ratios present in Calcutteroo xenoliths from South Australia (MCCULLOCH *et al.*, 1982) suggests AFC may have been important in their evolution. Present day isotope ratios for the mafic xenoliths show considerable scatter on an ϵ_{Nd} *vs.* $^{87}Sr/^{86}Sr$ diagram (Fig. 11a). However, a linear trend is obtained at 1300 Ma (Fig. 11b). Figure 11 also shows the north Queensland data at present (c) and at the pseudoisochron age of 570 Ma (d) for comparison. By analogy with the Queensland xenoliths, the 2.5 Ga age reported by MCCULLOCH *et al.* (1982) for the Calcutteroo xenoliths may be an artifact produced by mixing of 1300 Ma mafic magma with older silicic crust. Of course, there are large uncertainties associated with these ages, and factors such as whether the rocks are originally cogenetic or have undergone post-crystallization Rb depletion, will add to the uncertainty. Other mafic xenolith suites for which isochrons have been published either do not show high $^{87}Sr/^{86}Sr$ ratios (*i.e.*, Lesotho xenoliths), or do not back-calculate to linear trends in the past (Eifel xenoliths, STOSCH *et al.*, 1986). Therefore, this model may be applicable in only some cases and each xenolith suite clearly needs to be evaluated separately.

Composition of the lower crust

The majority of granulite facies xenoliths from eastern Australian volcanic pipes are mafic and probably represent basaltic melts with variable proportions of cumulate phases (EDWARDS *et al.*, 1979; WILKINSON and TAYLOR, 1980; KAY and KAY, 1983; WASS and HOLLIS, 1983; ARCULUS *et al.*, 1986; GRIFFIN and O'REILLY, 1986; RUDNICK and TAYLOR, 1986). Seismic refraction profiles across the Tasman fold belt in southern Queensland and New South Wales show a high velocity lower crust (V_p = 6.7 to 7.7 km/sec, FINLAYSON, 1982; FINLAYSON *et al.*, 1984), indicative of a mafic composition.

The data for the Queensland xenoliths presented here may be used to clarify when and how the lower crust formed. If the Queensland xenoliths are Cenozoic cumulates associated with intrusion of basaltic magmas into the lower crust, then they significantly postdate

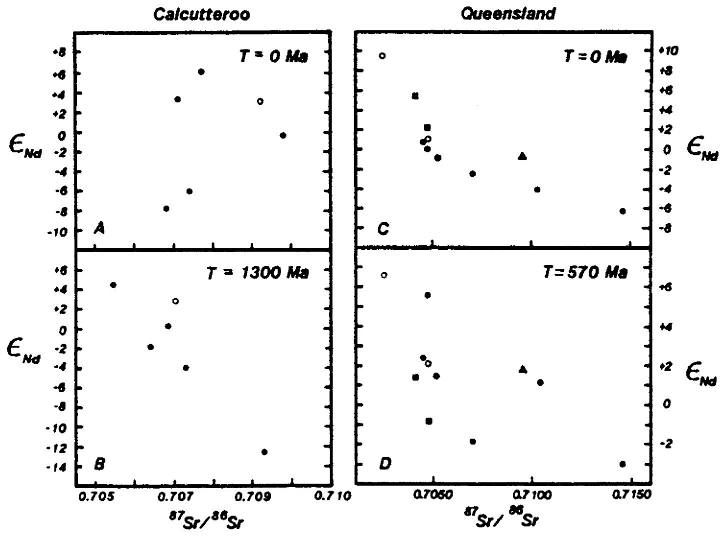

FIG. 11. (A) Present day $^{87}Sr/^{86}Sr$ *versus* ϵ_{Nd} values for mafic Calcutteroo xenoliths from south Australia (MCCULLOCH *et al.*, 1982). Filled circles are mafic granulites; open circle is an eclogite. (B) $^{87}Sr/^{86}Sr$ *versus* ϵ_{Nd} for Calcutteroo xenoliths at 1300 Ma. (C) Present day $^{87}Sr/^{86}Sr$ *versus* ϵ_{Nd} for Chudleigh province xenoliths compared with ratios for same xenoliths at 570 Ma (D) (pseudoisochron age). Symbols as in Fig. 4.

the sediments, lavas and granites of the Paleozoic Tasman fold belt. The observation that the parental magma to the xenoliths was affected by assimilation of isotopically evolved crustal material suggests the existence of felsic to intermediate rocks in the lower crust at the time of magma intrusion. Basaltic magmas ranging from highly silica undersaturated to saturated compositions have erupted in the highlands of eastern Australia from 70 Ma to Recent times (WELLMAN and MCDOUGALL, 1974). Of the three types of igneous provinces identified by WELLMAN and MCDOUGALL (1974), basalts of the central volcano provinces have been associated with deep crustal fractionation (EWART *et al.*, 1980; EWART, 1982; KNUTSON *et al.*, 1986) and extensive basaltic underplating is predicted to attend their formation (EWART *et al.*, 1980).

The eastern Australian central volcano provinces show a progressive decrease in age from north to south, which has been interpreted as a hot-spot trace (WELLMAN and MCDOUGALL, 1974; SUTHERLAND, 1983). The northernmost central volcano province is 32–33 Ma old and lies at 21° South. This is about 400 km east and 60 km south of the vents in the Chudleigh province. Assuming volcano spacing is regulated by the tensional stress field along the highlands (STEPHENSON and LAMBECK, 1985) and a migration rate of 66 km/Ma (WELLMAN and MCDOUGALL, 1974) for the central volcano-type activity, the hot spot would be predicted to be within the Chudleigh region some 33–35 Ma ago. A 35 Ma crystallization age is consistent with the chemical and isotopic data, thus the xenoliths may represent a lower crustal manifestation of basaltic magmatism in the region. Consequently, the Cenozoic igneous activity throughout eastern Australia may have provided more volumetrically significant crustal additions than are represented by the extruded rocks alone.

CONCLUSIONS

Integrated petrographic, geochemial and isotopic data for the granulite facies xenoliths from north Queensland indicate the rocks formed as cumulates from an evolving continental tholeiitic or alkalic basaltic magma which crystallized deep within the crust and isobarically re-equilibrated. The coherent geochemical and isotopic trends suggest that the basaltic liquid evolved through simultaneous crystal fractionation and assimilation of felsic crustal material. In particular, the good correlation between Sr and Nd isotopic composition and Mg# rule out mantle source heterogeneities as a means of producing the observed spread in isotopic compositions and suggests a young (Cenozoic) age for these xenoliths. The inferred isotopic composition of the mantle source region for this suite has a long term LREE and Rb depleted character, similar to the MORB source region. Features of this study which have wide ranging implications are:

(1) The enriched isotope compositions for these xenoliths are produced through simultaneous assimilation and fractionation, suggesting the use of caution when interpreting mantle source characteristics from continental tholeiites which have experienced even limited amounts of fractionation within the lower crust;

(2) The positive correlation between ^{147}Sm/^{144}Nd and ^{143}Nd/^{144}Nd is a product of mixing of a basaltic magma and an older, felsic crustal component and has no age significance. Thus, careful evaluation of trace element data along with isotopic results is required to interpret the meaning of possible "isochrons" from lower crustal xenolith suites.

(3) It may be possible to determine the age of genetically related lower crustal xenolith suites that have evolved through AFC-type processes by back-calculating their isotopic ratios to the time at which the samples plot along a trend on an ϵ_{Nd} *versus* ^{87}Sr/^{86}Sr diagram.

(4) These xenoliths provide evidence for Cenozoic basaltic underplating in the lower crust of eastern Australia, though the volumetric significance of this process is not constrained.

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APPENDIX

PETROGRAPHIC DESCRIPTIONS OF ANALYZED SAMPLES

Plagioclase-rich samples

83-107. Polygonal, optically zoned labradorite forms medium-grained (~0.3 mm) matrix around larger (up to 4 mm) deformed plagioclase (labradorite) with irregular grain boundaries, and elongate olivine-centered coronas. Olivine (Fo$_{54-70}$, variably altered to red-brown iddingsite) is rimmed by orthopyroxene which is generally rimmed by fine-grained spinel-pyroxene symplectite. Rare, large (~4 mm), optically continuous, poikilitic orthopyroxenes show some exsolution lamellae. Plagioclase within orthopyroxene have preserved lath-shaped crystal form. Plagioclase contains tiny (~5–10 μm), euhedral spinel inclusions.

83-112. Medium-grained (~0.5 mm), polygonal andesine matrix surrounds clusters of polygonal clinopyroxene (with thin exsolution lamellae)-orthopyroxene-magnetite (with ilmenite exsolution). Magnetite/ilmenite rimmed by dark alteration rims. Oriented oxide inclusions within clinopyroxene. Plagioclase devoid of spinel inclusions. Grain boundaries altered.

83-114. Medium-grained (~1.5 mm), zoned, deformed and broken labradorite (with andesine rims) with irregular grain boundaries surrounds irregularly-shaped, zoned and fractured clinopyroxene and orthopyroxene crystals and symplectic spinel-pyroxene intergrowths. Garnet forms completely kelyphitized thin rims around spinel. Grain boundaries altered. Plagioclase contains small (~75 μm), elongate spinel inclusions.

83-117. Medium-grained (0.6 mm), polygonal andesine surrounds symplectic intergrowths of pyroxene-spinel. Spinel surrounded by completely kelyphitized garnet. Orthopyroxene altered yellowish-brown with dark brown staining in fractures, some spinel altered to lemon yellow color. Much grain-boundary alteration. No spinel inclusions within plagioclases.

83-125. Coarse- to medium-grained (4 to 0.5 mm) andesine (large grains broken, small grains polygonal) forms matrix around euhedral garnet and garnet-clinopyroxene intergrowths or clusters. Clinopyroxene has typically smooth grain boundaries and no exsolution lamellae. Orthopyroxene rare. Rare, small (~250 μm) spinel cores occur at center of euhedral garnets. Garnets totally kelyphitized. Grain boundaries and fractures altered. Plagioclase devoid of spinel inclusions.

83-127. Coarse-grained (up to 3 mm), zoned, fractured labradorite, with andesine rims, surrounds clusters of clinopyroxene and coarse-grained symplectic orthopyroxene-spinel, which are sometimes rimmed by clinopyroxene. Plagioclase contains large (~ 150 μm), euhedral spinel inclusions.

83-131. Coarse-grained (up to 4 mm), zoned, deformed labradorite crystals (with andesine rims) form irregular grain boundaries with large (~ 2 mm) clinopyroxene crystals which show abundant exsolution lamellae. Smaller (~0.3 mm), polygonal clinopyroxenes have no exsolution. Euhedral garnet found within plagioclase matrix. Symplectic pyroxene-garnet rimmed by orthopyroxene. Some relict spinels at center of symplectic pyroxene-garnet intergrowths. Clinopyroxene rims orthopyroxene. Rare secondary amphibole. Some plagioclase crystals contain large (~ 150 μm), euhedral spinel inclusions. Grain boundaries relatively free of alteration.

83-133. Medium-grained (~0.5 mm), polygonal andesine forms matrix around mosaic-textured clinopyroxene clusters, symplectically intergrown orthopyroxene-garnet, and euhedral garnet. Occasional spinel cores at center of symplectites; no spinel observed at centers of euhedral garnets. Garnet within symplectite and garnet rims all kelyphitic. Some plagioclase crystals riddled with small (~30 μm), euhedral spinel inclusions. Grain boundaries have thin coating of brown material.

83-138. Coarse-grained (up to 4 mm), zoned, deformed and broken labradorite crystals with irregular grain boundaries form matrix around large (~ 5 mm) clusters of coarse-grained (up to 4 mm) clinopyroxene with smaller orthopyroxene and spinel. Coarse-grained clinopyroxene shows abundant thin exsolution lamellae and contains many CO_2-rich fluid inclusions. Spinel symplectically intergrown with pyroxene. Spinels sometimes have very thin, kelyphitized garnet rims. Orthopyroxene tends to be concentrated toward outside of clusters or within plagioclase matrix. Grain boundaries and fractures altered. Plagioclase does not contain euhedral spinel; some large clinopyroxenes contain spinel inclusions.

83-140. Coarse-grained (up to 4 mm), deformed and broken labradorite (rimmed by andesine), surround garnet-pyroxene symplectites and large, deformed clinopyroxenes and orthopyroxenes with exsolution lamellae. Rare spinel at center of garnet/pyroxene intergrowths. Orthopyroxenes rimmed by clinopyroxene when in contact with plagioclase. Some orthopyroxenes contain needle-like inclusions of rutile(?). Garnet heavily kelyphitized leaving only unaltered cores. Minor, small, red-brown amphibole. Rare ilmenite and zircons (<16 μm long). Grain boundaries altered. Plagioclase contains ~ 150 μm long spinel inclusions.

Pyroxene-rich samples

83-110. Coarse-grained (up to 3 mm), polygonal to irregular labradorite crystals with smaller, oval clinopyroxene and orthopyroxene crystals interlayered with coarse-grained clinopyroxene-orthopyroxene layers with minor plagioclase and rutile. Some of the larger pyroxene crystals have exsolution lamellae in two directions. Grain boundaries altered. Plagioclase does not contain spinel inclusions.

83-115. Coarse-grained (up to 4 mm), polygonal to irregular clinopyroxene and smaller orthopyroxene predominate with interstitial labradorite and rutile. Rare, thin exsolution lamellae in clinopyroxenes. Opaques occur along grain boundaries. Small rutile inclusions within pyroxenes. Plagioclase devoid of spinel inclusions.

Transitional samples

83-126. Coarse-grained (up to 3 mm), zoned, deformed labradorite, with andesine rims and irregular grain boundaries occurs with large (up to 3 mm) clinopyroxenes (with abundant exsolution lamellae) and orthopyroxenes. Clinopyroxene contains rutile lamellae. Spinel is intergrown with orthopyroxene and rimmed by clinopyroxene. Spinel and orthopyroxene rims altered dark brown. Grain boundaries and fractures altered and iron-stained. Plagioclase contains rare spinel inclusions.

BC. Medium-grained (~0.3 mm), generally untwinned, polygonal andesine crystals occur with euhedral garnets and large (up to 4 mm), recrystallized clinopyroxenes which often have an irregularly distributed, peculiar, vermicular-like texture. Rare, pale green spinels at center of some garnets. Garnets completely kelyphitized. Pyroxenes contain very small (~70 μm), irregular, pleochroic (biotite?) and opaque inclusions. Plagioclase devoid of spinel inclusions.

APPENDIX 2

Cenozoic Volcanism in North, East, and Central Otago

by D.S. Coombs, R.A. Cas, Y. Kawachi, C.A. Landis,
W.F. McDonough, and A. Reay

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Cenozoic Volcanism in North, East, and Central Otago

Douglas S. Coombs*, R. A. Cas, Yosuke Kawachi*, C. A. Landis*, W. F. McDonough*** and A. Reay***

Submarine basaltic activity occurred offshore of North Otago in Paleocene time. The Waiareka-Deborah volcanics result from late Eocene to early Oligocene volcanism extending from 40 ± 2 to about 32 m.y. before present. Fragmental deposits of largely Surtseyan shallow submarine eruptions show a variety of sedimentary forms some suggestive of surge deposits. They were reworked and redeposited by a variety of mechanisms including turbidity currents, mass flow, and grain flow. Products of the volcanism include shallow intrusives and pillow lava of olivine tholeiite which differentiated to high-silica residua, tholeiitic tephra, basanitic and nephelinitic tephra, and probably a range of mildly to more strongly alkalic shallow intrusives. The total volume was of the order of 100 km^3. Electron microprobe analyses of glasses from pillow margins and tephra confirm the tholeiitic nature of some of the tephra and the basanitic to nephelinitic nature of others. Early tholeiitic volcanism was followed by emplacement of tholeiitic and alkalic products, both voluminous. The basanitic tuffs, hitherto largely unrecognised, contain lherzolite fragments and high-pressure pyroxene megacryst fragments, analyses of which are given. The mineralogy and origin of the nephelinitic Kakanui Mineral Breccia are reviewed and new data on its pyroxenes and garnets are illustrated. Fluid inclusions of CO_2 in both tholeiitic and alkalic associations suggest the importance of CO_2 in the eruptive history.

It is proposed that the name Dunedin Volcanic Complex be amended to Dunedin Volcanic Group and redefined to include all late Tertiary volcanic rocks of eastern and Central Otago, including Waipiata Volcanic Formation. It includes a major shield volcano, the Dunedin volcano, active from 13 to 10 m.y. before present and numerous outlying, short-lived vents active from about 21 m.y. before present and overlapping with the lamprophyre dikes of northwest Otago and South Westland. In the Dunedin volcano a complex series of lineages gave rise to relatively voluminous phonolitic trachytes and phonolites by low-pressure fractionation of a range of mantle-derived basaltoid magmas of differing degrees of silica undersaturation and Na_2O/K_2O ratios. The outlying vents were characterised by rapid rise of relatively undifferentiated magma, in many cases carrying spinel lherzolite nodules. The Pigroot "mafic phonolite" has a high-pressure origin distinct from that of phonolites of the Dunedin shield volcano. Surge deposits amongst other pyroclastics indicate numerous phreatomagmatic eruptions. The region is one of fault-block topography controlled by post-volcanic reverse faulting, but there was low relief and northwest-southeast extensional stresses prevailed in the crust during the volcanism. Sr and Nd isotope compositions for Dunedin rocks, for the Kakanui Mineral Breccia, and for Banks Peninsula, are closely similar to those of the South Westland lamprophyric dikes, and occupy a distinctive position relative to the "mantle array". They also conform with those from Marie Byrd Land, with which the New Zealand – Campbell Plateau continental fragment was in juxtaposition 80 m.y. ago. The data imply derivation from a mantle source which had been depleted in light REE for some considerable time before recent enrichment in light REE and many other incompatible elements.

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INTRODUCTION

Three distinct periods of Cenozoic volcanism are recognised in the eastern part of the Otago region. One of these is known only from the presence of basaltic tuff of Paleocene age in an exploration well 17 km off the North Otago coast near Oamaru. Products of the second period, of late Eocene to early Oligocene age, are found in a triangular area about 60 km long and 30 km wide near the present northeast coast of Otago (Fig. 1). Extensive tephra and some pillow lavas were deposited on the continental shelf of the day by eruptions that were largely or entirely submarine. Doleritic

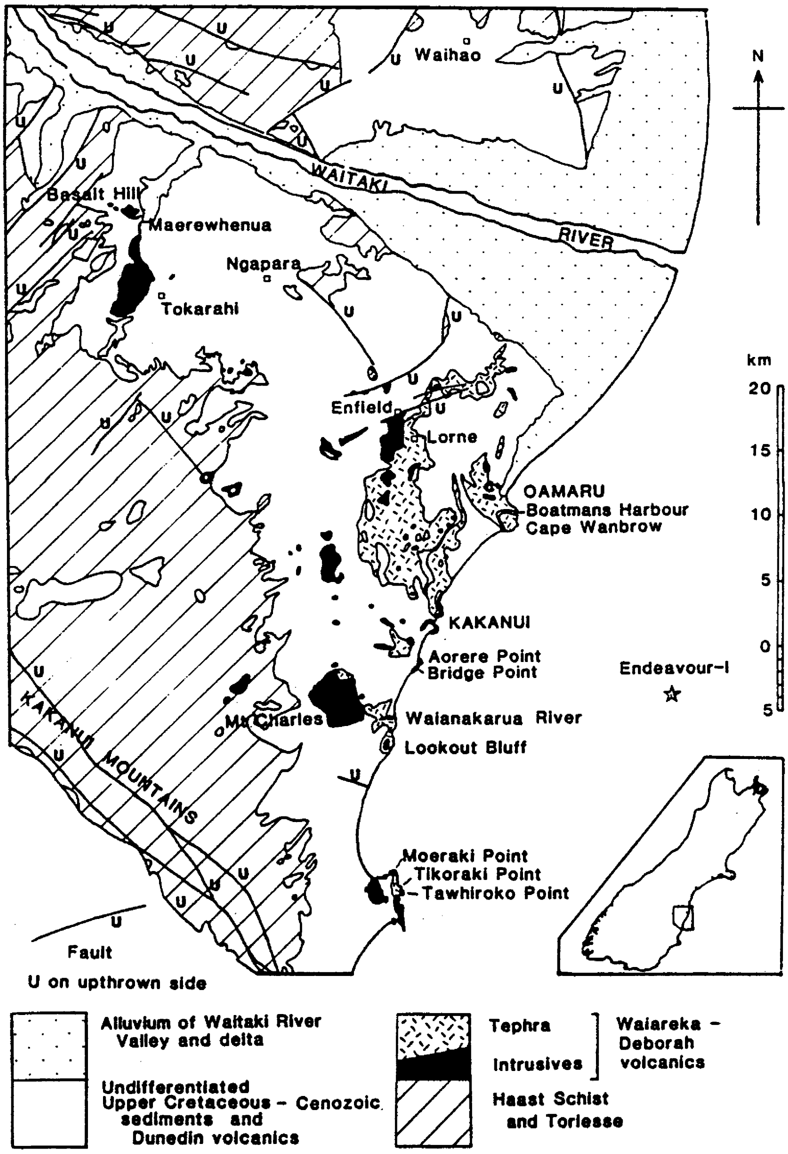

Fig. 1—Waiareka-Deborah volcanics, North Otago, mainly after Benson (1943), Gage (1957) and Mutch (1963).

sheets and dikes were emplaced within the shelf sediments which included limestones and more or less unconsolidated mudstones and siltstones. These rest on Upper Cretaceous to Eocene quartz sands and conglomerates with coal seams, themselves resting on a basement of Haast Schist. Many of the volcanic products were tholeiitic in composition, but substantial volumes of mildly to highly alkalic mafic magma were also involved, producing for example the nephelinitic Kakanui Mineral Breccia, well known for its suite of garnet pyroxenite ("eclogite") blocks and other deep-seated xenoliths and megacrysts.

Activity in the third period of volcanism was spread over a much larger area of eastern and Central Otago. It built up a substantial volcanic edifice, the Dunedin volcano, in late Middle Miocene time, but the activity of some of the outlying vents extends back to early Miocene, and overlaps with that of members of the lamprophyric dike swarm of Northwest Otago (Cooper, this volume). Products of the Miocene petrographic province of eastern and Central Otago are virtually entirely subaerial and alkalic, ranging in composition from mildly alkalic basalts through basanites to nephelinites, and from slightly quartz-normative trachytes to phonolites, with a wide range of intermediate types as well.

PALEOCENE SUBMARINE VOLCANISM OFFSHORE OF NORTH OTAGO

The log of the exploration well Endeavour 1 (Wilding and Sweetman, 1971), drilled 17 km southeast of Cape Wanbrow near Oamaru (Fig. 1), records glassy basaltic tuff at a depth of about 5960 ft and again from about 6000 to 6350 ft. The enclosing mudstones are dated as Teurian (Paleocene) to which Hoskins (1982) ascribes a radiometric age of about 65 to 54 m.y.. The tuff is described as having pseudomorphs after olivine, much montmorillonite and chlorite, an analcime matrix and some calcite. So far, no evidence for contemporaneous volcanism has been recognised in rocks of comparable age exposed onshore in eastern Otago. The fact that more than 100 m of basaltic tephra were penetrated without encountering, as far as is known, any dikes or other massive volcanic rocks, suggests that the drill hole passed through the flanks of a sizeable submarine volcano.

THE WAIAREKA-DEBORAH VOLCANICS: LATE EOCENE-EARLY OLIGOCENE VOLCANISM IN NORTHEAST OTAGO

Early work

The occurrence at Kakanui of tuff containing crystals of hornblende, augite and garnet, was reported by Mantell as early as 1850. In a schematic cross section, Hector (1864) showed "basalt and tuffaceous rocks" of Tertiary age at Moeraki and Oamaru and in 1884 he introduced the terms "Waireka series" and "Waireka tufas". Many observations on Tertiary volcanic rocks in northeast Otago have subsequently been published, but only the more important of these will be mentioned here. Hutton (1887) described four supposed eruptive centres as the Oamaru, Deborah, Enfield and Kakanui volcanoes. He also gave details of other occurrences further south at Mount Charles, Lookout Bluff and Moeraki, although he considered these to be much younger. He described tuffs, dolerites, glassy "tachylite" (sideromelane) breccias partly altered to palagonite, limestone veins or dikes cutting these as for example at the Oamaru breakwater quarry, and a "remarkable agglomerate" (occurring at Boatman's Harbour, Oamaru) in which the lower surfaces of the "bombs" curve round those below, each being encased in a coating of "tachylite", the interstices being filled with fossiliferous limestone. This celebrated occurrence was identified by Park (1905) as pillow lava, the first to be recognised in New Zealand.

Further details of the "gem gravels" at Kakanui were given by Thomson (1906, 1907). Park (1905) emphasised the essentially submarine nature of the volcanism, and in his 1918 Bulletin on the area he gave many more details of the pyroclastic and intrusive rocks, together with stratigraphic interpretations. Uttley (1918) provided further information on the pillow lavas and overlying pillow breccias at Oamaru. An important elucidation of stratigraphic relationships was effected by Gage (1957), and Benson (1943, 1944, 1945) published the results of a petrological study of the volcanic province as a whole. He paid particular attention to the petrology of the tholeiitic olivine dolerite sheet at Tawhiroko Point, Moeraki, introducing the new mineral name, subcalcic augite. He also pointed out the presence of alkalic intrusives.

Age and duration of volcanism

Although details were hotly debated in the early literature, it has long been considered that the bryozoan Totara Limestone (Gage, 1957) commonly intervenes between lower and upper volcanic horizons. These are the Waiareka and Deborah Volcanic Formations respectively, the latter including the Kakanui Mineral Breccia Member. In the discussion that follows, dates for the various New Zealand stages are taken from Hoskins (1982), slightly modified by N. de B. Hornibrook (pers. comm., 1985) according to the time scale of Berggren *et al.* (in press).

In the Oamaru area, Waiareka tuffs rest on the Raki Siltstone of middle Kaiatan age (43–38 m.y., Upper Eocene), *Chiasmolithus oamaruensis* zone (Edwards, 1971a). At Moeraki Peninsula, tuffs are underlain by mudstone and near their base contain thin bodies of mudstone (Coombs and Dickey, 1965) which appear to have been emplaced by upward injection as neptunic dikes. These mudstones also are of Kaiatan age (Hornibrook, pers. comm., 1985). In one case on the shore between Tikoraki Point and Tawhiroko Point, a fissure in tuff, some decimetres wide, is in part injected by a basaltic dike and in part by a neptunic dike of the mudstone. Near Lookout Bluff, strong load casting is visible at the contact and lobes and veins of lapilli tuff intricately penetrate underlying mudstone. Such observations suggest that the muds were quite unconsolidated when the tuffs were emplaced and presumably they are but little older. A mudstone sample from near the base of the volcanics at Lookout Bluff is of late Kaiatan age and the Waiareka tuffs themselves contain Kaiatan faunas at Lorne and Fortification Hill (Gage, 1957).

Inland where the Raki Siltstone is missing through non-deposition or erosion, typical occurrences of the volcanics are as sills and dikes in the underlying Tapui Glauconitic Sandstone of Bortonian age (46–43 m.y.). Near Tokarahi a columnar jointed sill, intrusive into the Tapui, appears to pass laterally into irregularly jointed basalt with locally developed glassy selvages suggesting crude pillow forms (Amies, 1952; Gage, 1957). Accepting the Bortonian age for the Tapui Sandstone, this could suggest either that the volcanic sheet was emplaced in Bortonian time, thus extending the period of volcanism at that locality backwards by several million years, or that the Tapui sands remained sufficiently wet for the magma emplaced within them to develop the pillow-like forms several million years after sedimentation.

The Totara Limestone and the Oamaru Diatomite both contain tuffaceous horizons and overlie the more massive tephra of the Waiareka Volcanic Formation. They are both placed in the Runangan Stage (Upper Eocene, 38–36.5 m.y.) on microfaunal evidence. The Oamaru Diatomite, consisting of 25 to 50 m of diatomaceous mudstone with interbedded tuffs, has long been regarded as part of the Waiareka Volcanic Formation and is now interpreted by Edwards (1971b) and Hornibrook (1983) as a lateral equivalent of the Totara Limestone, the diatomite accumulating in lows, while the limestone formed highs. The overlying Deborah Volcanic Formation is largely or entirely lower Whaingaroan (36.5–32 m.y., early Oligocene), again on microfaunal evidence (*Globigerina angiporoides* zone), as is the McDonald Limestone

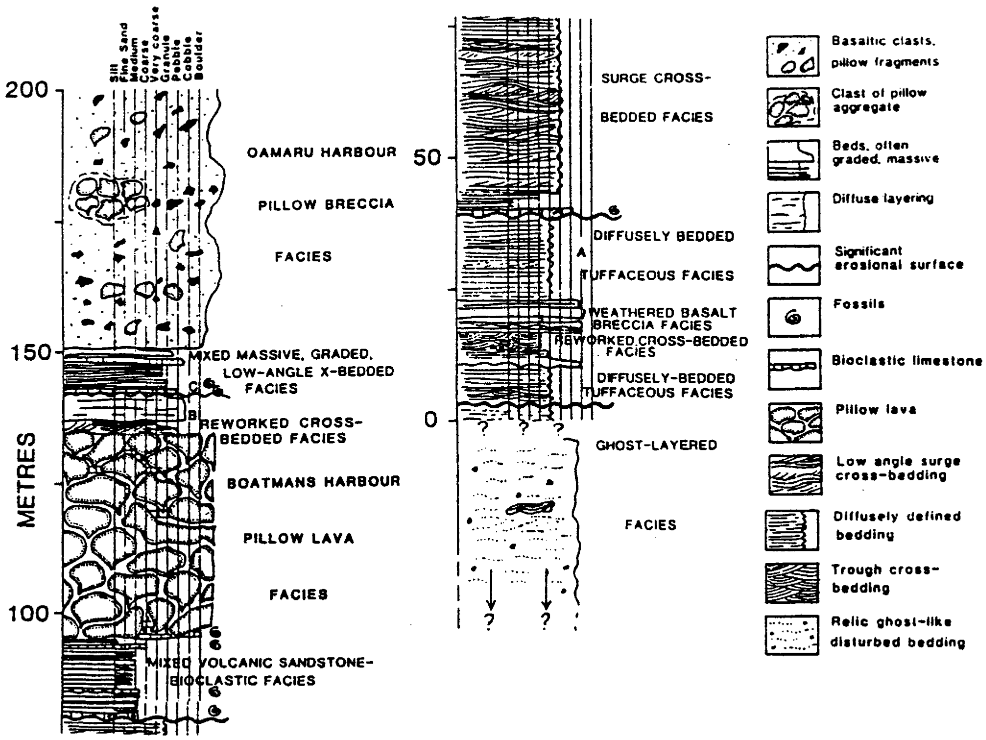

Fig. 2—Stratigraphic column, Waiareka-Deborah volcanics, Cape Wanbrow-Boatmans Harbour-Oamaru Harbour Board Quary section, North Otago. A. B. Basanitic cobbles and lapilli, lherzolite nodules and high-alumina clinopyroxene megacrysts. C. Fine-grained basanitic tuff.

which overlies it in turn and which contains little if any evidence of contemporaneous volcanism.

It is now known (Lee, 1980; Hornibrook, pers. comm., 1985) that a Runangan fauna with *Bolivina pontis* occurs in tuffs in the upper part of the Cape Wanbrow section, 4.5 m below the Boatmans Harbour pillow lava (Fig. 2) and within the type section for the Waiareka Volcanic Formation as proposed by Gage (1957). Above the pillow lava, which consists of tholeiitic basalt, are about 4 m of reworked, cross-bedded tuffs largely of basanitic parentage, followed by a 6 m sequence of calcareous coarse tuffaceous sandstones, a greenish-grey laminated argillised basanitic tuff, and further calcareous fossiliferous beds. The sequence between the pillow lava and overlying pillow breccia is correlated by Gage (1957) with the Totara Limestone. It contains *Bolivina pontis* with *Globigerapsis index* and is thus also Runangan in age (Hornibrook, pers. comm., 1985).

In view of the presence of tuffs within the Totara Limestone and the variable thickness and facies of this unit, its use as the basis for a two-fold subdivision of the volcanics into earlier Waiareka and later Deborah Volcanic Formations is at best a simplification. Furthermore, basaltic intrusives emplaced within the Waiareka and earlier formations in general cannot confidently be ascribed to either a Deborah or a Waiareka age. (The possibility exists that some of these bodies could even be much younger and correlatable with the Dunedin and Waipiata volcanics of later Miocene time). We will use the informal term Waiareka-Deborah volcanics as a collective name for all the late Eocene – early Oligocene volcanics and shallow intrusives of northeast Otago and as a suitable term for those occurrences of appropriate general age which are not specifically differentiated as Waiarekan or Deborah.

The only radiometric dating of the North Otago volcanism so far available is due to Dasch *et al.* (1970) who reported a K/Ar date of 31.6 ± 0.6 m.y. for kaersutite and anorthoclase megacrysts in the Kakanui Mineral Breccia, equivalent to 32.4 ± 0.6 m.y. on the basis of currently accepted decay constants (Harland *et al.*, 1982).

In summary, volcanism in the Northeast Otago province straddled the Eocene-Oligocene boundary and extended through parts of three stages, late Kaiatan, Runangan and early Whaingaroan. Eruption of the Waiareka Volcanic Formation commenced in Kaiatan time at about 40 ± 2 m.y. and continued into Runangan time at 38—36.5 m.y.. Eruption of the Deborah Volcanic Formation ceased in the early Whaingaroan at about 32 m.y.. Volcanism may have proceeded intermittently throughout the whole period but it appears to have been less voluminous in Whaingaroan than in earlier time. Precise correlation of some of the intrusives in the area is particularly uncertain.

Nature of the volcanism and emplacement of its products

Waiareka-Deborah volcanism was restricted to the relatively shallow continental shelf of the day. Volcanic islands may at times have been built up above sea level giving rise to subaerial eruptions, but otherwise the volcanic products were entirely submarine or intrusive. Included are sills and less regular sheets and bulbous intrusions as at Moeraki Point and Tawhiroko Point where basaltic magma has invaded soft muds. A massive dike at Enfield may have been a feeder for intrusive sheets in that area, and relatively numerous dikes cutting hyaloclastite tuffs at Moeraki Peninsula are believed to have been feeders for submarine eruption of the tuffs.

Certain dikes at Tikoraki Point on Moeraki Peninsula can be dated rather definitely as of the same age as the tephra into which they are emplaced since they are internally brecciated with chilled glassy selvages. This suggests that they were open to sea water and may have fed the tuffs (Nakamura and Coombs, 1973). Other Moeraki Peninsula dikes cutting the tuffs, and irregular intrusive sheets emplaced in the underlying mudstones, show remarkable petrological similarities including similar suites of xenoliths and are presumed to be of essentially the same age.

Pillow lava occurs at Boatmans Harbour and a number of other localities. The Cape Wanbrow-Boatmans Harbour sequence (Fig. 2) consists of tuffs more than 150 m thick followed by tholeiitic pillow lava about 30 m thick, then basanitic tuffs and impure calcareous beds, overlain in turn by more than 40 m of coarse tholeiitic pillow breccia which is exposed on the shore north of Boatmans Harbour to the old Oamaru Harbour Board quarry as first described by Hutton in 1887. This unit shows widely spaced crude bedding forms and is probably redeposited. In it sideromelane is partly replaced by palagonite; calcite and local pockets of foraminiferal sand or impure limestone occupy the interstices between broken pillows and smaller fragments. Like other volcanic mounds in the area such as those at Kakanui Mouth and Aorere Point, it is cut by spectacular bioclastic limestone dikes which are discussed by Lewis (1973).

Tuffs are much more voluminous than the pillow lavas and intrusive rocks and offer a fertile field for future researches in volcanology, sedimentation and alteration processes. They are exposed magnificently on the coast from Boatmans Harbour to Cape Wanbrow, north and south of the Kakanui River mouth, at Aorere Point and Bridge Point, Waianakarua Mouth and Lookout Bluff, and at Moeraki Peninsula. Near the inferred sites of volcanic centres, dips vary rapidly and are often steep. Near Punatoetoe Head, Moeraki Peninsula, dips approach 60° and must result from local collapse features. At Bridge Point and Aorere Point outward dips on shore and concentric lines of reefs offshore (Fig. 3a) suggest the site of a vent. The presence of large volcanic blocks or bombs and somewhat similar structures in bedding at Kakanui South Head and other localities near Kakanui, also suggest proximity to vents, even though the tephra may be proximally redeposited.

The tuffs show a variety of bed forms including planar laminated ash beds cut by channels containing volcanic debris flows which may contain 10–30 cm fragments of pillows, dikes, or bombs. For example, at Bridge Point sea cliffs and wave-cut platforms have created excellent exposures of a debris-filled submarine channel system (Fig. 3b) overlain by a marine volcaniclastic sequence of shallow water origin, deposited or redeposited below wave base. Thinly bedded ash and lapilli deposits are incised more than 7 m by channels filled with massive and weakly cross-bedded, unsorted, basaltic block and ash submarine debris flows. Channel walls are steep and locally undercut.

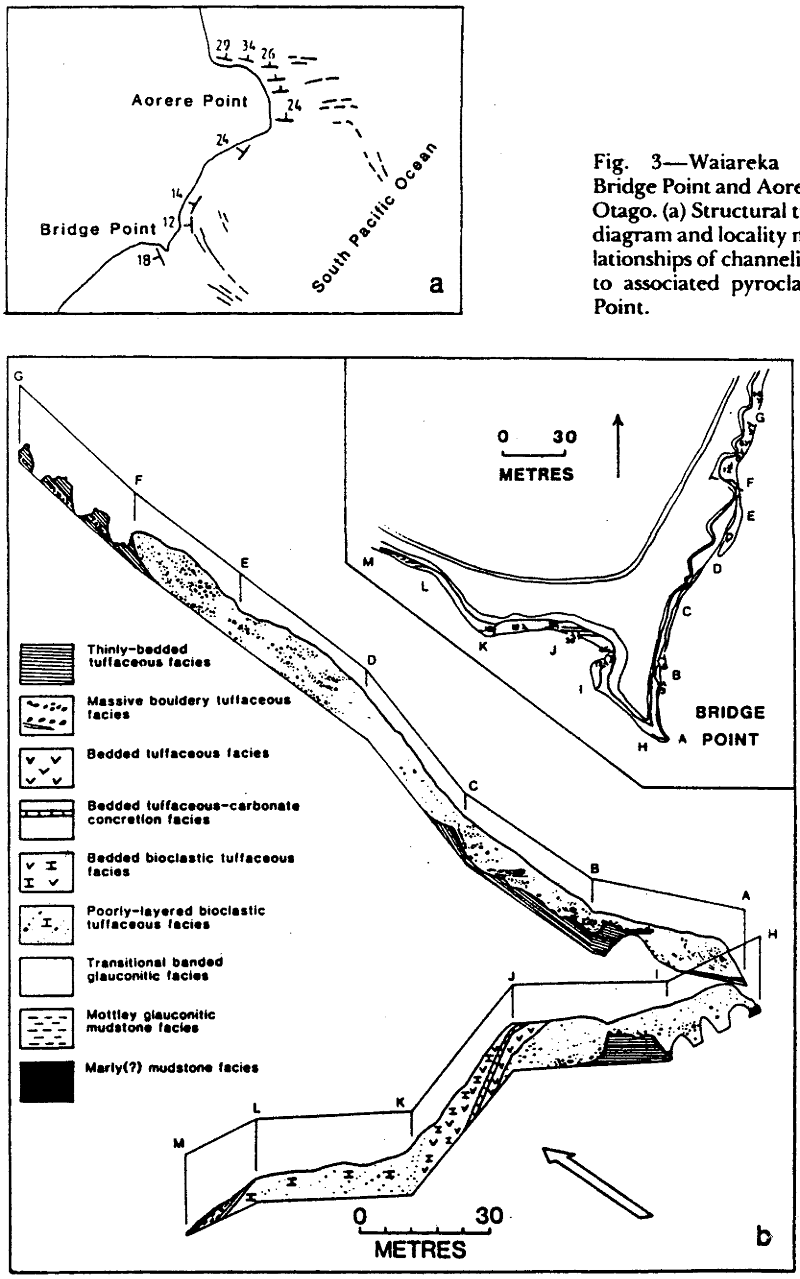

Fig. 3—Waiareka pyroclastics at Bridge Point and Aorere Point, North Otago. (a) Structural trends. (b) Fence diagram and locality map showing relationships of channelised debris flows to associated pyroclastics at Bridge Point.

They were probably carved by debris flows of detritus similar to that which now fills them. The debris flow deposits exceed 10 m in thickness. They are overlain by 17 m of variably bedded, commonly graded volcaniclastics which include an abundance of shallow marine fossils as well as large foreset beds (1–2 m thick) in which coarser blocks occur in the foreset toes. These are regarded as shallow marine angle-of-repose talus ramps flanking a wave-eroded platform cut in a newly deposited volcaniclastic pedestal.

Low-angle, long-wavelength cross-bedded units are exposed near Cape Wanbrow. These suggest pyroclastic surge deposition. Crudely graded units decimetres thick indicate repeated mass flow at various localities. Many local unconformities are present and most of them no doubt represent very little lapse of time. Others, as pointed out by Park (1918), Gage (1957) and other observers of the Cape Wanbrow section, represent pauses in volcanism and sedimentation of long enough duration for the surfaces concerned to be colonised by brachiopods, foraminifera, bryozoa, and other organisms, leaving thin beds, a few centimetres thick, of impure limestone studded with lag pebbles of volcanic origin. Such surfaces are interpreted as platforms cut by wave and current action and may be compared with the flat-topped surfaces which were cut at depths of about 28–44 m below sea level on the submarine hills Surtla, Syrtlingur and Jolnir near Surtsey within a few years of cessation of the activity which built up those piles (Jakobsson, 1982).

Tholeiitic tephra at Moeraki Peninsula, near Lookout Bluff, and at Bridge Point-Aorere Point, and partly tholeiitic, partly alkalic tephra in the Cape Wanbrow section, consist largely of highly vesicular sideromelane lapilli of probable phreatomagmatic origin and their palagonitised and zeolitised equivalents, often with a carbonate cement. The glassy selvages of the Tawhiroko intrusion at Moeraki, chilled against wet unconsolidated muds, contain about 12% vesicles, whereas vesicles in the glassy selvages of the Boatmans Harbour pillow basalt and the overlying Oamaru Harbour Board quarry pillow breccia are both very sparse (<<1%) and small (<0.5 mm), less abundant in fact than in many deep-sea, mid-ocean ridge basalts (e.g. Moore, 1979). Various writers such as Jones (1970), Moore and Schilling (1973) and Allen (1980) have found a transition from effusive eruption of pillow basalt to eruption involving explosive fragmentation (Surtseyan eruptions of Walker and Croasdale, 1972) at water depths between 100 and 200 m. For alkalic or other magma more highly charged with volatiles, the critical depth may be greater. Nakamura and Coombs (1973) felt that the water depth during sedimentation of the Kaiatan mudstones at Moeraki was unlikely to have been more than several tens or possibly hundreds of metres. This is compatible with the absence of pillow lava at this locality apart from one possible very restricted, slaggy occurrence.

We interpret the tuffs as the products of Surtseyan eruptions with vents originating below sea level but projecting ash, lapilli and larger blocks into the atmosphere. We envisage some deposition directly around the vents, some by pyroclastic surges, some by fall-out after passing through the atmosphere, and some by redeposition processes, including turbidity currents, mass flow, and grain flow. Much reworking would have taken place by wave and current action during and after eruptions. Thus the current-bedded, coarse-grained tuffs immediately above the Boatmans Harbour pillow basalt, though dominantly of basanitic parentage, are polymict and clearly reworked; in addition to altered glassy shards they contain many and relatively varied lithic volcanics suggesting a contribution from subaerial eruptions (Fisher and Schmincke, 1984), as well as occasional fragments of low-grade schist, glauconite and other non-volcanic material. The Boatmans Harbour and other pillow lavas were probably erupted in somewhat deeper water than that which prevailed for the Surtseyan eruptions, perhaps at depths of 150 m or more. In this context it may be significant that according to the stratigraphic correlations of Loutit and Kennett (1981) with the sea-level curve of Vail and Hardenbol (1979) global sea level was rising during Runangan time during which the Boatmans Harbour pillow basalt was erupted.

Volume of magma erupted

Order-of-magnitude estimates of the volume of the Waiareka-Deborah volcanics can be attempted. The two largest sheets preserved are the Mt Charles sill and the Tokarahi-Maerewhenua sheet. For a thickness of 50 m (Benson, 1943) and a surface area of about 25 km², the volume of the Mt Charles sheet would have been about 1 km³. A well at grid reference S127 255857 shows the Tokarahi sheet to be 25.5 m thick at that locality. If it had an average thickness of 20–40 m and an area of 50 km², its volume would have been about 1–2 km³; the original area and volume could conceivably have been up to several times that. The Enfield dike-sheet system may originally have had a comparable volume to these two bodies, but other intrusives of which remnants remain were probably smaller. The total volume of all the currently visible intrusives is thus likely to have been a few cubic kilometres and may have reached about 10 km³.

Thicknesses of the tuffs are highly variable, reflecting proximity to vents and the activity of ocean currents and other redepositional processes in reworking the materials. Gage (1957) points out that subsurface information is lacking for his cross sections through the Oamaru district and that the detail shown in the sections is largely hypothetical. Unfortunately this situation still prevails though it is now known that the Waiareka and Deborah Volcanic Formations are missing in the Endeavour no. 1 well, drilled 17 km offshore southeast of Oamaru. At Basalt Hill, 35 km northwest of Oamaru, is an inferred remnant of the Tokarahi sheet, here 15 m thick, but no volcanic materials are known from outliers of the Tertiary sequence still further to the northwest. Using the thicknesses hypothesised by Gage in his two main sections, a volume of 20–50 km³ for volcanic rocks between the Kakanui and Waitaki Rivers would seem reasonable. Riddolls (1968) reports 10 ft of tuffaceous beds (Kapua Tuff) in the Waihao River area north of the Waitaki River 35 km from Oamaru, but the total volume of volcanic materials in this region is probably not large.

Allowing for the volcanics south of the Kakanui River, it seems likely that the total volume of magma erupted at the surface or emplaced as shallow intrusives during the few million years of activity was in the range of a few tens of cubic kilometres, possibly reaching one or two hundred cubic kilometres.

Petrology and geochemistry

Tholeiitic tephra, pillow lavas and intrusives

The Waiareka-Deborah volcanics tend to be heavily charged with secondary minerals including carbonates, smectites, zeolites and chalcedony, no doubt resulting from their emplacement as subaqueous fragmental rocks and as intrusives into wet sediments. Consequently whole-rock analyses commonly do not reliably represent the magma chemistry. In many cases glass is more or less completely palagonitised, but sideromelane, clear and pale brown in thin section, is preserved in pillow selvages, in pillow breccias, as selvages to intrusions into wet mudstones, and locally in tephra. Its preservation is favoured in those deposits where early cementation by carbonates has sealed off the glass from further attack by aqueous fluids. In pillow interiors and in many intrusions such as those of Moeraki Peninsula, olivine is represented only by pseudomorphs. In contrast, olivine is often preserved in pristine fresh condition in the glasses, even in tiny pumiceous shards in carbonate-cemented tephra. In such cases small vesicles may be left unfilled and small olivines unaltered, whereas only a fraction of a millimetre away large vesicles and large olivines, more likely to have been intersected by hair cracks which allowed access by fluids, have been completely infilled or replaced.

Microprobe analyses of the glasses often give anomalously low totals indicating hydration. In these cases Na_2O tends to be anomalously low and loss of Na_2O through incipient alteration is suspected. As is well known (Neilsen and Sigurdsson, 1981), Na_2O also tends to be lost during microprobe analysis of glass. In other cases glass and phenocryst chemistry are compatible and the analyses are believed to approximate more closely to the original compositions. From modal analyses and microprobe analyses of glass and phenocryst phases a closer approximation to the composition of the erupting magma can be calculated than is given by the glasses alone, even in rocks that are highly amygdaloidal. To do so, we have used a glass density of 2.70 ± 0.02 as measured for a non-vesicular sideromelane in the Harbour Board Quarry pillow breccia OU 19883. Results of a reconnaissance study of some North Otago glassy tholeiitic rocks are given in Tables 1 and 2.

Bearing in mind the analytical difficulties and the fact that products of several quite distinct eruptions in both Kaiatan and Runangan time are involved, both the glasses and the whole rocks are respectively remarkably similar in composition. Compositions are comparable to those of typical continental intraplate tholeiites (cf. Wilkinson and Duggan, 1973), though with alkalis tending to be higher than usual. K_2O and P_2O_5 are substantially higher than in MORB. The whole-rocks concerned are olivine-normative whereas the glasses are quartz-normative and contain up to about 9% olivine phenocrysts Fo_{81-75}, in some cases euhedral, in some cases hollow or embayed indicating rapid growth. Small phenocrysts and microlites of medium labradorite usually accom-

Table 1: Tholeiitic glass and whole-rock (WR) compositions, Waiareka-Deborah volcanics, normalised to Fe_2O_3/FeO = 0.15; total anhydrous = 100%.

Spec. No.	47052		19882		19883	31408		52312A	31407		52301
	Glass	WR	Glass	WR	WR	Glass	WR	Glass	Glass	WR	Glass
Average of:	18		5			11		3	5		3
SiO_2	53.96	51.40	53.85	51.31	51.41	53.10	52.14	53.52	55.80	53.49	55.50
TiO_2	2.15	1.79	2.38	1.78	1.80	2.04	1.86	1.96	2.30	1.61	2.29
Al_2O_3	14.89	14.89	14.51	14.97	14.89	15.07	14.47	15.72	14.34	15.13	14.62
Fe_2O_3	1.30	1.37	1.33	1.37	1.39	1.37	1.43	1.21	1.36	1.26	1.45
FeO	8.64	9.16	8.86	9.14	9.24	9.17	9.53	8.09	9.06	8.40	9.64
MnO	0.15	0.15	0.16	0.19	0.15	0.18	0.17	0.19	0.19	0.16	0.16
MgO	5.17	8.21	5.13	8.39	8.05	5.57	7.67	5.60	4.63	7.94	4.14
CaO	8.98	8.49	9.11	8.24	8.59	8.72	8.27	8.93	8.52	8.53	7.94
Na_2O	3.53	3.41	3.45	3.46	3.33	3.75	3.53	3.61	(2.12)	(2.28)	(2.94)
K_2O	0.90	0.84	0.92	0.87	0.86	0.70	0.64	0.79	(1.32)	(0.94)	(1.06)
P_2O_5	0.33	0.28	0.30	0.27	0.28	0.32	0.29	0.38	0.36	0.26	0.26
Total	100.00	99.99	100.00	99.99	99.99	99.99	100.00	100.00	100.00	100.00	100.00
LOI (100 - Σ)	(1.68)	0.43	(0.20)	0.27	0.26	(0.34)		(1.77)	(2.85)		(2.01)
CIPW Norms, weight percent											
Q	3.10	-	3.40	-	-	0.85	-	1.86			
Or	5.32	4.96	5.44	5.14	5.08	4.14	3.78	4.67			
Ab	29.87	28.85	29.20	29.28	28.18	31.73	29.87	30.54			
An	22.13	22.84	21.39	22.75	23.14	22.22	21.75	24.36			
Di di	8.46	7.29	9.12	6.83	7.37	7.91	7.26	7.29			
en	4.35	4.24	4.67	4.00	4.25	4.03	4.07	3.94			
fs	3.89	2.70	4.22	2.50	2.78	3.68	2.89	3.10			
Hy en	8.53	8.44	8.11	7.92	9.03	9.83	11.56	10.01			
fs	7.63	5.37	7.32	4.95	5.91	8.99	8.20	7.87			
Ol fo	-	5.44	-	6.29	4.74	-	2.43				
fa	-	3.81	-	4.33	3.42	-	1.90				
Mt	1.88	1.99	1.93	1.99	2.02	1.99	2.07	1.75			
Il	4.08	3.40	4.52	3.38	3.42	3.87	3.53	3.72			
Ap	0.76	0.65	0.70	0.63	0.65	0.88	0.67	0.84			
Differentiation Index DI	38.3	33.8	38.0	34.4	33.3	36.7	33.7	37.1			
Method	WDS	XRF	WDS	XRF	XRF	WDS	Calc.	WDS	WDS	Calc.	EDS
Analyst	YK	RDJ	YK	RDJ	RDJ	YK		YK	YK		YK

Notes: For localities, see Table 2. LOI = loss on ignition; (100 -Σ) = 100-sum of oxides as determined by electron microprobe analysis.

Analysts: YK: Yosuke Kawachi; RDJ: R.D. Johnston.

Methods: WDS electron microprobe, wavelength dispersive method; EDS electron microprobe, energy dispersive method, MnO and P_2O_5 by WDS.

Specimens 31407, 52301. Glass presumed hydrated; serious Na_2O loss suspected from 31407 and some loss from 52301.

Table 2: Localities and modes for tholeiitic glassy selvages and lapilli, Waiareka-Deborah Volcanics.

OU 47052	Pillow lava, Boatmans Harbour, Oamaru. Waiareka Volcanic Formation.		
	Glass	83.2%	Table 1
	Olivine	6.3%	$Fo_{78.2}$ $Fa_{21.8}$ (Av. of 14, $Fo_{80.3-75.1}$)
	Plagioclase	10.4%	$An_{61.0}$ $Ab_{38.0}$ $Or_{0.9}$ (Av. of 17, $An_{62.1-57.8}$)
OU 19882	Basal part of Harbour Board Quarry pillow breccia, above limestone at Boatmans Harbour.		
	Glass	79.3%	Table 1
	Olivine	9.1%	$Fo_{77.1}$ $Fa_{22.9}$ (Av. of 7, $Fo_{78.0-76.7}$)
	Plagioclase	11.6%	$An_{59.7}$ $Ab_{39.3}$ $Or_{0.9}$ (Av. of 12, $An_{64.3-50.7}$)
	Augite	trace	
OU 19883	Pillow breccia, east side Oamaru Harbour Board Quarry.		
	Glass	73.1%	-
	Olivine	9.3%	$Fo_{77.3}$ $Fa_{22.7}$ (Av. of 6, $Fo_{78.2-76.1}$)
	Plagioclase	17.0%	$An_{59.7}$ $Ab_{39.4}$ $Or_{0.9}$ (Av. of 5, $An_{62.2-58.2}$)
	Augite	0.6%	
OU 31408	Lapilli tuff, shore near Maukiekie Island, Moeraki Peninsula		
	Glass	92.3%	Table 1
	Olivine	5.1%	$Fo_{77.7}$ $Fa_{22.3}$ (Av. of 10, $Fo_{79.9-75.9}$) very small crystals only preserved)
	Plagioclase	2.6%	$An_{59.4}$ $Ab_{39.8}$ $Or_{0.8}$ (Av. of 10, $An_{61.6-56.7}$)
OU 52312A	Pale brown glass, dominant component of calcified tuff band about 50 m below pillow lava, south of Boatmans Harbour, Oamaru		
	Glass	Table 1	
	Olivine	$Fo_{80.3}$ $Fo_{80.9}$ (two crystals)	
	Plagioclase	Microlites in some shards only	
OU 31407	Glassy selvage, Tawhiroko intrusion, Moeraki Peninsula		
	Glass	71.1%	Table 1
	Olivine	8.4%	Pseudomorphs only
	Plagioclase	18.2%	$An_{58.8}$ $Ab_{40.3}$ $Or_{0.9}$ (Av. of 9, $An_{63.8-57.0}$)
	Augite	2.3%	$Ca_{36.9}$ $Mg_{50.2}$ $Fe_{12.8}$ (Av. of 16, $Fe_{10.8-15.3}$)
OU 52301	Lapilli tuff in mudstone, near base of Waiareka Volcanic Formation, shore, north side of Lookout Bluff		
	Glass		Table 1
	Olivine		Mostly altered
	Plagioclase		$An_{64.1}$ $Ab_{35.2}$ $Or_{0.7}$ (Av. of 5, $An_{67.1-61.5}$)
	Augite		$Ca_{38.9}$ $Mg_{47.4}$ $Fe_{13.7}$ (Av. of 5, $Fe_{12.7-15.3}$)

pany the olivine, and where the total phenocryst content reaches about 15 to 20%, clinopyroxene appears as an additional phase, both as independent prisms and in glomeroporphyritic aggregates with plagioclase. It is a major component of quench products more than about 2 cm from margins. Predictably, whole-rock compositions and the phenocryst-poor glasses OU31408 and OU52312 plot in the olivine field of the Di-Ol-SiO_2 diagram (Fig. 4) as deduced for plagioclase-saturated Hawaiian tholeiitic basalts (Coombs, 1963), whereas those glasses containing augite plot within analytical error of the olivine-augite field boundary.

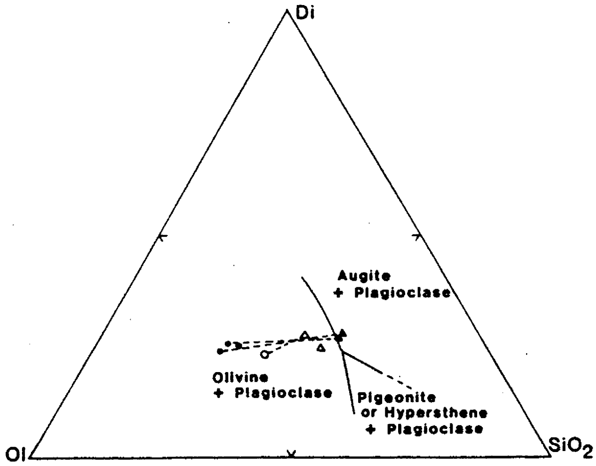

Fig. 4—Tholeiitic whole rocks and glasses, northeast Otago, on normative Di-Ol-SiO_2 diagram in molecular proportions. Field boundaries for plagioclase-saturated surface as inferred for Hawaiian tholeiites (Coombs, 1963). Filled circles: glassy selvages (whole-rock analyses). Open circles: whole-rock calculated from glass and phenocrysts. Filled triangles: glass containing phenocrysts of olivine, plagioclase and augite. Open triangles: glass containing phenocrysts of olivine and plagioclase alone. Dashed lines connect whole-rock and glass compositions. (Data from Tables 1 and 2).

Differentiation in the Main Moeraki, Mt Charles, and especially Tawhiroko sheets into olivine dolerite and coarser grained or pegmatoidal olivine-free quartz dolerite containing micropegmatite and often chalcedony has been described by Benson (1944) who considered that gravitational settling of olivine was the prime mechanism involved. Crystallisation behaviour of the pyroxenes in the Tawhiroko body has been related by Nakamura and Coombs (1973) and Nakamura (1973) to consolidation times ranging from a few minutes in the glassy selvages to several years for the coarser grained quartz dolerites. The glassy selvages contain intratelluric grains of augite approximating $Ca_{38}Mg_{50}Fe_{12}$, but with progressively slower cooling after high-level emplacement, compositions extended progressively towards the ferroaugite and subcalcic ferroaugite fields, especially in the $\{100\}$ growth sectors for which the miscibility gap with pigeonite is metastably reduced or effectively removed during the relatively fast cooling of such small intrusions. Pigeonite occurs as thin rims and small inclusions in augites more than 3 m from the intrusion contacts.

Benson (1944) referred to vesiculation throughout the Tawhiroko body and also to blotchy mingling and complex internal contacts, features not readily compatible with simple crystal settling as the only differentiation mechanism. A feature of the Tawhiroko intrusion, as with most other bodies on Moeraki Peninsula, is the presence 0.5–2 m from contacts of vesicles partially infilled with late-stage liquid. Larger globules and sheet-like segregation veins a few millimetres thick occur a little further in from the contacts. Blotchy vesicular patches occur further in still, and sparse late-stage dikelets, a few centimetres thick, cut the coarser grained interior. The partial infillings of the segregation vesicles, the globules, and the segregation veins in the outer few metres, are glassy and themselves vesicular. Elongate plagioclases and pyroxenes in the glassy segregations correspond in composition (Nakamura and Coombs, 1973) to the outer zones of the plagioclases and pyroxenes in the host rock and are accompanied by plates of ilmenite and magnetite. The glass is of high silica content, approximating the low pressure quartz-alkali feldspar minimum melting liquid; similar glass occurs within the matrix of the host rocks. Cooling in the interior of the sheet was slow enough for the dikelets emplaced there to have crystallised to holocrystalline tridymite-bearing assemblages, sometimes almost pegmatoidal in texture. It is hoped to discuss these segregations more fully elsewhere. Analyses of a pegmatoidal phase of the dolerite, of two segregation veins, and of high-silica glass are given in Table 3. It should be stressed that owing to the abundance of deuteric minerals including carbonates, smectite and chalcedony, the quartz dolerite and segregation vein analyses give only a general indication of the differentiation trend.

Table 3: Later differentiates, Tawhiroko Intrusion, Moeraki Peninsula.

	1	2	3	4
SiO_2	55.94	58.28	59.68	70.8
TiO_2	2.81	2.74	1.32	0.50
Al_2O_3	13.61	12.25	12.26	12.0
Fe_2O_3	7.83	8.99*	10.54*	-
FeO	3.36	-	-	1.97*
MnO	0.06	0.11	0.12	0.05
MgO	1.71	2.67	1.81	0.10
CaO	4.86	6.30	3.54	0.37
Na_2O	4.03	4.18	4.94	3.60
K_2O	1.33	1.30	1.94	3.85
P_2O_5	0.43	0.42	0.44	-
$H_2O\pm$, LOI	4.20	2.41	3.56	
Total	100.17	99.65	100.15	93.24

1. OU5750 Pegmatoidal quartz dolerite, interior of intrusion, (Benson, 1944; thin sections show much limonite after siderite ? in vugs).
2. OU20730 Micropegmatoidal segregation vein with tridymite and chalcedony, some carbonate. XRF analyses by B. Roser.
3. OU31388 Fine-grained magnetite-rich segregation vein with cristobalite, some carbonate and smectite. XRF analysis by B. Roser.
4. OU31393 Glassy matrix to globule about 3 m from outer contact of intrusion. Electron microprobe analysis (average of 6) by Y. Nakamura.

*Total Fe as Fe_2O_3 or FeO.

Quartzose xenoliths derived from the schist basement are conspicuous in Moeraki Peninsula intrusions and tephra and in the Mt Charles sill. They are also represented in tephra at Lookout Bluff and Bridge Point. Xenolith-rich zones tend to form an envelope 2–3 m in from the margins of bodies such as the Tawhiroko intrusion. Locally, as at the north tip of this under its inferred roof, they are present in extraordinary concentration, resembling sedimentary breccias ("pseudoconglomerates" of Benson, 1945) and contain quartzose slabs up to decimetres in diameter. Some are laminated and cross-cut by seams of glass and have quartz fabrics (Turner, in Benson, 1945) matching those of the underlying Haast Schist. In a few cases cordierite or hypersthene is present, but no remnants remain of the albite, muscovite, epidote and other minerals of the parent schist. Other xenoliths appear to have been derived from vein quartz. To judge from the composition of known Haast schists, the volume of low-melting fraction that must have been melted is likely to have been many times that of the quartzose refractory residue remaining. This must have contributed to the volume of high-silica glass and late stage siliceous segregation veins produced in the intrusions, at least in the xenolith-rich zones, but the quantitative importance of the effect is not known. Microxenolithic clots consisting of aggregates of fine-grained plagioclase ($An_{59}Ab_{40}Or_1$) with very tiny granules of spinel, while quantitatively insignificant, are also ubiquitous in the Tawhiroko and other Moeraki intrusions and tephra, as well as in at least some of the tephra at Lookout Bluff and Bridge Point.

Carbon dioxide is trapped as two-phase fluid inclusions up to about 6 µm in diameter in plagioclase phenocrysts of the Moeraki Peninsula intrusions and tephra, the Lookout

Bluff and Bridge Point tephra, and the Oamaru Harbour Board Quarry pillow breccia. The vapour-phase bubble often shows Brownian movement. The virtually ubiquitous occurrence of CO_2 inclusions in mantle-derived inclusions in alkalic volcanic rocks such as the lherzolite nodules and megacrysts of the Kakanui Mineral Breccia was described by Roedder (1965), while Moore (1979) has demonstrated the presence of CO_2 vesicles in mid-ocean ridge basalts. Although sparse and observed only in a small minority of plagioclase crystals in a thin section, the present examples show unequivocally that a CO_2 fluid phase was separating from the North Otago tholeiitic magmas, or coexisted with them, during the intratelluric growth of the plagioclase phenocrysts preceding eruption.

Alkalic tephra and intrusives

Coombs and Dickey (1965) reported an argillised ash of basanitic parentage between the pillow basalt and pillow breccia at Boatmans Harbour at a position corresponding to point *C* in Fig. 2. With Dickey (1968b) they also reported that the lower pyroclastic members of the Deborah Volcanic Formation at Kakanui are of basanitic (atlantite) composition and that bombs and lapilli of the Mineral Breccia Member are melanephelinite. More recently with Dr A. F. Cooper, we have recognised lherzolite nodules containing olivine, enstatite, chrome diopside and chrome spinel, together with black megacrysts of highly aluminous augite and rarer aluminous enstatite, in the coarse cross-bedded tuffs immediately above the Boatmans Harbour pillow lavas and also in tuffs more than 50 m below the pillow lava in the Cape Wanbrow section and thus within the Waiareka Volcanic Formation.

The occurrence of mantle-derived lherzolite nodules is effectively diagnostic of mafic alkalic magmas. Microprobe analyses of augite megacrysts from the Boatmans Harbour and Wanbrow localities (Table 4) show 8.5 to 9.7% Al_2O_3 and closely match those

Table 4: Representative pyroxene megacrysts in alkalic tuffs, Waiareka Volcanic Formation, Cape Wanbrow - Boatmans Harbour, Oamaru.

Spec.No.	49222 (3)	49222 (13)	52309 (2)	52312	49222 (17)
SiO_2	49.12	49.98	50.22	51.46	56.50
Al_2O_3	9.69	9.06	9.09	8.51	4.30
Cr_2O_3	0.14	0.22	-	-	0.18
TiO_2	1.80	1.36	1.21	0.56	-
FeO*	8.65	7.54	7.99	7.08	5.91
MgO	12.04	13.07	13.95	17.21	31.86
CaO	17.64	17.59	16.66	14.47	0.45
Na_2O	1.40	0.90	0.90	0.70	-
Total	100.48	99.72	100.02	99.99	99.20
Atomic proportions, O = 6					
Si	1.801	1.831	1.832	1.854	1.952
Al^{IV}	0.199	0.169	0.168	0.146	0.048
Al^{VI}	0.220	0.222	0.223	0.215	0.128
Cr	0.004	0.006	-	-	0.005
Ti	0.050	0.038	0.033	0.015	-
Fe	0.265	0.231	0.244	0.213	0.171
Mg	0.658	0.713	0.758	0.924	1.640
Ca	0.693	0.690	0.651	0.559	0.017
Na	0.100	0.064	0.063	0.049	-
Total	3.990	3.964	3.972	3.975	3.961
Ca	42.9	42.2	39.4	33.0	0.9
Mg	40.7	43.6	45.9	54.5	89.7
Fe	16.4	14.1	14.7	12.6	9.4

49222: In cross-bedded tuffs, 2-4 m above Boatmans Harbour pillow basalt.

52309, 52312: From tuffs about 50 m below Boatmans Harbour pillow basalt.

Analyst: Y. Kawachi, by EDS electron microprobe.

shown by Binns *et al.* (1970) also to be diagnostic of inclusions in mafic alkalic suites. The Oamaru megacrysts (Fig. 5a) show a trend with slightly increasing Fe/Mg ratios from subcalcic to less subcalcic, the trend line being at a high angle to the familiar low-pressure fractionation trends. It correlates with increasing Ti (Fig. 5b) and Na, and is the same as that found by Binns *et al.* who interpreted it as indicating high-pressure, deep-seated crystallisation with declining pressure during slow rise of the magma. The fact that no kaersutite has been found in the Wanbrow and Boatmans Harbour alkalic tephra indicates that these materials are not reworked debris from the kaersutite-rich Kakanui Mineral Breccia which outcrops 7 km to the southwest and which in any case is believed to be younger.

Lithic cobbles or blocks a few centimetres in diameter in the megacryst-bearing tuffs below the pillow lava, although severely altered, are recognisable as fine-grained vesicular basanitoids with tiny titanaugite prisms, plagioclase laths and abundant pseudomorphs after olivine. They contain plentiful lherzolite debris in addition to the dark aluminous augite megacrysts. The associated tuff fragments are highly vesicular, and are usually replaced and cemented by smectite, zeolites and carbonates. However vesicular glassy shards of two types are preserved in a thin calcite-cemented horizon above a minor unconformity at the approximate top of the megacryst- and nodule-bearing beds. The commoner ones are pale-brown and tholeiitic (Table 1, OU 52312A), but less common darker brown vesicular glass shards containing microlites of titanaugite and phenocrysts of olivine have a strongly alkalic nepheline hawaiite composition with 17% normative nepheline (OU 52312B, Table 5). The whole-rock composition including titanaugite and olivine would have been more basanitic. Higher in the section below the pillow lava, the distinctive lherzolite-bearing blocks and megacrysts are missing.

Blocks of basanitic aspect occur in tephra elsewhere in North Otago, as for example at a roadside locality 4 km northwest of Enfield. It is therefore clear that products of both tholeiitic and alkalic eruptions are widespread in tephra of both the Waiareka

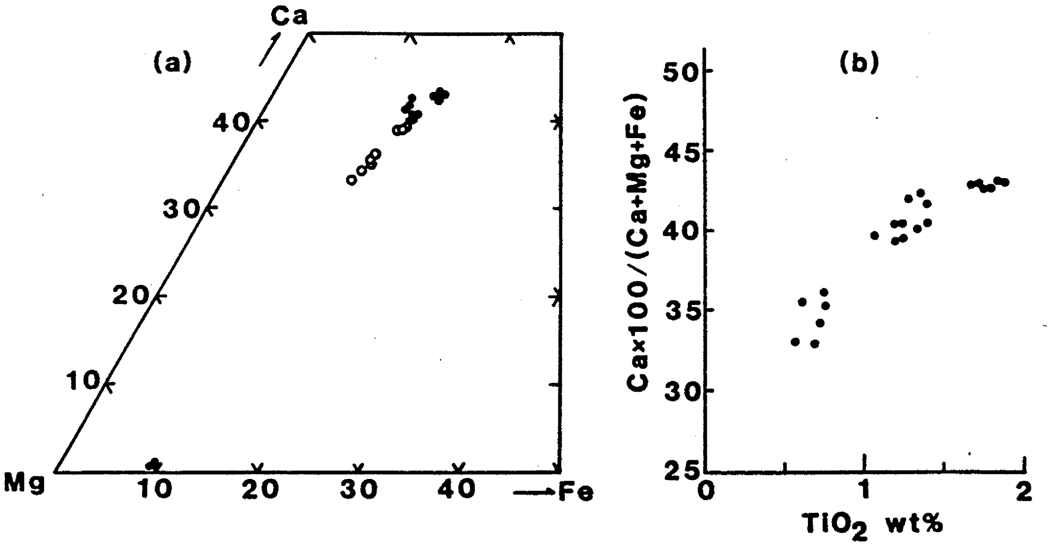

Fig. 5—Pyroxene megacrysts in tuffs of Waiareka Volcanic Formation, Oamaru. (a) Atomic proportions Ca:Mg:Fe. Filled circles: OU 49222, 2–4 m above Boatmans Harbour pillow basalt. Open circles: OU 52309, 52312, about 50 m below Boatmans Harbour pillow basalt. (b) TiO_2 (weight percent) as function of Ca content.

Table 5: Electron microprobe analyses of alkalic glasses in tephra, Waiareka Volcanic Formation and Kakanui Mineral Breccia.

Spec.No.	52312B	49352A	49352B	49322
SiO_2	45.52	44.56	44.17	45.53
TiO_2	2.36	2.55	3.22	2.28
Al_2O_3	15.72	17.77	16.48	16.50
FeO*	11.19	11.34	10.31	10.06
MnO	0.19	0.24	0.17	0.21
MgO	3.57	3.47	4.03	3.48
CaO	8.86	9.75	10.59	9.86
Na_2O	5.83	6.57	5.11	5.68
K_2O	1.90	3.68	2.73	3.17
P_2O_5	1.01	0.84	0.98	1.36
Total	96.15	100.77	97.79	98.13

CIPW Norms, normalised to 100% assuming $Fe^{3+}:Fe^{2+} = 1:3$

Spec.No.		52312B	49352A	49352B	49322
Or		11.68	13.60	16.45	19.04
Ab		19.97	-	6.23	8.56
An		11.46	8.04	14.24	10.33
Ne		16.92	29.79	20.51	21.82
Le		-	6.20	-	-
Di	di	11.38	14.36	13.70	12.67
	en	5.48	6.83	7.80	6.37
	fs	5.72	7.32	5.31	6.02
Ol	fo	2.62	1.20	1.71	1.71
	fa	3.02	1.42	1.28	1.78
Mt		4.67	4.52	4.23	4.11
Il		4.64	4.79	6.24	4.40
Ap		2.43	1.93	2.32	3.20
Differentiation Index		48.6	49.6	43.2	49.4

Notes: OU52312B. Dark brown vesicular shards with clinopyroxene microlites, in tuff of Waiareka Volcanic Formation, ∿50 m below Boatmans Harbour pillow basalt, Cape Wanbrow shore section. EDS analyses, av. of 6, Y. Kawachi, analyst (P_2O_5 and MnO by WDS).

OU49352A, 49352B, 49322. Vesicular lapilli containing olivine, clinopyroxene and magnetite, Kakanui Mineral Breccia, three separate outcrops, Kakanui South Head. WDS analyses each average of 5-7, P. Sipiera, analyst.

and Deborah Volcanic Formations as hitherto understood. Currently we do not know the relative proportions of tholeiitic, transitional, and strongly alkalic tephra. The Moeraki Peninsula volcanics, believed to be early products of the Waiareka Volcanic Formation, appear to be solely tholeiitic, and the Kakanui Mineral Breccia, possibly the last major product in the Deborah Volcanic Formation, was probably the most alkalic.

The Kakanui Mineral Breccia (Dickey, 1968a, 1968b) contains at Kakanui South Head large and small blocks of fine-grained melanephelinite with abundant inclusions of lherzolite and derivative debris including crystal fragments of olivine, chrome diopside, enstatite and chrome spinel, and abundant fragments of kaersutite. Also present are microphenocrysts of olivine and titanaugite, the latter sometimes mantling diopside, in a matrix rich in densely felted microlites of titanaugite together with magnetite and apatite. Small euhedra of nepheline are often apparent, but plagioclase is rare or absent. Shards in the tephra include many lithics of comparable aspect, together with shards containing similar suites of inclusions, phenocrysts, and microlites, but set in a clear brown glass or its palagonitised equivalent. Electron microprobe analyses of the glass forming lapilli in three separate samples are compatible with fractionation from melanephelinite or nepheline-rich basanite (Table 5). The variations between them are attributable to slightly different degrees of fractionation of the parent liquid to derivative glass and partly to possible element mobility during incipient alteration.

Many workers (Mason, 1966, 1968a, 1968b; Dickey, 1968a; Clark *et al.*, 1969; Griffin and Murthy, 1969; Dasch *et al.*, 1970; Philpotts and Schnetzler, 1970; Philpotts *et al.*, 1972; White *et al.*, 1972; Mason and Allen, 1973; Reay and Wood, 1974; Merrill and Wyllie, 1975; Basu and Murthy, 1977; Wallace, 1977; Saito *et al.*, 1977; Basu, 1978; Boettcher and O'Neill, 1980; Poreda and Basu, 1984) have contributed geochemical data on various mantle-derived megacrysts and other inclusions in the Mineral Breccia. Megacrysts tend to be rounded and highly polished. In a few cases they reach up to a decimetre in diameter. Included are pyropic garnet, omphacitic pyroxene, kaersutite, anorthoclase, ilmenite, chrome diopside, apatite, spinel and phlogopitic biotite. Blocks include lherzolites some of which are veined or layered with kaersutite and phlogopitic biotite (cf. Wilshire *et al.*, 1980) suggesting mantle metasomatism, various pyroxenites and garnet pyroxenites ("eclogites"), and a range of granulites which are believed to have been derived from the lower crust rather than the mantle.

The megacryst pyroxenes are distinctly more Fe-rich and more aluminous than the lherzolite pyroxenes (Reay, unpublished MS). They follow a similar trend to the much smaller megacrysts in the Waiarekan tuffs described above. Their field and that of the large garnet megacrysts are overlapped by those of the garnet pyroxenite minerals, which extend to still higher Fe contents (Fig. 6). The garnet pyroxenites, in which clinopyroxene predominates over garnet, are interpreted as re-equilibration products of a single low-calcium aluminous clinopyroxene. Their higher iron contents suggest crystallisation from more evolved melts, but still under high pressure conditions. Spinel pyroxenites, sometimes with fasciculate texture (Boyd *et al.*, 1984), occupy another distinct field.

On the basis of experimental studies on a kaersutite megacryst, compositionally equivalent to olivine nephelinite, and on a kaersutite eclogite, equivalent to a basanite, Merrill and Wyllie (1975) suggested a petrogenetic history involving pyrope-rich garnet and omphacitic pyroxene crystallising from rising hydrous magma at 75–85 km depth, temperature 1200–1300°C, and becoming trapped in lherzolitic mantle where kaersutite was precipitated from intercumulus melt during cooling. Subsolidus equilibration of the kaersutite assemblages is postulated at 700–800°C prior to incorporation in rapidly rising hydrous nephelinitic magma from which garnet, clinopyroxene and probably kaersutite precipitated at depths greater than 75 km, temperature

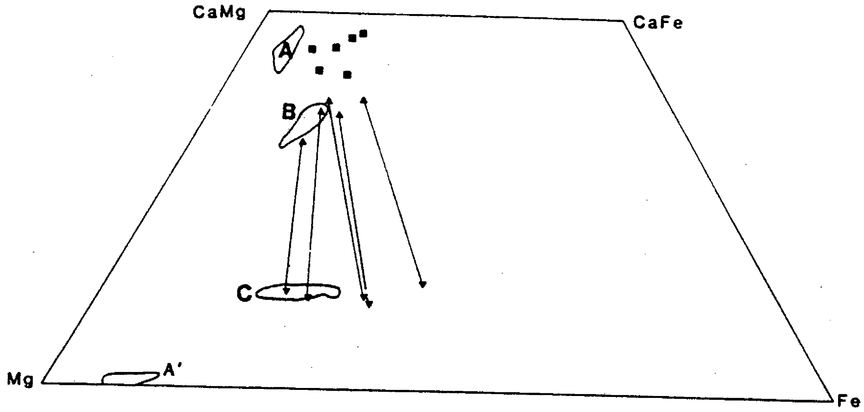

Fig. 6—Kakanui Mineral Breccia nodule and megacryst pyroxenes and garnets. A. Clinopyroxenes (chrome diopsides) and A' orthopyroxenes from lherzolite nodules. B. Clinopyroxene megacrysts. C. Garnet megacrysts. Triangles: clinopyroxenes from garnet pyroxenites. Inverted triangles: garnets of garnet pyroxenites. Squares: pyroxenes of spinel pyroxenites.

1100–1200°C. It may be noted that the melts were not only sufficiently hydrous to allow crystallisation of kaersutite and phlogopite, they were also saturated, locally at least, in CO_2 allowing entrapment of CO_2 fluid inclusions.

According to M. A. Menzies (pers. comm., 1984) apatite and kaersutite megacrysts from Kakanui have present day $^{87}Sr/^{86}Sr$ 0.70285, $^{143}Nd/^{144}Nd$ 0.51281. Dasch *et al.* (1970) and Basu (1978) give $^{87}Sr/^{86}Sr$ values for various Kakanui samples of 0.7029–0.7030. As discussed below, these data imply that the parent liquid was derived from a mantle source which had been depleted in light REE for a considerable period of time.

Alkalic intrusives of Waiareka-Deborah age are suggested by Benson (1943,1944) who indicated that basaltic sheets at Government Hill 7 km west of Mt Charles and at Trig S south of Maheno contain wisps of biotite, groundmass anorthoclase and analcime. Analyses of these two bodies (Benson, 1944) and of the olivine dolerite capping Lookout Bluff (Coombs and Dickey, 1965) indicate a range from hypersthene-normative.to slightly nepheline-normative hawaiite or hawaiitic basalt; the suite is clearly of transitional to mildly alkalic nature. A doleritic "basic analcime syenite" at Waimotu (Benson, 1944) is probably a pegmatoidal facies of a more strongly undersaturated intrusion. Other bodies on either side of Kakanui River, for example an analcime-bearing dolerite 2 km west of Maheno, also have transitional or alkalic affinities. In the absence of critical field data or radiometric dates, it is uncertain whether these bodies are to be correlated with the late Eocene — early Oligocene or with the Miocene volcanic periods of Otago. Nevertheless the demonstration of a number of quite separate and relatively voluminous alkalic ash beds of both Waiareka and Deborah age in close proximity to the intrusives makes it likely that at least some of those referred to will prove to be of Waiareka-Deborah age.

Summary

The available geochemical and especially isotopic data are still too sparse for thorough analysis of Waiareka-Deborah volcanism, in part because of difficulties arising from the commonly fragmental nature of the products and their pervasive alteration.

Nevertheless it is clear that substantial quantities of both tholeiitic and alkalic magmas were involved. The first eruptions in the Moeraki area were tholeiitic, whereas the last eruptions near Kakanui appear to have been the most alkalic, but there was a substantial period of overlap of tholeiitic and alkalic volcanism in Runangan time.

The tholeiites so far known are of normal intraplate olivine tholeiite composition and fractionated olivine, plagioclase and clinopyroxene to yield higher silica segregations and late stage glasses approaching the quartz-alkali feldspar minimum melting liquid composition. Some contamination of the tholeiites by crustal material is indicated by relatively abundant partially melted schist-derived quartz xenoliths. Tephra of basanitic to nephelinitic composition contain lherzolite nodules and high-pressure clinopyroxene megacrysts, and in the case of the Kakanui Mineral Breccia a very wide range of mantle- and lower crust-derived nodules and megacrysts implying a source as deep as 75–85 km. Transitional to strongly alkalic mafic intrusives are also present in the area and have been attributed to Waiareka-Deborah volcanism, but so far have not been dated unequivocally. It is thus not yet clear whether there was a spectrum of activity from tholeiitic to highly alkalic, or whether the volcanism was strongly bimodal. Fluid inclusions of CO_2 in mantle-derived inclusions in the alkalic tuffs and in plagioclase phenocrysts in the tholeiites show that CO_2 fluids were present during the rise of the alkalic magmas from the mantle, and during at least part of the crustal rise of the tholeiites.

THE DUNEDIN VOLCANIC GROUP: MIOCENE VOLCANISM IN EASTERN AND CENTRAL OTAGO

Earlier work

The volcanic rocks of the Dunedin district (Fig. 7) have long had a prominent place in the literature of alkalic volcanic rocks (e.g. Ulrich, 1891; Marshall, 1904, 1906, 1914; Benson, 1939, 1941a, 1941b, 1942a, 1942b, 1959; Benson and Turner, 1939, 1940; Turner and Verhoogen, 1960; Muir and Tilley, 1961). Benson's contributions, involving many years of his own field and laboratory study and consideration of the work of his predecessors and students, culminated in the postumous publication of the W. N. Benson Geological Map of the Dunedin District (Benson, 1968), but the major memoir which he had planned never appeared. He demonstrated a substantial volcanic edifice centred on Port Chalmers and Portobello for which he postulated an Initial and three Main (or Major) Eruptive Phases. The Initial Eruptive Phase was characterised by the eruption of slightly quartz-normative trachyte only, whereas each of the three Main Eruptive Phases, as well as three sub-phases of the Second Main Eruptive Phase, were characterised by a wide spectrum of rocks from alkalic olivine basalt or basanite to phonolitic trachyte or phonolite. Subsequently, Allen (1974) has demonstrated that basalts, the Careys Basalt, underlie the Initial Eruptive Phase trachytes (Koputai Trachyte) at Port Chalmers near the centre of the volcano. Products of Benson's First and Second, and Second and Third Main Eruptive Phases were separated, in Benson's view, by his Older and Younger Flood Plain Conglomerates, the former including the Kaikorai Leaf Beds with diatomite and oil shale.

Benson (1959) regarded his eruptive phases as discrete differentiation sequences commencing with basaltic effusions. In fact, the earliest flow of his First Main Eruptive Phase at Blanket Bay is phonolite (Coombs *et al.*, 1960) and near Aramoana it is benmoreite (phonolite, flow no. 2 of Marshall, 1914). However the repeated appearance of phonolitic and intermediate magmas as well as of more mafic ones during the history of the volcano is significant. Benson demonstrated the importance of intermediate types such as mugearites (Benson and Turner, 1940) and trachyandesites. He collected much data (Benson, 1941b, 1942a, 1942b; see also Williamson, 1939; D. A.

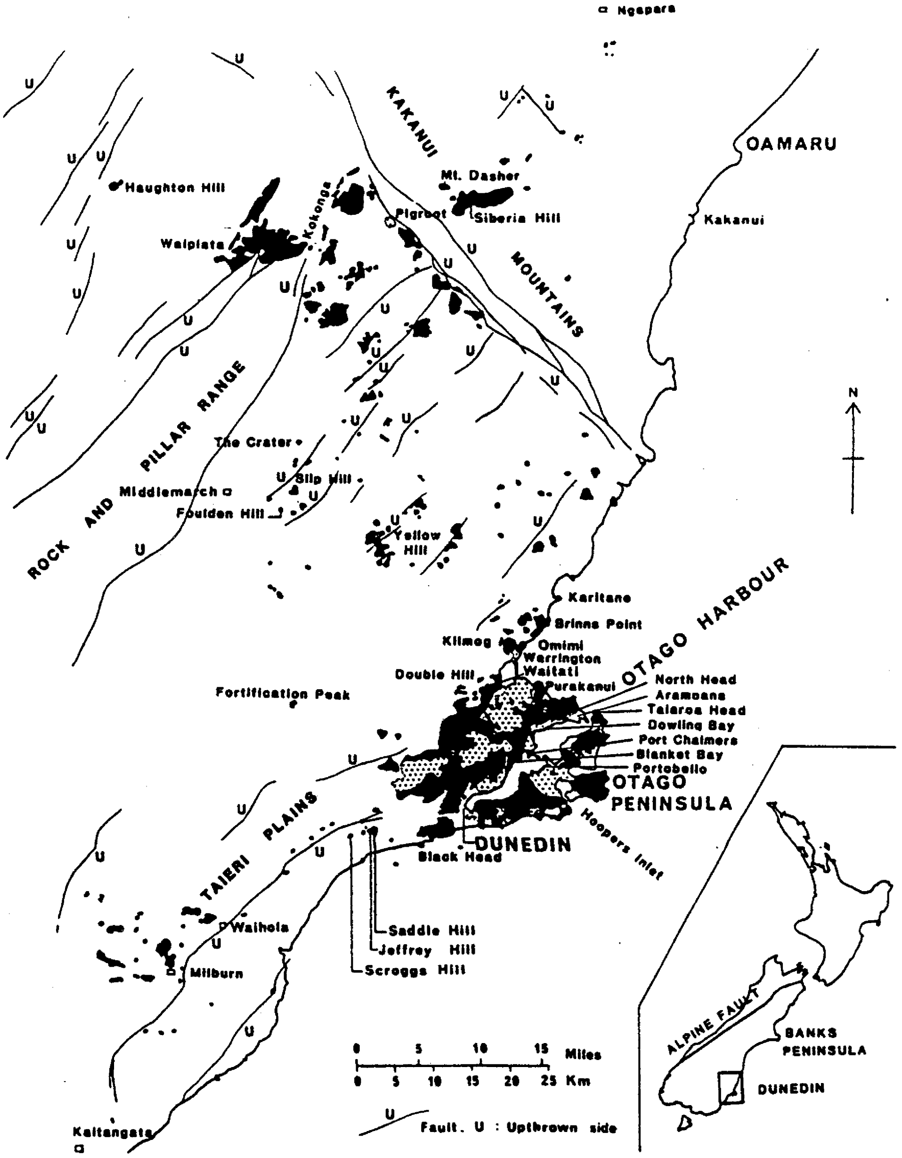

Fig. 7—The Dunedin Volcanic Group, mainly after Mutch (1963) and McKellar (1966). Black: Mainly mafic and intermediate tuffs, flows and shallow intrusives. Stippled: Mainly trachytic and phonolitic rocks.

Brown, 1955; E. H. Brown, 1964) on the numerous plugs, dikes and flow remnants, sometimes preserving tephra, in the widespread region of eastern and Central Otago peripheral to the main Dunedin volcano. Here basanites and alkalic olivine basalts predominate. Benson sought to correlate the intensity of volcanism and range of rock types with the extent of late Tertiary deformation, and in so doing he indicated a correlation between the volcanism and the initiation of Kaikoura movements in eastern Otago.

Lithostratigraphic terminology

The late Tertiary volcanic rocks of the Dunedin district and the associated "flood plain conglomerates" were called the Dunedin Volcanic Complex by Benson (1959, 1968). Basaltic lava flows and dikes of comparable age centred on Waipiata in northern Central Otago, but extending as remnants on the uplifted Kakanui Mountains to the northeast, have been termed the Waipiata Igneous Formation, Volcanic Formation, or Volcanics (e.g. Mutch, 1963) following Williamson (1933). Gage (1957) introduced the name Molehill Basalt for comparable rocks in the Waitaki Subdivision, in effect for those on the lower northeast slopes of the Kakanui fault block. This term is thus a synonym for Waipiata Volcanic Formation. Several formational units (e.g. Careys Basalt, Koputai Trachyte, Kaikorai Leaf Beds) have been proposed for units within the Dunedin volcano and many other names have been used formally or informally for specific bodies, e.g. Waihola olivine theralite. No general name has been formally proposed for the volcanic suite as a whole.

It is here proposed that the term Dunedin Volcanic Complex be amended to Dunedin Volcanic Group and redefined to include all the late Tertiary volcanic and shallow intrusive rocks of eastern and Central Otago, together with the tephra and other intimately associated sedimentary units such as Kaikorai Leaf Beds. Stratigraphically, Dunedin Volcanic Group, though overlapping in places onto Upper Cretaceous or Tertiary quartzose terrestrial beds or onto Haast Schist basement, intervenes between a major transgressive and regressive sedimentary marine sequence of early to mid Tertiary age, and later syn-orogenic terrestrial beds including piedmont gravels deposited during the movements of the Kaikoura Orogeny which are still in progress.

The term Dunedin volcano may be used informally for the major shield volcano centred on Port Chalmers and Portobello.

Extent of the province

The Dunedin volcano has a diameter of about 25 km and present vertical relief of 700 m. Peripherally to it, remnants of plugs, dikes, flows and tephra are known as far as 95 km north of Port Chalmers near Ngapara in North Otago, at Haughton Hill 95 km northwest of Port Chalmers, and in the Kaitangata area, 75 km southwest of Port Chalmers. Many cobbles of basanite occur 35 km to the west of Haughton Hill in Pleistocene gravels in the Manuherikia Valley above Alexandra, and indicate the possible existence of former vents in that catchment, now removed by erosion or covered by younger alluvium. A limburgite dike at Nevis Bluff, a further 50 km to the west, is chemically and petrographically similar to some Dunedin rocks and provides a link with the lamprophyric dikes and diatreme swarm of Northwest Otago. This suite in fact may not be sharply separable from the Dunedin Volcanic Group, a conclusion suggested by Adams (1981) on the basis of age determinations.

Age and duration of volcanism

In his earlier papers, Benson regarded the late Tertiary volcanics of the Dunedin district as being of probable Pliocene age, and unfortunately this age continues to be quoted. Coombs *et al.* (1960) showed that at Waipuna Bay and Blanket Bay on Otago Harbour, basaltic tuff, probably to be correlated with Careys Basalt, and trachytic tuff correlated with Koputai Trachyte, are interbedded with shallow-water sandstones dated as Waiauan or at youngest, early Tongaporutuan, i.e. within the range Middle to Upper Miocene. Potassium-argon dating (McDougall and Coombs, 1973) gave ages of 13.1 ± 0.1 and 13.0 ± 0.2 m.y. for two separate bodies of Koputai Trachyte, 12.1 to 11.3 m.y. for three flows of the Second Main Eruptive Phase and 11.3 ± 0.2 to 10.2 ± 0.1 m.y. for two basalt flows and two phonolite lava domes of the Third Main Eruptive Phase, of which only one, mafic phonolite (nepheline benmoreite) from Mt Cargill, was younger than 11 m.y.. Rubidium-strontium dating (Price and Compston, 1973) suggests generally compatible dates of about 13 to 14 m.y., though with less precision.

The main shield-building phase of the Dunedin volcano was thus in the Waiauan (late Middle Miocene), at about 13 to 11 m.y., with activity probably extending into early Tongaporutuan time (early Late Miocene) at about 10 m.y..

Two specimens from the Waipiata Volcanic Formation have given K/Ar dates of 12.8±0.2 and 15.6±0.6 m.y. (McDougall and Coombs, 1973) and Adams (1981) shows a date for an outlier in the Maniototo area (Haughton Hill) of 21 m.y.. Furthermore, Sikumbang (1978) has shown that on Karitane Peninsula, 20 km north of Port Chalmers, phonolitic trachyte is overlain by 4 m of carbonaceous siltstone, followed by 24 m of phonolitic trachyte tuff containing a large foraminiferal assemblage of probable Altonian age (late Early Miocene, 20–16.5 m.y. approximately), a period of rising sea level according to Loutit and Kennett (1981). He also found that tuffaceous beds containing foraminifera of probable Altonian age underlie the Waiauan Dowling Bay Limestone on Otago Harbour.

In summary, the main growth of the Dunedin shield volcano was from about 13 to 11 m.y. with some activity to 10 m.y. before present. More scattered alkalic volcanism had commenced by about 21 to 16 m.y. in Central Otago and probably on the east Otago coast. These dates overlap those of 28 to 16 m.y. given by Cooper (this volume) for the Wanaka lamprophyric dike and diatreme swarm of Northwest Otago.

Nature of the volcanism

The Dunedin volcano

The presence of tuff in shallow-water marine beds of the Waipuna Bay Formation shows that activity of the Dunedin volcano commenced before the sea had completely regressed from the area. The first eruptions may thus have occurred offshore. For most of its history the volcano was subaerial. It preserves evidence of explosive eruptions as well as of quieter effusions of basaltic lava and dome-building episodes of more felsic lava. Three million years is a substantial time span for one volcano, and there must have been long periods of quiescence and erosion followed by renewed activity.

Some flows were quite wide ranging. Thus a petrographically distinctive pair, the Roslyn Dolerite and the Leith Valley Andesite (trachyandesite), makes a useful mapping horizon on much of the western flank of the volcano. Some of the more felsic rocks, such as a phonolite which forms a thick coulée from Mopanui to Doctors Point, flowed distances of some kilometres, but as described by Price and Coombs (1975) most benmoreites, nepheline benmoreites, phonolitic trachytes and phonolites occur as lava domes with generally inward-dipping flow planes, sometimes almost schistose. In some cases, for example Hare Hill and the Mihiwaka domes, these appear to have risen into and overlapped the craters of more mafic cinder cones. Partially eroded domes of phonolite dominate the sky-line ridge on the north side of Otago Harbour and on the slopes to the north of it. Other domes of phonolitic rock, intrusive in nature, have arched up pre-volcanic sedimentary basement now exposed as inliers at Varleys Hill and Dicks Hill on Otago Peninsula and Dowling Bay on the north side of the Harbour.

The North Head cliff section (Marshall, 1914) is the most extensive through the flanks of the volcano and illustrates some of the structural features developed in lava flows of contrasting chemical and physical characteristics. Overlying tuff resting on Koputai Trachyte (flow no. 1 of Marshall) at the base of the section is a slabby-jointed flow-foliated benmoreite (flow no. 2) followed by a series of discrete basaltic flows with rubbly tops and then a thick series of innumerable thin, slaggy, aa flow units representing successive pulses in a single hawaiitic basalt eruptive event. These were followed after an interval by flow no. 13, "kaiwekite", a distinctive trachyandesite (Marshall, 1906; Benson, 1939) which produced a reddened baked horizon beneath it and which itself consists of two or three closely related flow tongues separated by rubble. The kaiwekite is the latest representative in this section of Benson's First Main Eruptive

Phase and flow no. 14, a flow-foliated phonolite 50 m thick including rubble, advanced over erosional relief cut in the kaiwekite. It in turn was followed by a range of more fluid basaltic rocks, including a nepheline mugearite, which locally have well developed columnar jointing where ponded. The upper part of the sequence is interrupted by a thin layer of pebbly volcanic alluvium and is terminated by nepheline benmoreites (flows no. 24 and 25). Two bodies of vitrophyric trachyandesite with closely spaced irregular columnar jointing, poorly exposed at the foot of the cliff, in one case as slumped blocks only, may represent small intrusive plugs.

Strombolian deposits with almond bombs, seen in a large fallen block at the foot of the same cliff section behind Aramoana, suggest that some of the basalt high in the First Main Eruptive Phase was derived from a vent nearby on the flanks of the main shield. The impression given by such cliff sections through the flanks of the volcano is that flow rocks, including rubbly flow tops and bases, strongly predominate over tephra, except near actual vents. To what extent this is an artifact of preservation is not clear at this stage.

The Port Chalmers Breccia is a remarkable rock, occupying a vent 1.3 × 2.5 km in diameter at Port Chalmers and four smaller vents 160 to 650 m in diameter south of Portobello on Otago Peninsula. It consists of carbonate-cemented, largely unsorted blocks locally up to a metre in diameter, down to fine grained particles of dark green phonolites, basalt, and other volcanics together with conspicuous fragments of basement schist and of subvolcanic crystallisation products, such as alkalic gabbros, nepheline-sodalite syenite and eucolite syenite (Allen, 1974). In the absence of clear juvenile material, the eruptive mechanism is obscure, but major gas eruptions are implied.

A variety of *pyroclastic deposits* are included in Benson's *Older and Younger Flood Plain Conglomerates* as well as volcanic-derived alluvium, diatomite with fossil leaves and fish as at Frasers Gully (Grange, 1930; Oliver, 1936; Campbell, 1985) and oil shale (Willett, 1943) grading into lignite. Deposits mapped by Benson (1940, 1968) as Older Flood Plain Conglomerate are particularly well developed (Harvey, 1978) along and to the west of the Leith Valley Fault Zone (Price and Coombs, 1975) which trends northeast across the west flank of the volcano. These deposits may have formed a more or less continuous sheet during deposition. Conglomerates in Frasers Gully and elsewhere contain a wide variety of volcanic clasts, and thus postdate substantial volcanism. In the Leith Saddle-Double Hill-Kilmog region, beds including oil shale, diatomite and trachytic tuff rest directly on pre-volcanic sedimentary rocks. It is unlikely that the entire deposit can be correlated with the interval between Benson's first two Main Eruptive Phases. There are even less strong grounds for regarding various lenses of volcanogenic sediments to the southeast of the Leith Valley Fault Zone, as for example leaf-bearing clays, tuffs and lapillistone at Taiaroa Head on the opposite side of the volcano, as being directly correlatable, and revision of the stratigraphy is called for. It is likely that the diatomites and oil shales accumulated where drainage was ponded on the western flanks of the actively growing volcano, and that alluvium, tuffs and laharic deposits also tended to be preserved in the same belt. These deposits were eventually overtopped by later flows. The more isolated occurrences to the southeast of these we regard as local pockets of sediment ponded and preserved during the intermittent growth and erosion of the volcano. A small occurrence on the southeast flank of the Scroggs Hill mugearite dome southwest of Dunedin (Benson, 1968) together with another on the flanks of a small mugearite or mugearitic hawaiite dome between Scroggs Hill and Jeffrey Hill, both referred to as "phonolitic mudflow" by Benson and Turner (1940), are now interpreted as remnants of mugearite cinder cones comagmatic with the lava domes that subsequently rose into them.

Pyroclastic surges, pyroclastic flow, and ash beds rich in accretionary lapilli are well developed along a 500 m stretch of coast near Warrington, 15 km north of the centre of the Dunedin volcano. With several hundred metres of strata exposed in sea cliffs, this is the best section dominated by stratified pyroclastics so far recognised in the Dunedin volcanics. Whereas the regional dip in eastern Otago is southeast at less than 10°, the Warrington pyroclastic sequence is near vertical, locally overturned, and strikes northwest. It appears to be part of a northwest-trending fault block and is cut by numerous steep northeast-trending faults and several dikes.

Surge deposits dominate a thickness of more than 60 m low in the section. Large scale dune cross stratification (wave length 2 m, amplitude 0.2 m) indicates transport from the north. Numerous asymmetric bomb sags within interbedded airfall tuffs rich in accretionary lapilli indicate that the vent that gave rise to these deposits was close by, in the same direction. This vent was thus to the north of, though closely peripheral to the main Dunedin volcano. The bulk of the Warrington sequence is made up of thick pyroclastic flow deposits, mostly block and ash beds, several of which contain charred wood. Thin surge deposits are intimately associated with several of these flows. Paleosols indicate substantial pauses between eruptions, as does an interbedded mudstone containing leaf and stem fossils.

Crustal magma chambers; volume of Dunedin volcano. Suites of coarse-grained xenoliths and megacrysts are found in various units in addition to the Port Chalmers Breccia. Examples include schist, syenite, nepheline syenite, magnetite-apatite-pyroxenite and other mafics in a basanitic flow at Purakanui (R. D. Johnstone, pers. comm., 1973, 1985), and kaersutite gabbro, rarer nepheline syenite, and megacrysts of kaersutite in the kaiwekite at North Head and Long Beach (Benson, 1939). Such occurrences provide evidence for partially disrupted subvolcanic magma chambers in which crystallisation and differentiation proceeded. Reilly (1972) has demonstrated a substantial positive gravity anomaly centred on the Port Chalmers-Portobello region. He modelled it with a cylinder 13 km in diameter extending to a depth of about 10 km and containing about 600 km^3 of olivine gabbro as well as less dense rock. It represents the inferred magma chamber complex in which mafic and some felsic differentiates accumulated complementary to the relatively more abundant felsic rocks erupted at the surface. The total volume of erupted rocks in the volcano is estimated as of the order of 78 to 150 km^3.

Peripheral vents of Eastern and Central Otago

Most of the peripheral vents appear to have been monogenetic, the sites of single, brief, eruptive events during which tephra and lava were produced. Only locally, as at Milburn Hill (Benson, 1942a) and Siberia Hill (Brown, 1955), do flows of distinctly different petrography overlie each other. Some quite extensive sheets are preserved or implied, notably the Waipiata doleritic basalt extending over an area of about 13 by 10 km. Most occurrences however have been reduced to much smaller flow remnants, plugs and dikes, sometimes preserving comagmatic tephra. The region was generally one of low relief, at least during the early stages of volcanism. This may have contributed to hydrological conditions promoting phreatomagmatic eruptions, indicated for example by surge deposits preserved in road cuts on the Pigroot as well as in the Warrington section.

Travis (1965) has shown that at three localities near Middlemarch, volcanism has been associated with local collapse features, the volcanics-schist or volcanics-Tertiary sediment contact now being below the general level of the surrounding schist erosion surface. In one of these cases, Foulden Hills, diatomite shown by drilling to be more than 75 m thick occurs in the basin. At another, The Crater (M. N. Gamble, pers. comm., 1983; and writers' observations), early explosive eruptions cleared a vent and produced a fall breccia and surge deposits (tuff ring?) containing copious blocks of basement schist together with blocks and vitreous lapilli of basanite and slabs of fossiliferous Upper Eocene sandstone which evidently thinly covered the schist at the time. Subsequently a larger cinder cone was built up and was diked and breached by basanite lava flows. Such a history may have been a typical one for vents in the province.

Phonolite occurs in the peripheral region at Karitane, 20 km north of Port Chalmers, and at nearby localities. Nearer Dunedin, vitrophyric nepheline trachyandesite occurs at Brinns Point and several bodies of mugearite or mugearitic hawaiite occur at Scroggs Hill and Jeffrey Hill. Other relatively evolved rocks are the Pigroot "mafic phonolite" referred to later, and nepheline mugearite near Middlemarch. Otherwise, rocks of the peripheral region are basanites, alkalic olivine basalts of various types, and nephelinites. At a large number of localities these contain spinel lherzolite and/or other deep-seated fragments, e.g. basalt at Kokonga (Turner, 1942), the Pigroot mafic phonolite, volcanic breccia at Omimi, basanites at Mt Dasher (Brown 1955), Yellow Hill (Brown, 1964), Slip Hill and Foulden Hills (Travis, 1965), The Crater, Fortification Peak, Saddle Hill, and many others. The lherzolites are often accompanied by small schist-derived xenoliths and attest to rapid rise of largely undifferentiated magma from mantle depths. High-pressure xenoliths are largely lacking in the Dunedin volcano, in which successive pulses of magma, rising from the mantle, were trapped in crustal magma chambers, there to lose their high-pressure enclaves and schist derived xenoliths, and there to fractionate to more evolved rock types.

Summary: contrasts between the central and peripheral volcanism

The Dunedin volcano was an intermittently active shield volcano with a life span of about 3 million years whereas most of the outlying vents were monogenetic, or at most the site of only a few distinct eruptive episodes. Mantle-derived xenoliths are rare in the Dunedin volcano and although blocks of schist are found in products of explosive eruptions such as the Port Chalmers Breccia and tuffs at Allans Beach, recognisable xenoliths of schist origin are found in few of the lavas. It is inferred that successive batches of magma rising through the schist basement from the mantle were trapped in crustal magma chambers, dense xenoliths settled out and any schist xenoliths were assimilated. Fractionation gave rise to a wide range of relatively voluminous felsic differentiates erupted at the surface, as well as complementary dense cumulates which can account for a substantial positive gravity anomaly. In contrast, magma feeding the peripheral vents is mostly relatively unfractionated and contains frequent mantle-derived nodules and incompletely assimilated schist xenoliths, all these features suggesting rapid rise.

Tectonic setting

Continental alkalic volcanism is commonly believed to be associated with extensional tectonics and the Dunedin volcano is situated at the northeast end of a graben-like tectonic depression, the Taieri Plains. It is to be emphasised however that the faults defining the prominent fault-block topography of eastern and central Otago, including examples near Dunedin, are reverse faults as currently observed.

Examples of both major northeast-trending and northwest-trending faults are known to have had major movement in the opposite (normal) sense in Late Cretaceous time (Mutch and Wilson, 1952; Bishop and Laird, 1976). Sedimentological and stratigraphic evidence suggests however that a terrain of low relief had been developed before the period of volcanism, 20 to 10 m.y. ago approximately. Although some faulting may have accompanied volcanism, the main period of faulting which developed the present topography undoubtedly came after the volcanic activity.

Molnar *et al.* (1975) and Walcott (1979) show that the motion of the Pacific plate relative to the Alpine Fault in the central South Island was slightly divergent from 38 to 10 m.y. before present indicating an extensional regime at that time in a direction making a high angle to the Alpine Fault, whereas since 10 m.y. before present it has been increasingly convergent. This permits northwest-southeast extensional stresses in the crust during the period of volcanism and the subsequent compressional tectonics and reverse faulting still active as part of the Kaikoura Orogeny in this part of New Zealand.

Farrar and Dixon (1984) have postulated that the New Zealand-Campbell Plateau continental segment of the Pacific Plate has overridden the site of mantle upwelling along a former spreading ridge, and that the alkalic volcanism of the area is the result of continued upwelling along this line. However the progressive southeast migration of alkalic volcanism postulated by Adams (1981) and cited by Farrar and Dixon, is not fully borne out by data in this paper. In particular, the substantial volume of early Tertiary alkalic volcanics in North Otago does not fit with Adams' generalisation.

Petrology, geochemistry and petrogenesis

From a consideration of major element chemistry, mineralogy and low-pressure fractionation trends as revealed by residual glasses and segregations, Coombs and Wilkinson (1969) postulated a spectrum of lineages for the Dunedin volcanics involving mantle-derived basaltic parents ranging from slightly hypersthene-normative to strongly nepheline-normative, and, for both of these types, ranging from sodic ($Na_2O:K_2O>2:1$) to moderately potassic ($Na_2O:K_2O<2:1$). High and low P_{H_2O} and P_{O_2} variants were also suggested.

Most Dunedin representatives of the sodic alkali olivine basalt, hawaiite, mugearite, benmoreite, trachyte lineage are slightly nepheline-normative. Members of the basanite, nepheline hawaiite, nepheline mugearite, nepheline benmoreite, phonolite lineage are more strongly nepheline-normative. Olivine nephelinites are widespread but volumetrically minor in the outlying areas of the province; no extended lineage derived from them has yet been recognised. The mafic and intermediate members of these more sodic lineages have relatively simple mineralogy of olivine and titaniferous Ca-rich augite which both show a tendency towards iron enrichment, titanomagnetite, plagioclase which except in the nephelinites is mantled by calcic anorthoclase in the groundmass, and nepheline in the feldspathoidal varieties. Kaersutite or its rhönite-bearing decomposition products is known in some members of the sodic series (Kyle and Price, 1975), but appears to be much more common in the more potassic series.

The more potassic rocks are represented by hypersthene-normative trachyandesites such as the Leith Valley "andesite" and the "kaiwekite" of North Head as well as by a nepheline-normative lineage from sanidine basanite (nepheline trachybasalt) through nepheline trachyandesite to phonolite. These rocks tend to be strongly porphyritic and feldsparphyric, and typically contain kaersutite partially or completely replaced by dense aggregates of its low-pressure magmatic decomposition products (Benson, 1939; Price and Chappell, 1975). High-Fe variants exist, but members of the more potassic lineages have a strong tendency to have lower Fe:Mg ratios than members of the sodic series, and to lack the Fe-enrichment trend shown by some typical hawaiites and mugearites. It is inferred that the more potassic magmas also tended to be the more hydrous with relatively high P_{H_2O} and P_{O_2} promoting crystallisation of kaersutite and/or early magnetite.

Rare-earth patterns (Price and Taylor, 1973) for 10 Dunedin rocks show strong enrichment in light REE as is typical of alkalic associations; La increases from about 100 times chondrite in a basalt to 500 in a phonolite (Fig. 8). The phonolites have very strong negative Eu anomalies. Quartz-normative trachyte (Koputai Trachyte) however has a flatter pattern with significantly lower light REE than all the others as well as higher $^{87}Sr/^{86}Sr$, higher K/Rb, and other trace element differences. It could

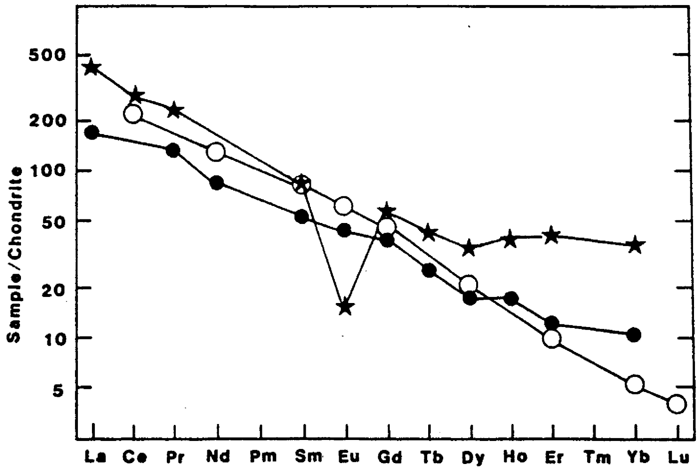

Fig. 8—Chondrite-normalised rare earth patterns for a Dunedin basanite and phonolite, and the Pigroot mafic phonolite (after Irving and Price, 1981). Open circles: Mafic phonolite, Pigroot. Filled circles: Basanite, Black Head. Stars: Phonolite, Mt Kettle.

not have been derived by simple fractionation from the known basaltic magmas of the province. A strong positive Eu anomaly indicates the importance of feldspar accumulation in its genesis.

Trace element and other data led Price and Chappell (1975) to postulate low-pressure fractionation involving olivine, clinopyroxene and titanomagnetite in the series basalt to mugearite, and of the same minerals plus apatite from mugearite to benmoreite. They suggest that kaersutite fractionation is involved in the basanite-nepheline benmoreite lineage and that this is a higher P_{H_2O} variant of the basalt-benmoreite lineage. Kaersutite fractionation could account for features of the REE pattern of a kaersutite-bearing nepheline hawaiite they studied, as well as for enrichment in Sr, Ba and Rb (cf. Kesson and Price, 1972), but whether their data are representative of this lineage is not clear. As they and Coombs and Wilkinson (1969) point out, the various lineages postulated are representatives of intergradational series involving several variables. For the more potassic series Price and Chappell postulate fractionation involving olivine, clinopyroxene and kaersutite and/or titanomagnetite.

The phonolites have a strong negative Eu anomaly and K/Rb values as low as 150 to 200 in comparison with about 300 in the benmoreites and nepheline benmoreites, and 300 to 500 in the basalts. Ba and Sr are strongly depleted with respect to the benmoreites. All these features indicate strong fractionation of feldspar in the transition from benmoreite or nepheline benmoreite to phonolite. Clinopyroxene, titanomagnetite and apatite are also involved and kaersutite and fayalitic olivine are usually present. Sodic amphiboles are less common. As indicated by Price and Chappell (1975) and by Coombs and Wilkinson (1969) the degree of silica undersaturation with which derivative magmas reach the silica-undersaturated thermal valley in the system Q-Ne-Ks reflects the degree of silica undersaturation of the mantle-derived parent basaltoid magma, and some phonolites may be derived directly from basanite (Wilkinson, 1966). Further alkali feldspar fractionation causes convergence on the low-pressure phonolite minimum melting point composition.

Dikes of analcime tinguaite in the Dunedin volcano are phonolite heteromorphs (Wilkinson, 1968) in which microlites of sanidine (Or_{75}) and needles of sodian salite or aegirine are set in a matrix of analcime, in contrast to the coexistence of anorthoclase (Or_{30-35}) with a potassium-bearing nepheline and mafic minerals in phonolite. These rocks presumably result from quenching of a hydrous phonolitic melt. Such occurrences of analcime contrast with those of late-stage analcime and other zeolites found in many Dunedin rocks (Coombs and Wilkinson, 1967). Sodalite is commonly present in the more evolved types, reflecting Cl contents of up to about 0.5%.

The Pigroot mafic phonolite (Wright, 1966; Philpotts *et al.*, 1972; Price and Green, 1972; Price and Wallace, 1976; Irving and Price, 1981) consists essentially of alkali feldspar, nepheline, and abundant clinopyroxene, olivine, and titanomagnetite, together with minor patches of zeolites. Fragments of partially assimilated schist are common. It is notable for the presence of abundant spinel lherzolite nodules and rarer corona-textured spinel metagabbro xenoliths in a chemically more evolved rock (100 $Mg/Mg + \Sigma Fe = 0.46$) than could be derived from partial melting of upper mantle peridotite containing olivine Fo_{88-92} (Price and Green, 1972). A $^{87}Sr/^{86}Sr$ ratio of 0.70297 ± 4 (Price and Compston, 1973) suggests that the extent of crustal contamination is not great, and like so many of the rocks of the outlying representatives of the Dunedin Volcanic Group, the relatively large lherzolite nodules attest to rapid rise from the upper mantle. The REE pattern (Fig. 8) lacks the Eu anomaly of the Dunedin shield volcano phonolites, and it is clear that this rock has a quite different, high-pressure origin. It is particularly high in Sr and Irving and Price (1981) suggest it might be the product of partial melting of a mantle source region previously enriched in Sr and light REE, followed by minor fractionation of olivine and kaersutite.

$^{87}Sr/^{86}Sr$ ratios for mafic alkalic lavas from the Dunedin volcano and a number of outlying vents range from 0.70277 to 0.70315 (Price and Compston, 1973) and with the Dunedin phonolites give an isochron-type diagram with an initial $^{87}Sr/^{86}Sr$ ratio of 0.70285 ± 5. Values for Koputai trachytes, 0.70400, are higher and imply a different origin; the kaiwekite at 0.70324 has an intermediate ratio. The ratios are low for continental basalts. Their limited Sr isotope variation and their nonradiogenic character restrict the nature and degree of contamination from crustal rocks although it should be pointed out that fragments of schist-derived quartz, partly melted and surrounded by coronas of clinopyroxene, are widespread in the mafic rocks of the peripheral province vents, especially those with lherzolite nodules indicating rapid rise and limited time for more complete assimilation. Furthermore as the Haast Schist and any other crustal materials through which the magmas have risen are unlikely to be older than Mesozoic or possibly late Paleozoic, the contaminating material may itself not have been particularly radiogenic. $^{87}Sr/^{86}Sr$ ratios for the Kakanui Mineral Breccia have been reported for megacrysts of kaersutite, aluminous clinopyroxene and apatite, and for kaersutite from a kaersutite garnet pyroxenite (Dasch *et al.*, 1970; Basu, 1978; Menzies, pers. comm., 1984). All are in the range 0.7029 to 0.7030. Similar $^{87}Sr/^{86}Sr$ ratios for mafic magmas of Early Oligocene and Middle to Late Miocene age from a wide area in the Otago province suggest that their upper mantle sources are related.

Sr and Nd isotope compositions have been determined for the Black Head and Saddle Hill basanites and the Pigroot mafic phonolite (Fig. 9). The positive ε_{Nd} values require that the source has been depleted in light REE for some time. This, coupled with the light REE enrichment of these lavas, indicates that the source has undergone a recent enrichment in light REE and many other incompatible elements (cf. Boettcher and O'Neill, 1980). The relatively high Mg values and Ni concentrations (Price and Chappell, 1976; Price and Taylor, 1973), low $^{87}Sr/^{86}Sr$ ratios, and the presence of lherzolite nodules implying rapid ascent, all suggest that these lavas have not been significantly crustally contaminated. Preliminary data for kaersutite and anorthoclase from the Kakanui Mineral Breccia show almost identical ε_{Nd} values and $^{87}Sr/^{86}Sr$ ratios (M. A. Menzies, pers. comm., 1984). For comparison, basalts from the Middle to Late Miocene

Akaroa and Lyttelton volcanoes, Banks Peninsula, have been analysed and show comparable isotopic compositions, although marginally higher in $^{87}Sr/^{86}Sr$ and distinctly higher in ε_{Nd}.

The Sr and Nd isotope compositions of these Otago Cenozoic basaltic rocks are equivalent to those measured for some of the South Westland lamprophyres (Barreiro, 1983; Cooper, this volume). The lamprophyres have high $^{206}Pb/^{204}Pb$ (Barreiro, 1983), and an overall Pb isotope character similar to that of St Helena and Tubuai (Sun, 1980; Vidal *et al.*, 1984); similar Sr and Nd isotopic compositions are observed for these localities also. This similarity in Pb, Sr and Nd isotope compositions is curious and suggests comparable long term parent/daughter isotope ratios in their source regions. By analogy, the Cenozoic Otago basalts with Sr and Nd isotope compositions similar to those of the South Westland lamprophyres may also have similar Pb isotope compositions.

Discussion

The Sr and Nd isotope compositions of Otago Cenozoic alkalic basalts are similar to other Cenozoic basalts from southeastern Australia, New Zealand and Antarctica (Futa and Le Masurier, 1983; Barreiro, 1983; Menzies and Wass, 1983; McDonough *et al.*, in press, unpublished data). These basalts lie on the low side of the oceanic mantle array (Fig. 9) and overlap with the fields of St Helena and Tubuai basalts (White and Hofmann, 1982; Vidal *et al.*, 1984). Few known basalts plot in this part of the Sr/Nd isotope diagram, and St Helena and Tubuai are the only examples reported of ocean island basalts. A Gondwanaland reconstruction of Australia, New Zealand and

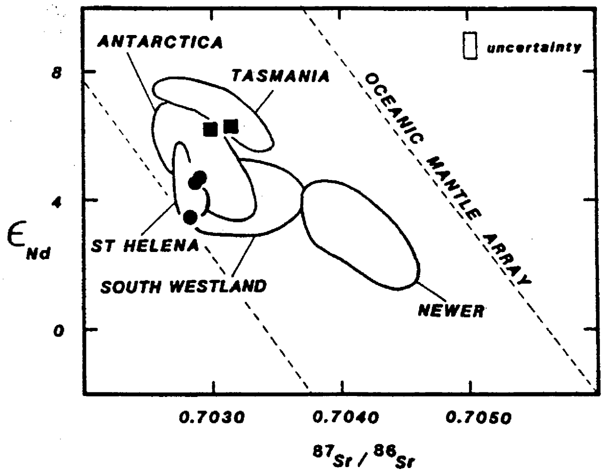

Fig. 9—ε_{Nd} versus $^{87}Sr/^{86}Sr$ variation for Cenozoic basalts from the South Island, New Zealand (McDonough *et al.*, unpublished data). Filled circles indicate the isotopic compositions of the Saddle Hill and Black Head basanites and the Pigroot mafic phonolite (Price and Chappell, 1975; Price and Taylor, 1973; Price and Green, 1972; Philpotts *et al*, 1972). Filled squares indicate the isotopic compositions of an Akaroa mugearite and a Lyttleton basalt from Banks Peninsula (Price and Taylor, 1980). Maximum uncertainty indicated by the open box $\pm 2\sigma_{mean}$ uncertainty). Also shown are the Sr and Nd isotope fields for Cenozoic basalts from St Helena (White and Hofmann, 1982; Cohen and O'Nions, 1982), Antarctica (Futa and Le Masurier, 1983), South Westland, New Zealand, (Barreiro, 1983) and Tasmania and Victoria/South Australia Newer Volcanic field, (McDonough *et al.*, 1985). The dashed field for the Oceanic Mantle Array includes Sr and Nd isotope data for MORB and OIB (DePaolo and Wasserburg, 1976; O'Nions *et al.*, 1977; White and Hofmann, 1982; Cohen and O'Nions, 1982; White and Dupré, 1984).

Antarctica suggests that prior to 100 m.y. these continental blocks were contiguous (Weissel *et al.*, 1977; Audley-Charles, 1983), with the southern New Zealand-Campbell Plateau area alongside Marie Byrd Land of Antarctica at 80 m.y. (Molnar *et al.*, 1975; Adams *et al.*, 1979). Similar isotopic compositions of Sr and Nd in these terranes and the fact that they were once adjacent land masses may reflect the involvement of a common mantle source component, possibly within the lithospheric mantle, in the genesis of these magmas.

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APPENDIX 3

Chemical and Isotopic Data on Continental and Oceanic Intraplate Basalts from the Southwest Pacific

A.3-2

GEOCHEMICAL AND ISOTOPIC SYSTEMATICS OF CENOZOIC INTRAPLATE BASALTS FROM CONTINENTAL AND OCEANIC REGIONS IN THE SOUTH PACIFIC

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Geochemical and isotopic comparisons are made between intraplate basalts from islands on the Campbell Plateau, and Chatham, Lord Howe and Norfolk Rises with intraplate basalts from Eastern Australia and New Zealand and ocean island basalts. We evaluate the effects of contrasting lithosphere on the chemical and isotopic compositions of these basalts and examine this region with respect to the proposed DUPALL isotope anomaly. Primary and near primary, Cenozoic basalts from Eastern Australia, North and South Islands, New Zealand and their adjacent ocean islands have incompatible element patterns similar to those found in oceanic intraplate volcanoes (e.g., Hawaiian Islands), suggesting that deep mantle plumes are involved in their genesis. Sr and Nd isotopic compositions for these basalts indicate that they are all derived from LREE-depleted and low Rb/Sr mantle source regions which have experienced a relatively recent LREE-enrichment.

There is considerable overlap in Sr and Nd isotope compositions for continental and nearby ocean island basalts for Australia, New Zealand, and West Antarctica. Eastern Australia continental basalts have Sr and Nd isotopic compositions (0.7028 to 0.7045 and +8.0 to 0.0, respectively) similar to basalts from Lord Howe (0.7041 and +3.0) and Norfolk islands (0.7030 and +7.5). Basalts from the Alexandra Volcanics (North Island) (0.7032 and +5.4) and from Banks Peninsula Volcanoes (0.7032 and +6.3), Dunedin Volcano (0.7028 and +3.5 to +4.5) and surrounding centers (0.7029 and +4.7) (South Island) have similar Sr and Nd isotope compositions to basalts from the sub-Antarctic ocean islands of New Zealand [Chatham (0.7033 and +4.0), Antipodes (0.7029 and +5.5), Auckland (0.7030 to 0.7036 and +5.6 to +4.9, respectively) and Campbell (0.7037)]. Alkali basalts from Marie Byrd Land (W. Antarctica) range in composition from 0.7026 to 0.7031 and +6.8 to +3.7 (Sr and Nd, respectively) (Futa and Le Masurier, 1983). Sr and Nd isotope data for the oceanic Tubuai and Rurutu islands, Austral Chain (0.7028 to 0.7034 and +5.7 to +3.6) are similar to those found for basalts in Australia and New Zealand. There is a large range in the Sr and Nd isotopic compositions for Pitcairn Island basalts (0.7035 to 0.7049 and +3.2 to -2.3).

All of these basalts plot on the lower left side of the oceanic mantle array, and in general they have a lower $^{87}Sr/^{86}Sr$ ratio for a given ε_{Nd} value when compared to Hawaiian alkalic and tholeiitic basalts. Combined Sr, Nd and (limited) Pb isotope data are not consistent with the proposed DUPALL anomaly (Hart, 1984). Instead the data indicate a non-systematic distribution of isotopically distinct plume components within this region, with some areas having extreme diversity in Sr, Nd and Pb isotopic composition over a rather small geographic region (e.g., French Polynesia).

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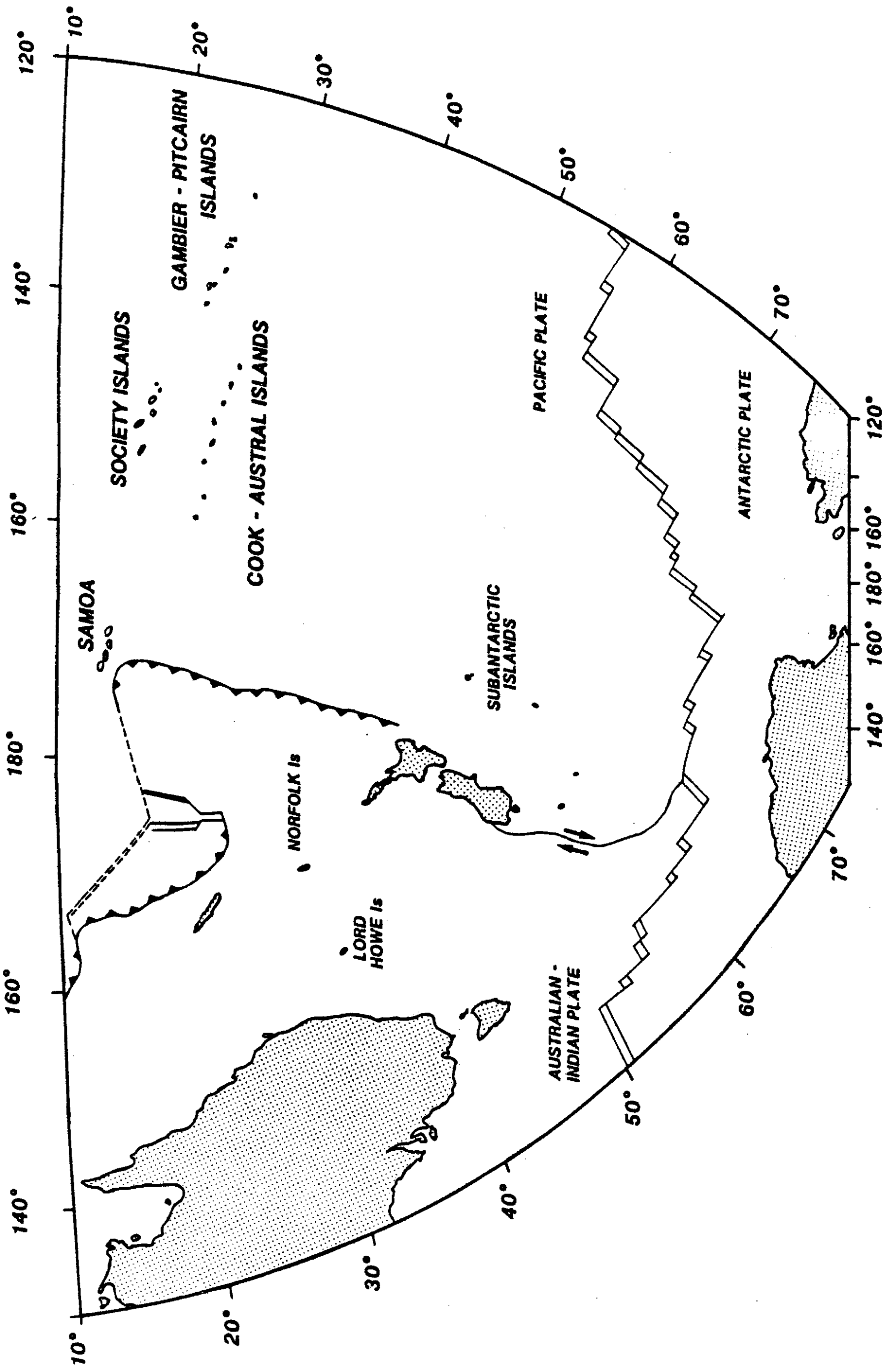
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SAMOA
SOCIETY ISLANDS
GAMBIER - PITCAIRN ISLANDS
COOK - AUSTRAL ISLANDS
PACIFIC PLATE
ANTARCTIC PLATE
SUBANTARCTIC ISLANDS
NORFOLK Is
LORD HOWE Is
AUSTRALIAN - INDIAN PLATE

Table 1. Geochemical and Isotopic Compositions of the Norfolk Island Basalts

	71-116	70-723	71-186	71-199	71-205	71-237
	(N-20)		(NF-56)	(NF-69)	(NF-75)	(PH-4)
	AOB.	Trans.	Thol.	Thol.	Thol.	Thol.
SiO_2	47.55	49.95	49.59	49.78	50.93	50.20
TiO_2	1.97	2.09	1.83	1.98	2.02	2.23
Al_2O_3	15.49	16.34	16.06	16.12	15.60	17.36
Fe_2O_3	1.92	4.31	3.39	4.67	4.24	6.70
FeO	7.82	5.64	6.61	5.34	5.50	3.01
MnO	0.17	0.15	0.16	0.14	0.12	0.12
MgO	8.57	6.19	7.04	6.41	6.32	3.98
CaO	8.97	8.74	9.02	8.11	8.34	7.69
Na_2O	3.91	3.85	3.56	3.63	3.47	4.10
K_2O	1.17	0.70	0.43	0.61	0.48	0.91
P_2O_5	0.46	0.37	0.31	0.31	0.29	0.44
Total	98.00	98.33	98.00	97.10	97.31	96.74
Rb	18	9	5	9	6	10
Sr†	583	479	425	401	328	534
Y	23	27	29	129	115	69
Zr	154	152	136	135	143	142
Nb	38	27	20	18	17	28
Cs	0.14	0.03	0.24	0.09	0.08	0.05
Ba	232	161	174	131	126	204
La	20.3	16.0	14.0	36.4	32.3	17.0
Ce	41.5	32.0	29.3	41.4	57.1	41.4
Pr	5.17	4.40	3.84	11.75	8.60	5.66
Nd	20.9	20.1	17.7	58.9	40.7	28.0
Sm	5.7	4.9	4.6	16.3	11.0	9.6
Eu	1.91	1.81	1.67	4.61	4.09	4.05
Gd	4.8	4.7	4.6	17.9	12.5	12.0
Tb	0.85	0.77	0.79	–	1.96	2.06
Dy	5.1	4.8	4.8	16.5	12.5	13.9
Ho	0.95	0.83	0.94	3.15	2.58	2.90
Er	2.5	2.2	2.4	7.7	6.8	7.8
Yb	2.2	1.7	1.9	5.3	5.0	6.8
Hf	3.28	2.80	2.60	2.84	2.27	3.59
Pb	1.36	1.35	2.38	1.25	1.50	2.90
Th	1.81	0.97	0.86	0.77	0.54	1.45
U	0.59	0.28	0.23	0.21	0.13	0.39
Sn	3.1	2.6	2.8	2.8	3.0	3.5
Mo	1.4	1.0	0.9	0.9	1.3	3.2
$^{87}Sr/^{86}Sr$	0.70283	0.70289	0.70294	0.70308	0.70299	0.70289
$^{143}Nd/^{144}Nd$	0.512208	0.512196	0.512215	0.512199	0.512189	0.512250
ε_{Nd}	+7.3	+7.0	+7.4	+7.1	+6.9	+8.1
$^3He/^4He$	1.82		1.93			

Major elements data from (Green, 1978) and trace element data were determined by SSMS (Taylor and Gorton, 1977). Sr and Nd isotopic compositions were determined according to the procedures described in McDonough et al (1985). He isotopic ratios are from H. Craig (personnal comm., 1986) and expressed in terms of R/Ra. Analytical uncertainties isotopic measurements for Sr are ≤ ± 0.00005 and for Nd are ≤ ± 0.000020. †Sr determined by isotope dilution. Major elements in weight %, trace element concentrations in ppm.

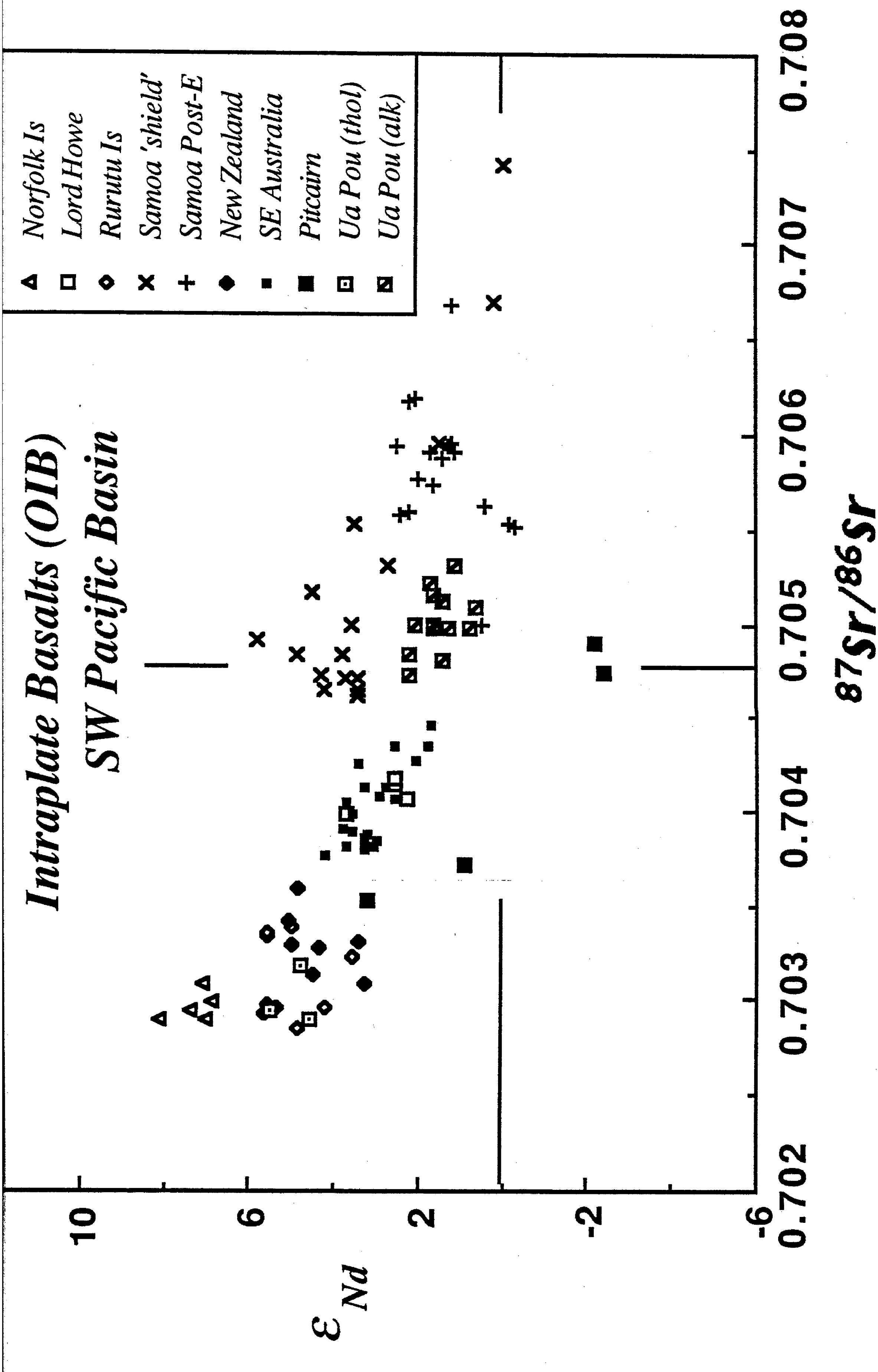
Intraplate Basalts (OIB)
SW Pacific Basin
△ Norfolk Is
□ Lord Howe
◇ Rurutu Is
× Samoa 'shield'
+ Samoa Post-E
◆ New Zealand
▪ SE Australia
■ Pitcairn
⊡ Ua Pou (thol)
⊠ Ua Pou (alk)
ε_{Nd}
10
6
2
-2
-6
0.702
0.703
0.704
0.705
0.706
0.707
0.708
$^{87}Sr/^{86}Sr$

TABLE 1. Major and Trace Element Concentrations and Sr and Nd Isotope Compositions for Basalts from the South Island, New Zealand

	Saddle Hill basanite	Black Head basanite	Pigroot ne. benmoreite	Akaroa mugearite	Lyttelton basalt
	30430[1]	30442[2]	21484[3]	T-102[4]	T-104[4]
SiO_2	42.96	42.12	46.70	49.17	44.18
TiO_2	2.91	3.38	2.21	2.07	2.98
Al_2O_3	13.33	14.38	13.55	16.96	13.26
Fe_2O_3	3.08	4.44	4.05	11.11	4.47
FeO	9.36	8.71	7.78	1.31	8.61
MnO	0.22	0.22	0.19	0.22	0.18
MgO	10.60	6.71	5.52	1.73	9.18
CaO	11.56	11.10	6.82	5.02	10.68
Na_2O	3.31	3.86	6.26	4.82	3.25
K_2O	0.84	1.75	2.79	2.39	0.94
P_2O_5	0.55	0.92	1.09	1.10	0.65
Mg value	66.9	57.9	55.9	23.9	65.5
V	253.	214.	61.	75.	220.
Cr	270.	114.	115.	—	420.
Ni	212.	85.	86.	—	245.
Cu	73.	47.	16.	21.	125.
Rb	12.	39.	73.6	52.	16.8
Sr	648.	935.	1612.	7.0	710.
Y	25.	29.	24.	50.	23.
Zr	214.	308.	633.	340.	240.
Nb	67.	83.	124.	93.	64.
Ba	388.	512.	728.	590.	360.
La	—	57.0	—	61.7	40.1
Ce	—	—	188.	137.	88.7
Pr	—	15.0	—	15.1	9.2
Nd	—	59.2	78.0	58.0	36.5
Sm	—	9.8	14.1	12.0	7.7
Eu	—	3.1	4.2	3.8	2.3
Gd	—	9.7	11.1	10.5	6.0
Tb	—	1.2	—	1.6	0.9
Dy	—	5.4	6.4	8.6	5.2
Ho	—	1.2	—	1.7	0.9
Er	—	2.5	2.0	4.0	2.0
Yb	—	2.1	1.0	3.4	1.3
Hf	—	5.	14.1	7.7	4.7
Pb	4.	4.	8.	6.	3.
Th	3.	5.	14.	6.	4.2
U	2.	2.	4.	1.7	1.0
$^{87}Sr/^{86}Sr$	.70282±5	.70287±5	.70289±3	.70298±x	.70314±x
$^{143}Nd/^{144}Nd$	.512015±14	.512069±14 .512059±18	.512075±18	.512154±14	.512157±20
ε_{Nd}	+3.5	+4.5	+4.7	+6.2	+6.3

Chemical data from [1] Price and Chappell (1976), [2] Price and Taylor (1973), [3] Major elements data from Price and Green (1972) for sample 30424, trace element data from Philpotts et al. (1972) for sample 21484 (GSFC 136), [4] Price and Taylor (1980). Mg value = [Mg/Mg + Fe]×100, with sample T-102 adjusted for $Fe_2O_3/FeO = 0.15$. Measured values for Sr and Nd isotope standards are $^{87}Sr/^{86}Sr = 0.70800 \pm 3$ for the E & A $SrCO_3$ and $^{87}Sr/^{86}Sr = 0.71022 \pm 1$ for the NBS-987 Sr standard, $^{143}Nd/^{144}Nd = 0.511833 \pm 10$ for BCR-1, and $^{143}Nd/^{144}Nd = 0.511101 \pm 8$ for Ndα (CIT standard, Wasserburg et al, 1981).

TABLE 1. Sr and Nd Isotopic Compositions of Alexandra Volcanic Group Basalts, North Island, New Zealand

Sample	Rb	Sr	$^{87}Sr/^{86}Sr$ unleached	$^{87}Sr/^{86}Sr$ leached	Sm	Nd	$^{143}Nd/^{144}Nd$	ϵ_{Nd}	Basalt Type
OKETE VOLCANICS									
104B	22.7	630.	0.70304	-----	7.03	34.46	0.512125 ± 24	+5.6	Basanite
111	26.2	571.	0.07315	0.70308	6.26	30.32	0.512123 ± 24	+5.6	Basanite
K 60	20.4	847.	0.70406	0.70351	6.23	29.89	0.512119 ± 18	+5.5	Alkali Ol. Basalt
118	17.2	479.	0.70320	0.70315	6.95	31.35	0.512107 ± 16	+5.3	Alkali Ol. Basalt
K 85	15.3	497.	0.70343	0.70333	5.04	22.26	0.512123 ± 22	+5.6	Olivine Tholeiite
121	16.5	418.	0.70361	0.70355	5.46	22.74	0.512124 ± 24	+5.6	Hawaiite
105C	11.7	333.	0.70340	0.70341	5.46	22.31	0.512118 ± 22	+5.5	Hawaiite
PIROGNIA, KAKEPUKU AND TE KAWA VOLCANICS									
P35	22	392		0.70482			0.511916 ± 18	+1.6	Trans. Ol. Basalt
P69	27	458		0.70365			0.512054 ± 24	+4.3	Basanite
P74	36	637		0.70357			0.512051 ± 24	+4.2	Basanite
P73	34	478		0.70481			0.511909 ± 16	+1.4	Trans. Ol. Basalt
U15	15	350		0.70424			0.512022 ± 20	+3.6	Trans. Ol. Basalt
T4B	12	322		0.70438			0.512017 ± 20	+3.5	Alkali Ol. Basalt

Element concentrations were determined for unleached powders. The leaching experiment was performed on basalt powders in 6.0 N HCl, overnight at 160°C, using open beakers, followed by rinsing of the residue with cold 6.0 N HCl and this residue was decomposed for Sr isotopic analysis. Measured $^{87}Sr/^{86}Sr$ ratio for E & A $SrCO_3$ is 0.70800 ± 2 and for NBS-987 is 0.71022 + 1. Nd isotopic ratios are normalized using $^{146}Nd/^{142}Nd = 0.636151$. Measured $^{143}Nd/^{144}Nd$ ratio for BCR-1 is 0.511833 ± 10, for La Jolla Nd standard 0.511040 ± 7, and for Ndα is $^{143}Nd/^{144}Nd$ is 0.511101 ± 8.

$$\epsilon_{Nd} = \left[\frac{(^{143}Nd/^{144}Nd)_{Sample}}{(^{143}Nd/^{144}Nd)_{Chur}} - 1 \right] 10^4, \quad \text{where } (^{143}Nd/^{144}Nd)_{Chur} = 0.511836$$

TABLE 1. Major and Trace Element Concentrations and Sr and Nd Isotope Compositions for Basalts from the Sub-Antarctic Islands, New Zealand

	82235	82262	82264	81/7	81/15
	Auckland Is.			Antipodes Is.	
SiO_2	48.25	46.55	47.36	42.65	42.11
TiO_2	2.86	3.17	2.86	4.23	3.92
Al_2O_3	12.37	14.81	12.75	11.53	12.97
Fe_2O_3	3.31	3.48	4.11	2.74	2.38
FeO	9.36	9.54	8.57	13.70	11.91
MnO	0.16	0.19	0.17	0.19	0.20
MgO	9.30	8.07	10.21	9.65	7.95
CaO	10.17	9.75	9.85	11.66	10.94
Na_2O	2.89	2.78	2.73	2.36	4.85
K_2O	0.83	1.06	0.87	0.76	1.57
P_2O_5	0.49	0.60	0.53	0.53	1.19
Mg value	60.4	56.3	62.7	54.7	53.4
Sc	24.	22.	25.		
V	222.	268.	250.		
Cr	305.	222.	410.		
Ni	201.	149.	223.	138.	117.
Cu	64.	65.	74.	58.	64.
Zn	121.	114.	112.	126.	178.
Ga	19.	21.	20.	21.	21.
Sr	495.	670.	480.	517.	1181.
Rb	13.	21.	19.	17.	45.
Ba	206.	322.	244.		
Pb	2.	1.	1.	4.	5.
Y	29.	33.	26.	29.	38.
Nb	42.	61.	44.	45.	100.
Zr	183.	229.	175.	228.	393.
La	24.	37.	24.		
Ce	56.	82.	60.		
Nd	28.	36.	29.	37.	78.
Th	5.	6.	4.	4.	11.
$^{87}Sr/^{86}Sr$	.70298±4	.70341±4	.70360±3	.70293±4	.70296±3
$^{143}Nd/^{144}Nd$	.512124±22	.512096±20	.512086±22	.512126±15	.512111±14
ε_{Nd}	+5.6	+5.1	+4.9	+5.7	+5.4

Mg value = [Mg/Mg + Fe]×100, with (Fe_2O_3/FeO = 0.15). Measured values for Sr and Nd isotope standards are $^{87}Sr/^{86}Sr$ = 0.70800 ± 3 for the E & A $SrCO_3$ and $^{87}Sr/^{86}Sr$ = 0.71022 ± 1 for the NBS-987 Sr standard, $^{143}Nd/^{144}Nd$ = 0.511833 ± 10 for BCR-1, and $^{143}Nd/^{144}Nd$ = 0.511101 ± 8 for Ndα (CIT standard, Wasserburg et al, 1981).

TABLE 1(cont). Major and Trace Element Concentrations and Sr and Nd. Isotope Compositions for Basalts from Chatham Island, New Zealand

	14423	14340	14432	14467	14469
Age(Ma)	≈75	≈75	≈35	5	5
SiO_2				43.66	
TiO_2				3.60	
Al_2O_3				14.37	
Fe_2O_3				2.29	
FeO				11.45	
MnO				0.17	
MgO				8.31	
CaO				11.90	
Na_2O				2.31	
K_2O				1.20	
P_2O_5				0.73	
Mg value				56.4	
Sc					
V				318.	
Cr				189.	
Ni				122.	
Cu				59.	
Zn				102.	
Ga					
Sr				784.	
Rb				24.	
Ba					
Pb					
Y				26.	
Nb					
Zr				211.	
La				184.	
Ce				145.	
Th				12.	
$^{87}Sr/^{86}Sr$	.70308±4	.70313±4	.70328±5	.70358±4	.70373±5
(leached)				.70331±4	.70329±4
$^{143}Nd/^{144}Nd$	.512004±14	.512065±14	.512059±18	.512008±18	.512090±22
ε_{Nd}	+3.3	+4.5	+4.4	+3.4	+5.0

GEOCHEMICAL AND ISOTOPIC CHARACTERISTICS OF EASTERN AUSTRALIAN CAINOZOIC "CENTRAL" VOLCANOES

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Geochemical and Sr and Nd isotopic data have been obtained on mafic rocks from four Cainozoic "central" volcanic provinces in eastern Australia. The provinces, namely Peak Range, central Queensland (mean age 30 Ma), Tweed Volcano (southern portion), northern N.S.W. (21 Ma), Comboyne Plateau, central coastal N.S.W. (16 Ma) and Warrumbungle Volcano, central N.S.W. (15 Ma) have rocks ranging from alkali and tholeiitic basalts through to trachyte or rhyolite. They are compared with associated "lava field" volcanism which typically has more restricted, predominantly basaltic compositional characteristics. The possible significance of source composition (plume and lowermost lithospheric mantle), hot spot traces, lateral compositional differences over a 550 km wide belt of contemporaneous volcanism, and the relative importance of fractionation and assimilation processes are assessed.

Basaltic rocks from Peak Range have initial $^{87}Sr/^{86}Sr$ ratios of 0.70327 to 0.70439 and ξNd +5.5 to +1.7, Tweed Volcano 0.70391 to 0.70541 and +0.3 to -2.8, Comboyne Plateau 0.70365 to 0.70400 and +3.2 to +2.1, and Warrumbungle Volcano 0.70360 to 0.70436 and +3.6 to +1.4 respectively. These isotopic compositions are similar to other eastern Australian provinces and are within the observed range for ocean island basalts. At a given Mg#(=100Mg/Mg+Fe^{2+}) there is a tendency for basaltic rocks from "central" provinces with low Mg# (<60) to have slightly higher $^{87}Sr/^{86}Sr$ ratios than "lava field" basalts. Similarly tholeiitic rocks generally have slightly higher $^{87}Sr/^{86}Sr$ ratios than associated alkaline basaltic rocks with comparable Mg#.

A tendency for basalts from the Peak Range and Warrumbungle Volcano with the lowest Mg#'s to have higher $^{87}Sr/^{86}Sr$ and lower ξNd suggests that crustal assimilation may be involved in the evolution of "central" type volcanoes. Primary and near primary basalts from the four provinces have incompatible element patterns typical of intraplate oceanic and continental alkaline basalts. In any one province incompatible elements are enriched in alkaline basalts relative to the associated tholeiitic basalts.

Internat. Volc. Congress Abst., New Zealand, 1986

sample#	rock type	Mg#	Ni	Cr	Rb	Sr	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	$^{87}Sr/^{86}Sr$	$^{143}Nd/^{144}Nd$	ϵ_{Nd}
			--------	ppm	--------				(initial†)		
					CLERMONT VOLCANICS			30 Ma			
CLM 5	hawaiite	70.6	308	236	23.5	550	0.123	0.70363	0.70358	0.512076 ± 22	+4.7
CLM 100	basanite	64.5	165		30.0	885	0.098	0.70331	0.70327	0.512119 ± 14	+5.5
CLM 43	ol. tholeiite	62.4	147		16.0	412	0.112	0.70407	0.70402	0.512001 ± 24	+3.2
CLM 77	hawaiite	44.1	37		31.5	490	0.186	0.70377	0.70369	0.511996 ± 20	+3.1
CLM 145	qz. tholeiite	63.8	93		107.	211	1.464	0.70501	0.70439	0.511922 ± 20	+1.7
					TWEED VOLCANICS		21 Ma				
28048	qz. tholeiite	57.1	78		31.0	516	0.173	0.70445	0.70430	0.511850 ± 24	+0.3
28060	qz. tholeiite	50.1	--	--	----	---	-----	0.70391	-------	0.511783 ± 18	-1.0
28062	qz. tholeiite	46.6	33		86.0	346	0.718	0.70562	0.70541	0.511694 ± 18	-2.8
					COMBOYNE VOLCANICS			16 Ma			
C 77	icelandite	50.9	--	--	40	386	0.299	0.70372	0.70365	0.511944 ± 16	+2.1
C 71	hawaiite	49.9	39	71	24	615	0.113	0.70403	0.70400	0.512000 ± 20	+3.2
MTB 6	hawaiite	45.9	22	40	30	633	0.137	0.70398	0.70395	0.511997 ± 16	+3.2
					WARRUMBUNGLE VOLCANICS			15 Ma			
WMB 171	alk. ol. basalt	60.1			24.0	1070	0.065	0.70361	0.70360	0.512021 ± 24	+3.6
WMB 35	hawaiite	64.3	183	253	31.5	498	0.183	0.70409	0.70405	0.511975 ± 20	+2.7
WMB 131/1	hawaiite	58.6	127	144	41.0	805	0.147	0.70437	0.70434	0.511938 ± 18	+2.0
WMB 136	mugearite	53.4	54	90	49.5	348	0.411	0.70409	0.70400	0.511938 ± 18	+2.0
WMB 8	hawaiite	49.2	42	36	49.0	1060	0.133	0.70439	0.70436	0.511906 ± 22	+1.4
WMB 162	benmoreite	31.5			61.0	475	0.371	0.70442	0.70434	0.511951 ± 22	+2.3
WMB 188	trachyte*				126.	108.	3.368	0.70520	0.70448		
WMB 5	trachyte	3.7	<1	<1	135.	34	11.47	0.71334	0.71090	0.511943 ± 20	+2.1
WMB 157	trachyte*				379.	2.5	442.2	0.81195	0.71775	0.511910 ± 20	+1.5
WMB 93	trachyte*	3.7	<1	2	520.	4	383.6	0.93226	0.85054	0.511871 ± 22	+0.7

All samples were leached in 6.0 N HCl at 160°C for at least 15 hours, rinsed in cold 6.0 N HCl and decomposed according to the technique of McDonough _et al_ (1985). *Samples are peralkaline. †Initial $^{87}Sr/^{86}Sr$ ratios were determined assuming a regional eruption age for each suite of volcanics; volcanic province ages are reported in Wellman and McDougall (1974). Elemental concentrations were determined by XRF. $Mg\# = [Mg/Mg + Fe^{2+}] \times 100$, and were determined using the measured Fe^{3+}/Fe^{2+} or by assuming a ratio of 0.20 in cases of obvious secondary oxidation. Calculated age for WMB 93 assuming an $^{87}Sr/^{86}Sr_i = 0.70400$ is 41.9 Ma. All uncertainties in the $^{87}Sr/^{86}Sr$ ratios is ≤ ± 0.00005. Uncertainties reported in the $^{143}Nd/^{144}Nd$ ratios are $2\sigma_m$. Measured $^{87}Sr/^{86}Sr$ for E & A $SrCO_3$ is 0.70800. Measured $^{143}Nd/^{144}Nd$ ratios are normalized to $^{146}Nd/^{142}Nd$. Measured $^{143}Nd/^{144}Nd$ ratio for BCR-1 is 0.511833 ± 10.

$$\epsilon_{Nd} = \left[\frac{(^{143}Nd/^{144}Nd)_{Sample}}{(^{143}Nd/^{144}Nd)_{Chur}} - 1 \right] 10^4, \quad \text{where } (^{143}Nd/^{144}Nd)_{Chur} = 0.511836$$

PART 2

SYNTHESIS

CHAPTER 4

Rb and Cs in the Earth and Moon and the Evolution of the Earth's Mantle

by W.F. McDonough, S.-s. Sun,
A.E. Ringwood, E. Jagoutz and A. W. Hofmann

Earth and Planetary Science Letters (Submitted)

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Abstract

Estimates of the Earth's Rb and Cs content and its Rb/Cs ratio vary considerably. The Earth's Rb content is best constrained by the bulk Earth's Rb/Sr ratio and by Sr and Nd isotopic systematics. The Earth's Cs content is poorly constrained and is dependent on its geochemical behavior relative to Rb.

Coarse and fine grained sedimentary rocks of all ages (including shales, loess, greywackes and deep sea sediments) have Rb/Cs ratios of 18±10 (±1σ). As this ratio is not affected by weathering, it is regarded as the upper crust Rb/Cs ratio. Differences in the mean Rb/Cs ratios of granulite facies terranes and xenoliths present difficulties in estimating the average Rb/Cs ratio of the lower crust. Archaean lavas and eclogites have low, subchondritic Rb/Cs ratios ($\leq$10), and many of these eclogites have high Cs concentrations. Altered oceanic crust and possibly sediments are considered important in establishing the low Rb/Cs ratio (25-30) in island arc lavas. A constant and high Rb/Cs ratio of 80 in mid-ocean ridge basalts (MORB) and ocean island basalts (OIB) does not reflect the Earth's primitive mantle Rb/Cs ratio. We propose a bulk Earth Rb/Cs ratio of ~20 which is close to the average crustal ratio. This estimate has about 50% uncertainty; a lower limit of Rb/Cs ~10 is defined by chondritic meteorites and Archaean komatiites, basalts and eclogites, as well as by summing the fractional proportions of the crust and MORB source reservoir contributions, the upper limit is harder to constrain but is necessarily much less than 80, the depleted mantle ratio.

There is a secular variation in the Rb/Cs ratio of the Earth's mantle, which is attributed to continental crust formation and mantle recycling. Archaean eclogites, with high Rb and Cs contents, may represent subducted oceanic lithosphere, and may constitute an important incompatible element enriched reservoir in the present day mantle. These rocks must be considered when taking an inventory of the Earth's Rb and Cs budget. The constancy of the Rb/Cs ratio in MORBs and OIBs, and its difference with respect to the bulk crust and bulk Earth Rb/Cs ratio indicates that the MORB - OIB source reservoirs have evolved together through a crustal depletion

event and limited subsequent intra-mantle differentiation. This has important implications for the present dynamic state of the Earth's mantle and its overall evolution.

The average Rb/Cs ratio for all lunar samples is 22±3. Lunar highlands anorthosites have lower Rb/Cs ratios, some of which are subchondritic. The Moon's Rb/Cs ratio is most likely dominated by the KREEP component. Within the uncertainties of these estimates, the Earth's Rb/Cs ratio is similar to the bulk Moon's ratio. Consequently, these data cannot be used to constrain the origin of the Moon, nor the relative contributions of the Earth and impactor, assuming an impact origin for the Moon.

1) Introduction

Knowledge of the concentration of Rb and Cs and the Rb/Cs ratio in the Earth's primitive mantle can contribute greatly to our understanding of the composition and evolution of the Earth's mantle (1-5). These elements, like K, are moderately volatile lithophile elements, with condensation temperatures slightly lower than moderately refractory major elements (e.g., Mg, Si and Fe). Because of their lower temperatures of condensation Rb, Cs, and K may have been fractionated relative to one another and relative to refractory lithophile elements during the Earth's accretion. Consequently, estimating their absolute abundances, their abundances relative to refractory lithophile elements, and/or the Earth's primitive mantle Rb/Cs ratio is difficult.

Most attempts use Rb - Sr isotope systematics to constrain the Earth's Rb content, and compare this with K/Rb and K/U ratios in the Earth and meteorites. However, estimates of the Earth's Cs content are most often constrained by its relationship with Rb and K, that is by determining a primitive mantle Rb and/or K concentration and assuming a Rb/Cs and/or a K/Cs ratio. A few recent estimates of the Earth's primitive mantle Rb/Cs ratio have been made.

Taylor and McLennan (6) developed a model composition for the continental crust which contains about 38% of the Rb and >45% of the Cs inventory of the Earth's primitive mantle and estimated a Rb/Cs ratio of 30 for the crust. From this they suggested the Earth's primitive mantle Rb/Cs ratio is equal to or greater than that of the continental crust. In a revised crustal model, these authors (7) argued that the continental crust contains only about 32% of the Earth's primitive mantle Rb and Cs budget, and suggested the Earth's primitive mantle has a Rb/Cs ratio of about 30. Sun (2) developed a model for the composition of the Earth's primitive mantle based on a mantle melting model and peridotite data. He suggested the Earth's primitive mantle Rb/Cs ratio can be constrained to be between the crustal ratio of ~30 and the oceanic basalt ratio of ~80. Hofmann and White (3) found a relatively constant Rb/Cs ratio of 80 in mid-ocean ridge basalts (MORBs) and ocean island basalts (OIBs) over a wide range of Rb contents. They suggested that this Rb/Cs ratio is the Earth's primitive mantle Rb/Cs ratio.

The Earth's primitive mantle Rb/Cs ratio has also been considered in the debate on the origin of the Moon (8-13). This debate focuses on the comparison of the bulk Earth's estimated Rb/Cs ratio that of the Moon's. If the Moon was derived from the Earth's mantle by a fission or an impact processes (see Hartmann *et al* [14] for a collection of papers on the lunar origins), then the Moon would necessarily have a Rb/Cs ratio similar to the Earth's, or higher, if contributions from the impactor are of minor importance (or the Rb/Cs ratio of the impactor is equivalent to the Earth's). If the Earth's estimated Rb/Cs ratio is considerably greater than the Moon's, then it would appear to be at odds with a terrestrial origin for the Moon. Critical to this whole debate is how well do we know the Rb/Cs ratio of the bulk Earth.

The aim of this paper is to examine in detail the data base available to constrain the Earth's primitive mantle Rb/Cs ratio and its bulk Rb and Cs content. In addition, we have compiled all of the available 'best analytical data' for the Moon and various meteorites in order to make comparisons with the Earth's primitive mantle Rb/Cs ratio and those of the Moon, and Mars (SNC meteorites). This information will be used to test whether Rb and Cs can be used to constrain models of lunar origin. An additional discussion on Rb - Cs mantle geochemistry and its secular evolution is included; new insights into this topic have come about as a result of this investigation.

2) *A Perspective on K, Rb and Cs in the Earth's Primitive Mantle*

A common assumption of all models which estimate the composition of the Earth's primitive mantle is that the refractory lithophile elements (e.g., Ca, Al, Ti, REE, etc.) are present in chondritic proportions. In contrast, many of these models differ on the absolute and relative proportion of moderately refractory (e.g., Mg and Si), moderately volatile and volatile lithophile elements. However, most models agree that the Earth experienced some depletion of the moderately volatile and volatile elements during accretion. The CI carbonaceous chondrites, with similar relative abundances to the solar photosphere (15), are considered to be a first order approximation to the composition of the solar nebula during the accretion of the planets, and as such these primitive meteorites are commonly used as a guide to the composition of the terrestrial planets. In order to estimate the moderately volatile lithophile element inventory of the Earth (e.g., Rb and Cs) we need to compare the relative concentrations of these elements to one another and to refractory lithophile elements in other meteoritic samples and in different major Earth reservoirs.

Current estimates of the primitive Earth mantle Rb/Cs ratio varies between 30 and 80, whereas Orgueil, a CI chondrite, has a Rb/Cs ratio of about 11 to 12 (15,16). The Rb/Cs ratio in all carbonaceous chondrites is about the same as in CI chondrites (17-20), but the Rb/Cs ratio in ordinary and enstatite chondrites is more variable (see later discussion). The absolute concentration of these elements relative to the refractory lithophile elements varies considerably when compared to CI chondrites and may reflect differences in the pressure and temperature conditions of formation of these meteorites and or their parent bodies. Because Rb has a slightly higher condensation temperature than Cs, the Rb/Cs ratio may be elevated above the primitive value (i.e., CI chondrite) during planetary formation by nebular processes and/or planetary surface volatilizations processes (21). However, experimental studies involving incremental thermal metamorphism of meteoritic samples have not been able to induce relative fractionation of Rb and Cs at temperatures up to 1400°C (e.g., 22).

It is useful to review the methods employed in estimating the absolute abundances of the moderately volatile lithophile elements in the Earth's primitive mantle. These estimates depend either on elemental ratios using an index refractory lithophile element or by employing relevant isotopic constraints. Estimates of the primitive mantle Rb abundance have been made using Rb-Sr isotope systematics and in some cases by combining the Sr and Nd isotopic systems. Similarly, estimates of the Earth's primitive mantle K abundance have used K-Ar isotope systematics and/or the K/U and K/Rb ratio relationships. Unfortunately, the Cs abundance in the Earth's primitive mantle is not constrained by any isotopic system and is generally only ratioed to K or Rb.

A consistent, and therefore commonly agreed upon, estimate of the Earth's Rb/Sr ratio is derived from three independent approaches: [1] the weighted mean Rb/Sr ratio for the bulk crust and mantle (23), [2] the time integrated ^{87}Rb/^{86}Sr ratio versus the ^{87}Sr/^{86}Sr for primitive basalts (24-26) and [3] the correlation of the ^{87}Sr/^{86}Sr with the ^{143}Nd/^{144}Nd ratio for recent primitive basalts (27, 28), as well as that between the MORB reservoir and the bulk crust. These approaches all yield a bulk Earth Rb/Sr ratio of 0.03. This ratio is known to within 10% and is probably the most secure constraint on the abundances of the moderately volatile lithophile elements available. If we assume the refractory lithophile elements are present in the Earth's primitive mantle at about 1.85 times their concentration in a volatile-free CI chondrite (2, 4, 29), this then yields a Sr abundance of 20 to 22 ppm and a Rb abundance between 0.60 to 0.66 ppm.

The various estimates of the Earth's K abundance differ considerably. It has been suggested that a portion of the Earth's K inventory resides in the core (30, 31). However, cosmochemical, geochemical and petrologic arguments suggest that the core would not contain a significant quantity of K (32-35). On this same point we would also add that we do not consider the Earth's core to contain a significant proportion of Rb and or Cs, although this viewpoint is difficult to defend or refute given our present lack of knowledge of the Earth's core and the partitioning behavior of Rb or Cs under these conditions.

Ar isotopic systematics provide a minimum estimate for the K abundance in the Earth. This approach is based on the ^{40}Ar/^{36}Ar composition of the atmosphere

(295.5) relative to the primitive planetary value ($<1.4 \times 10^{-3}$, 36) and the relative mass of the Earth's atmosphere to the bulk Earth. This estimate yields a bulk Earth K content of 77 ppm (for a review, Ozima and Podosek, 37) or a primitive Earth mantle K content of ~115, which is a minimum estimate since this does not take into account the existing ^{40}K in the crust and mantle, nor the ^{40}Ar in the mantle.

The absolute K abundance of the bulk Earth has also been estimated from the observed Earth K/U ratio and an assumed U content. If the bulk Earth's U content is assumed to be between 15 and 20 ppb (2, 4, 29) and we use a Ca content of about 2.5% (given Ca/U is $\sim 1.3 \times 10^6$ for all carbonaceous chondrites and enstatite chondrites), then this would yield a bulk Earth K content of between 150 and 200 ppm, or a primitive Earth mantle of between 225 and 300 ppm K. This calculation assumes that K and U have been equally incompatible in their partitioning behavior between the crust and mantle throughout geologic time. This assumption appears to be justified, given the Earth's continental crust has approximately the same K/U ratio ($\sim 10^4$) as the depleted mantle source region of MORB (1.27×10^4) (38, 39).

Given Rb is more incompatible than K during mantle melting, the K/Rb ratio in the Earth's primitive mantle must lie between the continental crust ratio and the present day depleted mantle ratio. Using the range of K and Rb contents just estimated for the Earth's primitive mantle, we calculate a range of K/Rb ratios from about 340 to 500; this range lies between the estimated K/Rb ratio of the crust and depleted MORB source mantle ratio. The continental crust K/Rb ratio is reasonably well established (K/Rb = 250, 7), and the depleted MORB source reservoir has a K/Rb of 513 (39). However only the depleted MORB-source mantle K/Rb ratio is well known among the myriad of present-day mantle reservoirs (e.g., 40). We can also consider the proportional contribution of these two reservoirs to the total Earth's primitive mantle K inventory. The fractional mass of the continental crust to primitive mantle is ~0.6% (7), and an estimate of the MORB source reservoir can be considered to be about ~50% of the mantle (see discussions in Hofmann et al [41] and Hart and Zindler [42]). Assuming the bulk continental crust has 9100 ppm K (7), and the MORB source reservoir has about 100 ppm K (39), this suggests the continental crust contains about 20%, and the MORB source reservoir would also contain about 20% of the total Earth K inventory. Together these reservoirs account for only 40% of the primitive mantle K inventory, and this being so, it is difficult to make a secure estimate of the bulk Earth K/Rb. This is worth considering when evaluating most models which propose that the Earth's primitive mantle K/Rb ratio is between 300 and 350 (2, 7, 25, 29).

The Cs abundance in the Earth's primitive mantle is not well constrained either by isotopic models or by a Cs/refractory lithophile element ratio. Generally, the Earth's primitive mantle Cs abundance is estimated from the mean Rb/Cs ratio of the Earth's crust (7) or the mean Rb/Cs ratio of recent MORB and OIBs (3). Therefore, we shall review the available data for Rb/Cs in these reservoirs.

2a) Rb/Cs in the Mantle

The Rb/Cs ratio in the mantle can be estimated from the available data on mantle-derived peridotites and lavas. Wänke *et al* (4) reported a Rb/Cs ratio of 190 for their most fertile (primitive) spinel peridotite SC-1, and estimated a Rb/Cs value of 80 for the primitive mantle, consistent with the study of Hofmann and White (3). We have not carried out a comprehensive literature survey for other Rb/Cs estimates in peridotite material, because these elements, due to their very low concentrations in peridotites, are readily affected by contamination, as excellently documented in the recent study of Zindler and Jagoutz (43). Therefore, we feel that Rb and Cs data for these rock types must be critically examined in order to establish the source of these elements.

By using the constant Rb/Cs ratios observed in MORBs and OIBs, Hofmann and White (3) suggested that the Rb/Cs ratio of the present day mantle is 80 and this reflects the Earth's primitive mantle Rb/Cs ratio. However, there are compelling reasons why this may not be so.

Hofmann and White (3) showed that modern oceanic basalts have a relatively constant Rb/Cs ratios of 80 over a wide range of Rb concentrations. They argued that these Rb/Cs ratios reflect the source ratio. By comparison then we have examined the variation in the Rb/Cs ratio in primary and near primary basalts and komatiites throughout time. Figure 1 is a plot of the mean Rb/Cs ratio and its $\pm 1\sigma$ for primitive basaltic and komatiitic lavas versus time. The Rb and Cs data for Archaean basalts and komatiites also includes data from carefully prepared fresh clinopyroxene separates from Archaean mafic lavas (44, 45). The clinopyroxene separates possess systematically lower Rb/Cs ratios than their mafic lavas, which is consistent with partitioning data obtained by Hart and Brooks (46) on recent (400 years old) clinopyroxenes and their whole rock matrix. In their study the two samples had $[Rb/Cs]_{clinopyroxene}/[Rb/Cs]_{matrix}$ ratios of 0.52 and 0.83 (46). If the Archaean lavas were contaminated by the continental crust during their ascent, eruption and/or emplacement (e.g., 47, 48), then the lava's subchondritic Rb/Cs ratio is still too low for what is known about Archaean crustal rocks; the average Rb/Cs ratio of Archaean sediments is 30 ± 20 (data from McLennan [49]). These data confirm the low and generally subchondritic Rb/Cs ratio in Archaean lavas and their source regions. The Rb and Cs data for Proterozoic basalts indicate that at this time the Earth's mantle had a relatively constant Rb/Cs ratio of about 20, and this ratio is higher than that found in Archaean lavas. Collectively this data suggests an increase in the Earth's mantle Rb/Cs ratio from the Archaean to the present. Alternatively, if it is argued that the Archaean and Proterozoic lavas have erupted through continental lithosphere and have possibly been contaminated, then we note that modern continental flood basalts (e.g., Karoo, Columbia River Plateau, Parana), which may be analogous to Precambrian basalts and komatiites, have Rb/Cs ratios of 50 to 70 (50-52). This too would also demonstrate a secular variation in the Rb/Cs ratio of komatiites and basalts which have erupted through the continental lithosphere.

It is also instructive to view the total range of Rb/Cs ratios for mantle derived magmas. Figure 2 shows this variation in detail and highlights the diversity of Rb/Cs ratios for mantle derived magmas through time and from a variety of tectonic settings. The highest Rb/Cs ratios are generally found in unaltered, modern MORBs and OIBs. Phanerozoic kimberlites, which possess some of the highest Rb contents of mantle-derived melts, generally have low Rb/Cs (~30) with many Group I kimberlites having lower Rb/Cs ratios than Group II, micaceous kimberlites and lamproites (53-55). The average Rb/Cs ratio for island arc rock suites and individual island arc lavas is generally around 25 to 30, and there is good agreement between the two data sets (56, 57).

In summary, this data indicates that the Earth's primitive mantle Rb/Cs ratio may not be defined by the constant Rb/Cs ratio in MORBs and OIBs. Additionally, there are a variety of Rb/Cs ratios to be found in present day mantle derived mafic lavas.

2b) Rb/Cs in the Crust

The continental crust is another significant reservoir for Rb and Cs in the Earth, with most Rb and Cs concentrated in the upper continental crust. In contrast to their ppb concentrations in the mantle, Rb and Cs concentrations in the upper crust are commonly estimated to lie between 70 to 110 ppm and about 1 to 3 ppm, respectively (7, 23, 58, 59), and generally bulk crust Rb/Cs ratios of about 30 are common. Taylor and McLennan (7) estimated that these elements are enriched in the upper crust relative to the lower crust by a factor of 20 to 40, and showed that fine-grained sediments and sedimentary rocks provide an excellent measure of the average upper crust composition. The variation in Rb/Cs ratios in sedimentary rocks from Precambrian and Phanerozoic continental terranes are shown in Figure 3. The mean Rb/Cs ratio for these rocks is 18 ± 10 ($\pm 1\sigma$). We suggest that this Rb/Cs ratio represents the mean ratio for the upper continental crust.

Before Rb/Cs ratios in sedimentary rocks can be used to constrain a crustal average it is necessary to examine how this ratio is affected by surface and/or low temperature processes. Nesbitt *et al* (60) studied the alkali and alkaline earth elements in the weathering profile of a granitic body and compared this to the overall mobilization and transport of these elements during continental weathering. They showed that the Rb/Cs ratio is not affected by the weathering process; they found the Rb/Cs ratio remained at 23 ± 3 from an unaltered sample to the most weathered sample. From this they concluded that Rb and Cs are quantitatively transferred to the weathering residues and subsequently transported on clays by mass wasting of the continents. Similarly, the Rb and Cs data of Kronberg *et al* (61) on intensely weathered soils did not document any relative fractionation, although their data quality was relatively poor. Nathan (62) compared the chemical compositions of different grain size fractions of sediments and found no difference in Rb/Cs ratios between coarse-grained (24 ± 2) and fine-grained (22 ± 2) clastic sediments. Taylor *et al* (63) used loess to derive an upper crustal composition because loess is derived by glacial milling and transported by aeolian processes so that weathering has had a relatively small effect on the chemistry. The mean Rb/Cs ratio of loess sediments is 24 ± 6 (63). Thus, we conclude that the Rb/Cs ratio in sedimentary rocks is not significantly affected by these surface processes and that their ratio reflects the average upper crust Rb/Cs ratio.

Additional support for an average upper crustal Rb/Cs estimate comes from the composition of tektites (Fig. 3). Tektites are generally accepted to be an impact produced glass made almost exclusively of terrestrial materials (64) and therefore may also provide an indication of the bulk upper crust Rb/Cs ratio. The average Rb/Cs ratio of tektites (australites) is 30 ± 10 (65, 66); this value compares favorably with the average upper crust Rb/Cs ratio.

In order to estimate the Rb/Cs ratio of the bulk crust, it is necessary to constrain the Rb/Cs ratio in the lower continental crust. The two types of lower crustal samples, granulite facies xenoliths, brought up in kimberlitic and basaltic magmas, and granulite facies terranes display a wide range of Rb and Cs concentrations and Rb/Cs ratios (Fig. 4). In general granulite facies terranes have high Rb/Cs ratios and high Rb concentrations, whereas granulite facies xenoliths have low concentrations of Rb and Cs and lower Rb/Cs ratios. These differences are probably primarily due to the inherently different rock type in these two occurrences: granulite xenoliths are dominantly mafic, whereas granulite facies terranes are generally dominated by intermediate to felsic rocks (67).

Currently, there is much debate concerning which of these two disparate rock types are best representative of the present-day lower crust. There are three main points that require consideration when evaluating the differences in Rb/Cs ratios between these two rock types. First, compositional models of the lower crust based on geochemical and isotopic data (7, 68, 69) and on heat flow data for Archaean areas (70) require a K, U and Th depleted (the heat producing elements) as well as a Rb and Cs depleted lower crust. This also considers a Scourian granulite model lower crust, which has been identified as one of the most depleted granulite facies terranes (69). Moreover, a Scourian granulite lower crustal model (71) also has too high a radiogenic heat producing budget to be viable in present day Archaean terranes (7). Second, the available Rb and Cs data show that granulite facies terranes have, for the most part, high K (≥ 1.0%) and Rb (> 60 ppm) contents, K/Rb ratios of 200 to 500 and contain stable K-feldspar. The presence of K-feldspar in these rocks is significant, because this phase (in contrast to plagioclase) has the ability to fractionate Rb and Cs given Rb's much more compatible behavior (72, 73). Therefore, this indicates a mineralogical control on the Rb/Cs ratio in granulite facies terranes, and it is critical to understand the distribution and modal abundance of K-feldspar in the lower crust. Third, sediments from granulite facies terranes have Rb/Cs ratios of about 20 (7, 74), with no evidence of systematically higher ratios.

Therefore, a mafic lower crust as indicated in the xenolith population may represent the best estimate of the lower crust composition. We do not see any immediate resolution to obtaining an accurate estimate of the lower crustal Rb/Cs ratio, nor its Rb and Cs content.

Given that the Rb/Cs ratio of lower crustal xenoliths is broadly similar to that of the upper crust; sediments sample broad regions of the upper crust including some granulite terranes; and the concentration of Rb and Cs in upper crustal rocks are much higher than in lower crustal rocks, we will use the upper crustal average as representative of the bulk crust. However, it must be kept in mind that this value may change with an increased understanding of the average lower crust composition.

3) Implication for the Evolution of the Earth's Mantle

The observed secular change in the Rb/Cs ratio of the MORB source mantle is somewhat analogous to the proposed secular changes in Rb/Sr and Sm/Nd ratios. There are greater differences in the degree of incompatiblitiy between Rb - Sr and Sm - Nd than is found in the Rb - Cs system. However, given this there is still a factor of 3 increase in the Rb/Cs ratio in the MORB source reservoir from the Earth's primitive mantle value. In contrast, the MORB source reservoir has experienced only about a 66% decrease in its Rb/Sr ratio and a ≤15% increase in its Sm/Nd compared to the Earth's primitive mantle ratios. Such a significant increase in the Rb/Cs ratio of the MORB source mantle is most likely not simply attributable to changes in partial melting during MORB genesis throughout time. Therefore, let us consider what processes have contributed towards the development of the secular variation in the Earth's mantle Rb/Cs ratio.

We suggest that the formation of the continental crust and the subduction of oceanic lithosphere has played a significant role in this respect. Using reasoning similar to that by Hofmann *et al* (41), we suggest that early continental crust formation resulted in the fractionation of Rb from Cs. This is demonstrated by the low Rb/Cs ratios in Archaean mantle-derived rocks compared to modern oceanic and continental intraplate basalts. This difference indicates that either during basalt genesis Cs was significantly more incompatible than Rb earlier in the Earth's history or that mantle recycling processes have greatly contributed to the fractionation of Rb and Cs. In contrast, during basalt genesis today Rb and Cs are nearly equally incompatible, as demonstrated by the constant Rb/Cs ratio in both MORB and OIB (3).

The subduction of oceanic lithosphere may influence the mantle Rb/Cs ratio. A mean Rb/Cs ratio of 25 to 30 is found in modern continental and island arc basalts. It is evident from Figure 2 that island arc basalts have much lower Rb/Cs ratio than MORBs and OIBs. The low Rb/Cs ratios of island arc basalts is consistent with the involvement of subducted altered oceanic crust and/or sediments, both of which have consistently lower Rb/Cs ratios than the MORB/OIB reservoirs (7, 75-77). Either or both of these sources must contribute to the low Rb/Cs ratios in the source regions of arc basalts.

Additional evidence for mantle recycling having a significant role in altering the Rb/Cs ratio of the mantle comes from the study of carefully prepared mineral separates from Archaean eclogites (type A). These rocks have relatively high Cs contents and low Rb/Cs ratios (77, 78). Jagoutz *et al* (77) argue that these eclogites represent fragments of old subducted oceanic lithosphere. Moreover, they calculate that <1% of this component in the mantle is sufficient to provide a CI chondrite K/Cs for the Earth's primitive mantle.

Taken in combination, these data support the proposition that the secular variation in the Rb/Cs ratio of the mantle is due to the development of continental crust (either episodically or continuously), and the re-injection of altered oceanic lithosphere ± a sediment component into the mantle. The sequestering of significant quantities of Rb and Cs in eclogites, and their low Rb/Cs ratios, suggests these rocks may be an important mantle reservoir.

Given the above observations we can estimate the proportional contribution of the continental crust and the present day mantle to the primitive Earth mantle Rb and Cs budget and its Rb/Cs ratio. Given a bulk continental crust with a Rb/Cs ratio of ~20 and an estimated Rb concentration of 32 ppm (7), we calculate a Cs concentration of 1.6 ppm, which is 60% higher than the estimated value given in Taylor and McLennan (7). To estimate the proportion of the total Earth Rb and Cs inventory contained in the crust, we need to know either the Rb and Cs content of the present day mantle or that of the primitive mantle, assuming the crust represents about 0.6% the mass of the mantle (or bulk silicate Earth). We propose that the Rb/Cs ratio of the Earth's primitive mantle can be set to be between the lower value found in CI chondrites and Archaean komatiites, basalts and eclogites, and an upper limit is set by the ratio in the present day depleted MORB source mantle. This upper limit is an absolute maximum value, since this reservoir is considered to have been depleted by crust formation. Moreover, the Rb/Cs ratio of Archaean lavas may provide a stronger indication of the Earth's primitive mantle ratio given these lavas came from a mantle which had not experienced as much depletion because of continental extraction. Given this, we propose that the primitive Earth mantle Rb/Cs value is close to 20, although this estimate would have a minimum of about 50% uncertainty. With this Rb/Cs ratio and given a Rb concentration of ~650 ppb (see Rb/Sr section) for the primitive mantle, we obtain a Cs concentration of ~33 ppb for the Earth's primitive mantle. These estimates indicate that the crust has about 30% of the total Rb and Cs compared to the Earth's primitive mantle inventory. This estimate is in agreement with Taylor and McLennan (7), however it is at odds with earlier estimates suggesting the continental crust contains about 40 to 60% (e.g., 3, 6, 79) or 60 to 85% (4) of the Earth's total Rb and Cs inventory.

Constraining the uncertainties in these models can be difficult, however these calculations indicate that the continental crust would contain on the order of 1/3 but less than 1/2 of the total Rb and Cs in the Earth's primitive mantle. Additionally, they indicate that the depleted MORB source mantle with about ~200 ppb Rb and ~2.4 ppb Cs and assumed to constitute about 25 to 50% of the present mantle (41, 42), would contain less than 10% of the total Rb and Cs in the Earth's primitive mantle. Considering the surprisingly high Rb and Cs concentrations in Archaean eclogites, which are interpreted to be fragments of subducted (altered?) oceanic crust, and the inferred subduction of oceanic lithosphere from the Precambrian onward, then it will be important to consider these rocks when making an inventory of the Earth's Rb and Cs budget. Furthermore, from the calculations and models used we note that the bulk crust plus the bulk MORB source reservoir contain only about 40% of the total inventory of K, Rb and Cs of the initial primitive mantle complement.

In summary, peridotites and modern basalts are not a good guide to the Rb and Cs geochemistry of the Earth's primitive mantle. The bulk continental crust has a Rb/Cs ratio of ~20 and this is established by upper crustal rocks. Rb/Cs ratios of 5 to 10 for Archaean mafic to ultramafic lavas (and their clinopyroxenes) provides a lower limit to the Rb/Cs ratio in the Earth's primitive mantle, although we feel that the CI chondritic Rb/Cs ratio of 12 may be a more realistic lower limit for the primitive mantle. Additionally, by summing the fractional contributions of Rb and Cs in the bulk crust and depleted MORB source reservoir we can also set a lower limit at about the CI chondritic ratio of 11. Thus, the bulk Earth Rb/Cs ratio is estimated to be 20 ±

10, which is close to the bulk continental crust ratio and the Rb/Cs ratio of primitive lavas from the Precambrian.

4) Importance of the constant Rb/Cs ratio in MORB and OIB

As was recently pointed out by Hofmann *et al* (41), the source regions of MORBs and OIBs have a constant and *non-chondritic* ratio for Nb/U, both Nb and U are refractory lithophile elements and thus should exists in the primitive Earth mantle in chondritic relative proportions. They argued that Nb and U were fractionated from one another as a result of continental crust formation, but these elements are presently equally incompatible during basalt genesis. Hofmann and White (3) showed that Rb and Cs are also presently equally incompatible during basalt genesis. Therefore, given the finding of this study concerning Rb/Cs and Hofmann *et al* 's (41) study on Nb/U, it is concluded that consistent elemental ratios in the MORB and OIB source regions do not reflect the Earth's primitive mantle ratio.

It is significant that the MORB and OIB source regions have near identical ratios of Nb/U, Rb/Cs, La/Nb, Ce/Pb and other elements and that these ratios are significantly different from the bulk crust ratio and primitive Earth mantle ratio. Also, only 40 to 50% of the total inventory of Rb and Cs in the Earth's primitive mantle can be accounted for. These points provide strong evidence for the co-evolution of the MORB and OIB source regions, and require that another mantle reservoir(s) exists, which would make up the remaining complement of Rb and Cs. If Archaean eclogites play a significant role in this mass balance, then we need to know whether they reside in the continental lithospheric mantle or in the underlying convective mantle? Alternatively, we wonder whether a significant proportion of these elements could reside in a primitive mantle reservoir, if still present. Furthermore, if there is a volume of primitive mantle which exists in the present day mantle, then we ask whether its is accessible to basaltic magmatism, and how is it sampled. However, it must be considered that when modelling the generation and evolution of OIB we cannot involve significant quantities of a primitive mantle reservoir based on Rb, Cs, Nb and U and their ratios found in MORB and OIB. In fact, we feel that the constancy of these (and other) ratios in MORBs and OIBs, and by analogy their source regions, argues against the significant involvement of another "mantle" component not wholly incorporated in the MORB/OIB source region.

Finally, given there is an apparent a secular change in the Rb/Cs ratio in the Earth's mantle, similar arguments may hold for Nb/U (and possibly other such element pairs). Therefore, it will be important to compare element ratios between OIBs and MORBs with those for Archaean and Proterozoic komatiites and basalts.

5) Constraints on Estimates of K, Rb and Cs in the Bulk Moon

Recently Kreutzberger *et al* (8) suggested that the Rb/Cs ratio of the bulk Earth and Moon were significantly different. Given this, they claimed that an impactor-type model for the origin of the Moon would not be consistent if it involved having a substantial proportion of the Earth's mantle contributing to the Moon's bulk composition. We have decided to re-evaluate the conclusions Kreutzberger *et al* (8) given that their interpretation was based on Hofmann and White's (3) earlier model that the Earth's primitive mantle had a Rb/Cs ratio of 80 as established by MORB and OIB.

We have compiled a comprehensive collection of data for Rb and Cs in lunar samples and this is shown in Figure 5. In general, Rb/Cs ratios for all lunar rocks varies between 10 and 40, with a grand average of 22 ± 3 (± 1 σ). This average value corresponds to the Rb/Cs ratio of KREEP materials, which generally have the highest concentrations of these elements for lunar rocks. Lunar highland anorthosites have lower Rb/Cs ratios than this average value; some anorthosite samples have subchondritic ratios. The average Rb/Cs ratio of the lunar highland component is not well constrained, given the analytical uncertainties in measuring the very low Rb and Cs contents in these rocks. Despite the large mass fraction of the lunar highlands crust, the low Rb and Cs contents of these anorthosites causes this part of the Moon to have a relative minor to insignificant role in the bulk Moon Rb/Cs ratio.

There may be some amount of heterogeneity in the Rb/Cs ratio of mare basalts. All analyses of Apollo 11 samples show a distinctly higher average Rb/Cs ratio of 30 ± 1 than all other Apollo samples, and this difference is also confirmed when cross referencing analyses between different laboratories for the same sample. The significance of this level of chemical heterogeneity cannot not be fully evaluated at present, but should be considered when future surveys of the Moon are considered.

Given this data we conclude that the bulk Moon has a Rb/Cs ratio of about 22 ± 3. When compared to the proposed bulk Earth Rb/Cs ratio of 20 ± 10. Furthermore, we conclude that the Earth's Rb/Cs ratio is, within the uncertainties of these model, similar to the Moon's Rb/Cs ratio. Thus, the claim by Kreutzberger *et al* (8) that the bulk Earth and bulk Moon have significantly different Rb/Cs ratios is without foundation.

6) Meteorites and Mars

We also have considered the available Rb and Cs data for various meteorite samples. Figure 6 presents Rb/Cs ratios for carbonaceous chondrites, ordinary chondrites and a number of achondrite meteorites. All of the carbonaceous chondrite meteorites have similar Rb/Cs ratios of about 10 to 13. There are some analyses of carbonaceous chondrite which fall just outside this range of values, however these are considered to reflect some of the analytical uncertainties involved in the measurements. The E chondrites have an average Rb/Cs ratio of 17 ± 8 (80), though some specimens have higher Rb/Cs ratios (up to 31). The H chondrites have Rb/Cs ratios that range between 16 and 123, though on average they have a Rb/Cs ratio of 41 ± 37 (Morgan *et al.*, 1985). The average Rb/Cs ratio for the L and LL chondrites is 280 ± 300, although this value has much less meaning given its standard deviation. Note however, the range of Rb/Cs ratios for L and LL chondrites is about 10 to 1130 (82-85). Overall, the chondritic meteorites have a broad range of Rb/Cs ratios, although the carbonaceous chondrites have a very limited range within this group. There is need to fully understand the cosmochemical processes which contribute to this range of Rb/Cs ratios in chondritic meteorites. Furthermore, the range of Rb/Cs ratios in chondritic meteorites is basically over a limited range of Rb contents; the Rb contents for these meteorites is generally between 1 and 4 ppm.

Rb/Cs ratios in eucrite and diogenite meteorites are between 100 and 10, and Rb concentration are ≤1.0 ppm (86-89). The aubrite meteorites have Rb concentrations of between 0.1 and 10 ppm and Rb/Cs ratios between 1 and 100 (89, 90). This difference in Rb concentrations is considered to be real, however the subchondritic Rb/Cs ratios reported in a few of the aubrites may be attributed to analytical problems.

The overall picture is one of the chondritic meteorites having Rb concentrations of between 1.0 and 4.0 ppm and Rb/Cs ratios of 11 ± 2 in the carbonaceous chondrites, and progressively higher Rb/Cs ratios in the E, H, L and LL chondrites, respectively. The achondrite meteorites generally have Rb/Cs ratios of between 10 and 100, and quite variable Rb concentrations.

Recently there has been much agreement as to the SNC meteorites (Shergottites, Nakhlites and Chassignites) having a Martian origin (see Shergotty Volume, GCA). Therefore, these meteorites may provide us with an estimate of the bulk Mars Rb/Cs ratio. Figure 7 presents the variation in Rb/Cs ratios for SNC meteorites. Based on this limited data base it would be difficult to estimate the *primitive* Martian Rb/Cs ratio, however the data is suggestive of a bulk Mars Rb/Cs ratio which is not too different from the CI chondrite ratio, nor the Rb/Cs ratios of the bulk Earth and Moon. Many of the SNC meteorites are cumulate rocks (Shergotty Volume), and if analogies can be made using rocks and minerals from the Earth (46), then we would postulate that the bulk Mars Rb/Cs ratio might be slightly higher than the average Rb/Cs ratios of ~14 for the SNC meteorites. It is worth considering whether the Earth, Moon and Mars all have approximately the same Rb/Cs ratio. In this same light we would point out that there is no obvious reason to assume that the Rb/Cs ratio of Venus and Mercury is 30 as was proposed by Morgan and Anders (91) and may be closer to the CI chondrite ratio (11) or the bulk Earth and Moon ratio of ~20. Overall we wonder whether the Rb/Cs ratio of the inner planets may be similar to one another, which is about ~1.5 to 2 times greater than the CI chondritic ratio.

8) Summary

(1) The Earth's upper crust Rb/Cs ratio is defined by sediments and sedimentary rocks and is estimated to be 18 ± 10.

(2) The Earth's lower crust Rb/Cs ratio is not well defined, although given (a) that all bulk crustal compositional models consider the lower crust to be depleted in Rb, Cs and the heat producing elements, (b) that there is a mineralogical control on the high Rb/Cs ratio in granulite facies terranes, (c) that sediments from granulite terranes have Rb/Cs ratios of ~20, and (d) that the upper crust has a high concentration of Rb and Cs, then it seems reasonable to assume the upper crust Rb/Cs ratio reflects the bulk crust Rb/Cs ratio.

(3) The bulk Earth's Rb/Cs ratio is estimated to be 20 ± 10 and it is constrained by (a) the bulk crust value, given that this represents a significant reservoir (~30%) of Rb and Cs, (b) Archaean komatiites and basalts which generally have subchondritic Rb/Cs ratios, reflecting the early Earth's mantle chemical composition, (c) Archaean eclogites which have subchondritic Rb/Cs ratios (similar to Archaean lavas) and high Cs contents and thus may represent an important group of rocks in the present day mantle.

(4) There is a secular variation in the Earth's mantle Rb/Cs ratio as recorded in primary and near primary basalts from the Archaean to the present.

(5) A secular variation in the mantle's Rb/Cs ratio and the subchondritic Rb/Cs ratios in Archaean eclogites suggests that mantle recycling has had a profound effect on the chemical evolution of the Earth's mantle.

(6) The Rb/Cs ratio of MORBs and OIBs is not equal to the Rb/Cs ratio of the bulk crust and is also not equal to the Rb/Cs of the Earth's primitive mantle. The homogeneous Rb/Cs ratio in MORBs and OIBs reflects their uniform source evolution, and differences in this ratio compared to the bulk Earth and crust suggest the presence of other mantle reservoirs.

(7) The Rb/Cs ratio for the bulk Moon is 22 ± 3 and is defined by lunar return samples, this ratio is dominated by the incompatible element enriched KREEP component, and within uncertainties of these estimates, the Earth's Rb/Cs ratio is similar to the Moon's Rb/Cs ratio.

(8) Thus, the claim by Kreutzberger *et al* (8) that the Rb/Cs ratio of the Earth is not equal to the Rb/Cs ratio of the Moon is without foundation.

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Appendix A -- References to Data Compilation

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Figure Captions

Figure 1. Rb/Cs ratio versus age for primary and near primary basalts and komatiites. The filled inner boxes represent the average Rb/Cs ratio for the suite of samples from the given time period. The size of the outer box reflects the $\pm 1\sigma$ for the Rb/Cs ratios and the range along the x-axis is an approximation of the spread in sample ages. See figure caption 2 for data sources.

Figure 2. Rb/Cs ratio versus Rb (ppm) concentrations for basalts and komatiites from the Archaean to the present. Data sources include: MORB/OIB (Hofmann and White, 1983), Archaean lavas and Cpx's (Hermann *et al.*, 1976; Hart and Brooks, 1977; BVSP, 1981; Machado *et al.*, 1986), Proterozoic lavas (BVSP, 1981), Island Arc lavas (BVSP, 1981; White and Patchett, 1984; White and Dupré, 1986), Island Arc Average (Morris and Hart, 1983), Kimberlites (Muramatsu, 1983; Muramatsu and Wedephol, 1985). The CI chondrite line (Rb/Cs = 11) is taken from the data of Anders and Ebihara (15) and Beer *et al* (16). The line for the average MORB/OIB Rb/Cs ratio of 80 is from Hofmann and White (3).

Figure 3. Rb/Cs ratio versus Rb (ppm) concentrations for sediments, sedimentary rocks of all ages and tektites. Data sources include: sediments and sedimentary rocks (Nathan, 1976; McLennan, 1981; Taylor *et al.*, 1983; Stern and Ito, 1983; Taylor and McLennan, 1985) and tektites (Taylor, 1962; 1966). The line for the average Rb/Cs ratio of 18 is derived by taking an average of the data.

Figure 4. Rb/Cs ratio versus Rb (ppm) concentrations for granulite facies rocks. These rocks are consider as representative samples of the lower continental crust. Data sources include: granulite facies terranes (Heier and Brunfelt, 1970; Condie and Allen, 1984; Condie *et al.*, 1986; Taylor *et al.*, 1986) and granulite facies xenoliths from kimberlites and basalts (Dupuy *et al.*, 1979; Rudnick *et al.*, 1986; Rudnick and Taylor, in press, Arculus *et al.*, in press). The line of Rb/Cs = 18 reflects the average upper crust value.

Figure 5. (a) Rb/Cs ratio versus Rb (ppm) concentrations for Lunar rocks and soils. Data sources are from laboratories which do not include the 'Chicago Group'; these are: Gast and Hubbard (1970), Taylor *et al* (1971; 1973; 1974), Tera *et al* (1970), Wänke *et al* (1970; 1971; 1973; 1975; 1976; 1977). Note that samples from the Apollo 11 survey are shown in filled symbols and have on average higher Rb/Cs ratios than the grand average. The horizontal line is the average Rb/Cs ratio of 22 ± 3 as determined by the 'Chicago Group'. This value was chosen

since it represents over 300 analyses of Rb and Cs on the same powders by one laboratory using a single analytical technique for both elements.

(b) Rb/Cs ratio versus Rb (ppm) concentrations for Lunar rocks and soils. Data sources are only from the 'Chicago Group' and include Keays *et al* (1970), Ganapathy *et al* (1970), Laul *et al* (1971), Morgan *et al* (1972a; 1972b), Ganapathy *et al* (1973), Krähenbühl *et al* (1973), Morgan *et al* (1973), Ganapathy *et al* (1974), Morgan *et al* (1974), Higuchi and Morgan (1975), Morgan (1976), Gros *et al* (1976), Hetrogen *et al* (1977), Janssens *et al* (1978) and Wolf *et al* (1979).

Figure 6. Rb/Cs ratio versus Rb (ppm) concentrations for chondrite and achondrite meteorites. Data sources include: CI and CM - CO - CV chondrites (Krähenbühl *et al*, 1973; Takahashi *et al.*, 1978; Wolf *et al*, 1980; Ebihara *et al.*, 1982; Beer *et al*, 1984), E chondrites (Tera *et al.*, 1970; Hertogen *et al.*, 1983), H chondrites (Tera *et al.*, 1970; Morgan *et al.*, 1985), L and LL chondrites (Tera *et al.*, 1970; Neal *et al.*, 1981; Biwas *et al.*, 1981; Walsh and Lipschitz, 1982; Hutson and Lipschutz, 1984), Aubrites (Wolf *et al.*, 1983), Eucrites (Tera *et al.*, 1970; Higuchi and Morgan, 1975; Gros *et al.*, 1976; Morgan *et al.*, 1978) and Diogenites (Biwas *et al.*, 1980; 1981; Wolf *et al.*, 1983).

Figure 7. Rb/Cs ratio versus Rb (ppm) concentrations for SNC (Shergotty, Chassigny and Nakhla) meteorites. These meteorites are considered to be from Mars (see papers in the Shergotty Volume, GCA). Data sources include McSween (1985) and Treiman *et al* (1986). Note that the average Rb/Cs value we give for the SNC meteorites is ~14, although the average Rb/Cs ratio for the data reported by McSween (1985) is 13 and by Treiman *et al* (1986) is 19. There is a need for more precise Rb and Cs data for each of these samples in order to obtain a better estimate of the Mars bulk Rb/Cs ratio.

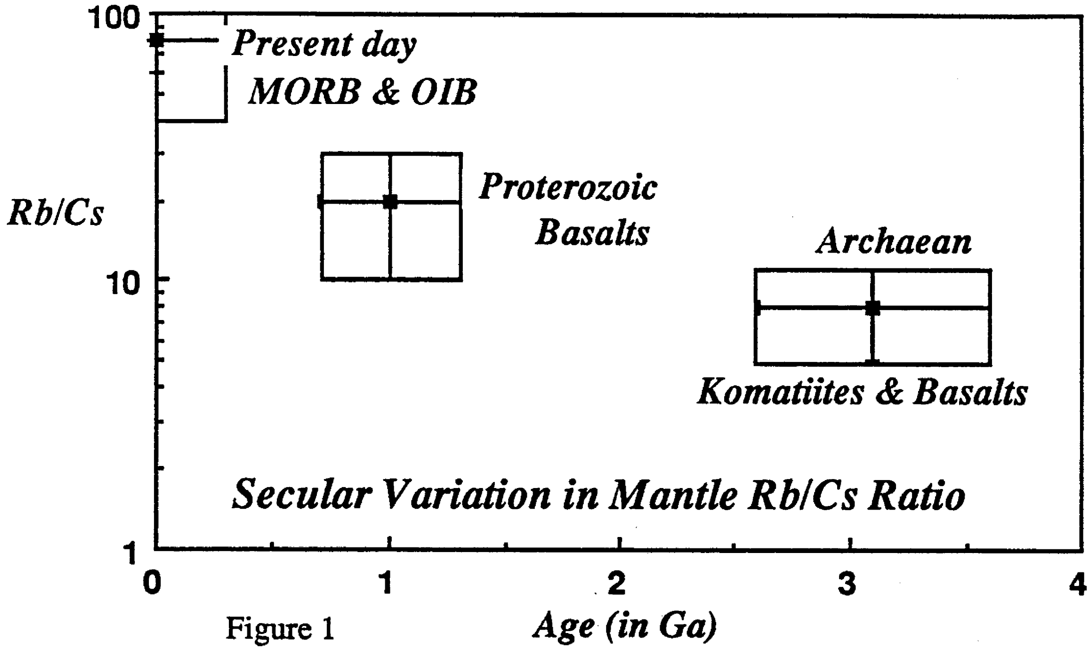

Figure 1

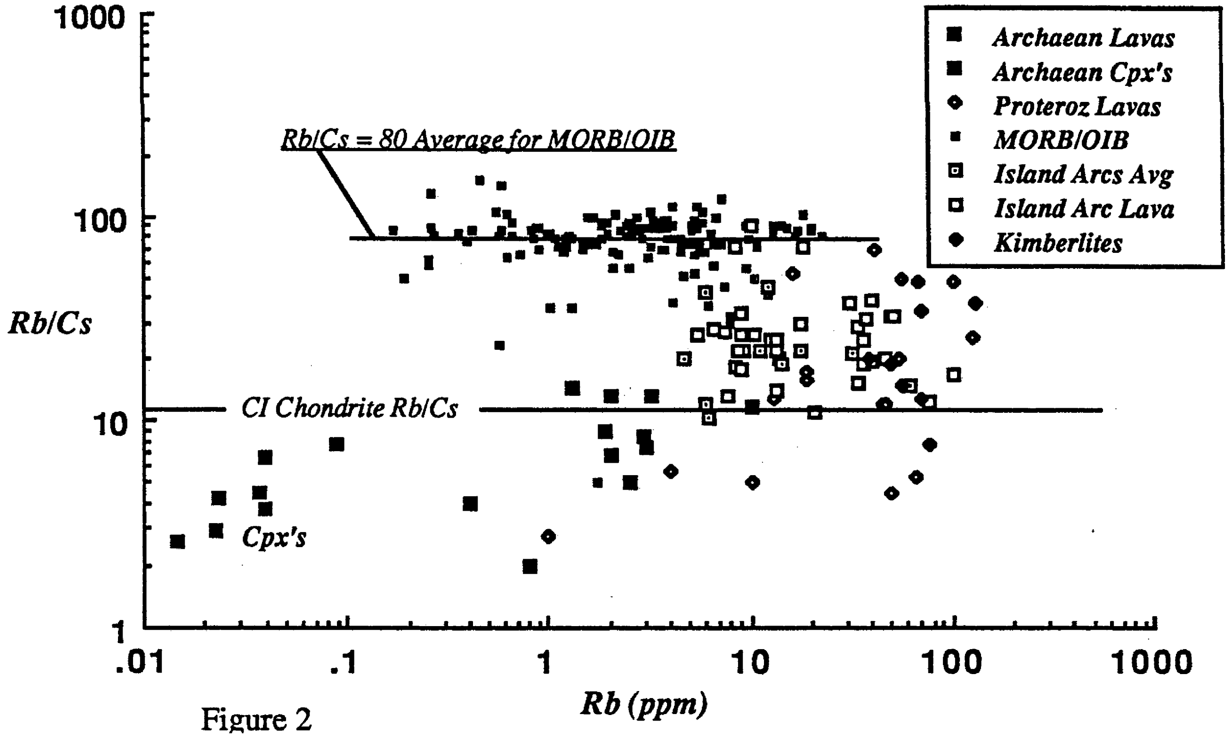

Figure 2

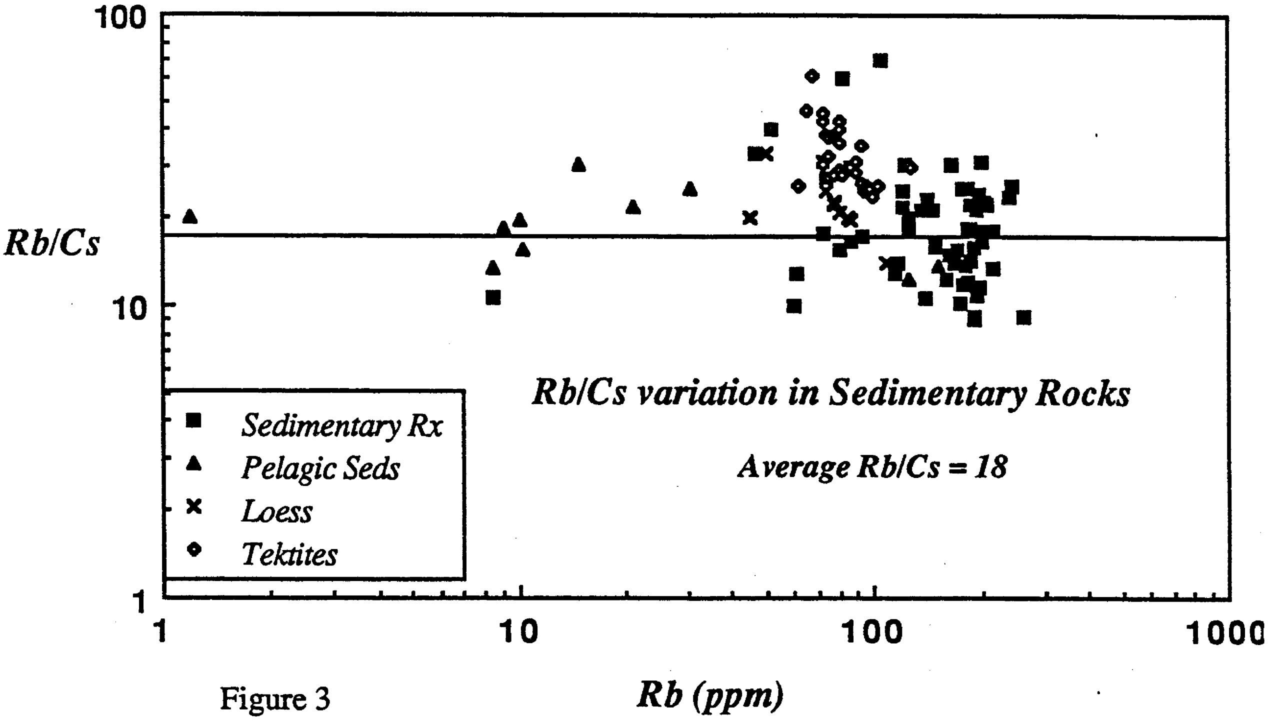

Figure 3

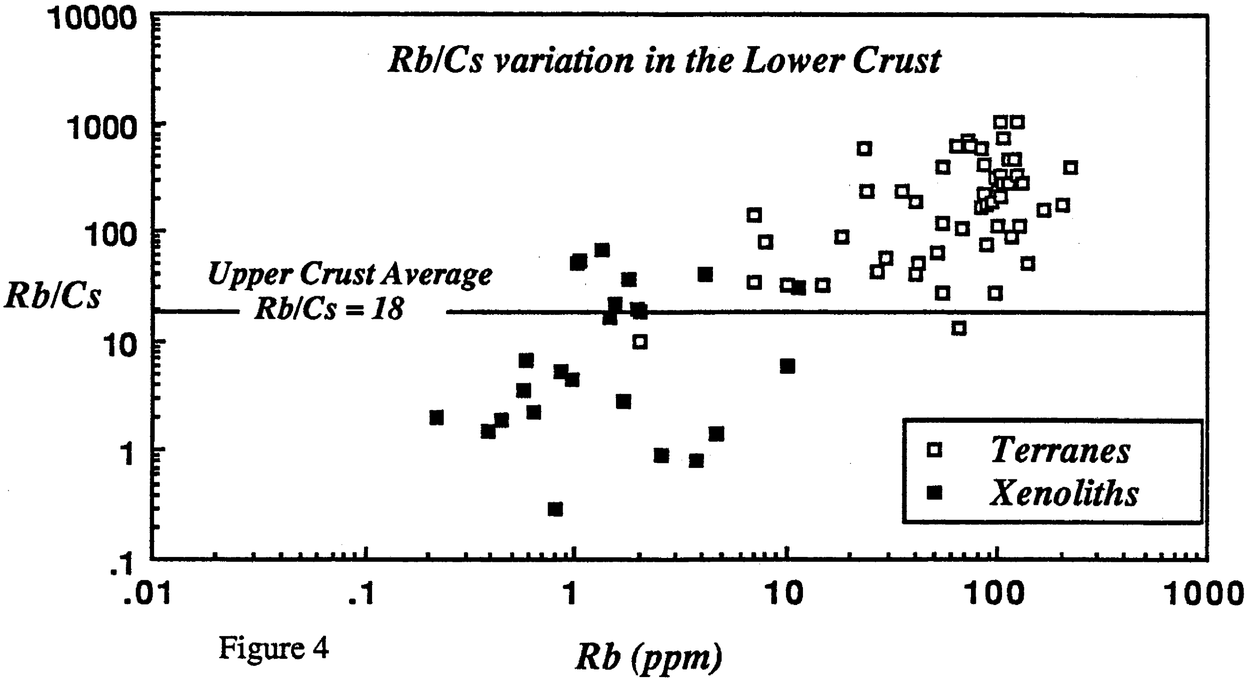

Figure 4

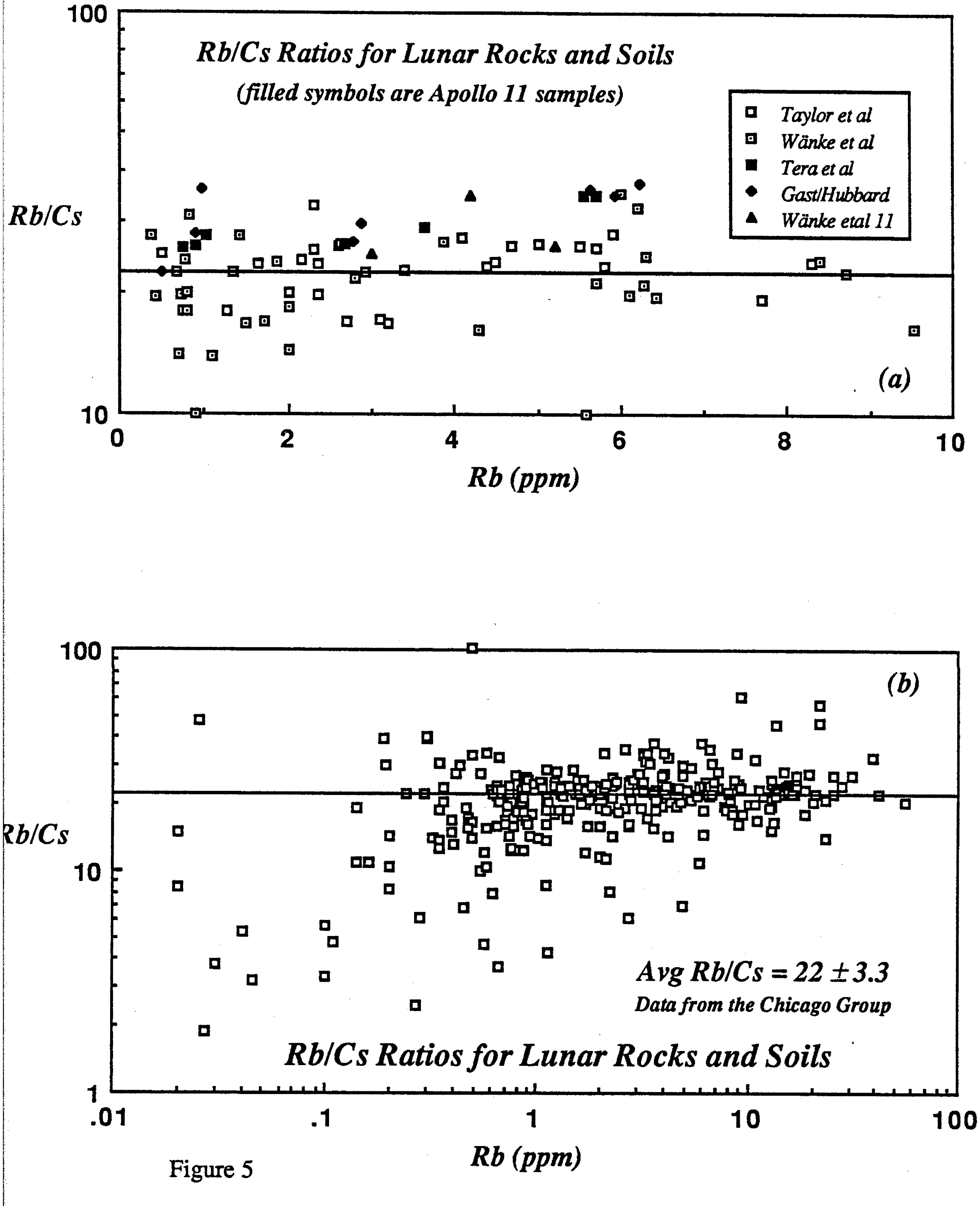
100
Rb/Cs Ratios for Lunar Rocks and Soils
(filled symbols are Apollo 11 samples)
Taylor et al
Wänke et al
Tera et al
Gast/Hubbard
Wänke etal 11
Rb/Cs
(a)
10
0
2
4
6
8
10
Rb (ppm)
100
(b)
Rb/Cs
10
Avg Rb/Cs = 22 ± 3.3
Data from the Chicago Group
Rb/Cs Ratios for Lunar Rocks and Soils
1
.01
.1
1
10
100
Rb (ppm)

Figure 5

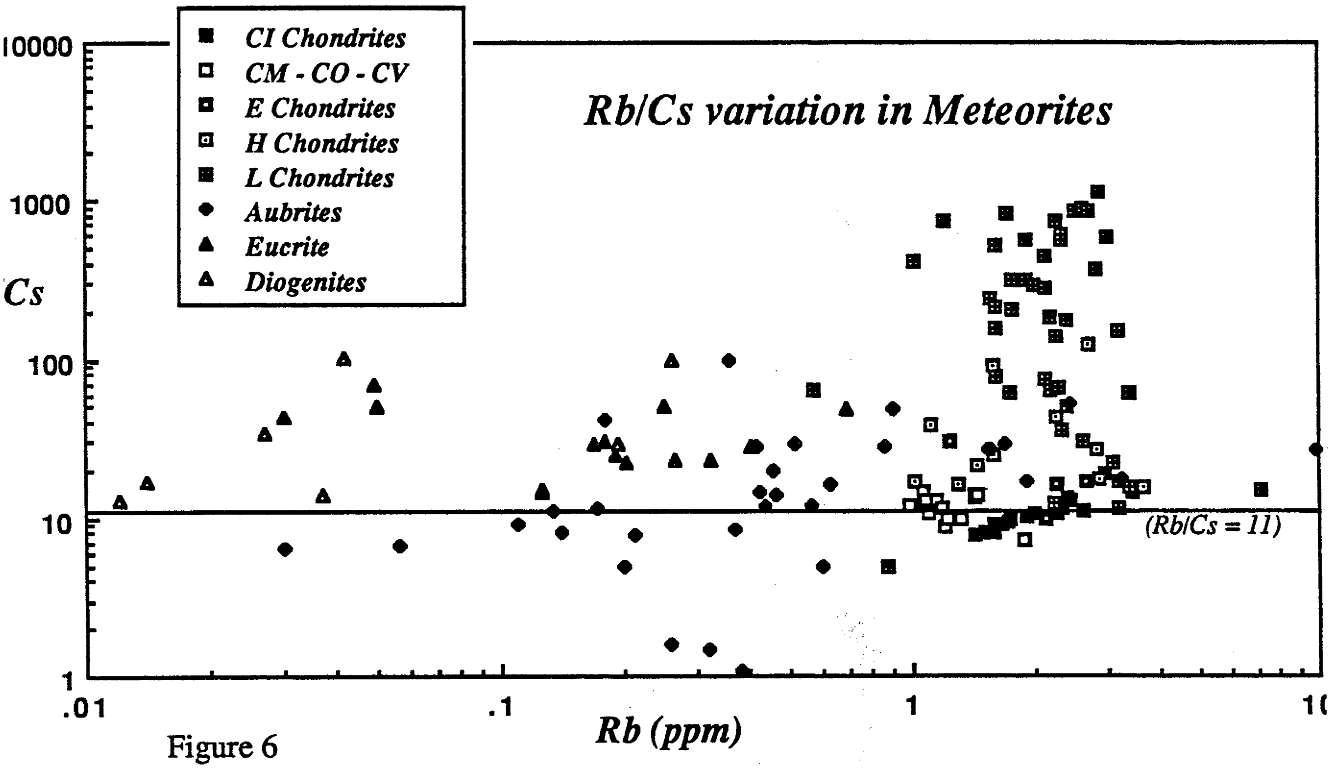

Figure 6

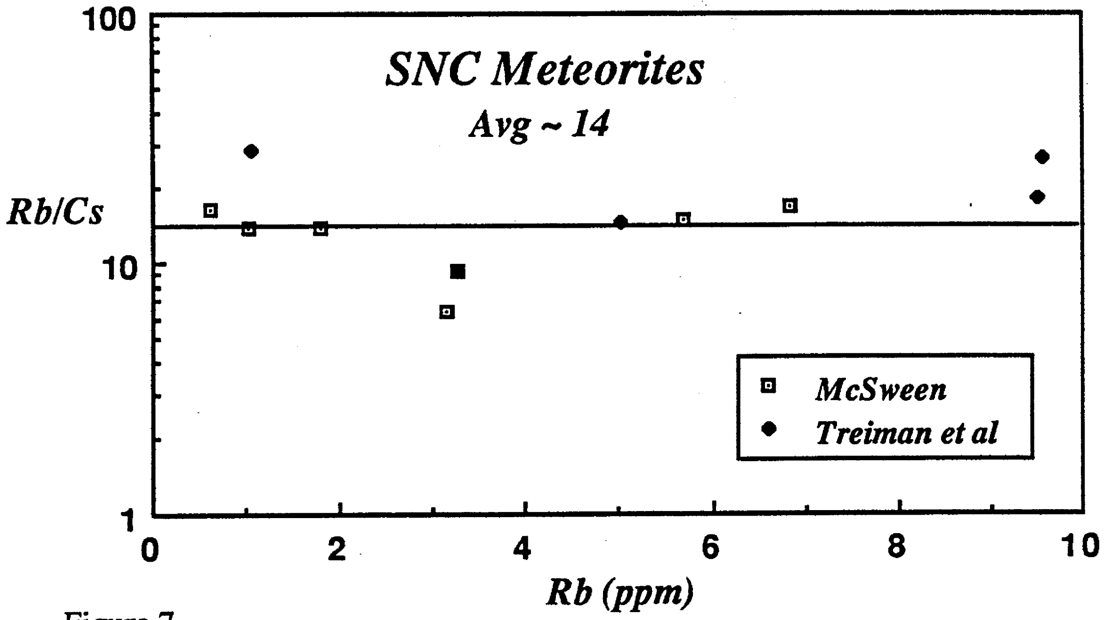

Figure 7

CHAPTER 5

Composition of the Earth's Primitive Mantle and Implications for its Evolution

by William F. McDonough

ABSTRACT

Ratios of refractory, non-refractory, lithophile, chalcophile and siderophile elements for Archean to modern komatiites and basalts, crustal rocks and mantle rocks are examined in detail. These data are used to constrain the composition and evolution of the earth's mantle.

Estimates for the absolute and relative abundances of non-refractory lithophile and siderophile elements in the earth's primitive mantle are given. Evidence is presented for a secular variation in the mantle's Rb/Cs ratio. Several factors have contributed to this, however recycling of altered (± sediment enriched) oceanic lithosphere back into the mantle and the sequestering of eclogitic material with high Rb and Cs contents and low Rb/Cs ratios are considered the most important. Other elemental ratios (e.g., Ba/W, Cs/Tl, Eu/Sb) may show similar secular variations.

Estimates for the absolute and relative abundances of refractory lithophile elements are presented for carbonaceous chondrite and ordinary chondrite meteorites. A revised bulk compositional estimate for an average CI carbonaceous chondrite is also presented, which has utilized data from previous compilations along with subsequent analyses to yield an internally consistent composition. These data are used to critically evaluate existing primitive earth mantle model compositions.

A chondrite normalized diagram, called a partitioning behavior diagram, is presented, which provides an effective illustration of the systematic behavior of major and trace elements during partial melting. This diagram demonstrates that fertile peridotite xenoliths have experienced a previous melting event which must be accounted for when deriving a primitive mantle composition. Using this diagram, the average initial, unmodified composition of fertile peridotite xenoliths can be estimated.

A compositional model for the earth's primitive mantle is derived by using a worldwide suite (Europe, Asia, North America, South America and Australia) of fertile peridotite xenoliths. This model avoids using unnecessary assumptions inherent in several existing models, and asserts that an empirical model based on such samples predicts an internally consistent primitive mantle composition with chondritic proportions of the refractory lithophile elements.

1. Introduction

A precise estimate of the chemical and isotopic composition of the earth's primitive mantle can yield much information on the earth's accretion processes, core - mantle fractionation processes, and any fractionation/differentiation due to a global melting event. These data can also be compared with compositional estimates for present day mantle reservoirs to provide constraints on their evolution. One method of evaluating the earth's primitive mantle composition is through the investigation of mantle derived samples. The mantle samples used in this study include peridotite xenoliths and primitive basalts. Peridotite xenoliths are generally considered to be fragments of lithosphere torn from conduit walls during magma ascent. Studies of these rocks provide direct information on the nature and composition of the upper mantle. Primitive basalts, ranging from Archean to modern, are partial melts of the mantle which have not experienced significant fractional crystallization or crustal contamination. They can thus provide additional, although less direct, data about the initial composition of their mantle source regions. Isotopic studies of these basalts and peridotite xenoliths can be used to construct a time integrated evolutionary model for the earth's mantle. Combined chemical and isotopic studies of past and present day mantle samples provide an important data base for developing an internally consistent model for the composition and evolution of the earth's mantle.

Peridotite xenoliths and primitive basalts may in part be derived from different regions of the mantle: the lithosphere and the asthenosphere. Peridotite xenoliths have a significant tectonic history associated with their incorporation into the continental lithosphere. They have substantially different ages, reflecting the times at which they were isolated from their source region (e.g., asthenosphere and/or recycled oceanic lithosphere (Hofmann and White, 1982; Ringwood, 1982)). In contrast, basalts are commonly believed to be samples of the asthenospheric mantle, although some are likely to be mixtures of asthenospheric and lithospheric sources. This would probably be true for some oceanic/continental intraplate basalts (OIB) and island arc basalts (IAB). Therefore, a study which integrates data for both basalts and xenoliths provides a more complete picture of the mantle. Furthermore, by comparing chemical and isotopic data from OIB and peridotite xenoliths from the same geographical region, we may be able to estimate the relative contributions of the plume and lithospheric mantle components in intraplate basaltic magmatism.

To understand the processes which have significantly contributed to the evolution of the present day mantle, we must first estimate the composition of the earth's primitive mantle. There have been many attempts to do this e.g., Ringwood (1966), Sun and Nesbitt (1978), Jagoutz et al (1979), Taylor and McLennan (1981), Sun (1982), Anderson (1983), Wänke et al (1984) and Hart and Zindler (1986). Most of these models assume that the relative abundances of the refractory lithophile elements (e.g., Ca, Al, Ti, Sc, Sr, Ba REE, etc.) are chondritic. However, there is no consensus as to the absolute abundances of these elements nor to the relative and absolute abundances of the moderately volatile (e.g., Na, K, Rb, Cs, As, Ag, Sb, etc.) and volatile elements (e.g., Cd, S, Pb, Bi, Tl).

The chondritic earth model relates the elemental abundances in the bulk earth to those observed in C1 carbonaceous chondrite meteorites. The C1 meteorites (also called the CI carbonaceous chondrites, where I = Ivuna) are free of chondrules and possess the highest moderately volatile and volatile element concentrations relative to refractory elements, of all meteorites. CI chondrites also have a composition that matches the relative composition of the solar photosphere (Anders and Ebihara, 1982), thus providing a scale by which to compare other meteorites. The chondritic meteorites are fragments remaining from the initial accretionary material which formed during the early development of the solar nebula (Wasson, 1985) and their chemical and isotopic diversity reflects the compositionally heterogeneous nature of the early solar nebula. It is from this heterogeneous collection of meteoritic materials that we attempt to construct and constrain our models of planetary compositions, in particular the bulk earth composition.

Studies of the earth's primitive mantle generally involve the integration of data from both terrestrial and meteoritic samples. These two distinctive rock suites provide different perspectives from which to view the composition and evolution of the earth's mantle. Geochemical and isotopic data gained from such studies are of fundamental importance to dynamical models that attempt to unravel the basic processes involved in the evolution of the earth's mantle.

2. Background to Estimating the Earth's Mantle Composition

2.1. Refractory Lithophile Element Abundance Models

Most primitive earth mantle models start with the basic assumption that the refractory lithophile elements (e.g., Ca, Al, Ti, Sc, Sr, Ba REE, etc.) accreted in chondritic relative proportions, but this is where the similarities in the models end. Debate continues about the absolute abundances of the refractory lithophile elements in the earth, whether Mg and Si were refractory elements during accretion and whether the earth has a CI chondritic Mg/Si ratio, among other topics.

There are two general methods used to estimate the composition of the earth's primitive mantle: 1) a cosmochemical approach and 2) a terrestrial petrological - geochemical approach. The terrestrial petrologic - geochemical approach, used by Ringwood (1966), Sun and Nesbitt (1977), Jagoutz *et al* (1979), Sun (1982) and Wänke *et al* (1984), estimates the earth's primitive mantle composition from the compositions of primitive, mantle-derived peridotite xenoliths, komatiites and basalts. The cosmochemical approach assumes, implicitly or explicitly, that the bulk earth has a CI chondrite relative composition for the refractory elements, including Mg and Si, and constrains model compositions accordingly (e.g., Taylor, 1980). Other investigators using the cosmochemical approach have developed complex, multi-component mixing models (Ganapathy and Anders, 1974; Morgan and Anders, 1980; Anderson, 1983), however these latter models generally are less specific regarding absolute concentrations.

One of the earliest and most significant petrologic - geochemical estimates of the earth's mantle composition is provided by the pyrolite model of Ringwood (1966). This model used the complementary melt - residuum relationship between basalts and alpine peridotites as a basis for estimating the major and minor element composition of the earth's upper mantle. Ringwood (1966) showed that this model was consistent with heat flow data, and found that the refractory lithophile element composition of the pyrolite model closely matched the composition of the CI carbonaceous chondrite group, minus the core component.

More recent petrologic - geochemical based compositional estimates of the earth's primitive mantle including estimates for its siderophile and lithophile, moderately volatile and volatile element abundances have been made by Sun and Nesbitt (1977), Jagoutz et al (1979), Wänke (1981), Sun (1982) and Wänke et al (1984). Jagoutz et al (1979), Wänke (1981) and Wänke et al (1984) used the composition of fertile (primitive) spinel lherzolites to estimate the earth's primitive mantle composition, whereas Sun and Nesbitt (1977) used the composition of primitive Archean mafic and ultramafic lavas to model the composition of the Archean mantle. The major element compositions of both models compare favorably with the pyrolite model. Sun (1982) evaluated primitive basalt and peridotite xenolith data sets and presented an integrated estimate for the composition of the earth's primitive mantle. Furthermore, using the reasoning of Ringwood and Kesson (1977), he proposed a model for the relative depletion of the siderophile, highly siderophile, moderately volatile and volatile element abundances in the primitive mantle. The above models show remarkable similarity to one another (e.g., Figure 1) and the pyrolite model (Ringwood, 1979). This is most significant in view of the separate data sets and independent methods of derivation used in constructing these models. Moreover, all of these models assume that the mantle is not significantly fractionated in its major element composition between upper and lower mantle, and the estimated compositions are generally consistent with this assumption. However, this assumption needs to be examined more closely.

Figure 1 illustrates the general similarity between the Sun (1982) and the revised model of Jagoutz et al (presented in Wänke et al, 1984), though small differences do exist. The absolute abundances for both models depend on mantle peridotites. Sun (1982) used the TiO_2 content of Jagoutz et al., 1979 and the correlation between MgO and TiO_2 in primitive mafic and ultramafic Archean lavas to determined the bulk earth's MgO content. The model of Jagoutz et al (1979) and Wänke et al (1984) depends on a few selected peridotites. A recent assessment of the peridotite data (Hart and Zindler, 1986), using 33 samples from xenolith suites and orogenic lherzolites, confirms these earlier estimates.

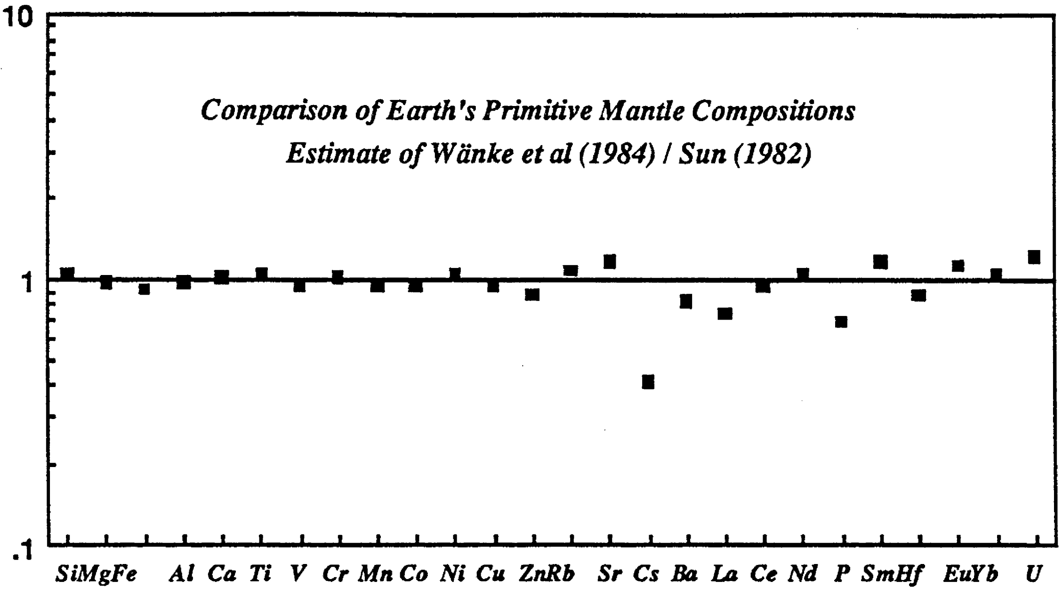

FIGURE 1. A comparison of 2 model estimates for the earth's primitive mantle. The model composition of Wänke et al (1984) is divided by the model composition of Sun (1982). Note that Cs in the Wänke et al (1984) model is about 60% less than the estimate from Sun (1982); this is discussed in Chapter 4.

One of the principal objections to the primitive mantle models of Wänke and coworkers and Sun has been their use of peridotites and basalts. These materials sample only the outer 200 to 400 kms of the mantle, which is less than 20% of the mass of the whole mantle. The 670 km seismic discontinuity in the mantle represents a significant phase change from a spinel-garnetite facies to perovskite + magnesiowüstite (Liu and Bassett, 1986). This discontinuity has been interpreted to be a chemical boundary (e.g., Liu, 1979), with the lower mantle being enriched in the perovskite component; consequently the lower mantle is believed to be more silica-rich than the upper mantle. In a similar vein, Ohtani (1984) proposed that early earth processes following accretion and core formation resulted in the silica enrichment of the lower mantle through the separation and sinking of denser picritic liquid plus garnet from an ascending, partially molten diapir of picritic liquid plus olivine and pyroxene. Walker (1986) used observations of Takahashi and Scarfe (1985), namely that the solidus and liquidus of a primitive mantle composition converge at about 14 GPa, to suggest that the upper mantle composition is the result of large scale mantle differentiation, and that the eutectic like upper mantle composition was probably produced by residual crystallization after melt extraction. If large scale mantle melting and differentiation occurred early in earth's history and a portion of the mantle remained isolated (see also, Anderson, 1983), then the usefulness of the peridotite and basalt data to derive the average bulk composition of the silicate portion of the earth would be limited. Palme and Nickel (1985) have also used ultramafic xenoliths to derive a primitive upper mantle composition for the earth. They concluded that the earth's mantle experienced early fractionation of the refractory lithophile elements, probably as a result of crystal fractionation during an early melting event which had produced a deep global magma ocean.

The CI chondritic primitive earth mantle models (e.g., Ganapathy and Anders, 1974; Morgan and Anders, 1980; Taylor and McLennan, 1985; Anderson, 1983) restrict the relative major element abundances (Si, Mg, Fe, Ca, Al, Ti) in their bulk earth (core + primitive mantle) composition to that found in the CI chondrite meteorites. They also generally agree that the absolute abundances of refractory lithophile elements are on average about 1.5 times a volatile-free CI chondrite. These estimates have similar relative refractory elemental abundances but different absolute abundances compared to estimates by Sun (1982), Wänke et al (1984) and Hart and Zindler (1986). Thus, compared to these latter models the CI chondritic models are 25% lower in the refractory elements, 5 to 10% lower in Mg and 8 to 12% higher in Si. A CI chondritic model is a good starting point from a historical perspective, but such a model cannot accurately predict the volatile lithophile element abundances of the earth's primitive mantle (Ringwood, 1975; Jagoutz *et al*, 1979; Sun, 1982). Furthermore, the oxygen isotopic compositions of carbonaceous chondrites are distinctly different from that of the earth and moon (Clayton and Mayeda, 1975; Clayton, 1977) suggesting their formation in a separate part of the solar nebula. Therefore, strict adherence to the CI bulk earth model, especially with respect to the Mg/Si ratio and its ultimate implications for the evolution of the earth's mantle is not a prerequisite of the bulk earth model. Discussion of this topic is further developed later in this study and in Appendix 4.

In using a chondritic earth model for the refractory lithophile elements (which is invoked in both the cosmochemical and the petrological - geochemical approaches) we need to fully understand the temperature and oxygen fugacity conditions during the earth's accretion. Additionally we need to understand lithophile/siderophile element fractionation during the core forming event. Therefore, we must attempt to determine which elements would behave as refractory or non-refractory and lithophile or siderophile/chalcophile elements (e.g., Mg?, Si?, Cr?, Mn?, etc.) in the earth during core - mantle and mantle - crust fractionation events.

2.2. *Non-refractory lithophile element abundances*

It has been recognized that the non-refractory lithophile element (e.g., Na, K, Rb, Cs and F) abundances in the primitive mantle are fractionated relative to their abundances in CI carbonaceous chondrites due to the volatility of these elements. Some 25 years ago a number of independent measurements and observations concerning the absolute and relative abundances of the moderately volatile and volatile lithophile elements in the earth gave strong support to this conclusion (e.g., Gast, 1960; Clark and Ringwood, 1964; Taylor, 1964; Wasserburg et al, 1964). Studies of the average K/U ratio in crustal rocks and the net mantle heat flow of the earth (Clark and Ringwood, 1964; Wasserburg et al, 1964) suggested that the K/U ratio of the bulk earth (1×10^4) was much lower than that of CI chondrites (6×10^4). Studies of Rb/Sr and $^{87}Sr/^{86}Sr$ ratios in terrestrial rocks led Gast (1960) to conclude that the earth possesses a Rb/Sr ratio which is about a factor of 10 lower than that of CI chondrites (0.03 versus 0.3, respectively). This and other data combined to quash the assumption that the earth possessed a complete CI chondrite inventory of elements.

Today many researchers are involved in attempting to constrain the absolute and relative abundances of the moderately volatile and volatile lithophile elements in the present day mantle as well as in the earth's primitive mantle. Most models constrain these elements using similar lines of evidence to those used in determining abundances of the refractory lithophile elements. Hence, the relative abundances of these elements as found in fertile peridotite xenoliths, and primitive, Archean to modern, komatiites and basalts (e.g., Jagoutz et al, 1979; Hertogen et al, 1980; BVSP, 1981; Sun 1982) are taken as a guide to those of the primitive mantle. Other approaches include looking at crustal abundances, secular changes in the mantle and changes in radiogenic isotope ratios (e.g., Rb-Sr, K-Ar and Pb-U-Th systems). In their studies of crustal rocks Taylor and McLennan (1985), have reviewed the evidence which suggests that a number of the non-refractory lithophile elements are concentrated in the earth's crust relative to the mantle. From this observation and their estimated composition of the earth's crust they have proposed values for the absolute and relative abundances of these elements in the earth's primitive mantle. In a study of Rb and Cs in the earth, McDonough et al (Chapter 4) showed that the Rb/Cs ratios of modern basalts are much higher than those found in Proterozoic and Archean basalts and in the continental crust. From this they proposed that the mantle Rb/Cs ratio has changed through time and that the bulk earth's ratio is similar to that of the bulk crust. Finally, the Rb-Sr, K-Ar and Pb-U-Th isotope systems have probably been the most important constraints for determining the relative abundances of K, Rb and Pb in earth's primitive mantle.

As an example of the determination of the relative and/or absolute abundances of non-refractory lithophile elements, some of the methods and problems associated with estimating the primitive mantle's Rb and K content will be reviewed.

A consistent, and therefore commonly agreed upon estimate of the earth's Rb/Sr ratio is derived from three independent approaches: (1) the weighted mean Rb/Sr ratio for the bulk crust and mantle (Gast, 1960), (2) the time integrated ^{87}Rb/^{86}Sr ratio versus the ^{87}Sr/^{86}Sr ratio for primitive basalts (Gast, 1968; Hurley, 1968a, 1968b; Jahn and Nyquist, 1976) and (3) the correlation of the ^{87}Sr/^{86}Sr ratio with the ^{143}Nd/^{144}Nd ratio for young, primitive basalts (De Paolo and Wasserburg, 1976; O'Nions et al, 1977), as well as the correlation between the MORB reservoir and the bulk crust. These approaches all yield a bulk earth Rb/Sr ratio of 0.030. This ratio is known to within 10% and is probably the most secure constraint on the abundances of the moderately volatile lithophile elements available. Therefore, given a Sr content of about 21 ppm for the earth's primitive mantle (Jagoutz et al, 1979; Sun, 1982; Wänke et al, 1984), the Rb content of the primitive mantle can be calculated as ~ 0.63 ppm.

Estimates of the earth's K abundance differ considerably. It has even been suggested that a portion of the earth's K inventory resides in the core (Lewis, 1971; Hall and Murthy, 1971; Goettel, 1976), however, many cosmochemical, geochemical and petrologic arguments demonstrate that this is not the case (Oversby and Ringwood, 1972; Ringwood, 1977; Bukowinski, 1976; Liu, 1986). Moreover, because of the similar behavior of Rb, Cs and K, it is unlikely that the earth's core contains a significant proportion of these other elements. However, more data are needed on the partitioning behavior of Rb and Cs under these very high pressure and temperature conditions.

Ar isotopic systematics provide a minimum estimate for the K abundance in the earth. This is based on the $^{40}Ar/^{36}Ar$ composition of the atmosphere (295.5) relative to the primitive planetary value ($<1.4 \times 10^{-3}$; Begeman et al, 1976) and the relative mass of the earth's atmosphere to the bulk earth. This suggests a bulk earth K content of 77 ppm (for a review, Ozima and Podosek, 1983) or a primitive earth mantle K content of about 115 ppm. This is a minimum estimate since it does not take into account the existing ^{40}K in the crust and mantle, nor the bulk $^{40}Ar/^{36}Ar$ composition of the whole mantle.

The absolute K abundance of the bulk earth has also been estimated from the K/U ratio (Clark and Ringwood, 1964; Wasserburg et al, 1964) and an assumed bulk earth U content derived from U-Th-Pb isotope systematics (e.g., Tatsumoto, 1978; Galer and O'Nions, 1985), heat flow (e.g., Sclater et al, 1981) and models of the earth's thermal evolution (e.g., Sleep and Langan, 1981; Richter, 1985). If the bulk earth has a U content of between 15 and 20 ppb (Jagoutz et al, 1979; Sun, 1982; Wänke et al, 1984), this then implies a bulk earth K content of between 150 and 200 ppm or a primitive earth mantle K content of between 225 and 300 ppm. This calculation assumes that K and U have been equally incompatible during crust-mantle differentiation, which is an assumption that seems to be justified given the bulk crust and mantle have similar K/U ratios ($\sim 10^4$) (Jochum et al, 1983; Taylor and McLennan, 1985).

Under most mantle melting conditions Rb is more incompatible than K, as indicated by its relative position on incompatible element diagrams for various types of basalts (Sun, 1980). The K/Rb ratio in the Earth's primitive mantle must, therefore lie between that of the continental crust and the present day depleted mantle. Using the range of K and Rb contents estimated for the earth's primitive mantle, we calculate a range of K/Rb ratios from about 340 to 500. These ratios appear to be consistent with the available data given that they are between the estimated K/Rb ratio of the crust (K/Rb = 250, Taylor and McLennan, 1985) and that of the depleted MORB source regions (K/Rb = 513, Jochum et al, 1983). However only the depleted MORB-source mantle K/Rb ratio is well known among the myriad of present-day mantle reservoirs (e.g., Hart et al, 1986; Appendix 4).

We can also consider the proportional contribution of crust and mantle reservoirs to the Earth's primitive mantle K inventory. The fractional mass of the continental crust to primitive mantle is ~0.6% (Taylor and McLennan, 1985), and it is estimated that the MORB source reservoir is about ≤50% of the mantle (see discussions in Hofmann et al, 1986; Hart and Zindler, 1986; Appendix 4). Assuming the bulk continental crust has 9100 ppm K (Taylor and McLennan, 1985), and the MORB source reservoir has about 100 ppm K (Jochum et al, 1983) and the earth's primitive mantle has on the order of 250 ppm K, it would suggest that the continental crust contains about 20%, and the MORB source reservoir about 20% of the bulk earth K inventory. Together these reservoirs account for only 40% of the primitive mantle K inventory. If this is so, it is difficult to make a secure estimate of the bulk earth K/Rb ratio. This must be considered when evaluating most models which estimate the earth's primitive mantle K/Rb ratio (Hurley, 1968a and 1968b; Jagoutz et al, 1979; Sun, 1982; Wänke et al, 1984; Taylor and McLennan, 1985).

2.3. Core - mantle fractionation (siderophile/chalcophile elements)

The siderophile and chalcophile element abundances in the earth's mantle have been effected by the formation of the earth's core. Estimations of their absolute and relative abundances are difficult. There are large depletions in the siderophile and chalcophile refractory elements (about a factor of 10 for the siderophile and much more than a factor of 100 for the highly siderophile noble metals) in the earth's mantle compared to CI carbonaceous chondrites (e.g., Ringwood, 1966; Jagoutz et al, 1979; BVSP, 1981; Sun, 1982; Chou et al, 1983; Morgan, 1986). Comparisons of the relative and absolute abundances of these elements in Archean to modern mafic to ultramafic lavas and in peridotite samples have provided much insight into their absolute abundances in the mantle. These data have in turn been used to understand the relative lithophile/siderophile partitioning behavior of the refractory siderophile elements during core - mantle fractionation.

Sun (1982; 1987) examined the data on siderophile and chalcophile element abundances in Archean to modern, mafic to ultramafic lavas and suggested that there has been no significant continuous core separation since the initial core forming event probably in the 100 Ma after the earth's accretion. More recently, additional support for this hypothesis was provided by Newsom et al (1986) who demonstrated that the Ba/W and Ce/Pb ratios in modern MORB and OIB are relatively constant over a range of Pb isotopic compositions, indicating there was no significant siderophile or chalcophile element fractionation in the sources of these basalts over the last ~ 2.0 Ga.

Other elements which can behave as lithophile or siderophile elements, depending on fO_2, pressure, and temperature (e.g., V, Cr, Mn), present even greater difficulties in obtaining well constrained estimates of their abundances in the earth's primitive mantle. Some of these elements may have been influenced by core formation, and their absolute abundances in the earth's primitive mantle, relative to other lithophile and siderophile elements of similar volatility, are likewise not well constrained. For example, compared to a CI chondrite composition, the depletions of Cr, Mn and V are not as great as those of Co, Ni, or P (i.e., moderately siderophile elements). However, V, Cr and Mn are believed to be more depleted than Mg and Si (i.e., lithophile elements) in the earth's primitive mantle (Sun, 1982; Wänke et al, 1984). In contrast, some moderately siderophile elements (e.g., P) are knownto behave like lithophile elements, as shown by the constant P/Nd ratio in many OIB and MORB (Sun and Hanson, 1975; Chapter 1). Therefore even reasonably well understood examples of moderately siderophile elements which have been strongly partitioned into the earth's core during its formation (Ringwood, 1966; 1983) have certain characteristics which are more akin to the lithophile elements.

Furthermore, studies of these elements (among others) have shown that there are strong geochemical similarities between the earth and moon in their relative abundances (e.g., Ringwood and Kesson, 1977; Ringwood, 1986). Therefore attempts to present a consistent chemical compositional model of the earth's primitive mantle for refractory and non-refractory, lithophile, siderophile and chalcophile elements also become important to our understanding of the earth with respect to other planetary bodies, as well as to our understanding of the evolution of the earth's mantle itself.

3. Elemental Ratios of the Earth's Mantle

3.1. Introduction

Observations regarding the initial composition of the primitive mantle and the secular chemical evolution of the mantle are discussed in this section. Any secular variation needs to be taken into account in attempts to create an internally consistent model for the composition of the earth's primitive mantle.

If cosmochemical fractionation processes have led to depletions in the moderately volatile and volatile elements, possibly including Si and Mg, then what percentages of these elements were lost during accretion? Does the bulk earth have a Mg/Si ratio equal to CI carbonaceous chondrites? Were other elements (e.g., V, Cr, Li and Mn) with condensation behavior similar to Mg and Si at or near the pressures and temperatures conditions believed to have existed during condensation, also partially depleted due to volatilization? The relative and absolute abundances of these elements need to be examined in detail in order to better understand the accretionary processes and initial composition of solar material in the collection zone of the growing earth. We also need to know the extent of element variation in refractory elements in chondritic meteorites in order to understand the uncertainties in compositional model estimates for the earth's primitive mantle. Finally, we must evaluate the available data on siderophile/lithophile element ratios in order to constrain the abundances of the siderophile elements in the earth's mantle, the various stages of the earth's accretion and core formation, and to examine the possibility of core growth through time.

3.2. The Mg/Si ratio of the earth's mantle

The earth's Mg/Si ratio provides a good example of many of the complications associated with estimating the earth's primitive mantle composition. Ringwood and Kesson (1977) and Sun (1982) suggested that the earth's primitive mantle had a Mg/Si ratio which is 10% to 20% higher than the CI ratio due to their preferential volatilization during the earth's accretion. In contrast, Ganapathy and Anders (1974), Anderson (1983) and Taylor and McLennan (1985) propose a CI Mg/Si ratio for the earth's primitive mantle with no volatilization of either Mg or Si during accretion. A third proposal put forth by Wänke et al (1984) suggests the earth's primitive mantle possessed a Mg/Si ratio which is about 10% higher than the CI ratio; this is because Si is thought to be the dominant light element in the core and to have partitioned into the core during its formation. Ringwood (1977; 1983) argued that partitioning of Si (and/or Mg) into the core is unlikely for thermodynamical and mass balance (with respect to FeO in the mantle) reasons, and proposed that the dominant light element in the earth's core is more likely to be oxygen.

Given that the earth has lost some amount of its volatile element inventory, then it is crucial to know if Mg and Si were inherently moderately volatile lithophile elements in the earth forming materials or if these elements were volatilized during accretion. Additionally it is necessary to know if any significant amount of Si (or Mg) was partitioned into the earth's core during its formation. An overall increase in the Mg/Si ratio of 10% (from CI < CM < CO < CV) is observed in the carbonaceous chondrites suggesting some Mg-Si fractionation due to volatility (Larimer, 1979; Kerridge, 1979). Furthermore, all non-CI carbonaceous chondrites have lost some proportion of elements more volatile than Mg and Si, relative to CI (Kallemeyn and Wasson, 1981; 1982). Moreover, enstatite and ordinary chondrite meteorites have substantially different Mg/Si, Si/Al and Mg/Al (i.e., Si or Mg/refractory elements) ratios than the CI chondrites (e.g., see Figure 2 in Jagoutz et al, 1979). Therefore, estimating the absolute and relative abundances of the moderately volatile and volatile element inventory for the earth is fraught with difficulties.

The cosmochemical approaches (e.g., models of Taylor and McLennan (1981) and Anderson (1983)) assume that Mg and Si are refractory lithophile elements accreted into the bulk earth in CI chondrite relative proportions and do not have Si or Mg as the light element in the earth's core. As a consequence, these authors are forced to conclude that the present day mantle is chemically heterogeneous on a major element scale, and that, it is chemically stratified with the lower mantle enriched in Si relative to the upper mantle. This assumption may be unjustified, although a Si enriched lower mantle (perovskite-rich) has been claimed to be consistent with geophysical observations (Liu, 1979; Anderson and Bass, 1984). However, Jackson (1983) and Ito et al (1984) argue that geophysical constraints cannot distinguish between a pyrolite model and a Si-rich lower mantle type model. More recently, Bukowinski and Wolf (1986) have emphasized that a lower mantle of pyrolite composition is consistent with density and seismic parameters.

The fractionation of the major element composition of the lower and upper mantle by the preferential enrichment of perovskite in the lower mantle would also have consequences for certain trace elements. Kato et al (1987) recently determined major and trace element crystal/liquid partition coefficients for the high pressure phases Ca-perovskite, Mg-perovskite and majorite garnet co-existing with ultramafic liquid. Their results demonstrate that crystal fractionation processes involving 10% or more of any one of these phases would result in non-chondritic ratios for key refractory lithophile elements (e.g., Ca/Al, Al/Sc, Al/Ti, La/Sm, LREE/HREE, Sc/Yb, etc.). However, these element ratios in fertile peridotite xenoliths and primitive komatiites and basalts are essentially similar to CI chondrites and unfractionated (Jagoutz et al, 1979; Sun, 1982; Wänke et al, 1984; and this study) providing strong, supporting evidence for the conclusions of Kato et al (1987) that the lower mantle has not experienced any significant enrichment of a perovskite (or garnetite) component relative to the upper mantle.

In conclusion, although some of the arguments are equivocal, the weight of evidence indicates that the upper and lower mantle have similar major element compositions. Consequently, this supports suggestions by Ringwood and Kesson (1977), Sun (1982) and Wänke et al (1984) that the earth's primitive mantle has a Mg/Si ratio that is 10% to 20% higher than the CI ratio. If oxygen is the dominant light element in the earth's core, then it must be concluded that the bulk earth's Mg/Si ratio is greater than the average CI chondrite ratio. Given this assumption, it becomes necessary to distinguish whether Mg and Si were depleted through an accretion -

volatilization processes or whether the earth formed from materials which were different from the CI carbonaceous chondrite meteorites in this respect.

3.3. Refractory lithophile element ratios in the earth's mantle

There are a number of elements which have been identified as refractory lithophile elements in chondritic meteorites (including carbonaceous chondrite, enstatite chondrite and ordinary chondrite (H, L and LL) meteorites), these include: Ca, Al, Hf, Lu, Zr, Y, Sc, Ti, Er, Ho, Dy, Tb, Gd, Th, Tm, Nd, Pr, Sm, La, Ce, Ta, Ba, Nb, Yb, Eu, Sr, U and V in order of their relative volatility as oxides (Kornacki and Fegley, 1986). These elements have 50% nebular condensation temperatures greater than about 1300°K - 1350°K at 10^{-4} atm (e.g., Wasson, 1985). There is also some suggestion that Be is a refractory lithophile element, although not much is known about its nebular condensation temperature. The earth's mantle is assumed to possess chondrite relative abundances of these elements and therefore if we independently know the absolute concentration of one of these elements we can calculate the absolute abundances for the rest of them. However, problems still exist in defining the chondritic ratios of many of these refractory lithophile elements, since minor variations in their relative abundances are observed in chondritic meteorites (e.g., Nb/Ta, Zr/Hf, Th/U). Several relevant elemental ratios are discussed below.

3.3.1. Ca/Al

There have been several problems in attempting to identify the Ca/Al ratio of the earth's primitive mantle. The Ca/Al ratio in the models of Wänke et al (1984) and Sun (1982) were adjusted to be consistent with the Ca/Al ratio of 1.08, the accepted constant value for both carbonaceous and non-carbonaceous chondrite meteorites. In adjusting their model, Wänke et al (1984) used the Al content of SC-1, their well documented primitive lherzolite, to estimate the Al content of the primitive mantle. However, in order to obtain a near-chondritic Ca/Al ratio (1.14) they used the *average* Ca content of their peridotite suite to estimate the Ca content of the primitive mantle, instead of the Ca content of SC-1 which has a Ca/Al ratio of 1.25. Sun (1982) suggested that the high Ca/Al ratio (>1.10) often found in the primitive, non-Barberton type, Archaean komatiites and basalts was due to partial melting effects (and to some extent, weathering). It was suggested that high Ca/Al ratios could be generated as a result of the separation of Al-rich orthopyroxene (high pressure phase) or an earlier melt extraction event from the komatiite source region (Nesbitt et al., 1979). These ideas led Sun (1982) to assume a chondritic Ca/Al ratio for the earth's primitive mantle based on the refractory nature of these elements and the assumed constant ratio in carbonaceous and non-carbonaceous chondrite meteorites.

The high Ca/Al ratios (>1.10) observed in many primitive spinel lherzolites led Palme and Nickel (1985) to suggest that either the bulk earth possesses a non-chondritic Ca/Al ratio or the mantle is chemically stratified, with the lower mantle possessing a sub-chondritic Ca/Al ratio. However, Hart and Zindler (1986), Sun (1987) and this study question the conclusions of Palme and Nickel (1985) concerning the Ca/Al ratio of the upper mantle and other observations they made concerning primitive lherzolites and the earth's primitive mantle. It is proposed here that the lherzolite data is consistent with a chondritic Ca/Al ratio for the earth's primitive mantle (Sections 4 and 5). Further discussion of the bulk earth's Ca/Al ratio is continued in Section 5, because I demonstrate in that section that high Ca/Al ratios in peridotites are expected, but do not require that the upper mantle have a non-chondritic Ca/Al ratio within the uncertainties of the data base. Here I will review only the meteorite data base.

Table 1 lists some refractory element ratios in carbonaceous chondrites using the data of Ahrens and coworkers for the major elements combined with the major and trace element data of Kallemeyn and Wasson (1981; 1982). Additional, meteorite data for enstatite chondrites and ordinary chondrites, and elemental ratios (for unpublished data) reported in Palme and Nickel (1985) were used to place some important constraints on the average major element composition of CI carbonaceous chondrites. The large data set of Kallemeyn and Wasson (1981; 1982) provides a strong foundation upon which to evaluate the chemical variation found in carbonaceous chondrites, because all of these data were determined at one well established (and dependable) laboratory, using one technique (neutron activation analysis) which has a standard deviation of replicate analyses for the Allende standard at ≤±5% for all elements. From this data set I have characterized the refractory element variations in carbonaceous chondrites.

An inspection of Table 1 shows that a number of element ratios are fairly well established in the carbonaceous chondrites (i.e., ≤10% variation at the 1 σ level). The average Ca/Al ratio for carbonaceous chondrites is 1.096 ± 0.072 (±1σ). Note, however, that this ratio and the 1σ variation was determined by using a selected data set and, the details of this selection procedure are given below.

> The average Ca/Al ratio is based on an evaluation of data from Wiik (1956), Mason (1962), Ahrens et al (1969), von Michaelis et al (1969), McCarthy and Ahrens (1972), Ahrens et al (1973), Fitzgerald (1979), Fitzgerald and Jaques (1982), Shima (1979), McSween (1976), Kallemeyn and Wasson (1981; 1982), Haramura et al (1981) and Jarosewich et al (1987). However, if all of the data was averaged unselectively it would yield a Ca/Al ratio of 1.09 ± 0.28 (±1σ); which shows remarkable agreement with the "selected sample" average. Data selection criteria can be arbitrary, and therefore I report here the criteria used.
>
> First, several samples with anomalous Ca/Al ratios (differing by more than 3σ) were excluded from the population. These samples were considered to be aberrant and their anomalous ratios may be due to analytical problems, terrestrial alteration processes or they are fundamentally rare and non-representative samples in the meteorite collections.
>
> Second, in trying to exclude presumably bad analytical data I compared replicate analyses of the same meteorite and chose analyses which were closer to the ~1.1 value, although some (but not all) of these excluded analyses may reflect heterogeneity in the sample.
>
> Third, I have rejected samples reported as having been affected by terrestrial weathering. To do this I have depended on it being indicated in the literature or through personal communication (G.W. Kallemeyn, 1987).
>
> Fourth, data sets were evaluated, where possible, to ensure that analytical bias was minimized. The analyses of Ahrens and co-workers and the comparisons available in Jarosewich et al (1987) for the Allende meteorite standard were used for this purpose. This procedure generally indicated that the earlier work of Wiik (1956) and analyses reported in Mason (1962) are of a lesser quality than the more recent reports.
>
> Fifth, the data of Haramura et al (1981) for Antarctic carbonaceous chondrites were not incorporated into the average. I. Kushiro (personal communication, 1987) has stated that sample Y-790112, 80 may be altered. However, even after excluding this sample from their other analyses, this group of carbonaceous chondrites have an average Ca/Al ratios of 0.88 ± 0.16, which is 20% lower than the "selected sample" average reported here.

Thus the Ca/Al ratio for carbonaceous chondrites is known to within 6.5% relative and the range in this ratio is from 1.02 to 1.17. The reported average Ca/Al ratio for ordinary chondrite meteorites is 1.12 ± 0.04 (von Michaelis et al, 1969; Fulton and Rhodes, 1984) and for enstatite chondrite meteorites is 1.05 ± 0.15 (von Michaelis et al, 1969; Sears et al, 1982; Weeks et al, 1985). These ratios all overlap the value reported here for the carbonaceous chondrite meteorites. Therefore assuming that the earth's primitive mantle accreted Ca and Al in chondritic proportions, then it is expected to have a Ca/Al ratio within the range 1.02 and 1.17.

Table 1. Elemental Ratios in the Carbonaceous Chondrites

Ratio	*Average*	*±1 Sigma*	*% Variation*	*Ref*
Mg/Si	0.906	0.031	3.4%	1
Ca/Si	0.087	0.012	14%	1
Al/Si	0.079	0.012	15%	1
Ca/Al	1.096	0.072	6.5%	1,2
Al/Ti	18.2	0.75	4%	1
Ca/Ti	20.0	0.89	4%	1
Al/Mg	0.0876	0.011	13%	1,2
Ca/Mg	0.0964	0.013	14%	1,2
Ca/Sc	1.490	0.015	10%	1,2
Sc/Si	0.0586	0.0076	13%	1,2
Sc/Mg	0.0647	0.0065	10%	2,3
Ti/Sc	74.3	7.4	10%	1,3
Al/Sc	1.353	0.074	5.5%	2,3
Yb/Eu	2.894	0.093	3.2%	2,3
Yb/Lu	6.536	0.209	3.2%	2,3
Sc/Lu	234.	10.	4.2%	2,3
Al/Yb	483.	20.	4.2%	2,3
Al/Lu	316	10.2	3.0%	2,3
Sc/Yb	35.7	1.75	4.9%	2,3

Si, Mg, Ca and Al are in mg/g, all others in µg/g. Ref. sources: 1= Mason (1962), Ahrens et al (1969), von Michaelis et al (1969), McCarthy and Ahrens (1972), Ahrens et al (1973), Fitzgerald (1979), Fitzgerald and Jaques (1982), Shima (1979), and McSween (1976). 2= Kallemeyn and Wasson (1981; 1982), excepting two analyses of Grosnaja, which have large differences in these element ratios. 3= this study.

A number of other elemental ratios are reasonably well established in the chondrite meteorites (e.g., Al/Ti, Ca/Ti, Al/Sc, Sc/Yb, Sc/REE and Al/REE). Thus, given sufficient justification for the earth possessing a chondritic refractory lithophile element budget, then these ratios can be used to critically evaluate the internal consistency in the proposed primitive earth mantle models.

3.3.2. Zr/Hf

It has been suggested that Zr and Hf, which are "super refractory" lithophile elements (Kornacki and Fegley, 1986), are fractionated between different types of carbonaceous chondrites (Shima, 1979; Knab, 1981; Hughes and Schmitt, 1985). Knab (1981) suggested that the Zr/Hf ratio systematically increases from CI < CM < CV2 = CV3 = CO3 < CV5 (from a low of 31 in CI to a high of about 40 in the CV5 Karoonda). Using published Zr and Hf data for terrestrial rocks (Table 2) and comparing this data with the meteorite data (see Table 3) McDonough et al (Chapter 1) proposed that the earth's primitive mantle has a Zr/Hf ratio of 38 ± 2, which they noted differed from the assumed CI ratio of 31 (Shima, 1979; Knab, 1981; Anders and Ebihara, 1982).

Table 2. Zr/Hf ratios in Terrestrial, Lunar and meteorite samples

Rock type	*Zr/Hf*	*Ref*	*Rock type*	*Zr/Hf*	*Ref*
kimberlite	36	1	CI chondrites	31	7,8
ocean island basalts	40	1	CM chondrites	34	7,8
continental alk basalts	40	2	CV2 chondrites	36	7,8
calc-alkaline basalts	39	1	CV3 chondrites	36	7,8
arc tholeiites	36	1	ordinary chondrites	35	8
MORB	36	3	CO3 chondrites	37	7
MORB	38	4	CV5 chondrites	42	7
BCR-1	39.4	5	KREEP basalts	41	9
GSP-1	40.5	5	Lunar Highlands (15405)	36	9
AGV-1	43.5	5	Lunar Highlands (67915)	33	9
W-1	38.2	5	Hi-Ti MARE basalts	32	9
Bulk Crust	33.3	6	Nakhla	32.4	10

Ref: 1= Fujimaki et al (1984), 2= Frey et al (1978), 3= Rhodes et al (1979), 4= Langmuir et al (1977), 5= Owen and Faure (1974), 6= Taylor and McLennan (1985), 7= Knab (1981), 8= Shima (1979), 9= Hughes and Schmitt (1984), 10= Ehmann et al (1979).

Table 3. Hf and Zr concentrations and Zr/Hf ratios in carbonaceous chondrites and enstatite chondrites

Sample	*Shima*	*Knab*	*Patchett*	*Shima*	*Knab*	*Shima*	*Knab*
	Hf (ppm)			**Zr (ppm)**		**Zr/Hf**	
Orgueil	0.123	0.124	0.1065	3.82	3.87	31.1	31.2
Murray	0.169	0.140	----	5.89	4.44	34.9	31.7
Murchison	0.285	0.157	0.140	9.59	5.18	33.6	33.0
"	0.167	----	0.150	5.71	----	34.2	----
Y-74662	0.231	0.131	----	8.02	4.85	34.7	37.0
"	0.174	----	----	5.96	----	34.3	----
Allende	0.217	0.172	0.199	7.40	6.29	34.1	36.6
"	0.219	----	----	7.37	----	33.7	----
Leoville	0.218	0.157	----	7.47	5.70	34.3	36.3
Y-6903	0.191	0.172	----	6.67	6.43	34.9	37.4
"	0.215	----	----	7.65	----	35.5	----
Stannern	1.23	----	2.344				
	----	----	2.397				
Y-74450	1.18	----	1.95				
Richardton	0.204	----	0.148				
BCR-1*	4.73	4.62	4.986	181.8	182.0	38.4	39.4

Data sources: Shima (1979), Knab (1981), Patchett and Tatsumoto (1980a, 1980b), Patchett

(1981), Tatsumoto et al (1981) and Beer et al (1984). *BCR-1 values in the Knab column are from Owen and Faure (1974).

More recently Jochum et al (1986) suggested the Zr/Hf ratio in CI carbonaceous chondrites and the earth's primitive mantle are both equal to 36. However, this conclusion was based upon their use of Knab's Zr data and not his Hf data (*n.b.* Knab's Hf data, which they claimed was inaccurate, is consistent with that reported by Shima, Table 3); they instead used the Hf concentrations reported in Beer et al (1984). The conclusions reached by Jochum et al (1986) may not be justified, given that they assumed the refractory element abundances reported in Beer et al (1984) are directly comparable with Knab's Zr data. A compilation of the available high quality Zr and Hf data in chondritic meteorites (using isotope dilution mass spectrometry methods only) is presented in Table 3.

It is evident from Table 3 that replicate analyses of the same powder can have markedly different concentrations of the refractory trace elements (e.g., compare repeat analyses of Y-74662 and Murchison). These observations suggest that the major and trace element data base for the chondritic meteorites will have large variations in some critical element ratios, especially when comparing different techniques, analysts and aliquots of the same powder. It is therefore important to attempt to eliminate any analytical uncertainties and laboratory/machine bias in making these comparisons. This example illustrates the need for identifying the refractory elements which show the least interelement variation in order to obtain a precise and internally consistent composition for the chondritic endmember. It is only after doing this that we can rigorously test the CI assumption for the primitive earth mantle models.

The Zr/Hf ratio reported for Nakhla (32.4), a meteorite believed to be from Mars (Laul et al, 1986), is lower than that estimated for the bulk earth, although the Nakhla data is of lesser quality. Precise measurements of Zr and Hf concentrations in this and other Martian meteorites would be useful to test for possible Zr - Hf fractionation between the planets. However, such data are not yet available.

3.3.3. Th/U

Several estimates have been made of the Th/U ratio (3.6 to 4.2) for the earth's primitive mantle (*e.g.*, Tatsumoto, 1978; Sun, 1982; Galer and O'Nions, 1985; Allègre et al, 1986). Recently, Allègre et al (1986) used radiogenic $^{208}Pb/^{206}Pb$ ratios of Archaean komatiites to suggest a Th/U ratio of 4.2 for the earth's primitive mantle (see also Table 5 in Sun 1982). Allègre et al (1986) highlighted some of the problems associated with determining this ratio, although they too made simplifying assumptions which may not be justified by the data. To support their estimate of a Th/U of 4.2 for the primitive earth mantle, Allègre et al (1986) plotted the variation in U versus Th/U for CI, H, L, and LL meteorites and an Allende chondrule (their Figure 4). From their diagram they conclude that the earth's data fit the correlation between Th/U ratios and U abundances as portrayed for these meteorites. However, a survey of published Th and U data for carbonaceous chondrites and ordinary chondrites does not substantiate this correlation (Figure 2); it is instructive to compare Figure 2 with Allègre et al's Figure 4 (inset diagram).

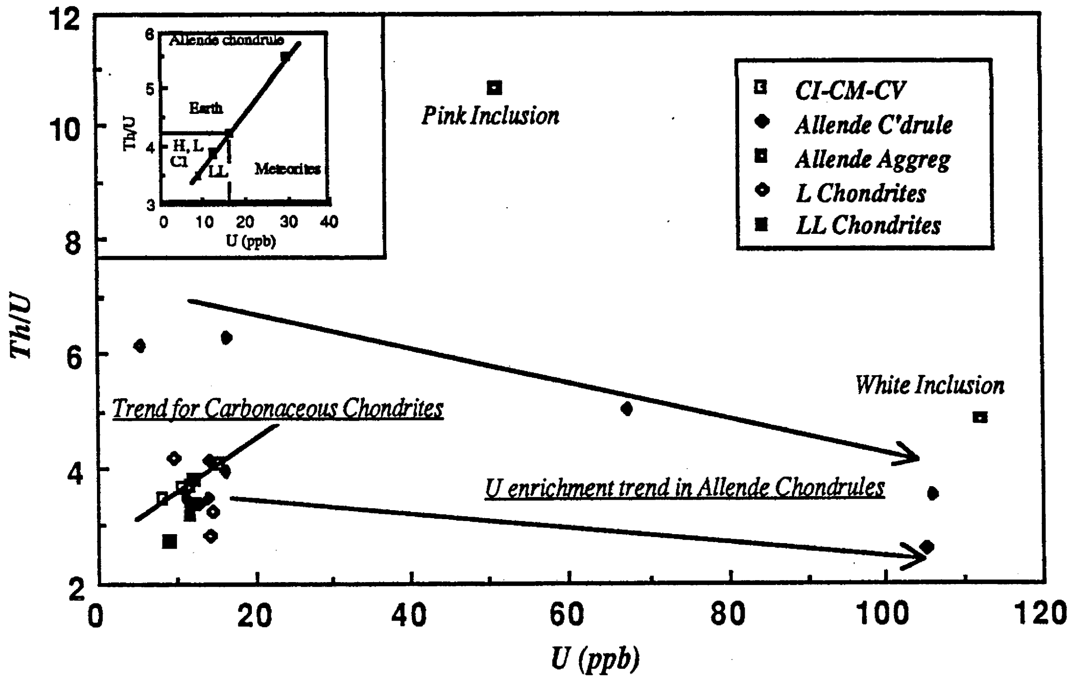

FIGURE 2. Th/U versus U for carbonaceous chondrites, ordinary chondrites and Allende chondrules. Data are from Tatsumoto et al (1976 and 1981) and Unruh (1982). Inset diagram is Figure 4 from Allègre et al (1986). Pink and White Inclusions are the Allende aggregates analyzed by Tatsumoto et al (1976) which differ considerably from that used by Allègre et al (1986).

Based on the comparisons between Allègre et al's Figure 4 (inset) and Figure 2 and the scatter displayed in the chondrules and ordinary chondrite for U versus Th/U, the bulk earth Th/U estimate of 4.2 of Allègre et al (1986) can be questioned. Alternatively, by using the methodology of Allègre et al (1986) but restricting the samples to the carbonaceous chondrites, a bulk earth Th/U ratio of 4.1 is plausible, based on 16 ppb U. However, this is not statistically significant given that $n = 4$ and $r = 0.993$. More analyses of carbonaceous chondrites are required to further test this promising approach. Clearly, the question of the Th/U ratio in the earth's primitive mantle remains an important issue of concern to geochemists. It is worth asking whether this high Th/U ratio (4.1 to 4.2) for the earth is pristine, or the result of mantle differentiation processes.

3.3.4 REE

The rare earth elements (REE) in chondritic meteorites have received much attention because of the available analytical techniques which are capable of providing precise analyses of them and the fact that the REE generally behave as a coherent suite of elements. Additionally, these elements play an important role in models of the composition of the earth. The REE are all refractory lithophile elements (some more so than others) and therefore are believed to occur in chondritic relative abundances in the earth's primitive mantle.

The REE relative abundances can be quite narrowly defined for most samples by comparing the REE abundances of one sample to a chondritic relative abundance (Masuda, 1962; Coryell et al, 1963). By normalizing REE concentrations, smoothed REE patterns are produced which can be used to compare relative REE abundances. Furthermore, because they behave in such a predictable fashion during melting and fractionation processes, we have been able to gain greater insights into a variety of mantle and crustal processes through measurements of these elements.

Table 4 presents estimates for the REE abundances in an average CI carbonaceous chondrite and for REE abundances in an average ordinary chondrite. Comparisons were made between existing data sets for all of the REE elements.

In presenting this estimate, the REE have been evaluated on the relative consistency of the existing data (mostly high quality, isotope dilution data was used). Recently reported REE measurements of Orgueil (a CI chondrite) (Beer et al, 1984), several ordinary chondrites (Shimizu and Masuda, 1986) and the Sm/Nd ratios of various chondritic meteorites (Jacobsen and Wasserburg, 1984) have been utilized. Considerable effort was invested to present a consistent set of element ratios for all of the REE based on the existing literature. In doing this an attempt was made to minimize the inconsistencies of individual measurements (which can be due to sample heterogeneity, laboratory bias, and/or analytical measurements).

Table 4 Chondritic Abundances of the REE and Selected Ratios

	CI Chondrite REE Values			*Ordinary Chondrite REE Values*			
Ref	**Preferred**	1	2	3	4	5	**Preferred**
La	0.2438	0.2446	0.2430	0.332	0.329	0.310	0.317
Ce	0.6320	0.6379	0.6259	0.835	0.865	0.808	0.822
Pr	0.09571	0.09637	--	--	--	0.122	0.124
Nd	0.4706	0.4738	0.4690	0.603	0.630	0.600	0.612
Sm	0.1520	0.1540	0.1529	0.196	0.203	0.195	0.198
Eu	0.05726	0.05802	0.05869	0.0825	0.0770	0.0735	0.0744
Gd	0.2032	0.2043	0.2020	0.270	0.276	0.259	0.264
Tb	0.03719	0.03745	--	--	--	0.0474	0.0483
Dy	0.2522	0.2541	0.2518	0.331	0.343	0.322	0.328
Ho	0.05632	0.05670	--	--	--	0.0718	0.0732
Er	0.1650	0.1660	0.1666	0.226	0.225	0.210	0.215
Tm	0.02546	0.02561	--	--	--	0.0324	0.0331
Yb	0.1657	0.1651	0.1671	0.223	0.220	0.209	0.215
Lu	0.02535	0.02539	0.02536	0.0362	0.0339	0.0322	0.0330
Ce/La	2.592	2.608	2.576	2.515	2.629	2.606	2.592
Nd/La	1.930	1.937	1.930	1.816	1.915	1.935	1.930
Sm/La	0.623	0.630	0.629	0.592	0.617	0.629	0.623
Ce/Nd	1.343	1.346	1.335	1.385	1.373	1.347	1.343
Sm/Nd	0.323	0.325	0.326	0.326	0.322	0.325	0.323
Sm/Eu	2.655	2.654	2.605	2.381	2.636	2.653	2.655
Gd/Eu	3.549	3.521	3.442	3.273	3.584	3.524	3.549
Dy/Er	1.528	1.531	1.511	1.465	1.524	1.533	1.528
Dy/Yb	1.522	1.539	1.506	1.484	1.559	1.541	1.522
Er/Yb	0.996	1.005	0.997	1.013	1.023	1.005	0.996
Yb/Lu	6.536	6.503	6.591	6.160	6.490	6.491	6.536
Nd/Pr	4.917	4.916	--	--	--	4.918	4.917
Gd/Tb	5.464	5.455	--	--	--	5.464	5.464
Dy/Tb	6.781	6.785	--	--	--	6.793	6.781
Dy/Ho	4.478	4.481	--	--	--	4.485	4.478
Er/Ho	2.930	2.928	--	--	--	2.925	2.930
Er/Tm	6.481	6.482	--	--	--	6.481	6.481

Ref: 1= Evensen et al (1978); 2= Average of isotope dilution data for CI chondrites in the literature. 3= Shimizu and Masuda (1986); 4= Nakamura (1974); 5= Boynton (1984); Preferred= this study.

3.4. Non-refractory lithophile element ratios

There are significant differences in the various estimates of the absolute and relative abundances of the moderately volatile and volatile lithophile elements in the earth's primitive mantle. These elements include: Li, Na, K, Rb, Cs, B, F, C, Cl, Br and I. In addition, other elements appear to behave as both lithophile or siderophile elements in the earth's mantle under some conditions (e.g., P, V, Cr, Mn, Cu, Zn, Tl, Ga, Ge, Mo, W, and Pb). All of these elements have variable relative and absolute abundances in different chondritic meteorites. Fractionation of the relative abundances of these non-refractory lithophile elements is thought to have been produced during accretion, rather than during post formational processes (e.g., surface weathering, impact metamorphism, etc.). Here I discuss some relevant elements and certain key ratios regarding their abundances in the primitive mantle.

3.4.1 Moderately volatile lithophile element ratios

The moderately volatile lithophile elements (MVLE) include Li, Na, K, Rb, Cs, B and F; Cr and Mn are sometimes included with these elements, but are discussed in the siderophile - chalcophile element section (3.5.3). MVLE are generally considered to have 50% nebular condensation temperatures between about 1300°K and 700°K at 10^{-4} atm (e.g., Wasson, 1985). Several ratios (e.g., Li/Dy, Na/Ti, K/Rb, Rb/Cs, Rb/Tl and Cs/Tl) are useful in establishing the earth's primitive mantle inventory.

3.4.1.a Li and Na

A number of studies have examined the systematics of Li in various rocks in order to determining its abundance in the earth's primitive mantle (e.g., Dreibus et al, 1976; Bailey and Gwozdz, 1978; Jagoutz et al, 1979; Sun, 1982; Ryan and Langmuir, 1987). During basalt generation Li has a liquid/crystal partition coefficient that is similar to Dy (Ryan and Langmuir, 1987; Appendix 4), and is generally considered to be more compatible than Na or Ti during MORB genesis (Sun et al, 1979). When compared to the estimated abundances of Dy or Ho in the earth's primitive mantle the abundance of Li is seen to be depleted relative to the refractory elements by 25% to 60% (Sun, 1982; Wänke et al, 1984).

Sodium also shows severe depletions in the earth's primitive mantle. The chondritic Na_2O/TiO_2 ratio is about 9, whereas in primitive, low TiO_2 MORB and Archean komatiites it is 1.8 (Sun and Nesbitt, 1977), which is comparable with that observed in fertile spinel lherzolite xenoliths (Jagoutz et al, 1979; Preß et al, 1986).

3.4.1.b K, Rb and Cs

The absolute abundance of K, Rb, and Cs in the earth's primitive mantle is of considerable interest to earth scientists, especially in terms of the earth's thermal budget and the evolution of the earth's $^{87}Sr/^{86}Sr$ system. The abundance of K can be constrained by Th and U concentrations and the Th-U-Pb isotope system, while the abundance of Rb can be constrained by the bulk earth Rb/Sr and $^{87}Sr/^{86}Sr$ ratio.

Our best constraint on the absolute Rb concentration in the earth's primitive mantle comes from Sr isotope studies of primitive mafic and ultramafic lavas through time, and from a comparison of Sr and Nd isotopes in these rocks (see also Section 2.2). Most workers are confident that the Rb/Sr for the earth's primitive mantle is 0.030, ± 10% uncertainty.

In contrast, there is considerable uncertainty in the estimate of the primitive mantle's Cs content. The estimated primitive mantle Rb/Cs ratio varies from 30 (Taylor and McLennan 1985) to 80 (Hofmann and White, 1983; Wänke et al, 1984). However, a compilation of Rb and Cs data for a variety of terrestrial rocks suggests that the mantle's Rb/Cs ratio may have changed through time (see Chapter 4). A Rb/Cs ratio between 5 and 15 is commonly found in Archaean komatiites and basalts (Figure 3), Proterozoic lavas generally have a Rb/Cs ratio of between 10 and 30, and modern MORB and OIB have Rb/Cs of about 80 (White and Schilling 1978; Sun, 1982; Hofmann and White, 1983). Interestingly, the Rb/Cs ratio of island arc basalts is generally between 10 and 40 (Hart and Brooks, 1977; Morris and Hart, 1983; White and Patchett, 1984). This lower ratio forces us to consider the role of oceanic lithosphere subduction in modifying mantle geochemistry. There is a real possibility that the earth's primitive mantle had a Rb/Cs ratio less than 30 and this ratio has increased through geologic time as a result of irreversible mantle differentiation processes such as lithospheric subduction, crust - mantle fractionation and intra-mantle fractionation.

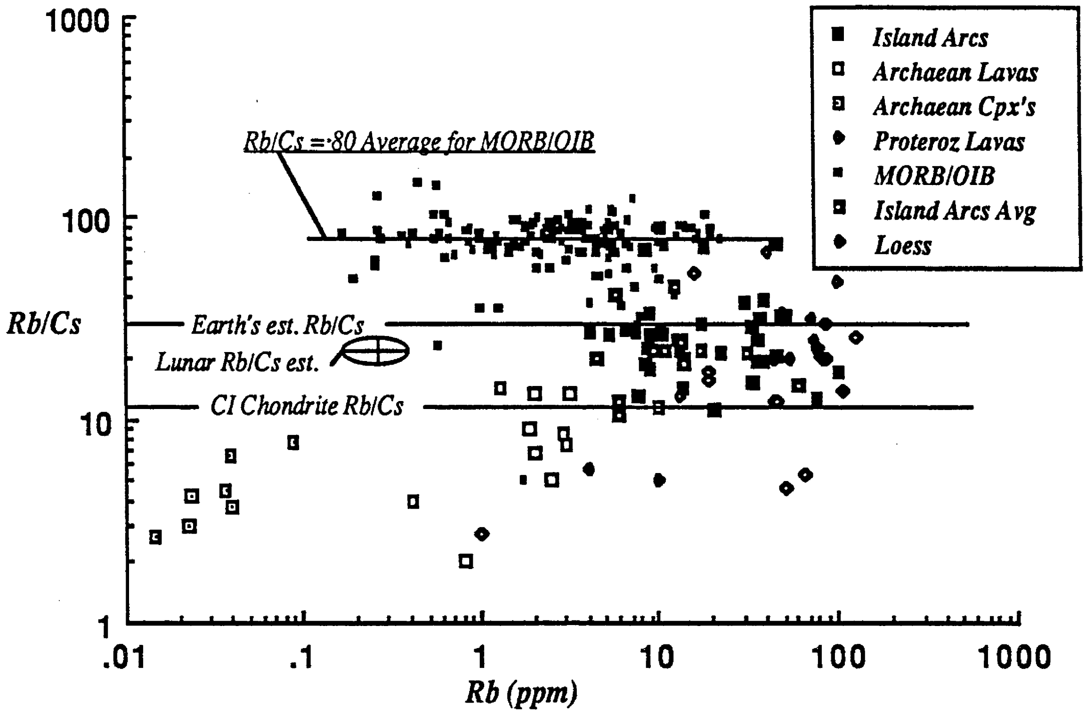

FIGURE 3. Rb/Cs versus Rb concentration for a variety of terrestrial rocks. Note the differences in the Rb/Cs ratio of mafic lavas through time. The Rb/Cs ratios of carefully prepared clinopyroxene separates from Archaean komatiites and basalts are comparable to those of their host lavas. Sources of Rb/Cs data are: the Moon, Taylor (1982); CI chondrites (see Section 4); loess, Taylor et al (1983); Island Arcs, White and Patchett (1984) and White and Dupré (1986); Island Arc Average, Morris and Hart (1983); MORB/OIB, Hofmann and White (1983); Archaean Clinopyroxenes, Hart and Brooks (1977); Archaean Lavas, Hart and Brooks (1977) and BVSP (1981); Proterozoic Lavas, BVSP (1981).

The estimated primitive mantle Rb/Cs ratio of 30 from Taylor and McLennan (1985) is based on their model crust composition (Figure 3). They noted that Rb and Cs are wholly partitioned into the melt during basalt genesis and thus are concentrated in the earth's crust. A precise determination of the Rb/Cs ratio in the bulk crust is therefore constrained by the averages of various crustal rocks and the models developed for crustal growth. McDonough et al, (Chapter 4) showed that the Rb/Cs ratio in the earth's primitive mantle can be constrained by integrating data from komatiites and basalts of all ages, peridotite xenoliths, and crustal rocks. In doing this they documented a secular change in the mantle's Rb/Cs ratio and derived an improved estimate of the bulk crust Rb/Cs ratio. They have also noted that eclogite xenoliths with very low Rb/Cs ratios and high concentrations of Rb and Cs may be a significant mantle reservoir for these elements. Finally, they determined that recycling of components with high Rb and Cs contents and low Rb/Cs ratios back into the mantle has played a significant role in the secular variation of Rb/Cs in the mantle, and suggested that the earth's primitive mantle has a Rb/Cs ratio of 20 ± 10.

An estimated Rb/Cs ratio between 10 and 30 for the earth's primitive mantle is similar to Taylor's (1982) estimated Rb/Cs ratio for the bulk Moon (Figure 3), and is consistent with models that invoke a terrestrial origin for the Moon (Ringwood, 1986; Hartmann et al, 1986). Furthermore, the uncertainty in this estimate weakens the credibility of arguments put forth by Drake (1986) for a non-terrestrial origin of the Moon based on the Rb/Cs ratio = 80 for the primitive earth mantle. The large variation in Rb/Cs ratios through time in a diversity of mantle derived rocks, peridotites and eclogites is not fully understood and needs further critical evaluation.

Estimated K/Rb ratios for the primitive mantle generally lie between 300 and 350 (Jagoutz et al, 1979; Sun, 1982; Taylor and McLennan, 1985), although estimates as low as 240 (Wänke, 1981) and as high as 500 (Jochum et al., 1983; Wänke et al, 1984) have been proposed (see also Section 2.2). Likewise, the K/Cs ratios in these models range from 10^4 to 2.7×10^4. The range in these estimated primitive mantle ratios illustrates the need for more work. Improved knowledge of the absolute and relative abundances of Cs, Rb and K in the primitive mantle can provide a greater understanding of the total earth budget of the heat producing elements, the bulk earth Rb - Sr isotope system and the overall abundances of the moderately volatile elements.

3.4.2 Volatile lithophile element ratios

The volatile lithophile elements include Cl, Br and I. During basalt generation Pb and Tl, both siderophile/chalcophile elements, behave like volatile lithophile elements, and have therefore been included in this section. The volatile lithophile elements have 50% nebular condensation temperatures below about 700°K at 10^{-4} atm (Wasson, 1985). Some of these elements and their mantle ratios are discussed here.

3.4.2.a Cl and Br

Estimates of these elements in the earth's primitive mantle are not well constrained compared to the refractory elements and some of the moderately volatile lithophile elements. This is in part due to the limited data base. Cl and Br are believed to behave similarly to Rb or Cs during modern MORB and OIB genesis (Schilling et al, 1980; Sun, 1982). Thus ratios of Cl/Cs, Cl/Rb and Cl/Br have been used to obtain the present estimate of these elements in the earth's primitive mantle (Schilling et al, 1980; Sun, 1982). With more data it will be important to find out if these ratios for the mantle have been constant through time.

3.4.2.b Boron

A recent study of the B content of fertile, peridotite xenoliths (Higgins and Shaw, 1984) allows a new estimate to be made for the primitive mantle concentration. Li/B ratios in these peridotites are relatively constant at about 3.5 (Jagoutz et al, 1979; Higgins and Shaw, 1984). The size and valency of B indicates that it should have a similar partition behavior to Li during basalt genesis. If the primitive earth mantle Li content is about 1.6 ppm (Jagoutz et al, 1979; Sun, 1982; Ryan and Langmuir, 1987; and this study) then the B content is suggested to be about 460 ppb.

3.4.2.c Tl

Tl is commonly considered to behave like K, Rb and Cs in the crust (Taylor and McLennan, 1985), however it has also been proposed as a sensitive indicator of sulfide saturation in silicate melts (McGoldrick et al, 1979). Data for Tl, Rb and Cs in in oceanic basalts (McGoldrick et al, 1979; Hertogen et al, 1980), suggest that the ratios of Rb/Tl (400) and Cs/Tl (5) are fairly constant in MORB and OIB. This, plus other evidence (e.g., Newsom et al, 1986), does not support the concept of sulfide saturation in the source regions of MORB or OIB. Tl data for three slightly LREE-depleted, although fertile (CaO ≈ 3.2% and Al_2O_3 ≈ 3.6), spinel lherzolite xenoliths (UM 4, 6 and 7; BVSP, 1981) suggest that there is a relatively constant La/Tl (100 ± 20) ratio in these rocks. After correction for the effects of melt depletion these data provide an estimate for the primitive earth mantle abundance for Tl; the estimated depletion of Tl in these samples ranges from about 80% to 96% which in turn suggests that the primitive mantle has a Tl content of between 10 and 11 ppb. This estimate implies a primitive earth mantle Rb/Tl ratio of about 60 and a Cs/Tl ratio of about 3, based on a primitive mantle Rb/Cs ratio of 20, and 630 ppb Rb and 31.5

ppb Cs (Chapter 4). These estimated Rb/Tl and Cs/Tl ratios are lower than those found in modern MORB and OIB and suggest a secular variation for these elements, consistent with observation on the Rb/Cs ratio (Chapter 4).

3.5. Siderophile element ratios

The mantle's siderophile elements, both refractory and non-refractory, have been strongly fractionated from their chondritic relative abundances as a result of core - mantle differentiation. These elements include: Re, Os, Ir, Pt, Au, Pd, Rh and Ru as the refractory, highly siderophile noble metals (partition coefficient (K_d) > 50,000), W, V, Fe, Ni, Co, Mo and P as the refractory siderophile metals (K_d = 50 to 10,000), (Cr and Mn), As, Cu, Ag, Ga, Sb, Ge and Zn as the moderately volatile siderophile metals and Cd, Sn, S, Se, Te, Pb, Bi, In, Tl and Hg as the volatile siderophile metals.

The absolute abundances of siderophile elements in the earth's primitive mantle is still debatable. Important questions include whether there have been secular variations in their concentrations, and which elements have been partitioned into the earth's core (e.g., Ringwood, 1983, 1986; Newsom *et al*, 1986; Jones and Drake, 1986). Accurate estimates of the concentrations of siderophile elements in the earth's mantle will provide strong constraints on core forming and mantle differentiation processes. Sun (1982) suggested that this could be accomplished through the study of refractory siderophile/lithophile element ratios in primitive, mantle derived melts and peridotite xenoliths. Some of these element ratios are considered below.

3.5.1 P/Nd in basalts, komatiites and peridotites

Sun (1982) estimated the phosphorous content of the earth's primitive mantle at 92 ppm, based on the constant TiO_2/P_2O_5 ratio of 10 in primitive Archaean mafic to ultramafic lavas and present day MORB with relatively unfractionated REE patterns. This phosphorous estimate yields a P/Nd ratio of 67 for the primitive mantle, this agrees with a P/Nd = 75 ± 13 recently proposed by McDonough *et al* (1985). In contrast, the primitive peridotite xenolith, SC-1, has a P content of 60 ppm, and from this Wänke et al (1984) proposed that the earth's primitive mantle has a lower P/Nd ratio of 45. This point will be further discussed in Section 5.

3.5.2 Platinum Group Elements

Many workers have estimated the absolute and relative abundances of the platinum group elements (PGE) in the primitive earth mantle based on studies of primitive basalts and komatiites and fertile peridotite xenoliths (Jagoutz et al, 1979; BVSP, 1981; Sun, 1982; Chou et al, 1983; Morgan, 1986). Investigations in the $^{187}Re/^{186}Os$ - $^{187}Os/^{186}Os$ isotope system using terrestrial and meteoritic samples suggest that the bulk mantle Os/Re ratio (~12) is within the range observed for chondritic meteorites (Allègre and Luck, 1980; Luck and Allègre, 1983). Morgan (1985) utilizing the Re-Os isotope systematics and PGE data for peridotite xenoliths has proposed that the earth's Os/Re ratio, as inferred from primitive mantle xenoliths, is more like those of enstatite chondrites and CV3-CO3 carbonaceous chondrites. Overall, there is reasonably good agreement between the various estimates of these elements in the earth's mantle.

3.5.3 V, Cr and Mn

Cr and Mn are moderately volatile lithophile elements, whereas V is considered a refractory lithophile element. However, there is evidence for each of these elements having some siderophile (± chalcophile) character. Controversy exists regarding the absolute and relative abundances of Cr, V and Mn in the earth's primitive mantle. Ringwood (1966) first noted that these elements are depleted in the earth's mantle relative to the CI chondrite composition.

Data for Cr, V and Mn in the carbonaceous chondrites (Kallemeyn and Wasson, 1981; 1982) show limited variations in Cr/V (40.8 ± 3.5) and Mg/Cr (39.0 ± 2.2) ratios, and large variations in Cr/Mn (2.08 ± 0.49), Mn/V (20.8 ± 6.2) and Mg/Mn (81.1 ± 18.2) ratios. Compared to CI chondrites, non-CI carbonaceous chondrites show depletions in Cr and Mn and enrichments in V relative to Mg in the approximate order CM ≈ CO > CV. However the enstatite chondrites have a Cr/V ratio (54.0 ± 3.6) which is distinct from those of carbonaceous chondrites, although their Cr/Mn (1.61 ± 0.33) and Mn/V (35 ± 6) ratios overlap (Kallemeyn and Wasson, 1986).

Sun (1982) and Wänke et al (1984) have suggested that V, Cr and Mn are depleted relative to Mg in the earth's primitive mantle. Sun (1982) has attributed the depletions in Cr and Mn to either their volatility during earth's accretion, or their partitioning into the earth's core during its formation, or a combination of these two factors. Sun (1982) also proposed that V, which is a refractory element, is depleted in the earth's primitive mantle due to its incorporation into the earth's core. In contrast, Wänke et al (1984) suggested that V, Cr and Mn were all partitioned into the earth's core, based on the experimental studies of Dreibus and Wänke (1979). Additional experimental evidence suggests that Cr, V and Mn are siderophile at temperatures above 1500° C and within the fO_2 of the earth's mantle (Brey and Wänke, 1983; Rammensee et al 1983; McCammon et al, 1983). By and large these data support the suggestion that core - mantle fractionation is an important factor (most particularly for V) contributing to the depletion of these elements. However the possibility still exists that some volatilization of Cr and Mn may have occurred.

3.5.4 Mo/Pr, Ba/W, Eu/Sb and Eu/Sn ratios and sulfide saturation

The ratios of Pr/Mo, Ba/W, Eu/Sb and Eu/Sn are all refractory lithophile/(siderophile - chalcophile) element ratios; such ratios have been used to estimate the relative abundances of these siderophile (or chalcophile) elements in the earth's primitive mantle. Fortunately, data are available for these elements in MORB, OIB, island arc basalts (IAB), crustal rocks and some peridotite samples. In addition, these ratios (and others e.g., Rb/Tl, Cs/Tl) can be used to test for sulfide saturation in the source regions of various modern basalts as well as basalts and komatiites in the past (Sun and Hanson, 1975; Sun and Nesbitt, 1977; BVSP, 1981; Sun, 1982; Newsom and Palme, 1984; Jochum et al., 1986; Newsom et al, 1986).

Before an estimate of the primitive mantle can be made, we must first determine whether sulfide saturation occurs in the source regions of MORB, OIB and or IAB since it would greatly affect the observed lithophile/chalcophile element ratios in these lavas. Mo, W, Sn, and Sb are siderophile and/or chalcophile elements with sulfide melt/silicate melt partition coefficients of between 1 and about 1500 (Rammensee and Palme, 1982; Newsom et al, 1986). Comparison of Pr/Mo, Ba/W, Eu/Sb and Eu/Sn ratios in MORB and OIB shows that these element ratios do not change over a range of source melting conditions (P, T, fO_2, and percentage of partial melting). A comparison of Pr/Mo (4 to 4.5) and Eu/Sn (about 1.0) ratios in MORB, OIB and IAB (Taylor and White, 1966; Bence and Taylor, 1977; BVSP, 1981; Newsom et al, 1986; Appendix 3) shows that these ratios are constant and comparable between these different magmatic environments. [Note that earlier data (pre-1982) for Sn from Taylor's lab need to be increased by about a factor of 1.7 based on a revision of standards by Taylor and McLennan (1983).] Furthermore, ratios of Pr/Mo and Eu/Sn in both upper and lower crustal rocks are comparable to those in MORB and OIB (Taylor and McLennan, 1985; Rudnick et al, 1986; Rudnick and Taylor, 1987), suggesting no significant crustal - mantle and intracrustal fractionation of these element ratios. Therefore, even though there are substantial differences in the average S contents of MORB and OIB magmas (800 to 1200 ppm) compared to IAB magmas (about 120 ppm) these data do not support the suggestion of sulfide saturation in the source regions of these basalts (e.g., McGoldrick et al, 1979; Hamlyn et al, 1985).

Data for MORB, OIB, IAB and crustal rocks have relatively constant ratios of Pr/Mo (~4.4), Ba/W (~620), Eu/Sb (~0.9) and Eu/Sn (~1.0) (Newsom and Palme, 1984; Taylor and McLennan, 1985; Jochum et al, 1986; Newsom et al, 1986; this study). If these ratios do not exhibit secular variations in mantle derived melts, they can be used to estimate the primitive mantle relative abundances of Mo, W, Sn, Sb, P and Tl (Sun and Nesbitt, 1977; Sun, 1982; Newsom et al, 1986). The Pr/Mo ratio of basalts, crustal rocks and primitive peridotite xenoliths is constant at about 4.0 to 4.5, whereas the Ba/W ratio differs between basalts and crustal rocks, which have Ba/W ratios of about 620, and primitive peridotite xenoliths, which have Ba/W ratios of about 260 ± 40 (Jagoutz et al, 1979). This difference is only a factor of 2.3, but it seems to be genuine and not due to analytical uncertainties. It is important to determine whether Archean basalts and komatiites have Ba/W ratios similar to primitive peridotite xenoliths (260) or to modern MORB/OIB samples, in order to resolve whether secular variation in the Ba/W ratio occurs in the earth's mantle.

There is an urgent need for detailed documentation of the secular variation of elements in the earth's mantle. This information will be crucial to evaluating core forming processes, mantle - crust differentiation and intra-mantle fractionation. Furthermore, by identifying which elements show such variations we will be able to elucidate processes of mantle evolution through time. Only when there is an internally consistent set of element abundances for the earth's primitive mantle will we be able to clearly document the nature of the accreting material in the earth's early orbit.

4. The Average Composition of CI Chondrites

4.1 Background

A primary purpose of this study is to evaluate the existing models for the composition of the earth's primitive mantle and to present a revised model. To do this and to compare this estimate to chondritic meteorites, it was necessary to examine in detail the average composition of the CI carbonaceous chondrites. It therefore became necessary to critically evaluate and update the existing 'average CI chondrite composition' (Palme et al., 1981; Anders and Ebihara, 1982). Special emphasis was given to ensuring that an internally consistent data set was used for comparison with the earth's primitive mantle composition. The compilation of Anders and Ebihara (1982) was used as a foundation on which revisions were made, since their study is the most recent and thorough evaluation of these data. The earlier work of Palme et al. (1981) was used as a cross reference to the Anders and Ebihara (1982) study.

4.2 An average CI chondritic meteorite composition

Table 5 presents the average composition for CI carbonaceous chondrite meteorites as determined in this study and compares it with those of Anders and Ebihara (1982) and Palme et al. (1981). The data in this table generally agrees with both estimates, however differences between this study's estimates and that reported by Anders and Ebihara (1982) are indicated. These differences are discussed below, or have been discussed previously in the text.

A revised average major element composition for CI carbonaceous chondrites was based on the available literature data and a compilation of critical element ratios known to remain constant in various chondritic meteorites. These parameters provided a rigid set of constraints for these elements. Reasons for the revisions in the estimated REE element abundances are discussed in section 3.3.4. Estimated abundances of K, Rb, Sr, Ba, and Cs were based on literature data, with greater emphasis placed on measurements done by IDMS for a large number of elements on a single aliquot dissolution procedure.

Table 5 Average Composition of CI Carbonaceous Chondrites

Element	Preferred	A & E	Palme	Element	Preferred	A & E	Palme
Li (ppm)	1.57	1.57	1.45	Ag† (ppb)	200	216	210
Be	0.027	0.027	0.025	Cd†	710	720	770
B	0.983	0.983	0.27	In	80	80	80
C%	5.05	5.05	3.5	Sn	1720	1720	1750
F	60.7	60.7	54.	Sb	162	162	130
Na†	5000	4960	5020	Te†	2260	2370	2340
Mg† %	9.15	9.90	9.36	I	433	433	560
Al† %	0.801	0.868	0.820	Cs†	188	187	190
Si† %	10.10	10.64	10.68	Ba†	2410	2270	2200
P (ppm)	1220	1220	1010	La†	244	236	245
S%	6.26	6.26	5.8	Ce†	632	616	638
Cl (ppm)	700	704	678	Pr†	95.7	92.9	96
K†	550	545	517	Nd†	471	457	474
Ca† %	0.882	0.928	0.900	Sm†	152	149	154
Sc† (ppm)	5.92	5.76	5.9	Eu†	57.3	56.0	58.0
Ti	440	440	440	Gd†	203	197	204
V	57	57	55.6	Tb†	37.2	35.5	37
Cr†	2650	2640	2670	Dy†	252	245	254
Mn	1960	1980	1820	Ho†	56.3	54.7	57
Fe %	18.2	19.0	18.3	Er†	165	160	166
Co	502	502	501	Tm†	25.5	24.7	26
Ni†	10800	10960	10800	Yb†	166	159	165
Cu	124	123.7	108	Lu†	25.4	24.5	25
Zn	312	312	347	Hf†	107	119	120
Ga	9.98	9.98	9.1	Ta†	14	15.5	14
Ge	32.4	32.4	31.3	W	95	95	89
As	1.927	1.927	1.85	Re	35.8	35.8	37
Se	18.6	18.6	18.9	Os	517	517	49
Br	3.57	3.57	2.53	Ir	481	481	48
Rb†	2.32	2.30	2.06	Pt	1012	1012	1050
Sr†	7.26	7.90	8.60	Au	140	140	140
Y†	1.57	1.56	1.44	Hg	395	395	530
Zr†	3.85	3.70	3.82	Tl	140	140	140
Nb† (ppb)	246	250	300	Pb	2470	2470	2430
Mo	920	920	920	Bi	110	110	110
Ru	712	712	690	Th	29	29	29
Rh	134	134	130	U	8.1	8.1	8.2
Pd†	555	560	530				

Preferred = this study, A & E = Anders and Ebihara (1982), Palme = Palme et al. (1981)
† differences between this study and A & E are noted.

The revised abundance estimates of Pd, Ag, Cd and Te are based on the recent study of Loss et al. (1984). Replicate isotope dilution mass spectrometry measurements were made on Orgueil and Ivuna, two CI carbonaceous chondrite meteorites, and Murray (CM2) and Allende (CV3), two non-CI carbonaceous chondrite meteorites. The estimated average concentrations of Pd, Ag, Cd and Te in CI chondrite meteorites reported here are similar to those given in Anders and Ebihara (1982). However, the precision of the analyses by Loss et al. (1984) and the variation found in different CI chondrite meteorites were considered in this study.

The revised abundance estimates of Nb, Ta, Zr, Hf and Y were based on the work of Jochum et al (1986), Beer et al (1984) and a comparison of the absolute concentrations of refractory element abundances in the different analyses of Orgueil.

5. Composition of the Primitive Earth Mantle

5.1 Introduction

In this section I present a model for the composition of the earth's primitive mantle based on available data for relatively undepleted, primitive spinel lherzolite xenoliths. This model has several features in common with models discussed in earlier chapters, however this study is able to demonstrate that the available samples are capable of providing a consistent chondritic model for the refractory lithophile elements, contrary to the suggestion of Palme and Nickel (1985) and without having to correct for clinopyroxene enrichments assumed to be due to sampling bias as suggested by Hart and Zindler (1986). Several features of this model are contrasted with other existing models.

5.2 The Data Set

Studies of primitive mafic and ultramafic lavas and fertile peridotite xenoliths provide good evidence for near chondritic ratios of incompatible refractory lithophile elements in the upper mantle (Ringwood, 1966; Sun and Nesbitt, 1977; Jagoutz et al, 1979; Sun, 1982). Ringwood (1966), Sun and Nesbitt (1977) and Sun (1982) considered the melt - residuum relationship of the mantle samples and made certain corrections in order to "see through" previous melting events. In contrast, Jagoutz et al (1979) intentionally selected xenoliths which best represented relatively "unmodified" (e.g., SC-1) mantle materials, however even these samples have experienced some degree of melt extraction, as evidenced by their LREE depletions (Jagoutz et al, 1980).

There is debate as to whether these different mantle samples possess chondritic proportions of the refractory elements. Palme and Nickel (1985) suggested that fertile peridotite xenolith samples, including the relatively "unmodified" samples of Jagoutz et al (1979), have non-chondritic Ca/Al ratios and concluded that either the upper mantle is fractionated from an initially chondritic composition or that the primitive upper mantle does not possess a chondritic Ca/Al ratio. In contrast, Hart and Zindler (1986), after examining the available peridotite data, suggested that the samples used have been selectively biased in favor of the clinopyroxene enriched xenoliths. Earlier, Ringwood (1975; Chapter 3.4, 5.1, and 5.2) reached this same conclusion where he suggested that the peridotite data may be biased towards samples with "deep-green chrome diopside and dark spinel". He recommended that the Ca/Al ratio in these peridotites should be corrected to that of the chondritic Ca/Al ratio (Ringwood, 1975; e.g., p. 189). Following the suggestion of Ringwood (1975), Hart and Zindler (1986) corrected the Ca/Al ratios in a number of relatively fertile peridotite xenoliths back to the assumed chondritic value in order to obtain a bulk silicate earth composition.

Data for fertile peridotite xenoliths have been examined in detail in order to solve the question of chondritic proportions of refractory lithophile elements in the bulk earth. Given evidence for a complex, multi-stage history in even the more fertile xenoliths (e.g., Jagoutz et al, 1980), the residua characteristics of each xenolith were characterized. After identifying the nature and relative amount of melt depletion, these xenoliths were collectively used to uniquely define a primitive mantle composition. These data were then compared with those from Archean komatiites and basalts (e.g., Sun and Nesbitt, 1977; Sun, 1982) and integrated into a consistent model for the earth's primitive mantle.

The samples used in this study are spinel-bearing lherzolite xenoliths; they include samples from Jagoutz et al (1979), Stosch and Seck (1980), BVSP (1981), Nickel and Green (1984), Chauvel and Jahn (1984), Preß et al (1986) and Stern et al (1987). These samples are from Europe, North and South America, Asia and Australia, and thus encompass any global chemical variation in the upper mantle.

I established two selection criteria for choosing the xenolith samples used in this study, namely that all samples: (1) have < 40 wt. % MgO and (2) have less than 9 wt. % FeO content (with all Fe was assumed to be FeO). The first criterion eliminated samples which have experienced excessive "loss of basalt". The second criterion eliminated only 3 additional samples (UM 5, LE76-1L and A-6/47), but its purpose was to reject samples which have been modified by secondary enrichment processes. For example, one of these samples (LE76-1L) was described by Irving (1980) as being a composite xenolith (spinel + amphibole + olivine clinopyroxenite in contact with a group I spinel lherzolite), with distinct chemical zonation in its mineral phases from the spinel lherzolite to the contact with the clinopyroxenite. However, Hart and Zindler (1986) have included this xenolith in their study.

Figure 4 is a plot of MgO versus CaO, Al_2O_3, TiO_2, NiO, Sc and Yb for the xenoliths used in this study. The systematic trends shown by these xenoliths are typical of lherzolite and harzburgites worldwide (e.g., Maaløe and Aoki, 1977; BVSP, 1981), suggesting that similar magmatic and metamorphic processes operated in all environments. Isotopic and chemical evidence imply that none of these samples are pristine, some have had a melt component extracted, while others may have experienced a limited degree of secondary melt enrichment. However their initial compositions can be determined by using a melt - residuum relationship to "see through" previous melting event(s).

The unmelted, initial composition of these xenoliths provides an empirical method for estimating the earth's primitive mantle composition. Similar modelling has been used previously to identify the initial composition of peridotite massif samples and Archean ultramafic and mafic lavas (Loubet et al, 1975; Sun and Nesbitt, 1977; Sun, 1982). This approach is used here to determine the initial compositions of these xenoliths, and the data are then used to derive a consistent model for the composition for the earth's primitive mantle.

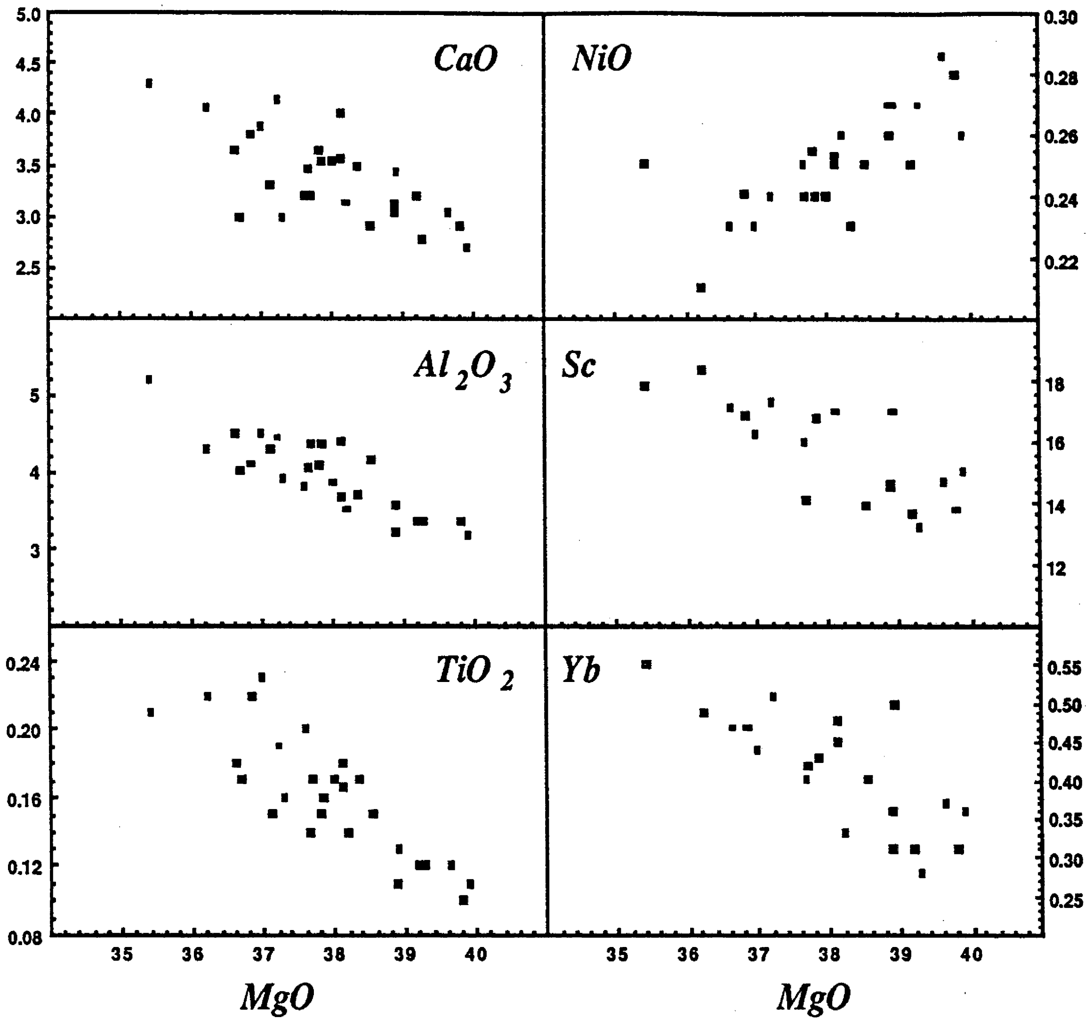

FIGURE 4. MgO (wt.%) versus CaO, Al_2O_3, TiO_2, NiO (all in wt %), Sc (ppm) and Yb (ppm) for spinel-bearing lherzolite xenoliths. Data sources for samples are given in the text.

5.3 The Model

Figure 5 presents chondrite normalized (excepting Mn and Cr) plots for several of the peridotite xenoliths used in this study, and illustrates the systematic behavior of several major and trace elements. Elements are positioned according to their relative bulk partition coefficients for a basaltic melt - peridotite system, with increasing partition coefficients from left to right (adapted from Sun et al., 1979). This diagram is called a partitioning behavior diagram. Before continuing with the discussion on the peridotite xenoliths, I will highlight several important features of this diagram.

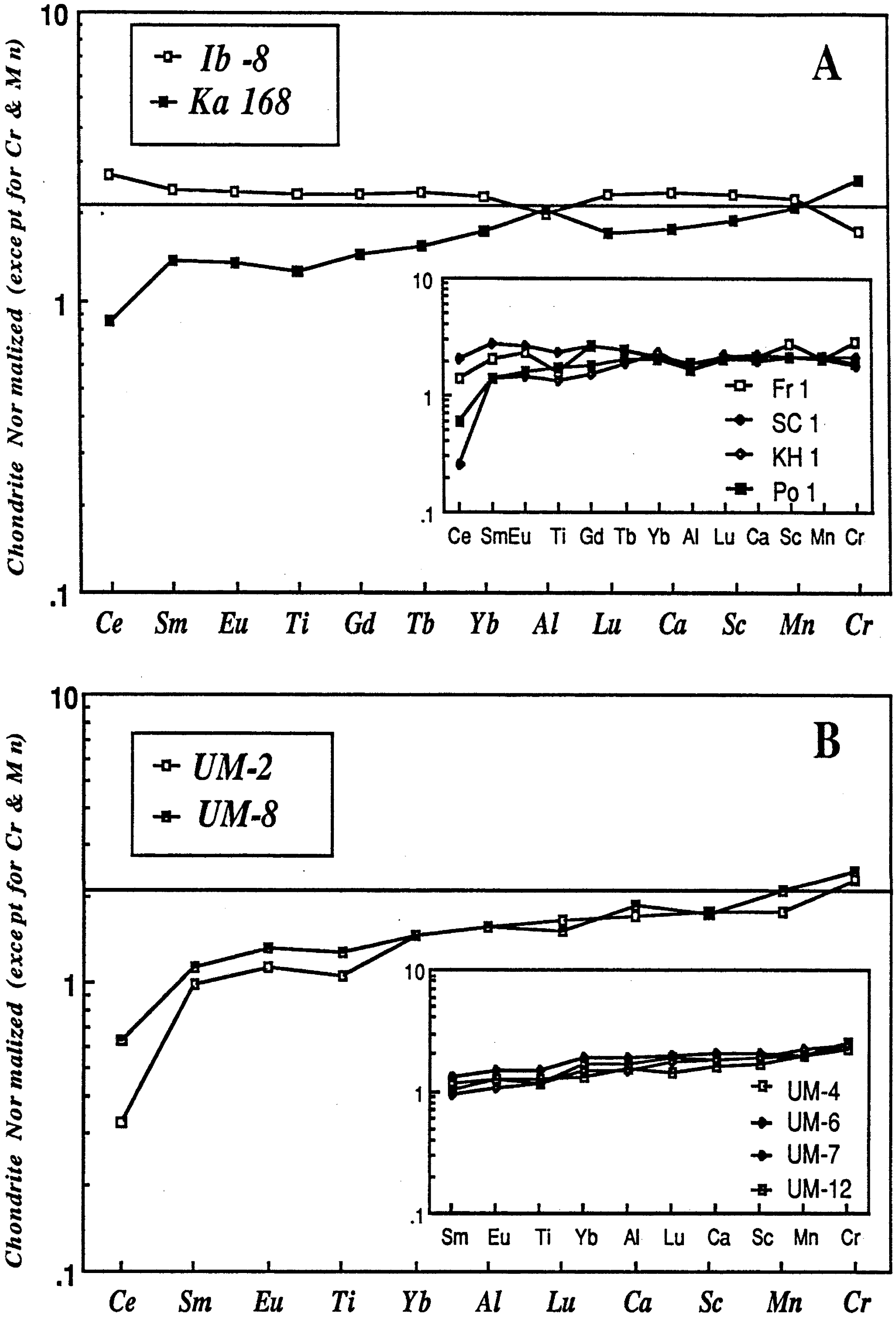

FIGURE 5. Partitioning behavior diagrams for several of the peridotite xenoliths used in this study. Data are normalized to the average ordinary chondrite (Section 3), except for Mn and Cr, which have been normalized to values (480 and 1350, respectively) which are relatively comparable for their primitive mantle concentrations (Sun, 1982; Wänke et al, 1984).

5.3.1 The Partitioning Behavior Diagram

First, in all but the Jagoutz et al (1979) study both Mn and Ti were treated as major element oxides. This means that MnO and TiO_2, which have average concentrations of about 0.13 wt.% and 0.21 wt.%, respectively, can be estimated to within only about ±8% and ±5% certainty, respectively. This is an unfortunate historical feature and should be overcome in order to improve our understanding of these important geological samples. More precise Mn and Ti data may resolve apparent small relative depletions or enrichments in some samples, for example, UM-2 and UM-8 (Figure 5b).

Secondly, smooth patterns were obtained by positioning Ti, Al, Ca, Sc, Mn and Cr in this order, relative to the REE, on the diagram. This order is consistent with the relative enrichment factors for these elements in basalts (basalt/PM). Given that these peridotites have experienced the removal of a small degree of partial melt it was considered appropriate to compare the enrichment factors for a basanite with the primitive mantle composition (Sun, 1982). The enrichment factors for a primitive basanite sample (2769, with a Mg-number = 69) are:

Element	Enrichment Factor (basanite 2769)
Sm	20.0
Eu	18.2
Ti	13.1
Tb	11.1
Yb	3.7
Al	2.9
Lu	2.6
Ca	2.4
Sc	1.22
Mn	1.17
Cr	0.11

(Frey et al, 1978). These data indicate that Mn has a partition coefficient of about one for MORB in equilibrium with a primitive or pyrolite mantle, which is consistent with mineral/melt partition coefficient studies (Irving, 1978). This is significant because it provides us with an element which undergoes little change during partial melting.

Thirdly, other elements such as FeO, MgO, Ni, Co, V, Cu and Zn, can be added to this diagram; their position would be determined by their relative bulk partition coefficients or by their relative enrichment factors. For example, Cu, V and Zn have concentrations of 30, 177 and 56, respectively in this sample. This would suggest they have enrichment factors of about 0.7 for Cu, 2.2 for V and about 2.4 for Zn, thus indicating that the relative bulk partition coefficients for these elements are:

$$\mathrm{Mn} < \mathrm{Cu} < \mathrm{Cr} \quad \mathrm{Ca} < \mathrm{V} < \mathrm{Sc} \quad \mathrm{Zn} \sim \mathrm{Ca}.$$

Fourthly, the positions of Ti, Al, Ca, Sc, Mn and Cr relative to the REE, and their relative enrichment factors are significantly different if we were to consider a MORB and/or its harzburgitic residue. Using a primitive MORB sample (482/11, with a Mg-number = 69, from Sun et al, 1979) the relative enrichment factors indicate that the ordering shown here would not produce a smooth pattern and must be changed. This is due to the fact that MORB tholeiites are derived from sources in which clinopyroxene has been nearly or totally melted out. The relative enrichment factors for this MORB sample are:

Element	Enrichment Factor (MORB 482/11)
Eu	5.7
Dy	5.7
Yb	5.3
Lu	5.2
Ti	4.6
Al	3.6
Ca	3.1
Sc	1.8
Mn	1.0
Cr	0.15

Moreover Cu, V and Zn, which commonly have primary MORB concentrations of about 75, 200 and 80 ppm, respectively would have enrichment factors of about 2.5 for Cu and V and 1.4 for Zn. This indicates that during MORB genesis the relative positions of these elements are:

$$\mathrm{Ca} < \mathrm{Cu} \sim \mathrm{V} < \mathrm{Sc} < \mathrm{Zn} < \mathrm{Mn}$$

5.3.2 Characteristics of the Peridotite suite

There are several important observations regarding the compositions of xenoliths which arise from these diagrams. Sample Ib-8 from Dreiser Weiher (Stosch and Seck, 1980) has a flat, unfractionated pattern for most elements, except Al and Cr

(Figure 5a). Its relative depletions in Al and Cr can be explained by a small depletion in spinel, which commonly contains about 50 to 60 wt.% Al_2O_3 and 7 to 15 wt.% Cr_2O_3 (e.g., Frey and Green, 1974; Frey and Prinz, 1978; BVSP, 1981). The loss of a small spinel component could be due to metamorphic and/or igneous processes, or possibly mineral fractionation during sample processing and analysis. Though the origin of this depletion in Ib-8 is not yet understood, it is clear from the relative abundances of the other elements that there is no anomalous clinopyroxene component which needs to be corrected for, as suggested by Zindler and Hart (1986).

In comparison to the Al and Cr depletion found in Ib-8, sample Ka 168 from Kapfenstein (Jagoutz et al, 1979), with a slightly depleted pattern, displays positive enrichments in Al and Cr relative to the other elements. This feature is not likely to be a characteristic of a clinopyroxene component, but rather reflects spinel enrichment. It is also noteworthy that xenoliths which are relatively coarse-grained are comparatively small, with diameters typically less than 30 cm across. Therefore, it is always possible that their spinel content is non-representative. Given that both element patterns point towards an anomaly in a spinel component and not a clinopyroxene component, this would indicate that the Ca/Al correction of Hart and Zindler (1986) may be unnecessary.

The two UM samples (2 and 8, from BVSP, 1981), both from Kilborne Hole, US, have relatively smooth patterns (Figure 5b) with slight depletions in incompatible elements, a slight enrichment in Cr and no significant variation in Mn (compare also Mn contents in Figure 5a and the inset in Figure 5b). Little or no variation in the Mn value reflects its partition coefficient of about 1.0 (see also section 5.3.1), which suggests that these xenoliths should possess Mn abundances which are close to the primitive mantle Mn abundances. The pattern found in these 2 UM samples shown in Figure 5b is characteristic of fertile, peridotite xenolith from Kilborne Hole (e.g., UM 4, 6 and 7 see inset) and San Carlos, SW, US (UM-12 sample, see inset).

These diagrams can also be used to evaluate the relative abundances of various elements in a particular sample or model composition which is suggested to be representative of the primitive mantle. For example, samples MHP 79/1 and more so MHP 79/2 are 2 samples thought by Preß et al (1986) to be least affected by partial melting processes and indicative of the primitive mantle composition. However, these samples have fractionated patterns (not shown), especially for Ca, Al and Sc relative to the HREE.

Overall these diagrams illustrate the systematic behavior of various major and trace elements in peridotite samples. They clearly display the relative depletion and enrichment of elements in a peridotite xenolith, which can be used to document the character and amount of partial melt extracted, given that the xenolith has experienced a relatively simple history. These diagrams can also be used to identify enrichments or depletions in a specific mineral (e.g., spinel versus clinopyroxene). Finally, in light of the recently acquired mineral/melt partition coefficient data for the high pressure phases, Ca-perovskite, Mg-pervoskite and majorite garnet (Kato et al, 1987), the smooth patterns exhibited by the peridotite xenoliths suggest that they have not experienced any high pressure fractionation involving these phases. Consequently these peridotites cannot be residua of a terrestrial magma ocean nor its crystallized melt products (see discussions in Section 2.1).

5.3.3 Evidence for a chondritic primitive mantle

Samples with systematic element patterns in the partitioning behavior diagrams also define coherent trends on ratio - ratio plots, in which the trends pass through the uniquely defined chondritic value for these two ratios. An example of this is presented in Figure 6, which includes all of the data for the xenolith suite including samples with irregular LREE-enrichments and those with one or more elements displaying anomalous relative abundances (e.g., the Sc content of Fr-1 relative to the other samples; inset Figure 5a). The fact that the data trends pass through the chondritic value (Figure 6) provides strong evidence that these xenoliths originally possessed chondritic relative proportions of these elements, and supports the assumption of chondritic relative abundances of refractory elements in the earth's primitive mantle.

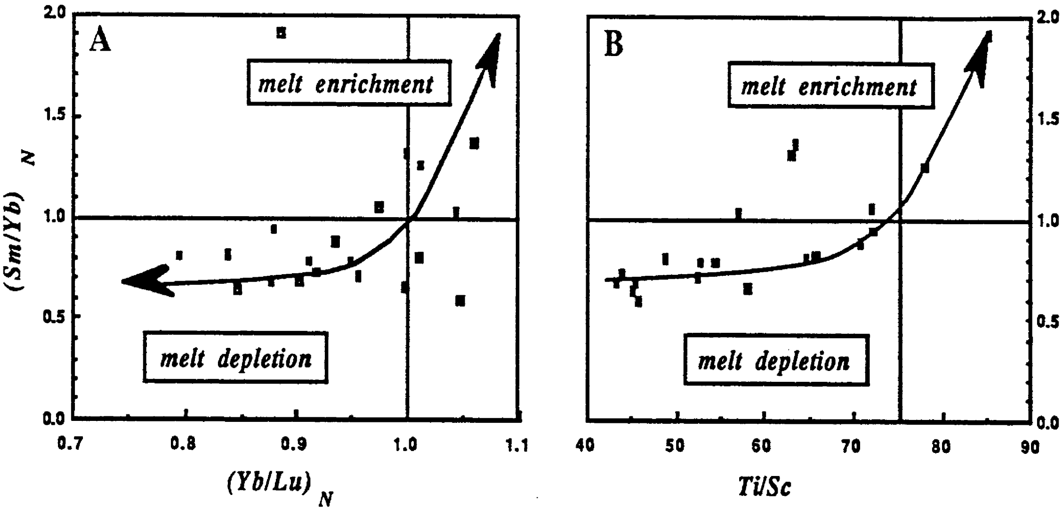

FIGURE 6. $(Yb/Lu)_N$ versus $(Sm/Yb)_N$ and Ti/Sc versus $(Sm/Yb)_N$ for the xenoliths. Samples with relatively smooth patterns on the partitioning behavior diagram follow a trend which intersects the chondritic composition, as indicated by the intersection of the solid lines.

5.3.4 Calculating a Primitive Mantle Composition

The compositions of these xenoliths can be used to estimate the composition of the earth's primitive mantle given that:

(1) they originally possessed chondritic relative proportions of the refractory elements and are not chemically fractionated, and

(2) they display coherent chemical depletion and enrichment patterns which are consistent with most of them having lost a basaltic melt component, whilst a few others experienced secondary melt enrichment (Figure 6).

It is necessary to correct the present composition of these xenoliths for the effects of partial melting in order to calculate the initial source composition. Figure 7 schematically presents such a correction. It can be seen that the removal of a partial melt will deplete the peridotites in elements more incompatible than Mn (i.e., Ce to Sc) and enrich those which are more compatible than Mn (e.g., Cr). Therefore in order to derive the initial composition of these xenoliths, we have to restore each of the depleted components by a relative proportion dependant on its relative bulk partition coefficient, and in the same fashion subtract the enriched components.

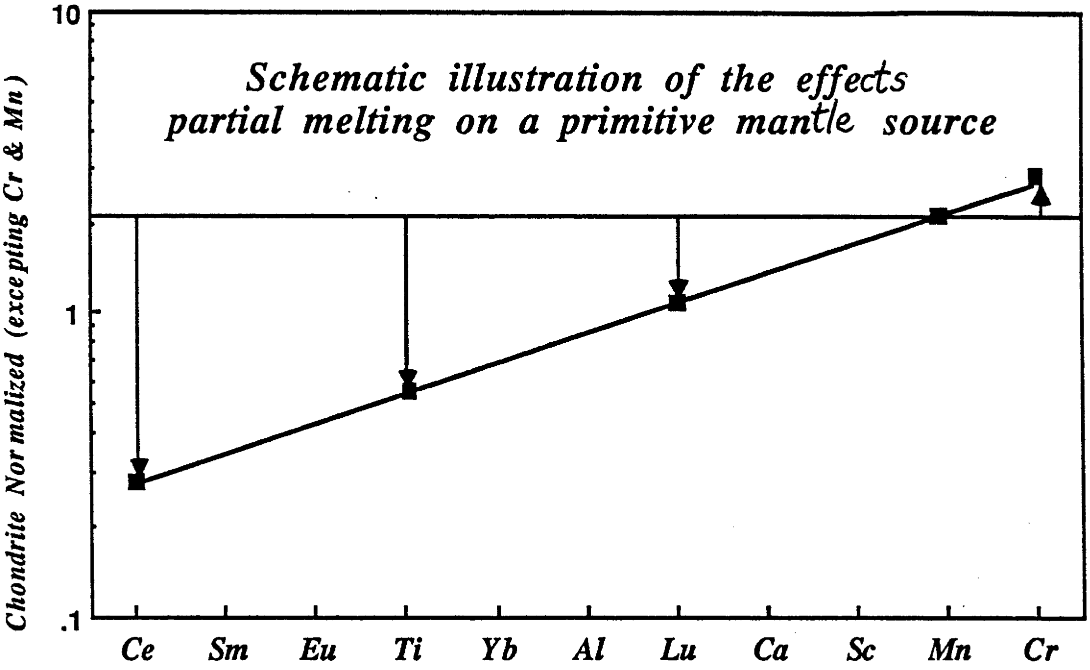

FIGURE 7. Schematic partitioning behavior diagram showing the compositional changes resulting from the removal of a partial melt from a primitive mantle source. Depletions in the incompatible elements (Ce to Sc) are shown in contrast to the enrichment of Cr. Under most conditions Mn will have a partition coefficient of about 1.0 and thus it will be a neutral pivot-point.

The relative positions of Ca and Al in this diagram are of particular interest. In correcting for the effects of partial melting it is important to remember that the proportional depletion of Al is greater than that of Ca. This in turn will cause a residual peridotite xenolith to possess a Ca/Al ratio which is higher than its initial value. This observation provides a simple resolution to the ongoing debate concerning the elevated Ca/Al ratios found in relatively fertile peridotite xenoliths (see discussion in section 5.2).

An effective way of correcting the composition of these xenoliths to their initial value is to use element - element, element - ratio and ratio - ratio variation diagrams. Figure 8 illustrates the Sc/Yb versus Yb and the Ti/Sc versus TiO_2 variation found in the xenoliths considered here. A unique Yb, Sc and Ti content for this suite be can determine given that these xenoliths originally possessed chondritic ratios of the refractory lithophile elements. Using the relationship given in Figure 8 these xenoliths initially possessed on average 0.475 ppm Yb, 17.1 ppm Sc and 1270 ppm Ti. These data in combination with other chemical variation diagrams were used to calculate the average initial composition for this suite and this is reported in Table 6. Given the data base this approach provides a more accurate and precise estimate of the earth's primitive mantle composition.

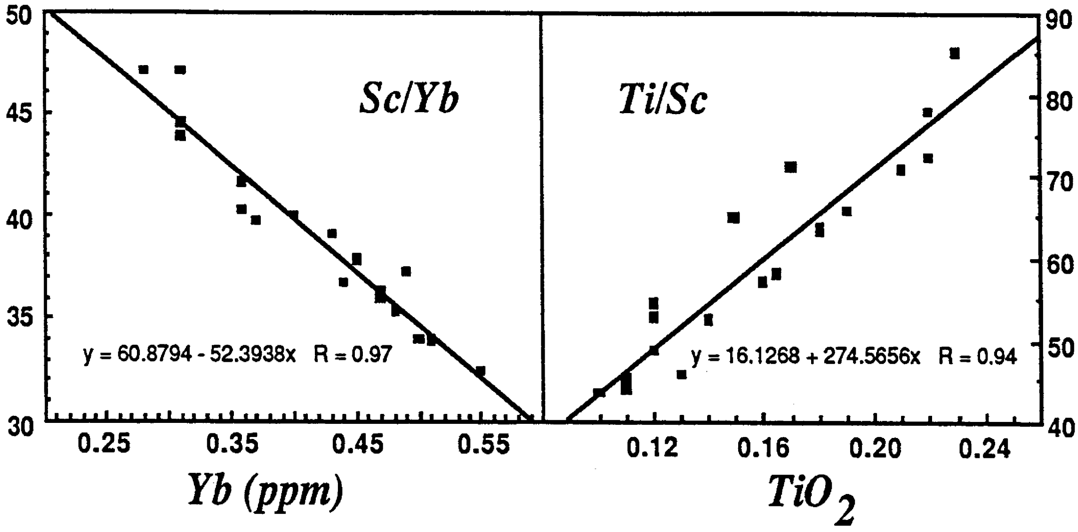

FIGURE 8. Yb (ppm) versus Sc/Yb and TiO_2 (wt.%) versus Ti/Sc for the peridotite xenoliths studied here. Least squares regression and their correlation coefficients are given.

5.3.5 Comparisons of Primitive Earth Mantle Models

Table 6 presents several compositional models for the earth's primitive mantle, along with a number of critical element ratios which allow easy comparisons to be made. A strong point of the model presented here is that it is based on data from some 30 relatively fertile spinel-bearing lherzolite xenoliths from around the world. In comparison Jagoutz et al (1979) used only 6 such samples and they were limited to Europe and North America. Wänke et al (1984), in a revision of the Jagoutz et al (1979) model have further restricted this suite to only one sample (SC-1) and have attempted to integrate into it a crustal component. Considering uncertainties in the estimates of the upper and lower crust compositions and the proportions involved this procedure simply compounds the uncertainties. Additionally, there are several aspects of the crust model composition that are questionable (e.g., $[Rb/Cs]_{crust}$ = 60, compare with Chapter 4, and Taylor and McLennan, 1985).

A second positive feature of my model is that the effects of partial melting on the composition of the xenoliths have been taken into account. This contrasts with previous models which have not accommodated this factor (e.g., Jagoutz et al, 1979; Palme and Nickel, 1985) or have attempted this correction based on an invalid assumption (e.g., Hart and Zindler, 1986).

Table 6. Compositional Models of the Earth's Primitive Mantle

Model	1	2	3	4	5	6	7	8	**Preferred**
SiO_2	21.62	45.10	44.52	45.98	45.96	49.90	47.95	46.20	45.39
TiO_2	0.0734	0.200	0.217	0.225	0.181	0.160	0.204	0.230	0.212
Al_2O_3	1.514	3.300	4.310	4.200	4.060	3.640	3.817	4.750	4.366
Cr_2O_3	0.387	0.400	0.440	0.440	0.468	0.440	0.342	0.430	0.426
FeO	23.41	8.000	8.170	7.580	7.540	8.000	7.860	7.700	7.814
MnO	0.256	0.150	0.140	0.130	0.130	0.130	0.131	0.130	0.136
NiO	1.374	0.200	0.250	0.270	0.277	0.250	0.250	0.230	0.230
MgO	15.17	38.10	38.00	36.85	37.78	35.10	34.02	35.50	36.69
CaO	1.234	3.100	3.500	3.540	3.210	2.890	3.078	4.360	3.696
Na_2O	0.674	0.400	0.390	0.390	0.332	0.340	0.275	0.400	0.390
K_2O	0.0663	0.030	0.030	0.030	0.032	0.020	0.018	–	0.030
P_2O_5	0.280	0.020	0.022	0.015	0.019	—	0.013	–	0.022
Total	66.06	99.00	99.99	99.65	99.99	100.87	97.95	99.93	99.40
Mg#	53.6	89.5	89.2	89.6	89.9	88.7	88.5	89.1	89.3
Si %	10.10	21.07	20.80	21.48	21.47	23.31	22.40	21.58	21.21
Ti (ppm)	440	1199	1300	1350	1085	960	1225	1379	1270
Al %	0.8010	1.75	2.28	2.22	2.15	1.93	2.02	2.51	2.31
Cr (ppm)	2650	2737	3000	3011	3200	3000	2342	2942	2915
Fe %	19.00	6.22	6.35	5.89	5.86	6.22	6.11	5.99	6.07
Mn (ppm)	1980	1162	1100	1021	1010	1000	1016	1007	1053
Ni (ppm)	10800	1572	2000	2108	2180	2000	1961	1807	1807
Mg %	9.15	22.98	22.90	22.23	22.79	21.20	20.52	21.41	22.13
Ca %	0.8822	2.22	2.50	2.53	2.29	2.07	2.20	3.12	2.64
Na (ppm)	4960	2968	2890	2889	2460	2500	2040	2968	2893
K (ppm)	550	249	230	231	265	180	151	–	230
P (ppm)	1222	87	96	65	83	–	57	–	95
Co (ppm)	502	100	110	105	102	100	101	104	110
V (ppm)	57	81.0	87.0	82.1	87.0	128.0	77.0	–	82.0
Sc	5.92	–	17.0	17.0	17.0	13.0	15.0	17.0	17.1
Yb	0.166	–	0.498	0.490	0.420	0.372	0.320	0.440	0.475
Mg/Si	0.906	1.09	1.10	1.03	1.06	0.91	0.92	0.99	1.044
Ca/Si	0.087	0.105	0.120	0.118	0.107	0.089	0.098	0.144	0.125
Al/Si	0.079	0.083	0.110	0.103	0.100	0.083	0.090	0.116	0.1090
Mg/Ca	10.37	10.37	9.15	8.79	9.93	10.26	9.33	6.87	8.38
Ca/Al	1.10	1.27	1.10	1.14	1.07	1.07	1.09	1.24	1.14
Mg/Al	11.42	13.16	10.04	10.00	10.61	11.00	10.16	8.52	9.58
Mg/Ti	208	192	176	165	210	221	168	155	174
Al/Ti	18.2	14.57	17.55	16.47	19.80	20.07	16.49	18.23	18.18
Ca/Ti	20.0	18.48	19.24	18.74	21.14	21.52	17.96	22.60	20.78
Ti/P	0.36	13.74	13.54	20.62	13.09	–	21.49	–	13.38
Ti/Mn	0.22	1.03	1.18	1.32	1.07	0.96	1.21	1.37	1.21
Ti/V	7.72	14.80	14.94	16.44	12.47	7.50	15.91	–	15.50
Cr/V	46	34	34	37	37	23	30	–	36
Na/K	9.02	11.92	12.57	12.51	9.28	13.89	13.51	–	12.58
Na_2O/TiO_2	9.18	2.00	1.80	1.73	1.83	2.13	1.35	1.74	1.84
Mg/Cr	35	84	76	74	71	71	88	73	76
Fe/Mn	96.0	53.5	57.7	57.7	58.0	62.2	60.1	59.5	57.7
Mg/Mn	46	198	208	218	226	212	202	213	210
Si/Mn	51	181	189	210	213	233	220	214	201
Sc/Yb	35.7	–	34.1	34.7	40.5	34.9	46.9	38.6	36.0
Ti/Sc	74.3	–	76	79	64	74	82	81	74.3
Al%/Sc	0.135	–	0.134	0.131	0.126	0.148	0.135	0.148	0.135
Al%/Yb	4.83	–	4.58	4.54	5.12	5.18	6.31	5.71	4.86

Models 1 = CI chondrite, 2 = Ringwood (1979), 3 = Sun (1982), 4 = Wänke et al (1984), 5 = Hart and Zindler (1986), 6 = Taylor and McLennan (1985), 7 = Anderson (1983), 8 = Palme and Nickel (1985), Preferred = this study.

Thirdly, in attempting to derive a primitive mantle composition it is desirable to minimize the number of assumptions involved. Previous models commonly assumed, for example, that the refractory lithophile elements (RLE) accreted in chondritic proportions and/or that the mantle is chemically layered. The model used here is an empirical one and does not make assumptions of this kind. As a result it independently provides support for the chondritic assumption. Moreover, this study has demonstrated that the earth's primitive mantle has a Mg/Si ratio which is about 15% higher than the CI carbonaceous chondrite ratio and that the RLE are enriched by about 40% relative to Si and CI chondrites. It is thus shown that the earth's primitive mantle does not possess Mg/RLE and Si/RLE ratios similar to those found in CI carbonaceous chondrites.

This conclusion is at odds with the assumptions used in the models of Taylor and McLennan (1985) and Anderson (1983). These authors have assumed CI chondrite Mg/Si, Mg/RLE and Si/RLE ratios, although it is known that this ratio is not only fractionated between the carbonaceous chondrites and the enstatite and ordinary chondrites (Larimer, 1979; Kerridge, 1979), but that it is also fractionated between different groups of carbonaceous chondrites. In fact Mg/Si, Mg/RLE and Si/RLE ratios are all fractionated between the different groups of chondritic meteorites. Therefore, I see no justification for assuming any one particular ratio. Furthermore, given other chemical (volatile element abundances) and isotopic (e.g., O isotope) compositional differences (see Section 2) between the earth and CI carbonaceous chondrites, it would seem that the assumptions used by the aforementioned authors are unjustified.

The proposed Mg/Si and Al/Si ratio for the earth's primitive mantle are shown in Figure 9 and are compared to the cosmochemical and geochemical fractionation trends identified by Jagoutz et al (1979). Data for the peridotite xenolith suite used in this study are also included. The geochemical fractionation trend proposed by Jagoutz et al (1979) describes a broad band which is controlled by the degree of partial melting, the amount of melt extracted and the proportions of olivine, orthopyroxene, clinopyroxene and an aluminous phase remaining in the residuum. More depleted peridotites have higher Mg/Si ratios (more olivine) and lower Al/Si ratios (less pyroxene component). The cosmochemical trend is defined by enstatite chondrites, ordinary chondrites and CI carbonaceous chondrites. The other carbonaceous chondrites define a separate trend with a shallower slope (see Jagoutz et al, 1979).

Finally, there are some significant differences between the various compositional models of the earth's primitive mantle (Table 6); some of these differences are listed below. The following observations are presented as a guide to data in Table 6 and can be considered as a point of discussion and a guide to areas of future research :

(1) The model of Palme and Nickel (1985) has the lowest ratios of Mg/RLE and Si/RLE of all the proposed models. Furthermore, this model has a high Ca/Al ratio.

(2) The model proposed by Anderson (1983) yield certain ratios in common with other models, however in detail this model is much less precise than most of the others. It is based on a 5 component mixing scenario and appears more to constrain these model components than to define the earth's primitive mantle composition. Several inconsistencies have been identified in his model, especially between various refractory element ratios (this includes ratios involving Mg and Si, which in his model are in CI chondritic relative proportions).

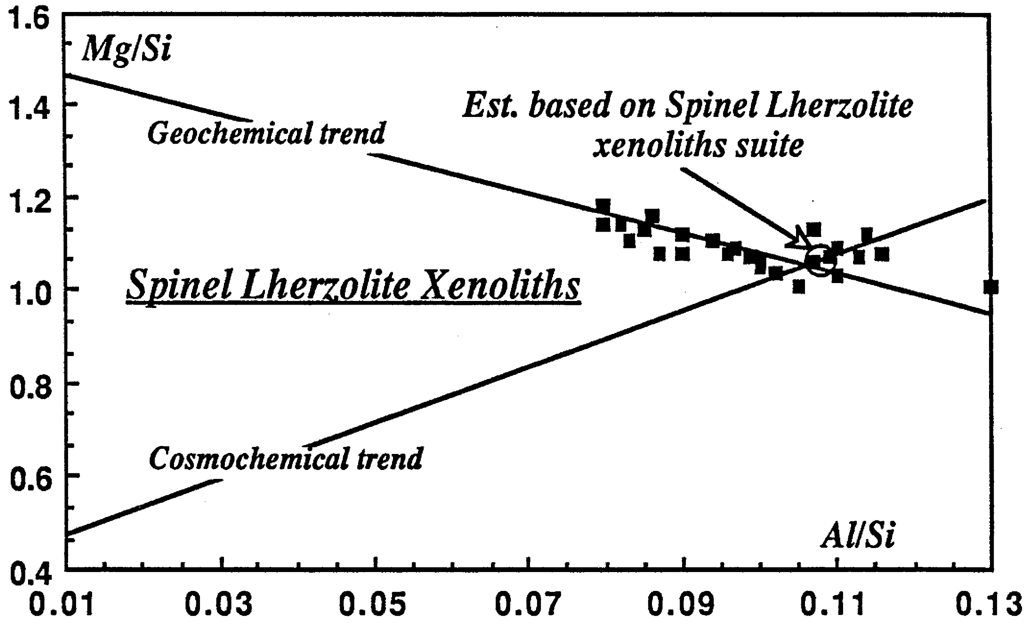

FIGURE 9. Mg/Si versus Al/Si (weight ratios) for the peridotite xenoliths studied here (filled squares). The proposed Mg/Si and Al/Si for the earth's primitive mantle is indicated by the open circle. This estimate falls within the region suggested by Jagoutz et al (1979) to represent the intersection of the cosmochemical and geochemical trends. This diagram has been adapted from the study of Jagoutz et al (1979). The peridotite xenolith with a Al/Si ratio of 0.13 is Mo-105 from Preß et al (1986).

(3) Cr/V and Ti/V ratios are lowest in the model of Taylor and McLennan (1985), because they assume the absolute abundances of Ti and V in the earth's primitive mantle are about 1.5 times that of the CI chondrite composition and base their Cr estimate, of 3000 ppm, on peridotite xenolith data. They are therefore implying that the earth's primitive mantle Ti/V ratio is equal to the CI chondrite value. This also forces their Cr/V ratio to be about 30% to 40% lower than the other estimates.

(4) The model of Taylor and McLennan (1985) has the highest Na/K and Na_2O/TiO_2 ratios of all of the models. In contrast, Anderson proposes a mantle with a high Na/K ratio, but the lowest Na_2O/TiO_2 ratio. Estimates of the earth's primitive mantle abundances of Na relative to various other elements are poorly constrained and this problem has been discussed in section 3.4.1.a.

(5) The model of Hart and Zindler (1986) possesses an anomalously low Ti content relative to various other refractory lithophile elements. Moreover, related to point (4), these authors propose a Na/K ratio which is approximately chondritic, and a Na_2O/TiO_2 ratio similar to the models of Ringwood (1979), Sun (1982), Wänke et al (1984) and the model presented here. Given that there is evidence for Na/K fractionation between the different groups of chondritic meteorites and that they have suggested that the earth has a non CI chondritic Mg/Si ratio, there is some question concerning their Na/K ratio.

(6) The Ca/Al ratio proposed by Ringwood (1979) is rather high and is similar to that proposed by Palme and Nickel (1985). This ratio may indeed be high, as suggested by internal consistency with other ratios (e.g., Al/Ti, Mg/Al and Al/Si) which in turn suggests that the estimated Al content of his model is too low.

(7) The model of Sun (1982), Wänke et al (1984) and the one presented here share a number of factors in common. However, even though the absolute and relative abundances of many elements are similar they are derived by different methods, and in some cases are attributed to different processes (e.g., Wänke et al suggest that Si, Mn and Cr have been fractionated by core forming processes, whereas Sun has suggested that these elements were volatile during accretion). The relative abundance of P in the models of Sun (1982) and this study are in agreement, whereas Wänke et al (1984) require about 30% less P in the earth's primitive mantle.

5.4 Comparisons of Models for the Earth's Primitive Mantle Composition and for the Earth's Bulk Crust Composition

In this concluding section I present 2 summary data tables of compositional models of the earth's primitive mantle and the bulk crust. Table 7 presents 3 models of the earth's primitive mantle, the preferred model is the model determined in this study and models 1 and 2 are from Wänke et al (1984) and Taylor and McLennan (1985), respectively. These three models provide a repesentative view of the variations which exists in the current models. Table 8 presents 3 different compositional models of the earth's bulk crust and compares these models with the preferred model composition of the earth's primitive mantle. This tables provides a first order indication of the extent and nature of the chemical fractionation involved in the crust - mantle differentiation. Below are a series of observations which highlight some of the differences and similarities of the various models presented, they can be considered as points of discussion and a guide to future research.

The preferred compositional model of the earth's primitive mantle has been derived almost completely from the chemical and isotopic data of the xenolith suite, and, where appropriate, the data of Sun (1982) were used as a guide and to check for internal consistency of this model. I have also used the combined data for MORB, OIB and crustal rocks to provide a further check on the consistency of the model. The absolute abundances of the refractory lithophile elements in the preferred model are generally about 1.28 to 1.30 these of CI carbonaceous chondrites when normalized to Mg (Table 7). Note that the relative abundance of Ca is slightly higher (1.34) and Th is still higher yet (1.42), whereas U is slightly lower (1.21) when compared to other refractory lithophile elements. The higher Ca abundance is derived from the xenolith data and, as previously mentioned, the estimated Ca/Al ratio is still within the uncertainties of the estimate for all chondritic meterorites. The Th and U abundances were determined using a Th/U ratio of 4.2 as determined from Pb isotope constraints (Section 3.3.3 and Sun, 1982). The Th and U relative and absolute abundances in various chondritic meteorites is only poorly known and further work is need to fully understand the spectrum of variation in these meteorites. The Sn abundance was calculated from the abundance of Eu, a refractory lithophile element, and the Sn/Eu

Table 7. Compositional Models of the Earth's Primitive Mantle

		Abundances in Primitive Mantle			*Normalized to Mg and CI*		
Element	CI	**Preferred**	1	2	**Preferred**	1	2
Li (ppm)	1.57	1.60	2.15	0.83	0.46	0.61	0.25
Be	0.027	0.078	--	0.060	1.29	--	1.04
B	0.983	0.5	--	0.6	0.23	--	0.29
F	60.7	26.0	19.4	--	0.19	0.14	--
Na	5000	2890	2889	2500	0.26	0.26	0.23
Mg %	9.15	22.13	22.23	21.20	1.08	1.08	1.08
Al %	0.801	2.31	2.22	1.93	1.29	1.23	1.13
Si %	10.10	21.21	21.48	23.30	0.94	0.95	1.08
P	1220	95	64.5	--	0.035	0.024	--
S	62550	350	13.2	--	0.0025	0.0001	--
Cl	700	30	11.8	--	0.019	0.008	--
K	550	230	231	180	0.19	0.19	0.15
Ca %	0.882	2.64	2.530	2.070	1.34	1.28	1.10
Sc	5.92	17.1	17	13	1.29	1.28	1.03
Ti	440	1270	1350	960	1.29	1.37	1.02
V	57	82	82	128	0.64	0.64	1.05
Cr	2650	2915	3011	3000	0.49	0.51	0.53
Mn	1960	1055	1021	1000	0.24	0.23	0.24
Fe %	18.20	6.07	5.89	6.22	0.15	0.14	0.16
Co	502	110	105	100	0.098	0.093	0.093
Ni	10800	1800	2108	2000	0.075	0.087	0.086
Cu	124	30	29	28	0.11	0.10	0.11
Zn	312	56	49	50	0.080	0.069	0.075
Ga	9.98	4.8	3.8	3.0	0.22	0.17	0.14
Ge	32.4	1.1	1.3	1.2	0.02	0.018	0.017
As	1.927	1.3	0.152	0.100	0.30	0.035	0.024
Se	18.6	0.05	0.0135	0.041	0.0012	0.0003	0.0010
Br	3.57	0.075	0.0456	--	0.009	0.006	--
Rb	2.32	0.630	0.74	0.55	0.12	0.14	0.11
Sr	7.26	20.9	27.7	17.8	1.29	1.70	1.14
Y	1.57	4.52	--	3.4	1.29	--	1.01
Zr	3.85	11.1	--	8.3	1.29	--	1.01
Nb (ppb)	246	710	--	560	1.29	--	1.06
Mo	920	64	--	59	0.031	--	0.030
Ru	712	4.2	--	4.3	0.003	--	0.003
Rh	134	1	--	1.7	0.003	--	0.006
Pd	555	5	--	3.9	0.004	--	0.003
Ag	200	8	2.9	19	0.018	0.007	0.044
Cd	710	40	26.1	40	0.025	0.016	0.026
In	80	13	18.5	18	0.073	0.103	0.105
Sn	1720	165	--	<1000	0.043	--	--
Sb	162	5.0	5.7	25	0.014	0.016	0.072
Te	2260	13	19.9	22	0.003	0.004	0.005
I	433	11	13.3	--	0.011	0.014	--

Table 7(contd.). Compositional Models of the Earth's Primitive Mantle

		Abundances in Primitive Mantle			*Normalized to Mg and CI*		
Element	CI	**Preferred**	1	2	**Preferred**	1	2
Cs (ppb)	188	31.5	9.1	18	0.075	0.022	0.045
Ba	2410	6910	5600	5100	1.28	1.03	0.99
La	244	700	520	551	1.28	0.95	1.05
Ce	632	1810	1730	1436	1.28	1.22	1.06
Pr	95.7	275	--	206	1.29	--	1.01
Nd	471	1350	1430	1067	1.28	1.35	1.06
Sm	152	435	520	347	1.28	1.52	1.07
Eu	57.3	165	188	131	1.29	1.46	1.07
Gd	203	580	740	459	1.28	1.62	1.06
Tb	37.2	105	126	87	1.26	1.51	1.09
Dy	252	723	766	572	1.28	1.35	1.06
Ho	56.3	161	181	128	1.28	1.43	1.06
Er	165	473	460	374	1.28	1.24	1.06
Tm	25.5	73	--	54	1.28	--	0.99
Yb	166	475	490	372	1.28	1.32	1.05
Lu	25.4	73	74	57	1.28	1.30	1.05
Hf	107	305	280	270	1.28	1.17	1.18
Ta	14	40	38	40	1.28	1.21	1.33
W	95	21	24.1	16.0	0.10	0.11	0.08
Re	35.8	0.28	0.24	0.25	0.003	0.003	0.003
Os	517	3.4	3.11	3.80	0.003	0.003	0.003
Ir	481	3.3	2.8	3.2	0.003	0.003	0.003
Pt	1012	8	--	8.7	0.004	--	0.004
Au	140	0.75	0.52	1.30	0.002	0.002	0.004
Hg	395	--	--	--	--	--	--
Tl	140	10.5	--	6.0	0.034	--	0.020
Pb	2470	200	--	120.0	0.036	--	0.023
Bi	110	2.5	--	10.0	0.010	--	0.042
Th	29	92	--	64.0	1.42	--	1.03
U	8.1	22	29.30	18.00	1.21	1.61	1.04

From Li to Zr element concentrations are in ppm, Nb to U are in ppb, and Mg, Al, Si, Ca and Fe are in wt. %. CI from Table 5, 1 = Wänke et al. (1984), 2 = Taylor and McLennan (1985).

Table 8. Comparison of Bulk Crust with the Primitive Mantle

		Crustal Abundances			*Crust/PM*		
Element	PM	T & M	W & T	Wed.	T & M	W & T	Wed.
Li	1.6	13	--	13.8	8.1	--	8.6
Be	0.078	1.5	--	--	19	--	--
B	0.5	10	--	--	20	--	--
Na%	0.289	2.30	3.12	2.45	8.0	10.8	8.5
Mg%	22.13	3.20	1.69	2.39	0.14	0.08	0.11
Al%	2.31	8.41	8.52	8.24	3.6	3.7	3.6
Si%	21.21	26.8	29.5	28.1	1.3	1.4	1.3
P	95	--	830	760	--	8.7	8.0
K%	0.023	0.91	1.74	1.76	40	76	77
Ca%	2.64	5.29	3.36	4.86	2.0	1.3	1.8
Sc	17.1	30	--	21	1.8	--	1.2
Ti	1271	5400	3600	5320	4.2	2.8	4.2
V	82	230	--	134	2.8	--	1.6
Cr	2915	185	56	146	0.06	0.02	0.05
Mn	1055	1400	620	830	1.33	0.59	0.79
Fe	6.07	7.07	3.81	4.87	1.16	0.63	0.80
Co	110	29	--	25	0.26	--	0.23
Ni	1800	105	35	69	0.06	0.02	0.04
Cu	30	75	--	47	2.5	--	1.6
Zn	56	80	--	77	1.4	--	1.4
Ga	4.8	18	--	18	3.8	--	3.8
Se	0.05	0.05	--	0.15	1.0	--	--
Rb	0.63	32	61	79	51	97	125
Sr	20.9	260	503	293	12	24	14
Y	4.52	20	14	30	4.4	3.1	6.6
Zr	11.1	100	210	140	9.0	19	13
Nb	0.71	11	13	14	16	18	20
Mo	0.064	1	--	--	16	--	--
Pd	0.005	0.001	--	--	0.20	--	--
Ag	0.0075	0.08	--	0.07	11	--	9.3
Cd	0.0040	0.098	--	0.1	25	--	25
In	0.0125	0.05	--	--	4.0	--	--
Sn	0.165	2.5	--	--	15	--	--
Sb	0.005	0.2	--	--	40	--	--
Cs	0.0315	1.0	--	1.3	32	--	41
Ba	6.95	250	707	543	36	102	78
La	0.703	16	28	29	23	40	41
Ce	1.82	33	57	54	18	31	30
Pr	0.276	3.9	--	--	14	--	--
Nd	1.356	16	23	25.6	12	17	19
Sm	0.438	3.5	4.1	5.60	8.0	9.4	13
Eu	0.165	1.1	1.09	1.40	6.7	6.6	8.5
Gd	0.585	3.3	--	--	5.6	--	--
Tb	0.107	0.6	0.53	1.00	5.6	5.0	9.3
Dy	0.726	3.7	--	--	5.1	--	--
Ho	0.162	0.78	--	--	4.8	--	--
Er	0.475	2.2	--	--	4.6	--	--
Tm	0.0734	0.32	0.24	--	4.4	3.3	--
Yb	0.478	2.2	1.53	3.30	4.6	3.2	6.9
Lu	0.0732	0.3	0.23	0.56	4.1	3.1	7.7
Hf	0.308	3.0	4.7	3.40	9.7	15	11
Ta	0.0403	1.0	--	2.20	25	--	55
W	0.021	1.0	--	--	48	--	--
Tl	0.0105	0.36	--	0.4	34	--	38
Pb	0.2	8	15	12	40	75	60
Bi	0.11	0.06	--	0.07	0.55	--	0.64
Th	0.092	3.5	5.7	7.0	38	62	76
U	0.022	0.91	1.3	1.2	41	59	55

Concentrations in ppm unless otherwise specified. T & M = Taylor and McLennan (1985), W & T = Weaver and Tarney (1984), Wed. = Wedepohl (1981), PM = Primitive Mantle (from this study).

ratio (1.0) in MORB, OIB and the bulk crust, which appears to be relatively constant. There is not sufficient data available to present an estimate for Hg in the earth's primitive mantle, and the other existing models have not attempted this either.

Table 8 can be used as a guide to indicate which elements have been enriched in the earth's crust as a result of crust - mantle differentiation. I have not attempted an extensive review of the composition of the bulk crust, nor a critical evaluation of these models. These compositional models were selected because they provide an estimate of a large number of elements. There are a few points of interest. First, there are significant differences in the estimate of the bulk crust's Fe content. The Taylor and McLennan model predicts a much higher Fe content (~7%), whereas the others are between ~4 and 5%. The high Fe content of the Taylor and McLennan crustal model suggests that Fe has been enriched into the crust over the mantle, and in fact they have suggested that the lower crust is strongly enriched in Fe. This has significant implications for the long-term stability of a mafic Fe-rich lower crust, and it must be considered whether this region would be less dense than the underlying lithospheric mantle and asthenosphere. If a Fe-rich lower crust is denser than the underlying mantle, then is it possible that this material could be incorporated back into the convective mantle? Along with the higher Fe component, it can be seen that many of the Fe-Mg group elements are enriched in the crustal model of Taylor and McLennan. It is possible that more detailed investigations of these elements may provide clues about the nature of this component in the crust. Second, there are some significant differences in the bulk K, Th and U contents of these models which have implications for crustal heat production. These elements are strongly partitioned into the crust, and thus improved crustal abundances can help to provide further constraints on our estimates of these elements in the earth's primitive mantle. Finally, there is a significant difference in the relative abundance of Ba in these models and a two fold difference in the estimate of Ta. Ba is enriched and Ta is depleted relative to the REE in calc-alkaline rocks, whereas these elements are not as strongly fractionated during MORB - OIB genesis. Further work is needed to understand the absolute and relative abundances of these and related elements in order to understand the processes involved in crustal growth.

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APPENDIX 4

Chemical and Isotopic Systematics of Oceanic Basalts: Implications for Mantle Composition and Processes

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Summary

Trace element data for mid-ocean ridge and ocean island basalts are used to formulate chemical systematics in the oceanic basalts. The data suggest that the order of trace element incompatibility in oceanic basalts is:

Cs~Rb(~Tl)~Ba(~W)>Th>U~Nb=Ta~K>La>Ce~Pb>
Pr(~Mo)~Sr≥P~Nd(>F)>Zr=Hf~Sm>Eu~Sn(~Sb)~Ti>(Li)>Ho=Y>Yb.

This rule works in general and suggests that the overall fractionation processes operating during magma generation and evolution are relatively simple, involving no significant change in the environment of formation for MORB and OIB.

In detail, minor differences in element ratios do correlate with the isotopic characteristics of different types of OIB reservoir (HIMU, EM, MORB). These systematics are interpreted in terms of partial melting conditions, variations in residual mineralogy, sediment subduction, recycling of oceanic lithosphere and low velocity zone processes.

Nb data indicate that the mantle sources of MORB and OIB are not conjugate reservoirs to the continental crust. Subduction of oceanic lithosphere or subtraction of refractory eclogite material from the former oceanic crust into the lower mantle is required.

The negative Eu anomalies observed in some EM type OIB suggest the addition of subducted sediment to their mantle sources. However, a general lack of a crustal signature in OIB indicate that sediment recycling is not an important process, at least not in more recent times (≤ 2 Ga), in the convecting mantle.

Upward migration of silica undersaturated melts from the low velocity zone can generate an enriched reservoir in the oceanic lithosphere. We propose that the HIMU type (e.g., St. Helena) OIB source can be generated in this way by recycling of the enriched oceanic lithosphere back into the mantle.

> That much good ensues and that the science is greatly advanced by the collision of various theories cannot be doubted. Each party is anxious to support opinions by facts. Thus, new countries are explored and old districts re-examined; facts come to light that do not suit either party; new theories spring up; and in the end, a greater insight into the real structure of the earth's surface is obtained.
>
> Henry Thomas De la` Beche (1830)

It is now well established that chemical and isotopic heterogeneities of different scales, ranging from centimeters to thousands of kilometers, exist in the earth's mantle. Such heterogeneities reflect variations in elemental abundances generated by depletion and enrichment processes that have operated in the earth's mantle throughout geological time.

In this paper we attempt to integrate the chemical and isotopic data from oceanic basalts in order to establish coherent relationships between isotopic compositions and the consistent (but variable) trace element patterns observed in oceanic basalts. These regularities are then interpreted in terms of the physical and chemical processes that have operated in the mantle.

Our discussion is preceded by an outline of some of the major issues in the chemical evolution and geodynamics of the earth's mantle. This is followed by some ideas on forward modelling, developed by investigating the possible consequences of major physical and chemical processes in the mantle. Finally, we discuss factors which influence the chemical and isotopic compositions of oceanic basalts.

1. Major issues in the chemical evolution and geodynamics of the mantle.

A first order aim in the study of oceanic basalts is to improve our understanding of the chemical and dynamic processes which have operated in the past and present within the earth's mantle. To achieve this it is necessary to delineate the major issues, which requires the integration of data derived from different branches of earth sciences. We need to

1. Undertake complete chemical and isotopic characterization of the earth's primitive mantle (the silicate sphere of the earth) and the timing and processes involved in core growth.

2. Characterize the behavior of elements and the melting and extraction processes involved during magma genesis under different tectonic environments (e.g., is sulfide saturation important?).

3. Delineate the processes responsible for development of ocean island basalt (OIB) source characteristics.

4. Document the secular variations of element abundances and their ratios in the mantle in order to understand mantle differentiation processes involved in crust formation.

5. Firmly establish the extent of crustal recycling in the mantle and document its effects on the chemical and isotopic evolution of the mantle.

6. Establish whether the chemical and isotopic characteristics shared between mid-ocean ridge basalts (MORB) and OIB reflect a complementary relationship with the continental crust.

7. Clarify the geometric and dynamic relationship amongst the different mantle reservoirs.

8. Determine the survival time of chemical and isotopic heterogeneities in the continental lithosphere and in the underlying convecting mantle.

9. Determine the fate of subducted oceanic lithosphere: is it simply recycled and resorbed back into the upper mantle, or is part of it transported into the lower mantle during irreversible mantle differentiation processes?

2. *Forward modelling of mantle differentiation and crustal formation*

The combined processes of plate tectonics, mantle convection, magma generation, crust recycling and upper and lower mantle exchange contribute to the geochemical and isotopic evolution of mantle reservoirs. The nature of mantle convection processes through time (whole mantle or layered mantle) is critical to our understanding of the chemical and thermal evolution of the earth.

In essence each mantle reservoir carries an identifiable chemistry and isotopic fingerprint of the specific processes and environments which have acted upon it. These compositional fingerprints reflect the responses to such factors as partial melting under different P-T-X (CO_2, water rich, melts or fluids) conditions, sediment subduction, and recycling of oceanic crust and asthenosphere through the island arc environment.

a. Mantle differentiation processes through time

Our understanding of mantle differentiation associated with the earth's accretion, core formation and the early history of mantle - crust fractionation relies upon chemical and isotopic studies of Archean volcanic rocks, other planetary bodies, petrological and chemical experiments carried out under high temperature and pressure conditions, and numerical modelling of the thermal evolution of the earth.

Even if some thermal models predict the presence of upper and lower mantle convection cells at present (e.g., Richter, 1985), there is no obvious reason to argue against whole mantle convection during the early history of the earth. It is generally assumed that the early earth's (> X Ga) mantle temperature was higher (e.g., 2000°C surface potential temperature, Richter, 1985), which would favor vigorous, and probably chaotic, whole mantle convection with possible consequences for large scale mantle melting. Consequently, it is very likely that the lower mantle would have been involved in the formation of the earliest lithosphere, resulting in an incompatible element depleted character, i.e., a non-primitive, fractionated lower mantle. At the same time, dense, early-formed, severely hydrothermally altered mafic to ultramafic crust and lithospheric mantle would be rapidly recycled back into the convective mantle by meteorite bombardment and lithosphere subduction. Vigorous convection in the early earth's mantle would quickly stretch and mix this oceanic lithosphere with the convective mantle. Some of this lithosphere may have been subducted into the lower mantle. The magnitude of these activities decreased as the earth's heat engine slowed down. Two-layered mantle convection may have eventually been initiated due to a density barrier imposed by temperature dependant phase transformation at 670 km (e.g., Sawamoto, 1987).

If the mantle differentiation scheme discussed above is realistic then the high $^{3}He/^{4}He$ ratios (≥20x atmospheric) observed in some OIBs do not indicate an origin from a primordial, unfractionated lower mantle. These ratios may instead result from the cooling of the outer core. Similarly, the ^{129}Xe anomaly observed in some MORB samples (Allegre et al., 1987) are unlikely to result from the early (4.4 Ga) separation of the upper mantle from the lower mantle.

The stabilization of the Archean continental crust was accompanied by the formation of thick refractory harzburgitic lithosphere. This subjacent mantle formed as a residual product of mantle melting. Occurrences of diamonds of Archean age from kimberlite pipes in the Kaapvaal craton, South Africa (Kramer, 1977; Richardson et al., 1985) suggest the early existence of Archean continental lithosphere up to ~175 km thick. Such lithosphere could have been developed through underplating of residual mantle related to mantle plume activity and/or depletion of the mantle wedge above a subduction zone.

Studies of modern island arc basalts suggest that subduction of the oceanic lithosphere, with or without associated sediment, can continuously modify the chemical, isotopic and mineralogical composition of the overlying mantle wedge. The release of fluids and hydrous silicate melts from the downgoing altered oceanic crust can result in the enrichment of incompatible elements in the mantle wedge above the subduction zone. Stabilization of phlogopite in the mantle wedge provides a site for the introduced alkalis and Ba (e.g., Sekine and Wyllie, 1982) and formation of titanate minerals (such as sphene, rutile and perovskite) in the subducted slab or in the mantle wedge may have played an important role in the depletion of high field strength elements (e.g., Ti, Nb, Ta) in arc basalts. Recycling of this mantle wedge or the overlying lithosphere could introduce subduction zone related chemical and isotopic characteristics into the convecting asthenosphere.

The upward migration of highly incompatible element-enriched silicate melts from the low velocity zone (LVZ) beneath the continental and oceanic lithosphere (e.g., kimberlites, carbonatites, nephelinites) can be a continuous or episodic process responsible for local enrichments of incompatible trace elements. Although such enrichment processes should not be limited to the Archean and early Proterozoic, the more vigorous melting possible in the Precambrian mantle would promote such enrichment processes. This type of enrichment can be superimposed upon earlier enrichment events related to subduction zone processes. Such enriched lithospheric mantle commonly has a refractory major element composition, reflecting residual products of earlier melting event(s) (e.g., Frey and Green, 1974).

Recycling of the continental lithosphere by delamination (McKenzie and O'Nions, 1983) or thermal erosion, and the subduction of oceanic lithosphere (Hofmann and White, 1982, Ringwood, 1982) introduces compositionally distinctive sources into the convecting mantle. Such material can be preserved as coherent entities through billions of years of convection. Thermal reactivation of enriched ancient continental lithosphere by plume activity or rifting may also play an important role in the generation of some continental basalts.

There are different opinions regarding the fate of the subducted oceanic lithosphere. It could have been continuously stretched and eventually well mixed back into the convective upper mantle (e.g., Allegre and Turcotte, 1986). Alternatively, due to the density barrier at 670 km caused by phase transformations, the subducted oceanic crust and refractory harzburgite lithosphere beneath it may buckle and accumulate at the base of the upper mantle (e.g., Ringwood, 1982; 1986). Subduction of some part of the oceanic lithosphere into the lower mantle may be possible (Creager and Jordan, 1984). In Ringwood's model, the megalith accumulates at the base of the upper mantle and warms up after some hundreds of millions of years. Partial melts of the former oceanic crust may fertilize the surrounding refractory harzburgite. The dense former basaltic oceanic crust may then sink into the lower mantle. Once the harzburgite is thermally equilibrated it becomes intrinsically lighter than the surrounding and overlying mantle and ascends. These refractory peridotite diapirs are considered to give birth to mantle plumes or blobs that are enriched in incompatible elements due to equilibration with residual garnetite minerals, which are stable at 400-600 km depths (Ringwood, 1982).

b. Factors influencing chemical and isotopic characteristics of basaltic magmas

The distinctive chemical and isotopic characteristics of basalts from different tectonic environments can be attributed to the following factors:

1. The source characteristics, which are a function of its previous history
2. Present tectonic environment of magma generation
3. Magma generation conditions and processes
4. Mixing of different mantle source regions

As discussed in the earlier section, core - mantle - crust differentiation and geodynamic processes have contributed to the formation of a chemically and isotopically heterogeneous mantle. Modern processes operating in the source regions produce further modifications to the chemical compositions of basalts.

In addition to the effects of source mineral composition, pressure, temperature and mineral/melt partition coefficients (K_d), magma generation processes can also affect the composition of the resulting melt. Segregation of melts from a mantle diapir involves mixing of migrating melts formed under different conditions (e.g., Oxburgh and Turcotte, 1968; Langmuir et al., 1977; Hanson, 1977; McKenzie, 1984). At present numerical modelling of melt migration and separation is very much dependant upon basic assumptions. Detailed studies of ophiolites, alpine peridotites and ultramafic xenoliths greatly help in evaluating the dynamic processes involved in melt generation and segregation (e.g., Nicolas, 1986). If the mantle is veined as a result of melt migration, low temperature melting will selectively sample areas near these fertile veins. At higher temperatures the degree of partial melting increases, and the refractory non-veined peridotite becomes progressively more involved in melting (e.g., Sun and Hanson, 1975a; Hanson, 1977; Zindler et al., 1984). Finally, mixing of a diapiric plume with the asthenosphere and/or lithosphere through which it passes can be reflected in the erupted basalts. Hot and dense tholeiitic and picritic magmas may interact extensively with the lithosphere and crust to induce further melting. On the other hand, due to their volatile-rich character, alkali basalts rise rapidly to the earth's surface, often carrying mantle xenoliths, and generally escape significant contamination.

3. *Chemical sytematics of oceanic basalts*

Since chemical and isotopic characteristics of basalts are governed by their source character, the tectonic environment of magma generation, and magma generation processes, it is logical to expect systematic compositional variations caused by these factors. In this section we will present some chemical regularities observed in oceanic basalts (OIB and MORB) and relate the detailed chemical variations in different groups of oceanic basalts to their isotope character.

a. Systematic relationships amongst incompatible trace elements

During partial melting of mantle peridotite the incompatible elements are concentrated into the magma. When two incompatible elements have identical mineral/melt K_d during partial melting their abundance ratio in the magma reflects that of their source, regardless of the degree of partial melting, i.e., their abundance ratios do not vary with increasing concentrations in the magma. In contrast, the ratios of incompatible elements having different K_d values will vary with the degree of partial melting. The more incompatible an element, the more it will be preferentially enriched in the melt. On the basis of this simple rule we can establish the degree of incompatibility of trace elements in oceanic basalts during magma generation. Obviously, in different tectonic environments with different physical conditions and mineral assemblages, the order of element incompatibility may change significantly. Thus, such an approach is very useful in evaluating the viability of possible mantle processes.

To present trace element data graphically for the purpose of pattern recognition it is convenient to normalize it to the trace element abundances of the primitive mantle composition. This type of plot, established by Sun et al. (1979), has been called a 'spidergram' by Thompson et al., (1983) and an extended Coryell-Masuda diagram by Hofmann et al (1986). This is similar to the practice of chondrite normalization for the rare earth elements. Hofmann et al (1986) pointed out that there are potential problems in such normalization plots if the relative incompatibility of elements change with time. They found that the Ce/Pb and Nb/U ratios observed in OIB and MORB are nearly constant, 25±5 and 47±10 respectively, but quite different from the primitive silicate mantle ratios (9 and 30), indicating that processes operating in the early history of the earth (≥2 Ga) caused fractionation of Ce from Pb and Nb from U. Rb and Cs show similar behavior. Oceanic basalts have nearly constant Rb/Cs ratios of about 80, which is distinct from the primitive mantle value of 20±10 (McDonough et al., 1987). Taking these observations into account we have calculated our primitive mantle values for Pb based on a Ce/Pb ratio of 25 and Cs based on a Rb/Cs ratio of 80. The primitive mantle values used here are given in Table 1, the element concentrations in CI carbonaceous chondrites and the three different types of oceanic basalts shown for comparison.

Figure 1 presents the primitive mantle normalized patterns for typical N-type and E-type MORB and an oceanic alkali basalt with $^{87}Sr/^{86}Sr \sim 0.7035$. The data suggests that the order of trace element incompatibility in oceanic basalts is:

Cs~Rb(~Tl)~Ba(~W)>Th>U~Nb=Ta~K>La>Ce~Pb>Pr(~Mo)
~Sr≥P~Nd(>F)>Zr=Hf~Sm>Eu~Sn(~Sb)~Ti>(Li)>Ho=Y>Yb.

This order is mainly based upon the depletion pattern of N-type MORB and the systematics of concentration ratios observed in E-type MORB and OIB (Sun and Hanson, 1975a, 1976; Sun and Nesbitt, 1977; Sun et al., 1979; Sun, 1980; Newsom et al., 1986; Hofmann et al., 1986; Ryan and Langmuir, *in press*). The relative incompatibilities of these elements appear constant within oceanic basalts suggesting that fractionation processes involved in the generation of these basalts are simple and involve no drastic differences between the MORB and OIB sources. The consistent behavior of some characteristic elements, e.g., Y-Ho, Nb-Ta, Sr-Pr, Zr-Hf-Sm, Ti-Eu^{3+}, Ce-Pb, Nb-U, are consistent with the idea that the main control of mineral/melt K_d for these elements during oceanic basalt genesis is the presence of residual clinopyroxene and garnet (Fujimaki et al., 1984; Watson et al, 1985; Jochum et al., 1986). Furthermore, these constant elemental ratios suggest that zone refining melting and magma chamber processes such as mixing and extensive fractionation and replenishment (as discussed by O'Hara and Mathews, 1981), which could fractionate incompatible elements efficiently, are not dominant processes operating during the generation of primitive oceanic basalts. On the basis of this spidergram rule, when accurate analytical data are available for a few critical trace elements (e.g., Y, Ti, Zr, Sr, P, Nb, K, Rb), the concentrations of other elements on this plot can be estimated quite accurately. It can also be suggested that any large deviation from Nb/Ta = 17 and Zr/Hf = 36 in MORB and OIB are most likely due to analytical errors.

Since Sr ~ Pr, Pb ~ Ce and Hf ~ Sm on the spidergram plot (Fig. 1) and Sm, Pr and Ce are close to Nd , mixing of different mantle reservoirs having different spidergram patterns is expected to generate linear trends in plots of isotope ratios, e.g., $^{143}Nd/^{144}Nd$ versus $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$ versus $^{176}Hf/^{177}Hf$ and $^{87}Sr/^{86}Sr$ versus $^{206}Pb/^{204}Pb$.

The chemical regularities observed in basalts can be used to obtain information on the composition of the source and the processes and mineralogy involved in magma generation. The relatively constant but low concentration of K, coupled with high concentrations of Nb and La in some highly undersaturated alkali basalts, kimberlites and carbonatites suggests that K in the melts could be buffered by residual amphibole, phlogopite and clinopyroxene (under very high pressure) during source enrichment processes and/or magma generation (e.g., Sun and Hanson, 1975a; Clague and Frey, 1982). Such residual K-bearing minerals could also cause depletions of Rb, Cs and Ba in these magmas relative to their neighboring spidergram elements. If phlogopite is indeed the mineral holding back K, Rb and Cs in the source regions of undersaturated nephelinites, basaltic kimberlites and melilitites (Sun and Hanson, 1975a; Clague and Frey, 1982), then the near constant Ba/Rb (~12) and Rb/Cs ratios (~80) for most OIB requires that Ba and Cs have similar phlogopite/melt K_d's relative to Rb. Studies of U-disequilibrium series isotopes in OIB indicate that ≥20% U has been held back in the source, assuming that Th is perfectly incompatible (e.g., Oversby and Gast, 1968; Newman et al., 1984). Therefore, the variable K/U ratios observed in OIB alkali basalts (> a factor of 2) could be due to these combined effects in addition to original source variations.

b. Modification of the spidergram rule and exceptions to the rule

Among OIB samples with La ≥50 ppm, decoupling and lowering of Ti, Zr, Sr, P, K and Th abundances from their corresponding REE is common. A new set of relationships is developed for this suite of rocks (Table 2). These features may be due to factors such as saturation of minor minerals, changes in the residual mineral proportions (e.g., increase of garnet abundance with depth), a change of mineral/melt K_d, mantle metasomatism, and/or melting processes (e.g., if zone refining becomes important). For example, nephelinites from Oahu island have Ti/Eu ratios less than half of that commonly observed in alkali basalts (3000 versus ~6600 ± 700, respectively) and they are also depleted in Nb, Ta, Zr and Hf. It is very likely that these depletions are due to saturation of a titanate mineral in the source region (Clague and Frey, 1982).

Examination of the chemical and isotopic compositions of Group I and II kimberlite samples (Kramer et al., 1981; Smith, 1985; Smith et al., 1986; Muramatsu, 1985; Muramatsu and Wedepohl, 1985) reveals that in many respects Group I kimberlites are comparable to Bouvet type OIB, whereas Group II kimberlites are more akin to DUPAL type OIB (le Roex, 1986; and this volume). However, exceptions to these general comparisons are that both groups of kimberlites have higher La/Ce ratios, lower Sr/Nd ratios and commonly show Zr and Hf depletions relative to Sm. These differences are most likely due to melting under very different conditions (e.g., variable clinopyroxene/garnet ratios, P-T conditions and/or K_d's).

There are several reports of tholeiites and alkali basalts that are enriched in REE and Y relative to other incompatible elements (e.g., western Victoria, Australia [Frey et al., 1978; McDonough et al., 1985], Norfolk Island [Green, 1978], and the Hawaiian islands [Clague et al., 1982; Jacobs et al., 1986]). Some samples have negative Ce anomalies and concave downward REE patterns with relative enrichment of the middle REE. Recently, detailed microprobe studies by Nagashima et al (1986), Jacobs et al (1986) and Price (1987, pers. comm.) have detected small amounts of REE-rich carbonates and phosphates of secondary origin. It is therefore likely that post-magmatic alteration is responsible for REE-Y enrichment in these unusual samples.

c. Trace element-isotope correlations in major types of mantle sources of oceanic basalts

Combined Pb, Sr and Nd isotope studies of oceanic basalts demonstrate that the observed isotope variations in these rocks cannot be generated by a single mantle process or mixing of two distinct mantle reservoirs (e.g., Sun and Hanson, 1975b; Sun, 1980; Zindler et al., 1982; Cohen and O'Nions, 1982; Zindler and Hart, 1986; White and Hofmann, 1982; White, 1986; Hart et al., 1986; Allegre et al., 1986). To estimate the minimum number of end members required, different approaches have been taken. Zindler et al (1982) suggested that on a 3-dimensional plot of Pb, Sr and Nd isotopes, most oceanic basalts fall on or near a mantle plane defined by average N-type MORB ($^{206}Pb/^{204}Pb \sim 18.5$, $^{87}Sr/^{86}Sr \sim 0.7029$, $\varepsilon_{Nd} \sim +13$), St. Helena (~20.8, 0.7029, +5) and Kerguelen Island (~18.4, 0.7054, -1). White (1986) subdivided oceanic basalts into five distinct groups on isotope plots: MORB group (including Iceland, Galapagos, Easter Islands), St. Helena group (including Austral, Comores, Ascension), Kerguelen group (including Gough, Tristan da Cunha) Society group (including Marquesas, Samoa, Sao Miguel) and Hawaii island group. Most Society group samples clearly fall above the mantle plane of Zindler et al (1982) with higher $^{87}Sr/^{86}Sr$ at the same Pb and Nd isotope ratios. Zindler and Hart (1986) used different terminology to define the characteristics of mantle end members: DMM (depleted MORB mantle), PREMA (prevalent mantle, including Iceland, Galapagos, Easter Islands of White's MORB group and Hawaiian islands), HIMU (long term high U/Pb in the source, including St. Helena, Tubuai, Mangaia), EM 1 (enriched mantle type 1 for Kerguelen type), and EM 2 (enriched mantle type 2 for Society Island type). Their EM 1 samples from Walvis Ridge clearly fall below Zindler et al's (1982) mantle plane with lower $^{87}Sr/^{86}Sr$ at the same Pb and Nd isotope ratios (Fig. 2).

Different mantle processes have been proposed for the generation of the different isotope groups and end members. Since isotope variation is a function of parent-daughter abundance ratio and isolation time, the same mantle process taking place at different times and with different degrees of elemental fractionation will result in variable but coherent Pb, Sr and Nd isotopic compositions. Consequently, the "end members" proposed by Zindler and Hart (1986) would not be expected to have fixed isotopic compositions.

It is not surprising to find that the different mantle processes responsible for generating a variety of isotope groups also create distinct chemical signatures. Variations in spidergram patterns for the various mantle reservoirs reflect the effects of the different processes and environments involved. A comparison of Nb/Pb, Ce/Pb, Nb/U, K/U, K/Nb and Rb/Cs ratios, ratios which encompass elements considered to behave similarly during generation of oceanic basalts, for different OIB end members is presented in Table 3. The contrast between St. Helena and Gough samples is quite clear and there are consistent differences, especially for Nb/Pb and Ce/Pb ratios, in other OIB samples. Ratios involving K may be affected by the retention of K (Rb, Ba and Cs) in K-bearing residual minerals, as discussed in section 3a.

In Fig. 3 a St. Helena (2882) and a Gough island (G111) sample are used to illustrate the differences in their spidergram patterns. HIMU type mantle with low

$^{87}Sr/^{86}Sr$ (0.7027 to 0.7030) and very radiogenic $^{206}Pb/^{204}Pb$ ($\geq$ 21) is characterized by a low Rb/Sr ratio (0.01 to 0.03) and a high $^{238}U/^{204}Pb$ ratio ($\geq$30); such mantle materials tend to have low K/U and K/Nb ratios (related to K, Rb and Ba depletions). The spidergram patterns of St. Helena type mantle display a continuous decrease in the abundances of Nb to Cs, similar to typical MORB. In contrast, for EM type OIB with $^{87}Sr/^{86}Sr$ $\geq$0.7040 and lower $^{206}Pb/^{204}Pb$ ratios than St. Helena type mantle (<18.6 for EM1, 18.6 to 19.7 for EM2), the spidergram shows increased abundances of elements more incompatible than Nb (Cs, Rb, Ba, Th, U, K) and Pb as compared to the St. Helena type. Moreover, such OIB often have Ba spikes and high La/Nb ratios (sometimes higher than the chondritic ratio). This later point is illustrated by Fig. 4 which shows a linear correlation between Ba/Nb and La/Nb among OIB. These two ratios also correlate with $^{87}Sr/^{86}Sr$ in general. However, there are "exceptions", some EM samples (e.g., Group I kimberlites and Tutuila) have Ba/Nb $\leq$8 and La/Nb $\leq$0.8. Such differences are most likely due to the multiple origins of EM type OIB.

Lamproites from western Australia could also represent the extremely enriched EM2 type. They have a highly fractionated spidergram pattern (Fig. 5) especially from Nb to Rb. They have low in Sr and P, but high Pb and Zr abundances, reflecting a sedimentary component. Often, but not always, they have depletions of Nb relative to La.

4. *The generation of different mantle types and the Nb issue*

Ocean island alkali basalts with high K_2O ($\geq$ 2%) do not always have low μ values ($\leq$ 16) but it is generally true that ocean island alkali basalts with low K_2O (~1%) always have high μ values ($\geq$ 20). This correlation must be related to the source character and partial melting conditions. Several mechanisms have been proposed to generate the isotopic and chemical characteristics of different types of OIB mantle sources. The HIMU and low $^{87}Sr/^{86}Sr$ character of St. Helena type OIB have been attributed to the recycling of altered oceanic crust into the OIB source region (e.g., Zindler et al., 1982; Palacz and Saunders, 1986), mantle enrichment through melt migration from the low velocity zone into oceanic and continental lithosphere (e.g., Sun, 1980; Hart et al., 1986) or derivation of OIB from the lower mantle which has lost Pb by continuous core formation (e.g., Vidal and Dosso, 1978). However, Newsom et al (1986) showed that St. Helena basalts have the same Mo (highly chalcophile) to Pr (highly lithophile) abundance ratios as MORB and other OIB, effectively arguing against continuous core formation. The EM type character is generally considered to be related to processes associated with convergent margins, such as the recycling of sediments with oceanic crust (e.g., Hawkesworth et al., 1979; Cohen and O'Nions, 1982; White, 1985; Weaver et al., 1986). The formation of these OIB sources from remobilization or delamination of metasomatized continental lithosphere has also been proposed (e.g., McKenzie and O'Nions, 1983; Richardson et al., 1982; Hawkesworth et al., 1986).

Multiple origins for EM type is likely, including supperposition of different processes. Menzies (1983) suggested that EM 1 could be related to enrichment by the introduction of CO_2-rich silicate melt (e.g., kimberlite, nephelinite) whereas the high Rb/Sr, $^{87}Sr/^{86}Sr$ character of EM 2 is similar to some modern island arc basalts (e.g., White, 1985). Hart (1984) and Zindler et al (1986) emphasized that EM 2 is almost exclusively restricted to the southern hemisphere. It could have originated from the delamination of subduction zone related metasomatized continental lithosphere of Gondawanaland. However, they do not preclude the earlier suggestion by Hart (1984) that this regional EM type anomaly in the southern hemisphere existed since the Archean and might be controlled by global convection patterns. Hawkesworth et al (1986), on the other hand, favor the idea that the EM type mantle in the southern Atlantic (Gough, Walvis Ridge, Tristan da Cunha) has a shallow origin due to the thermal remobilization and detachment of the continental lithosphere of southern Africa from south America during the breakup of Gondawanaland. More recently, Hart et al (1986) pointed out that HIMU and EM 1 mantle types are often spatially related, and share the characteristic of lying below the mantle array on the ε_{Nd} (vertical axis) versus $^{87}Sr/^{86}Sr$ plot (Fig. 2). They suggested a subcontinental lithospheric mantle origin for both HIMU and EM 1 mantle types through mantle metasomatism by silicate melts.

Weaver et al (1986) emphasized the positive correlation between Ba/Nb, La/Nb and $^{87}Sr/^{86}Sr$ ratios of OIB (Fig. 4). They suggested that low Ba/Nb, La/Nb and the $^{87}Sr/^{86}Sr$ ratios of the HIMU type source can be explained by the melting of recycled subducted oceanic crust. Dehydration and partial melting of the oceanic crust during subduction may decrease its Ba and La (and other light REE) abundances relative to Nb (held back by a residual titanate mineral); whereas high Ba/Nb and La/Nb ratios of EM type samples can be explained by the mixing of ancient (1.5 to 2.0 Ga) subducted pelagic sediments with the subducted oceanic crust. However, when data of Koolau tholeiites, Oahu and the extended field of MORB are added (Fig. 6), it becomes obvious that Weaver et al.'s (1986) interpretations are nonunique. A more thorough evaluation of factors which can change the La/Nb and Ba/Nb ratios is needed.

a. The Nb issue

The low La/Nb ratio (relative to the chondritic value of 0.95) observed in some OIB, especially the HIMU type (Figs. 4 and 6), could reflect the mantle source character (Weaver et al., 1986) or be the result of small degrees of partial melting, since Nb is more incompatible than La (Fig. 2). The high La/Nb ratio found in many (most?) EM type basalts could be due to introduction of subducted sediment (with high La/Nb ratios) into the OIB source, or it could be due to the presence of a residual titanate mineral during magma generation. The effects of partial melting on La/Nb ratios can be assessed by several observations. Two MORB samples from 45°N in the mid-atlantic ridge (Chain 43- 104-16 and 104-18) have identical Pb, Sr and Nd isotopic compositions (Fig. 7 and data in the appendix). The sample that is light REE-enriched also has a much lower La/Nb ratio, consistent with it representing a lower percentage of partial melt derived from the same source as the light REE-depleted sample. Figure 8 shows similar partial melting effects on the La/Nb ratio of basalts from Loihi seamount and Haleakala flows on Maui. The tholeiites and basanites have similar isotopic compositions but the La/Nb ratios of the tholeiites are near chondritic, whereas the basanites have La/Nb ratios as low as the HIMU samples of Fig. 6. These data argue strongly against the idea that the HIMU source must have a low La/Nb ratio as a result of subduction of oceanic crust. Either the recycled oceanic crust model is incorrect, or the La/Nb ratio of the recycled oceanic crust has been increased before final diapiric rise. In terms of Ringwood's megalith model (1982), the increase of La/Nb might be caused by partial melting of the former oceanic crust in the presence of garnetite if the resulting melt fertilizes its neighboring refractory harzburgite. There are some preliminary experimental mineral-melt K_d data which are consistent with this interpretation (Kato et al., 1987). However, more precise and quantitative data are needed in order to further evaluate this possibility.

In addition to reflecting the source character, high La/Nb ratios in OIB can be produced if a residual titanate mineral is present during open-system processes in the source (e.g., metasomatic enrichment or partial melting). Nephelinites and basanites of the Honolulu series from Oahu are good examples (Fig. 8). They are depleted in Ti, Nb, Ta, Zr and Hf and have Ti/Eu ratios (~3000) less than half those normally observed in OIB (~6600, close to the chondritic ratio of ~7800). Clague and Frey (1982) suggested that a residual titanate mineral is responsible for the Nb depletion relative to La. In contrast to the Oahu case, EM samples from Walvis Ridge and Gough (Fig. 4) with high La/Nb ratios have Ti/Eu ratios close to the chondritic ratio, suggesting that a titanate mineral does not play a role in the generation of these basalts. We therefore agree with Weaver et al (1986) that the high La/Nb ratios of these EM type basalts reflect a mantle source characteristic, possibly resulting from the involvement of subducted sediments. However, we would emphasize that sediment subduction, along with the oceanic crust, is not an unique solution for the generation of EM type mantle. The addition of a fluid or melt derived from an altered subducted oceanic crust, with or without sediment, into the overlying mantle wedge or adjacent continental lithospheric mantle may also produce high Ba/Nb and La/Nb ratios.

b. MORB source connection of the HIMU type mantle

HIMU type OIB are characterized by very low $^{87}Sr/^{86}Sr$ (as low as 0.7027) similar to some N-type MORB, and high $^{206}Pb/^{204}Pb$ (~21.0), but low inferred Th/U ratio in the source (~3.3, see below). It is now generally accepted that the HIMU type mantle was originally derived from the MORB source reservoir more than a billion years ago, however there is disagreement regarding the processes responsible.

On Pb isotope ratio plots (Fig. 9) each HIMU island exhibits a small range of isotopic variation except for one St. Helena sample which has a much lower $^{206}Pb/^{204}Pb$ than the other St. Helena samples (19.68 compared to 20.70 to 20.96)(Cohen and O'Nions, 1982), which fall on the trends of most OIB data and point towards the MORB fields. To estimate the time of isolation for the HIMU type mantle, we use the Pb isotopic composition of the depleted upper mantle to calculate a two stage Pb isotopic evolution (Zartman and Doe, 1981) . The version II Pb isotopic growth curves for the depleted mantle suggested by Zartman and Doe (1981) are quite consistent with the available Pb isotope data for Archean and Proterozoic komatiites and basalts derived from depleted mantle, as well as Phanerozoic ophiolites. Feasible solutions to our calculations are evaluated by comparing the calculated μ_2 values ($^{238}U/^{204}Pb$) needed to generate the observed HIMU $^{206}Pb/^{204}Pb$ and the resulting $^{207}Pb/^{204}Pb$ values with the measured μ and $^{207}Pb/^{204}Pb$ values. These results (Fig. 10), indicate that the isolation time must be greater than one billion years, otherwise the μ value in the source would have to be higher than that measured in the magma, which is contrary to the fact that U is more incompatible than Pb (Fig. 1). However, the calculated $^{207}Pb/^{204}Pb$ value after one billion years of isolation is lower than the measured value, therefore a longer isolation time is required. Using a reasonable μ_2 value and considering $^{207}Pb/^{204}Pb$ heterogeneity (±0.05) in the Precambrian depleted mantle, we obtain an isolation time of 2.0 ± 0.2 Ga (Fig. 10). Since the HIMU source is related to the MORB source through mantle fractionation processes, it is not surprising that similar age information can be derived from the slope connecting HIMU data with the MORB field on Figure 9, assuming the slope represents an isochron. A mantle source isolation age calculated in this way for the other two oceanic islands - Tubuai and Mangaia, give 1.7 Ga (Palacz and Saunders, 1986), similar to the St. Helena case. An isolation time of about 1.0 ± 0.2 Ga is required to derive the most radiogenic $^{206}Pb/^{204}Pb$ ratio in the Ua Pou (Marquesas Archipelago) tholeiites (19.99) from a depleted MORB type mantle, assuming a reasonable μ_2 value of 20±2 in the mantle source. This is the youngest isolation time calculated for HIMU type OIB.

It is important to point out that if St. Helena, Tubuai, Mangaia and Ua Pou samples are not derived from pure HIMU end members, but either (1) contain an EM type component with low $^{206}Pb/^{204}Pb$ but high $^{207}Pb/^{204}Pb$, or (2) they are derived from a recently enriched high μ reservoir (e.g., St. Paul's Rock; Roden et al., 1984) followed by mixing with depleted asthenosphere, then the age of the HIMU isolation could considerably younger. Such an interpretation may apply to much of the non-HIMU OIB Pb isotope data (see section 5).

Model calculations for the $^{208}Pb/^{204}Pb$ evolution of St. Helena samples (Fig. 10) yield a Th/U ratio of 3.30 ± 0.05 in the mantle source. This value is lower than the measured Th/U ratios in St. Helena samples (3.5 to 3.8, Weaver et al., 1986; this paper), consistent with the fractionation of Th from U during OIB magma generation. Similar conclusions are reach through $^{230}Th/^{232}Th$ studies on young OIB (e.g., Oversby and Gast, 1968; Newman et al., 1984).

Recently, Dupuy et al (1987) presented a strong case for the presence of recycled oceanic crust in the HIMU type OIB sources based on their study of Ua Pou Island, Marquesas Archipelago. They emphasized that Ua Pou tholeiites are highly depleted in most incompatible elements (Ba, Rb, Th, U, K, Nb and light REE) and have spidergram patterns (Fig. 11) showing mirror images to those of island arc basalts, i.e., these tholeiites have high Nb/La, Ce/Pb, U/Pb, Hf/Lu ratios. Dupuy et al. suggested that the mantle source of Ua Pou tholeiites contains residual oceanic crust formed by dehydration and partial melting during subduction.

These unusual samples with concave downward REE patterns (Fig. 11) offer a rare opportunity to evaluate the recycled oceanic crust model. The tholeiites have high Ni (155-550 ppm), TiO_2 (3.7-4.1%) and Ce (61-78 ppm), comparable to other HIMU OIB considered in this study. Consequently, based on the arguments presented in section 4a, it would be reasonable to expect more than 20% fractionation of the La/Nb ratio during magma generation. The measured La/Nb ratio (0.85) of these tholeiites is higher than other HIMU OIB (St. Helena = 0.69, Ascension = 0.65, Mangaia = 0.77) but similar to EM type OIB of Tristan da Cunha (0.86). After a 20% correction for the partial melting effect is made, the mantle source for Ua Pou tholeiites has La/Nb = 1.06, which is greater than the chondritic ratio (0.96), i.e., it actually shows Nb depletion relative to La. The lack of a positive Nb kick relative to

La in their mantle source argues against the recycled oceanic crust model for the Ua Pou tholeiites, or at least makes it unnecessary.

The high Hf/Lu ratios (22-28) observed in the Ua Pou tholeiites have been used by Dupuy et al. to support the recycled oceanic crust model. However, since Hf is much more incompatible than Lu during OIB generation, this argument may not be valid. A comparison of Sm/Hf is more appropriate because these elements are similarly incompatible (Fig. 1). In fact, the Sm/Hf ratio of Ua Pou tholeiites (1.43) agrees well with the Sm/Hf value of our primitive mantle (Table 1) suggesting that Hf has not been fractionated from Sm by processes involved in the generation of HIMU type mantle. However, we agree with Dupuy et al. that the very high Ce/Pb ratios of Ua Pou tholeiites (38-78) are very unusual for OIB (25±5), but they are also much higher than other HIMU type OIB shown in Table 2. We do not have a good explanation for this anomaly.

The Nd isotope data presented by Dupuy et al. (1987) require that the mantle source of Ua Pou tholeiites has a Sm/Nd ratio lower than chondrite, after isolation from the MORB type source about 1 billion years ago. To combine this information with Nb and REE data, we suggest that this mantle has a concave downward REE pattern with Nb depletion similar to the pattern of many Hawaiian tholeiites (e.g., Fig. 8).

In order to make a correct choice between the two processes proposed for generation of the HIMU type mantle, i.e., through recycling of altered oceanic crust or migration of silicate melt from the depleted mantle into the lithosphere, critical evaluation of the two processes is required. If the oceanic crust recycling model is correct, then alteration and subduction of this crust (dehydration and partial melting) must increase the U/Pb ratio by a factor of 2 without significantly affecting the Rb/Cs, Rb/Sr, Th/U, Ce/Pb ratios. This does not seem likely. Furthermore, dehydration and partial melting is an effective "depletion" mechanism. In order to generate a St. Helena type OIB source character an enrichment process after subduction, such as megalith melting (Ringwood, 1982), is required. At present, there is no experimental data to show how these trace elements (and La/Nb ratio discussed earlier) will be fractionated during partial melting in the garnetite stability field. On the other hand, upward migration of CO_2-rich silicate melts such as kimberlite, carbonatite and nephelinite from the low velocity zone at the top of the depleted asthenosphere can be an effective mechanism to achieve the HIMU characteristics (e.g., Green, 1971; Kay, 1979; Sun, 1980; Menzies and Murthy, 1980; Hart et al., 1986). These CO_2-rich silica undersaturated melts have low Rb/Sr but high U/Pb ratios (see section 3a) and match the characteristics of the HIMU type. The choice between oceanic and continental lithosphere for the HIMU reservoir will be evaluated in section 4d.

c. Subduction zone processes and EM type mantle

EM 2 type mantle with high Rb/Sr and $^{87}Sr/^{86}Sr$ is commonly considered to be a product of the migration of water-rich fluids or melts enriched in K, Rb and Ba associated with subduction zones (e.g., Menzies, 1983; White, 1985; Zindler and Hart, 1986); whereas the chemical and isotopic character of EM 1 type mantle, with high Ba/Nb and La/Nb ratios, has been interpreted by Weaver et al (1986) as the product of sediment subduction. In this section we will point out some weaknesses of the subduction zone related models, emphasize the need for alternative mechanisms and propose more definite tests for sediment involvement in OIB sources.

As discussed earlier, high Ba/Nb and La/Nb ratios observed in many EM type OIB are not necessarily indications of sediment involvement in their source. Except for Gough, Walvis Ridge, Kerguelen and Aitutaki (Table 3), there is a general lack of strong trace element indication of sediment recycling. Mixing 1% of pelagic sediment with subducted oceanic crust (or 0.2% for MORB type peridotite mantle) is expected to change the Nb/U, Ce/Pb and Rb/Cs ratios considerably from nearly constant values (47± 10, 25 ± 5, 80 ± 20) for MORB and OIB (Hofmann and White, 1983; Hofmann et al., 1986). However, if subduction of sediment is invoked to explain the isotope evolution and the development of negative Eu anomalies in some EM type mantle (see below), then some modification of this simple mixing is required. In this connection, it is interesting to note that the Nb/U ~ 34, Ce/Pb ~ 13, Rb/Cs ~123 (Fig. 5) of Miocene lamproites from western Australia (Jaques et al., 1987) are not very different from values for MORB and OIB mentioned above. Isotope and trace element studies of these lamproites (extreme EM 2 types) strongly suggests the involvement of sediments in their mantle source (Fraser et al., 1985; Nelson et al., 1987; Jaques et al., 1987). Since the EM type OIB in Table 3 require much less sediment involvement than these lamproites, the lack of a large amount of variation in Nb/U, Ce/Pb and Rb/Cs ratios may not be a strong argument against involvement of a minor amount of sediment in some EM type mantle. Le Roex (this volume) has reached a similar conclusion for DUPAL type OIB in the South Atlantic. However, mixing of small amount of pelagic sediment with oceanic crust is not capable of generating the $^{208}Pb/^{206}Pb$ characteristics of the EM 1 type mantle in the South Atlantic. Using Pb isotope evolution curves for the depleted mantle and upper crust (sediment source) given in Zartman and Doe (1981), model calculation for sediment - oceanic crust mixing at 1.5 to 2.0 Ga and 50% Pb contributed by the sediment (as suggested by Weaver et al., 1986), requires a Th/U ratio of 5.0 to generate the observed $^{208}Pb/^{206}Pb$ ratio. This value (5.0) is much higher than the value (~3.7) estimated for the Tristan da Cunha source. In general, most oceanic basalts (EM, MORB, HIMU) come from source regions with Th/U ratios of ≤3.8, as has been demonstrated by $^{230}Th/^{232}Th$ studies, or by a reduction of 15% ± 5% of the measured Th/U of fresh basalts to correct for the Th/U fractionation during melting. In our opinion, EM 1 type OIB in the South Atlantic does not represent a mixture of sediment and oceanic crust. It is more likely to be derived from an enriched mantle wedge or lithosphere above the subduction zone, with some in put from the subducted sediments.

Secondly, the subduction zone environment is not required for at least some EM 1 type mantle. Enrichment can be achieved by silicate melt migration from mantle plumes with less depleted character than a MORB source (e.g., Bouvet, Hawaii or isotopically close to the primitive mantle). EM 1 generated this way will have higher Th/Nb and Th/Ta ratios than the HIMU type, whereas Ba/Nb, Rb/Nb and La/Nb ratios could be similar to the HIMU type due to low alkali character controlled by residual K bearing minerals and the fact that Nb is more incompatible than La. These characters are shared by some Group I kimberlites with $^{87}Sr/^{86}Sr = 0.704$ to 0.705 and some EM 2 - OIB such as Sao Miguel (White et al., 1979; le Roex, 1986). Le Roex (1986) emphasized that the trace element and isotope data for Group I kimberlites cannot be explained by the sediment subduction model. Instead they are probably evolved from less depleted or close to primitive mantle material.

Although the discussion presented above sounds negative towards the connection between sediment subduction and the formation of EM type mantle, we do believe that sediment subduction has left an important fingerprint on the geochemistry of at least some EM type OIB (e.g., Walvis Ridge, Gough, Kerguelen, Society Island, Samoan Islands). A recent carbon isotope study of OIB by Exley et al (this volume) lends some support to this belief. Further detailed geochemical studies of both EM 1 and EM 2 end members are required to firmly establish this case. We would suggest that accurate estimation of Eu anomaly in OIB can be of special importance. Sun and Hanson (1975a) suggested that the 2% to 5% positive Eu anomaly commonly observed in OIB is due to the existence of Eu^{2+} (≥ 10%) in addition to Eu^{3+} under mantle oxidation conditions and the fact that Eu^{2+} is more incompatible than Eu^{3+} and its neighboring Sm^{3+} and Gd^{3+}. Sediments derived from various terranes have different amounts of negative Eu anomaly (e.g., McLennan and Taylor, 1981), with up to 35% for modern crustal rocks. The available accurate REE data indicate that HIMU OIB have 4% to 6% positive Eu anomaly whereas EM 2 OIB from Samoan Islands and EM 1 OIB from Kerguelen show up to a 4% to 6% negative Eu anomaly (e.g., Sun and Hanson, 1975a, Palacz and Saunders, 1986; Newsom et al., 1986), consistent with the sediment subduction model. In contrast, EM type OIB from Gough and Tristan da Cunha have a 2% to 5% positive Eu anomaly despite our belief that sediment has been involved in their mantle source. Either the sediment subducted and ultimately incorporated into their source has a small negative Eu anomaly (i.e., from Archean terranes) and/or more likely the sediment effect has been compensated by an increase of the Eu^{2+}/Eu^{3+} ratio during source modification and magma generation under more reducing environments than other OIB.

d. Continental lithosphere connection of the DUPAL anomaly and the low Nd array.

Hart (1984) pointed out that EM type OIB are concentrated in the southern hemisphere, are globe encircling in extent, and are centered at latitude 30°S. He named this isotopically anomalous region the DUPAL anomaly region and suggested that it may have been in existence in the southern hemisphere since Archean times. In terms of the model, the occurrences of EM type OIB in the northern hemisphere, e.g., the Azores, Oahu Island (Koolau tholeiites) and the Japan Sea and continental alkali basalts, tholeiites and kimberlites, have to be considered as exceptions to the general rule or due to crustal contamination. Later, Zindler and Hart (1986) suggested that the enhanced rate of Pangean subduction into the DUPAL mantle (Anderson, 1982) may account for localization of EM2 type OIB in the southern hemisphere. If this interpretation is correct, then EM2 anomalies in the southern hemisphere are a relatively young, subduction related phenomena surrounding the Pangean continents, but are not circum-global. Furthermore, Archean and Proterozoic DUPAL-like anomalies observed in komatiites and galena and feldspar in granites of the southern continents (Africa, Australia, India), where there is abundant early Archean crust, are likely to be a result of crustal contamination. For example, some late Archean komatiites (and associated NiS mineralization) of the Yilgarn Block, Western Australia, have been contaminated by early Archean felsic crust which resulted in DUPAL-type Pb anomalies. In contrast, Hawkesworth et al. (1986) suggested that the DUPAL anomaly in the southern Atlantic (i.e., Walvis Ridge, Gough, Tristan da Cunha and the Discovery Table Mounts) may be of shallow origin and due to the thermal reactivation and detachment of the metasomatized lithosphere of southern Africa and South America before the breakup of Gondwanaland. The continental lithospheric delamination model of McKenzie and O'Nions (1983) is attractive because there is the opportunity to generate a variety of mantle types in the continental lithosphere within close proximity through subduction zone related and unrelated processes. The superposition of the products of different processes is possible. It also allows long term isolation of the enriched mantle within the lithosphere before delamination and recycling back into the convecting mantle.

More recently, Hart et al. (1986) also seem to favor an ultimate origin of the DUPAL anomaly from the continental lithosphere. They pointed out that EM1 and HIMU type OIB often show close association in occurrence and share the same character of long term low Rb/Sr ratio as compared to OIB within the mantle array on an $^{87}Sr/^{86}Sr$ versus ε_{Nd} plot (Fig. 2). HIMU and EM1 type OIB have lower ε_{Nd} values than the mantle array. There appears to be a lower limit on this plot for OIB data defined by connecting the HIMU and EM1 end members. Hart et al. (1986) named this limiting line a "LoNd" (low ε_{Nd}) array. (Since HIMU and EM1 are characterized by having lower $^{87}Sr/^{86}Sr$ values due to lower Rb/Sr ratios than samples within the mantle array, it might be more appropriate to call the array a "LoSr" (low $^{87}Sr/^{86}Sr$) array). They suggested that this LoNd array was developed within the subcontinental lithosphere through migration of silicate melts of different chemical and isotopic compositions (p. 1556): " . . . EM1 end member being slightly modified primitive mantle, and the HIMU end member being metasomatically produced, possibly during subduction episodes preceding lithosphere accretion." It is interesting to note that many of the Mesozoic and Cenozoic carbonatites of worldwide occurrences, not limited to the southern hemisphere, also fall on or close to this LoNd array (e.g., Bell and Blenkinsop, 1987; Dudas et al., 1987; Nelson et al., 1987). This is also true for some group 1 kimberlites (Kramer et al., 1981; Smith et al., 1983).

The close association of HIMU and EM type OIB in some ocean island or island groups of the southern Pacific (Vidal et al., 1984; Palacz and Saunders, 1986; Dupuy et al., 1987) and Walvis Ridge (Palacz, pers. com., 1986, and Fig. 6) does not offer a firm argument for identifying their birthplaces (e.g., continental lithosphere). Alternative mechanisms can be suggested, for example, mixing of different types of mantle reservoirs within the convective upper mantle. In addition, we would like to emphasize that isolated occurrences of HIMU (e.g., St. Helena, Ascension, Cameroon Line, Guadalupe) or EM (Gough, Tristan da Cunha, Kerguelen, Samoa) without the company of the LoNd counterpart are quite common.

The long isolation time (up to 2 Ga) required by the isotope data of OIB has been a major consideration of many people in favoring the model of continental lithosphere delamination. In this respect, it is surprising to see that the OIB members of the LoNd array have well defined isotopic correlations on Sr versus Nd and Pb versus Sr plots (Hart et al., 1986). Since the extent of low ε_{Nd} values below the main array is a function of Rb/Sr fractionation and isolation time, in addition to other

Hart et al. (1986) correctly pointed out that there are many EM1 type continental peralkaline basalts (e.g., Leucite Hills, Smoky Butte, etc.) which fall well below the LoNd array. The lack of an obvious influence of the low Nd array by these extremely low ε_{Nd} components from the continental lithosphere formed in the Archean (e.g., Dudas et al., 1987) may imply that (1) delamination of continental lithosphere with Archean isotopic signatures is not feasible or very minor in modern times, (2) metasomatized continental lithosphere formed at ≤ 2 Ga is abundant on the worldwide scale and dominates the scene, or (3) delamination of continental lithosphere is sufficient but not necessary for OIB generation, and survival times of ≤ 2 Ga in the convection mantle are possible (Gurnis and Davies, 1986). The last option will be further discussed in later sections.

A major drawback for the continental lithosphere delamination model is that there is a general lack of OIB samples showing strong subduction zone related chemical and isotopic characteristics which are commonly found in many continental mafic and ultramafic volcanic rocks. As shown in Figs. 5 and 12, strong depletion of Ti, P, Nb, Ta and Sr, but extreme enrichment of Pb and the presence of up to 20% negative Eu anomalies, reflecting sediment subduction effects (McLennan and Taylor, 1981), have been observed in many least fractionated post-orogenic and intraplate mafic to ultramafic peralkaline volcanics (group II kimberlites of southern Africa and lamproites from western Australia) which are considered to be derived form continental lithosphere modified by subduction zone processes (e.g., Thompson et al., 1984; Duncan et al., 1984; Jaques et al., 1987; Nelson et al., 1986). Among these samples there is often a positive correlation between the size of the negative Eu anomaly and the $^{87}Sr/^{86}Sr$ ratio (and Sr/Nd ratio?), reflecting the effect of subducted sediment which has high $^{87}Sr/^{86}Sr$, large negative Eu anomalies (~30% but variable depending on the source rocks) and low Sr/Nd ratios. In this connection, negative Eu anomalies observed in Samoan and Kerguelen alkalic basalts can be considered as a good indication of sediment involvement in their mantle sources.

Detailed chemical and isotopic studies of Mesozoic Karoo basalts of southern Africa, Parana basalts of South America, African kimberlites and modern DUPAL OIB in the south Atlantic (e.g., Duncan et al., 1984; Hawkesworth et al., 1986; Smith et al., 1983, 1987; le Roex, 1986) have offered a great opportunity to evaluate different models suggesting their source relationships and mechanisms of magma generation. Based on hot spot trace reconstructions and geochemical data, le Roex (1986) concluded that group I kimberlites are not DUPAL type (represented by Walvis Ridge and Gough Island) but are related to Bouvet and Marion-type hot spots, whereas group II kimberlites are related to the DUPAL islands. The group II kimberlites have higher $^{87}Sr/^{86}Sr$ (0.707 to 0.710), lower ε_{Nd} values (-5 to -12), and less radiogenic Pb isotopic compositions ($^{206}Pb/^{204}Pb \sim 17.2$ to 17.9) compared with the high P-Ti basalts of Parana and northern Karoo as well as the DUPAL islands of the southern Atlantic. As shown in Fig. 13, northern Karoo basalts have similar but still not quite the same spidergram as DUPAL OIB. If we accept the asthenospheric origin of DUPAL OIB and group II kimberlites, it seems reasonable to suggest that the geochemical difference between them as well as the northern Karoo basalts is due to the involvement of the continental lithosphere of southern Africa which has strong signature of sediment subduction combined with subduction zone processes (i.e., depletion in Nb, Sr, P and Ti, a negative Eu anomaly and an enrichment in Pb). Alternatively, this crustal signature is may be derived from Pangean sediment subduction.

A magnification of this subduction zone related character is shown in the southern Karoo basalts (Fig. 12) and Mesozoic low P, Ti Parana basalts of South America, which have more radiogenic Pb and Sr isotopic compositions but lower ε_{Nd} values than group II kimberlites and the high P, Ti northern Karoo and Parana basalts (Mantovanni et al., 1985; Hawkesworth et al., 1986; Smith et al., 1983). It is important to note that these isotopic and chemical characteristics of southern Karoo basalts are shared by Ferrar dolerites of the Trans-Antarctic mountains and the Tasmanian dolerites (Hergt et al., 1987). Cox (1978) suggested that the Mesozoic Gondwanaland flood basalts are probably a product of back arc volcanism related to subduction along the Pacific margin (i.e., close to the southern Karoo occurrence, Trans-Antarctic Mt. range and Tasmania versus northern Karoo). If his model is correct, involvement of subduction zone processes as well as melting of the Gondwanaland lithosphere could be responsible for the crustal characteristics (i.e., low Sr, P, Ti, Nb, and high Pb) of these types of basalts.

In our opinion, mantle plume activity induced by the thermal blanketing of the Gondwanaland supercontinent (Anderson, 1982) or induced by lithosphere subduction in the back arc environment could be the long lasting hotspot source for the DUPAL anomaly in the southern Atlantic and the Indian Oceans. Chemical and isotopic characteristics of the plume material can be modified by contributions from the subduction zone related processes (e.g., sediment subduction for low P, Ti basalts of southern Karoo and Parana) or interactions with the continental lithosphere (e.g., group II kimberlites). In this connection, we agree with Zindler and Hart (1986) that Pangean sediment subduction may have left its influence on the EM 2 type OIB in the south Pacific region too (e.g., Samoan and Society Islands OIB with negative Eu anomalies). Some residual effects from the recycled mantle wedge on the source character of the mid ocean ridges and volcanic arcs is also likely.

The alternative interpretation that the DUPAL anomaly in the south Atlantic is a result of thermal reactivation, remobilization and detachment of the southern African and south American lithosphere (e.g., Hawkesworth et al., 1986) has difficulty in explaining the lack of a strong signature of subduction zone processes (observed in southern Karoo, some Parana basalts) in the DUPAL OIB. Furthermore, the long lasting (>100 Ma) distinctive chemical and isotopic character of hotspot traces of the Cameroon line - St. Helena, Ninety East Ridge - Kerguelen, Walvis Ridge - Tristan da Cunha also favors a deep stable mantle origin.

On a worldwide scale, the lack of a strong subduction zone signature in OIB and MORB suggests that the effect of sediment subduction has been short-circuited in the volcanic arc, mantle wedge and continental lithosphere above it. The sediment does not subduct to as great a mantle depth (e.g., ≥500 Km) as the oceanic crust. Although earlier subduction zone effects have been detected in some young oceanic basins (e.g., Woodlark basin, SW Pacific; Perfit et al., 1980) and backarc basins (e.g., Cohen and O'Nions, 1982), the recycled wedge material in most cases is probably very refractory and poor in incompatible elements. Thus, it will have limited or no effect on MORB and OIB chemistry. However, delamination of continental lithosphere once situated above subduction zones should introduce a strong subduction zone signature into the convecting mantle. Unless the continental lithosphere is generally formed by non-subduction zone related processes such as plume underplating (e.g., Ringwood, 1982; McDonough and McCulloch, 1987) or alternatively, after subduction ceased, it has been strongly modified, on a worldwide scale, by upward migration of CO_2-rich silicate melts from the asthenosphere and/or intraplate magmatism (as observed in many mantle xenoliths), then the available chemical and isotope data of OIB raises serious doubts about the delamination of continental lithosphere in more recent times (≤ 2 Ga?).

5. *Mixing of OIB mantle reservoirs and interpretations of Pb isotope data*

On a combined Pb, Sr and Nd isotope ratio plot, the fields for 5 OIB groups defined by White (1985) all extend towards, and overlap with, the MORB group, suggesting mixing with MORB type reservoir. Little mixing appears to have occurred between the four other groups. Detailed geochemical studies of seamount basalts from the north Pacific by Zindler et al. (1984) document small scale heterogeneities in the mantle sources for the basalts. On the other hand, systematic studies of MORB collected circum-global have shown large scale regional heterogeneities and large scale mixing of different mantle types (e.g., Schilling et al., 1985).

Since the isotopic characteristics of distinct mantle types is an integrated product of fractionation of parent-daughter elements and isolation time, no fixed end member should be expected. Consequently, mantle mixing with 4 to 5 component fields in Sr, Nd and Pb isotope space will generate a volume of mixing products. The mantle plane suggested by Zindler et al. (1982) contains most of the OIB data, but it is only an approximation.

Often in a single island or island group, more than one mantle type can be sampled. For example, Li and Hart (in press) suggested that four mantle components (PREMA, primitive mantle, ancient recycled oceanic crust and MORB source) are required to explain the Pb, Sr and Nd isotopic variations observed in Hawaiian basalts. Combined isotope and trace element studies can offer important constraints on the geometric relationships of different types of magma sources and magma generation processes. It is now well established that Hawaiian post-erosional alkali basalts have lower $^{87}Sr/^{86}Sr$ but higher ε_{Nd} than the underlying shield-building tholeiites and associated pre-erosional alkali basalts (e.g., Chen and Frey, 1983; Li and Hart, in press). In terms of the relative isotopic characteristics of alkali basalts versus tholeiites, the Hawaiian situation is the opposite of that observed for seamount basalts by Zindler et al. (1984), who suggested that the isotopic differences between the alkali basalts and tholeiites are due to different degrees of melting of a veined mantle. The isotope data suggest that interaction of the mantle plume (source for tholeiites) with the oceanic lithosphere and/or its immediately underlying asthenosphere is important, especially for the post-erosional alkali basalts (e.g., Sun, 1980; Chen and Frey, 1985; McDonough et al., 1985). The inverse correlations between La/Ce, Nb/La and Ba/La with $^{87}Sr/^{86}Sr$ observed in many Hawaiian basalts have been interpreted as the result of a combination of mixing of different mantle sources and the effects of variable degrees of partial melting. In Fig. 14 a and b, $^{87}Sr/^{86}Sr$ versus Ba/La and La/Nb, respectively, are shown for the Hawaiian basalts. Post-erosional alkali basalts with low $^{87}Sr/^{86}Sr$ are mainly derived from a MORB-type source at the base of the Hawaiian oceanic lithosphere and/or in the asthenosphere immediately below it. Strong fractionation of Ba/La and La/Nb ratios from those of the MORB source is consistent with the idea that they have quite different incompatibility on the spidergram.

In view of the high frequency of inferred mantle mixing phenomena, it is desirable to reconsider the age significance of the Pb isotopic data for OIB. Earlier we suggested that Pb isotope data for HIMU type OIB indicated source isolation ages ranging from 1.0 (Ua Pou) to 2.0 Ga (St. Helena). Except for those OIB samples from individual islands having negative slopes on $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagrams indicating mixing of different types of mantle, the interpretation of other OIB data is not so straightforward. Some EM2 type OIB from the Society Islands and Sao Miguel have high $^{207}Pb/^{204}Pb$ values and each island group exhibit a steep slope on a plot of $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$. It is likely that this high $^{207}Pb/^{204}Pb$ character is related to sediment subduction (see section 4a), as suggested by White

(1985). This interpretation may also apply to Kerguelen samples.

Good regression lines are also found for basalts from the Hawaiian Islands (0.94 Ga), Canary Island (1.7 Ga), Iceland (1.5 Ga), Ross Island (1.3 Ga) and the northeastern Pacific seamounts (1.8 Ga). Gough Island and the Discovery Tablemount basalts have small range of $^{206}Pb/^{204}Pb$ and shallow slope on the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram and yield an age close to zero, whereas Walvis Ridge data give an age of about 0.8 Ga. Whether or not these regression lines have any age significance is not clear. For example Stille et al. (1986) emphasized the mixing character of the Hawaiian basalts and suggested that the ~0.9 Ga regression slope has no real age significance, although they felt that the general OIB-MORB trend reflects an 1.5-2.0 Ga isolation age from the MORB source for Iceland, Galapagos and Easter Island.

A good example to illustrate the nonunique solution of the ~1.8 Ga Pb-Pb isochron of OIB data is given by the study of the St. Paul's Rocks in the equatorial Atlantic (Roden et al., 1984). These peridotites have young Sm-Nd and Pb-Pb isochron ages ($\leq$ 200 Ma) corresponding to the time of metasomatism in the mantle. The high $^{206}Pb/^{204}Pb$ (up to 19.8) and $^{238}U/^{204}Pb$ ratios in the rocks allow $^{206}Pb/^{204}Pb$ to evolve to high values quickly. Mixing of this type of mantle with depleted MORB source can generate Pb-Pb slopes similar to those of Canary and Ross Islands. However, it is important to point out that the St. Paul's sample SE-6 with the least radiogenic Pb ($^{206}Pb/^{204}Pb = 18.63$, $^{87}Sr/^{86}Sr = 0.70347$) has unusually high $^{207}Pb/^{204}Pb$ (15.61) for OIB of this type with low $^{206}Pb/^{204}Pb$ and $^{87}Sr/^{86}Sr$.

On the basis of this analysis, we conclude that the available Pb isotopic data for OIB allows for mantle isolation ages ranging from a few hundred Ma to up to 2.0 Ga. Further research is required before an unique solution for individual island and island groups can be obtained.

6. Mass exchange between the crust and mantle

Ever since the plate tectonic theory became well accepted, the idea of continuous recycling of crustal material into the mantle has received attention. It is hydrothermal alteration, back into the mantle through meteorite bombardment (during the early history of the earth) and lithosphere subduction or delamination must have generated chemical and isotopic heterogeneity in the mantle. The survival of large scale and long term mantle heterogeneities became possible when the earth's thermal engine slowed down and mantle convection became less vigorous. The magnitude of crustal recycling processes would also be expected to be reduced with time. In this section we present arguments to (a) support Hofmann et al.'s (1986) suggestion that sediment recycling has not been a dominant mechanism in producing isotope variations observed in the mantle since ~2 Ga ago, (b) show that the upper mantle is not an exact complimentary reservoir to the continental crust and that irreversible mass exchange and elemental fractionation between the upper and lower mantle is required.

a. mass exchange between the crust and upper mantle

Armstrong (1968, 1981) suggested that the continental crust is mainly formed during the Archean and has reached a steady-state growth at present. Recycling of continental crustal material is required to keep Pb and Sr isotope growth in the depleted mantle. In contrast, Hofmann et al. (1986) emphasized that the observation of constant Ce/Pb (25±5) and Nb/U ratios (47±10) in MORB and OIB would argue against significant amounts of sediment recycling into the convecting mantle since ~2 Ga ago, as sediment involvement will greatly affect these ratios. We have also shown in this paper that, except for some EM type OIB, there is a general lack of sediment signature in the spidergrams of OIB and MORB. We would suggest that subduction of sediment at the convergent margins has been short-circuited within the mantle wedge above the subduction zone. This idea is consistent with a detailed geochemical study of alkali basalts in the Japan Sea region by Nakamura et al. (1985). Consequently, in order to keep the depleted MORB source isotopically alive, input from OIB source and subcrustal lithosphere in the upper mantle and/or from the lower mantle is required.

b. Mass exchange between upper and lower mantle

Gast (1968) first suggested that the geochemical characteristics of MORB sources are mainly a product of extraction of small amounts of alkali basalts. In contrast, some lithosphere recycling models require resorption of the subducted oceanic crust into neighboring fertile mantle peridotite in order to regenerate the MORB source (Allegre and Turcotte, 1986). It is obvious that a combination of these two processes is likely to be operative in the mantle. In terms of the lithosphere recycling model, the MORB source in the upper mantle is most likely to be the compliment to the continental crust. This hypothesis can be tested by a mass balance calculation.

There are various model estimates of elemental abundances in the bulk crust, but they generally vary within a factor of two (e.g., see summary by Taylor and McLennan, 1985). In Table 4 we use the primitive mantle composition presented in Table 1 and estimates of crustal abundances by Taylor and McLennan (1985) to perform some simple calculations. To satisfy crustal abundances of highly incompatible elements (e.g., Ba, Rb, Cs, Th and U), 25-30% (volume of the upper mantle) of primitive mantle is required. Using higher estimates of element abundances in the crust, up to 50% primitive mantle is required. Furthermore, if the continental lithosphere is globally or locally enriched in incompatible elements, then depletion of an even higher portion of the convecting mantle is required. According to the calculations in Table 4, the residual MORB source in the upper mantle should have a fertile major and trace element composition, similar to those of the fertile ultramafic xenoliths studied by Jagoutz et al. (1979). Despite all uncertainties involved in this calculation, it is clear that a major discrepancy between the calculated and observed La/Na ratios requires special attention. We have argued that the lack of obvious positive Nb kicks in the MORB and OIB sources and continental lithosphere requires a mechanism to fractionate Nb from La, or preferentially withdraw former oceanic crust with low La/Nb ratios from the upper mantle. This can be achieved by subduction of oceanic lithosphere (Creager and Jordan, 1984) or subtraction of refractory eclogitic material from the megalith into the lower mantle (Ringwood, 1984). Preferential withdrawal of Nb from the upper mantle can also reduce the discrepancy between the calculated and measured Nb/U ratio of the depleted mantle shown in Table 4. A plot of La/Ta versus La/Sm ratios for MORBs from the literature, along with our estimates of the primitive mantle, is shown in Fig. 15. It is quite clear that transitional type MORB and some N-type MORB with light REE depleted to slightly enriched patterns (La/Sm ~ 0.8 to 1.8) have Ta kicks (La/Ta < 17). These results are consistent with the idea of recycling and resorption of the subducted former oceanic crust into the asthenospheric mantle source for these MORB.

c. formation of heterogeneous MORB sources

In our opinion, recycled former oceanic crust is not simply resorbed and mixed into neighboring fertile peridotite and refractory former oceanic lithosphere to regenerate a homogeneous MORB source. The heterogeneities in the trace element and major element abundances observed in MORB call for a more sophisticated model. It is important to note that light REE enriched MORB from plume-ridge segments (e.g. Azores platform) commonly show refractory residual characters in major elements (very low in FeO, Na_2O) compared to samples from normal ridge segments (e.g., Langmuir and Hanson, 1980). The chemical and isotopic data for this type of MORB would imply that the plume source is refractory in major elements (former lithospheric harzburgite?) and was fertilized before plume diapirism. Such enrichment could be achieved through upward migration of silica undersaturated melts from the low velocity zone into oceanic lithosphere before subduction (Kay, 1979). It could also be achieved through the megalith melting process suggested by Ringwood (1982). In contrast to the case of the Azores platform, low-K tholeiites from Iceland often show high abundances of FeO and they have positive Nb kicks on the spidergram plot (e.g., Wood et al., 1979). It is likely that the Iceland plume has received more than its share of recycled former oceanic crust.

A uniformly depleted MORB reservoir which is homogenized through convective mixing may also have added to it a component from the recycled mantle wedge above the subduction zone, and plumes or blob components derived from the lower mantle or base of the upper mantle where subducted former lithosphere may accumulate. A veined and plum-pudding type upper mantle with various scales of old and young heterogeneity can be generated this way.

7. *Towards an integrated mantle evolution model*

A Combined trace element and isotope approach is very useful for evaluating the various mantle processes involved in the generation of OIB sources. Figure 16 emphasizes some controlling factors which can generate distinct features on the OIB spidergram. The effect of sediment subduction can superimpose a crustal signature (e.g., positive Pb and negative Eu anomaly) onto the general pattern. Residual phlogopite may not only hold back K and Rb, but also Ba and Cs. Partial melting under very high pressure conditions (e.g., kimberlite generation) with changing mineral assemblage, mineral-melt K_d and melting process, may greatly modify the spidergram rules. Ringwood (1982) suggested that enrichment of refractory harzburgite in a subducted megalith by partial melting of the former oceanic crust near the 650 km phase transition can be a potential source for OIB. It is expected that during high pressure melting, fractionation of some elements between minerals with either a garnetite or perovskite structure and the coexisting melt can be quite different from melting under low pressure (Kato et al., 1987). Consequently, detailed studies of element ratio systematics (e.g., Ba-Rb-Cs, Nd-Sr, Nb-La, P-Nd, Ti-Eu, Sm-Zr) and the effect of changing mineralogy on K_d under different pressure and temperature conditions, are worthwhile to pursue. Such differences in mineral assemblage and melting condition may also be responsible for two types of light REE patterns observed in OIB: (1) the predominant pattern showing a continuous increase from heavy REE to light REE with La/Ce = 0.46 (±10%) and (2) a less common type shows concave downward light REE patterns as in Ua Pou tholeiites (Fig. 11) and most Hawaiian tholeiites.

Fairly constant Ce/Pb (25±5) and Nb/U (47±10) ratios observed in MORB and OIB (Hofmann et al., 1986) are fractionated from values in the primitive mantle. Hofmann et al suggested that these ratios were fractionated in the early history of the earth (≥2 Ga) through subduction zone process. Since then, subduction zone processes have only introduced minor noise. The depleted mantle was rehomogenized before intra-mantle differentiation to form various types of OIB and MORB sources. At this time no further significant fractionation of Ce/Pb and Nb/U ratio has been observed. In terms of this model, mantle heterogeneities found in the various OIB type sources are mainly related to subduction and recycling of the oceanic lithosphere.

Since the bulk crust has a factor of two higher La/Nb ratio and the MORB and OIB mantle sources have La/Nb ratios about equal to the primitive mantle value, then a Nb rich component is missing from the upper mantle - crust system. We suggest that this component has been introduced into the lower mantle through lithosphere subduction and is identified with sinking refractory eclogite (former oceanic crust) from the megalith (Ringwood, 1982). This irreversible process could continuously modify the geochemical (e.g., possibly explaining the Rb and Cs budget of the earth McDonough et al., 1987) and geophysical character of the lower mantle. Furthermore, subduction of oceanic lithosphere, possibly with a metasomatized enriched base, may introduce enriched reservoir material into the lower mantle.

If whole mantle convection was important in the early earth history then we suggest that element fractionation in the lower mantle has also been affected as a result of its involvement in crust formation and mantle differentiation (MORB-OIB). The total absence of OIB with primitive mantle element ratios (Rb/Cs ~ 20, Nb/U ~ 30, Ce/Pb ~ 9) or ratios very different from those observed suggest that the different OIB type sources are only derived from a limited portion of the earth's mantle (≤ 1000 Km?) which has been previously well mixed with the MORB reservoir.

Pb and Nd isotope data of HIMU type OIB require source isolation age 1.0 to 2.0 Ga with long term, slightly light REE enriched pattern. The 2.0 Ga age may correspond to a major thermal event in the earth's crust. Large amounts of HIMU and possibly EM 1 type OIB reservoirs might have been formed from the depleted asthenosphere through migration of silica undersaturated melts from the low velocity zone into oceanic and continental lithosphere. In view of the limited amount of continental lithosphere available for recycling and a general lack of crustal and subduction zone signatures in OIB, we favor the idea that the HIMU source character is generated by the recycling of oceanic lithosphere.

Due to the problem of mantle mixing, no unique isotope isolation age can be established for EM 1 type mantle with confidence; whereas trace element and isotope data of the EM 2 type mantle seem to suggest the involvement of recently subducted sediments. A range of source isolation ages from a few hundred million years to 2 billion years are possible for EM type reservoirs.

The geometric relationship between the different types of OIB type sources and the depleted upper mantle asthenosphere (MORB source) cannot be clearly established as yet. However, it is evident that many of the OIB sources are derived from greater depths in the form of mantle plumes or isolated blobs.

Forward modelling, combining information from high pressure (≥ 200 Kb) experimental petrology, geophysical observations and more sophisticated numerical modelling of mantle convection, will greatly improve our understanding of the physical consequences of plate tectonic activities. Only after we have a better understanding of these physical processes will numerical modelling of mantle evolution become more realistic.

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Figure Captions

Figure 1. Primitive mantle (modified) normalized abundance patterns for moderately to highly incompatible elements in average N-type and E-type MORB and oceanic alkali basalts with $^{87}Sr/^{86}Sr \sim 0.7035$.

Figure 2. Schematic diagram of ε_{Nd} versus $^{87}Sr/^{86}Sr$ plot of OIB data to show fields of different types of oceanic basalts, and the end member assigned by Zindler and Hart (1986). Modified from Hart et al. (1986).

Figure 3. A comparison of spidergram patterns of basalts from St. Helena (2882) and Gough Iland (111).

Figure 4. Shows positive correlation between Ba/Nb and La/Nb ratios of HIMU (low $^{87}Sr/^{86}Sr$) and EM (high $^{87}Sr/^{86}Sr$) type OIB. Data sources: Weaver et al. (1986), Palacz and Saunders (1986), Richardson et al. (1982) and this paper.

Figure 5. Spidergrams of EM2 type Miocene lamproites from the West Kimberley and 1.2 Ga lamproites from East Kimberley of Western Australia. Data source: Jaques et al. (1987).

Figure 6. Shows correlation between Ba/Nb and La/Nb ratios of basalts from St. Helena, Ascension, Tristan da Cunha and Walvis Ridge (modified from Weaver et al., 1986). Data of Koolau tholeiites, N-type MORB, Group II kimberlites and sediments are added for comparison.

Figure 7. Comparison of spidergrams for two MORB samples from 45°N on the mid-Atlantic ridge. they have the same Pb, Sr and Nd isotope composition. Data sources: Whtie and Hofmann (1983), and this paper.

Figure 8. Comparison of primitive mantle normalized patterns of Rb-Ba-Th-K-Nb-La-Ce-Nd for selected Hawaiian basalts. Data sources: Clague and Frey (1983), Frey and Clague (1983), Staudigel et al. (1984), Chen and Frey (1985).

Figure 9. Simplified $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ plot for oceanic basalts from mid-ocean rige (MORB), Walvis Ridge (W), Hawaiian Islands (H), Kerguelen (K), Gough (G), Tristan da Cunha (T), Society Islands (S), Ascension (A), Ua Pou (U), Ross Island (R), Canary Islands (C), Bouvet (B), St. Helena (St. H.), Tubuai (T) and Mangaia (M). Data sources: Sun (1980), Stille et al. (1986), Richardson et al. (1982), Vidal et al. (1984), Palacz and Saunders (1986), Wright and White (1986), Dupuy et al. (1987), Cohen and O'Nions (1982).

Figure 10. Model calculations for Pb isotope evolution of a St. Helena sample (2882) assuming it was derived from a depleted upper mantle MORB type source some time ago. When an isolation time is assigned, specific values of μ_2 and κ_2 are required to match the measured $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios. At 2.0 Ga, model calculations give the best solution to match the measured $^{207}Pb/^{204}Pb$ and μ value.

Figure 11. Spidergrams of two HIMU type OIB samples from Ua Pou. They have concave downward patterns in the light REE region. Data from Liotard et al. (1986) and Dupuy et al. (1987).

Figure 12. Spidergrams of two selected, least fractionated basalts from southern Karoo and central Karoo. They show strong signatures of sediment and subduction zone related processes. Data from Duncan et al. (1984).

Figure 13. Spidergrams of two selected, least fractionated basalts from northern Karoo. They have similar $^{87}Sr/^{86}Sr$ ratios but have lower ε_{Nd} values than DUPAL-type OIB from the south Atlantic ocean. Data from Duncan et al. (1984).

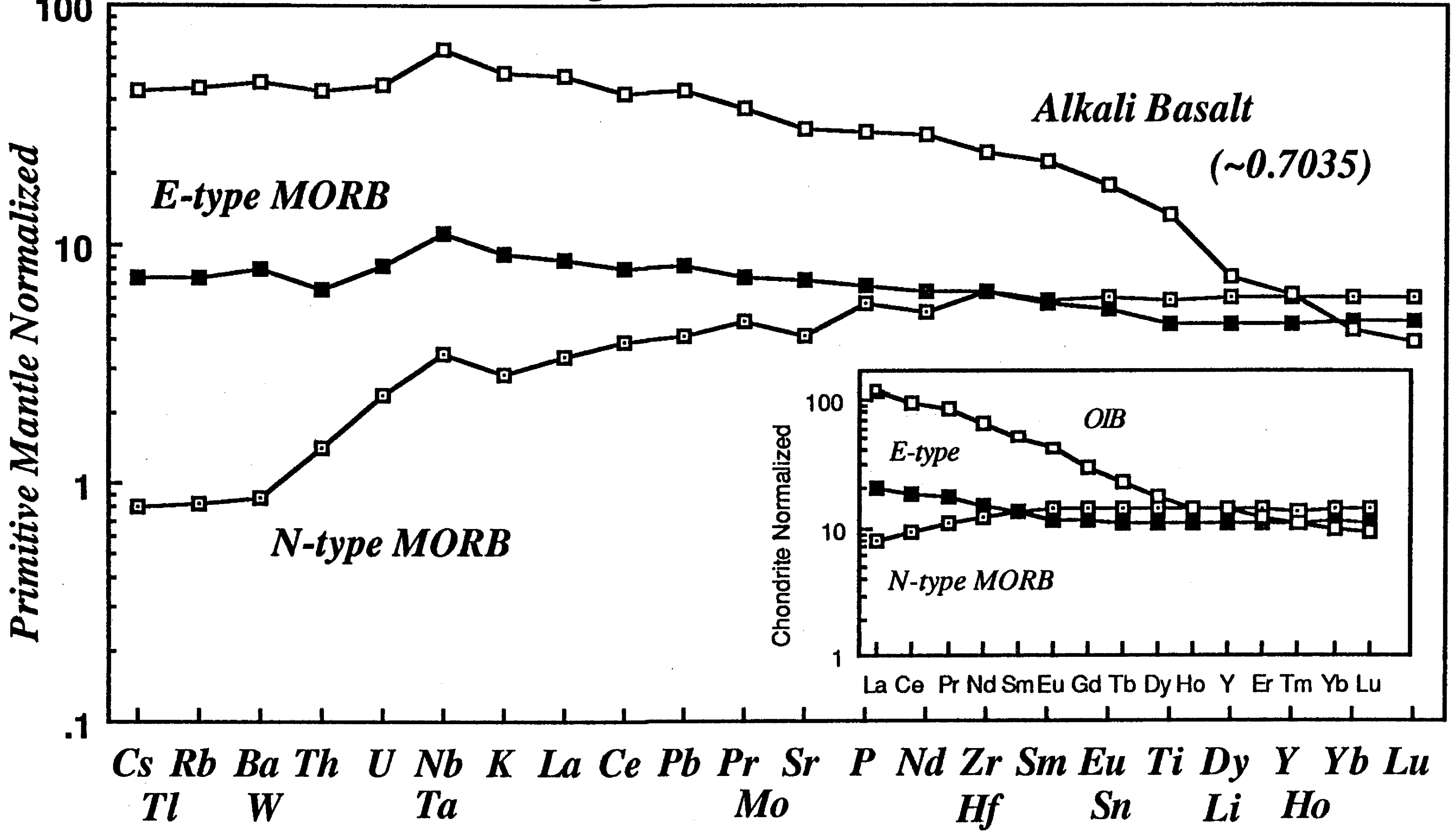
Figure 14. (a) $^{87}Sr/^{86}Sr$ versus La/Nb and (b) $^{87}Sr/^{86}Sr$ versus Ba/Nb plots for data of seleced Hawaiian basalts to illustrate the combined effects of mixing of two types of mantle sources and different degrees of partial melting. The trend of changing La/Nb and Ba/Nb raitos caused by different degrees of partial melting is indicated by the arrow direction.

Figure 15. Schematic diagram showing La/Sm versus La/Ta (Nb) ratios for N-MORB, T-MORB and plume-enriched MORB/OIB. The estimate for the earth's primitive mantle is form Table 1. The region which encompasses N-MORB and T-MORB with Ta (Nb) "kicks" ($La/Ta > 17.5$) is shaded.

Figure 16. Schematic description of the effects of various factors which can modify the spidergram pattern of OIB. See text for explanation.

Figure 1

Mid Ocean Ridge Basalts and Ocean Island Basalts



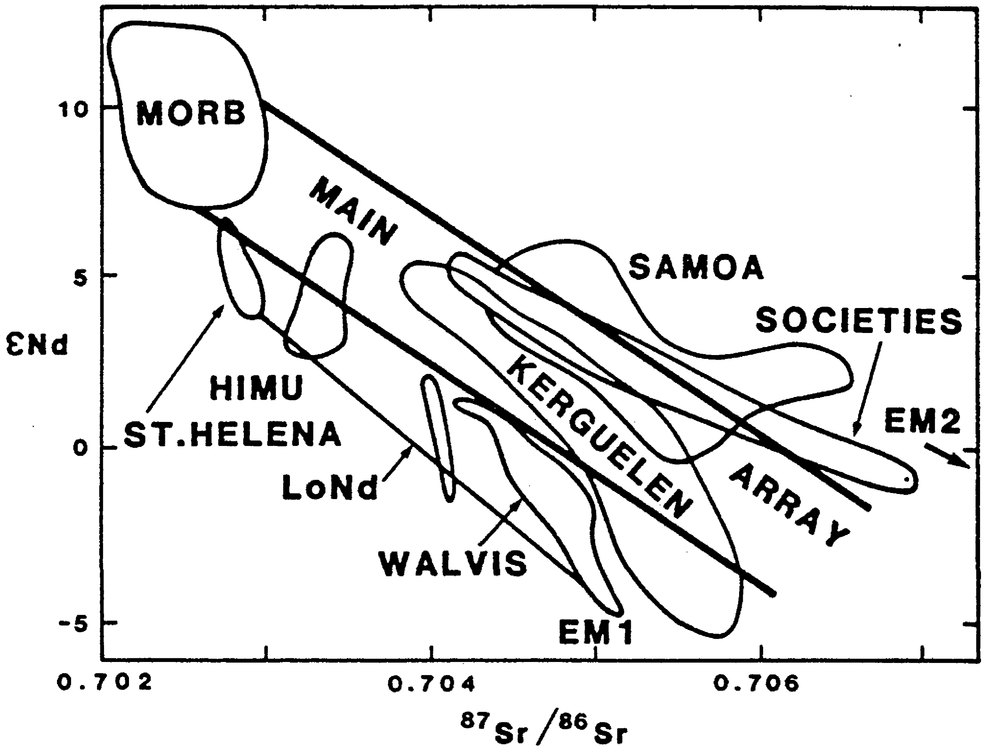

MORB
MAIN
KERGUELEN
ARRAY
SAMOA
SOCIETIES
EM2
HIMU
ST.HELENA
LoNd
WALVIS
EM1
εNd
10
5
0
-5
0.702
0.704
0.706
^{87}Sr/^{86}Sr

Fig. 2

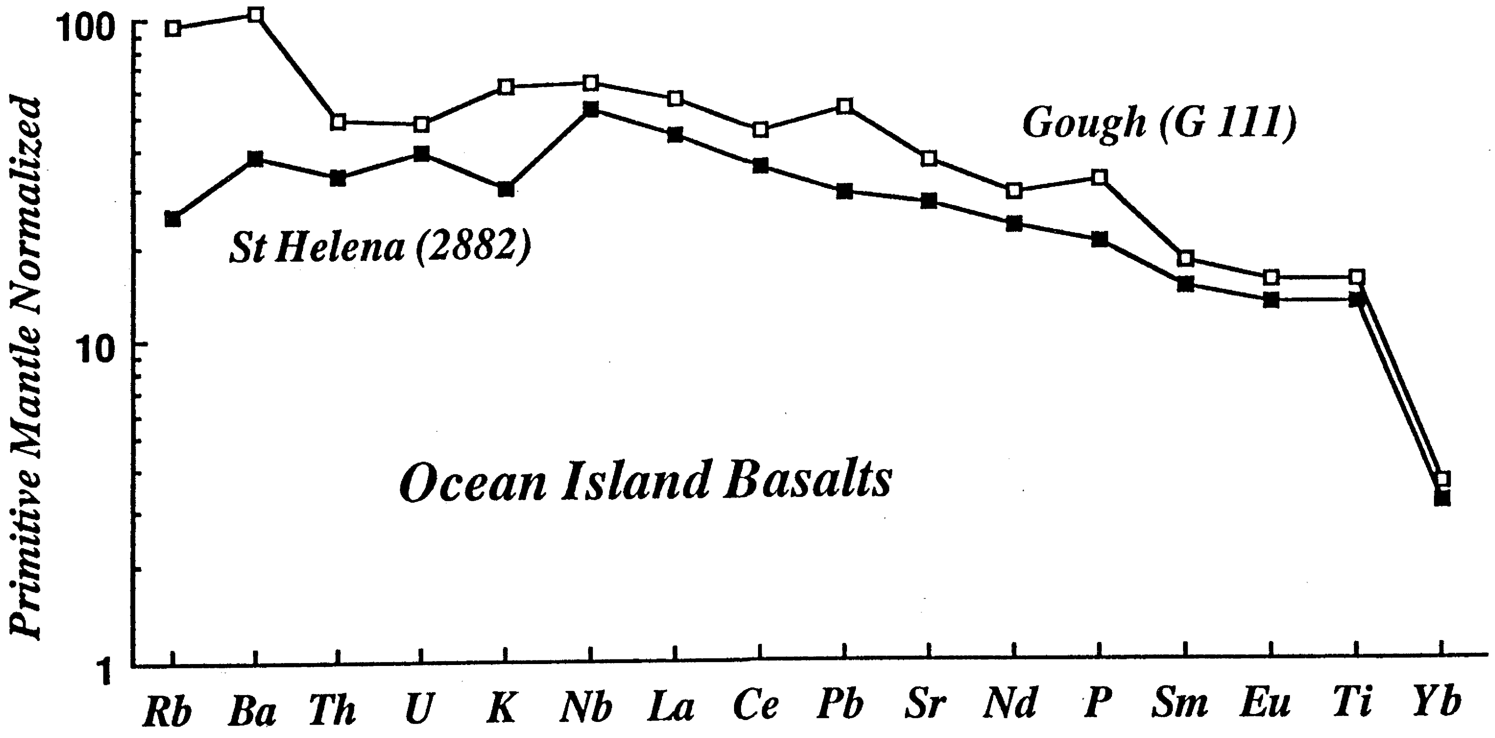

100
10
1
Primitive Mantle Normalized
Gough (G 111)
St Helena (2882)
Ocean Island Basalts
Rb
Ba
Th
U
K
Nb
La
Ce
Pb
Sr
Nd
P
Sm
Eu
Ti
Yb

Fig 3.

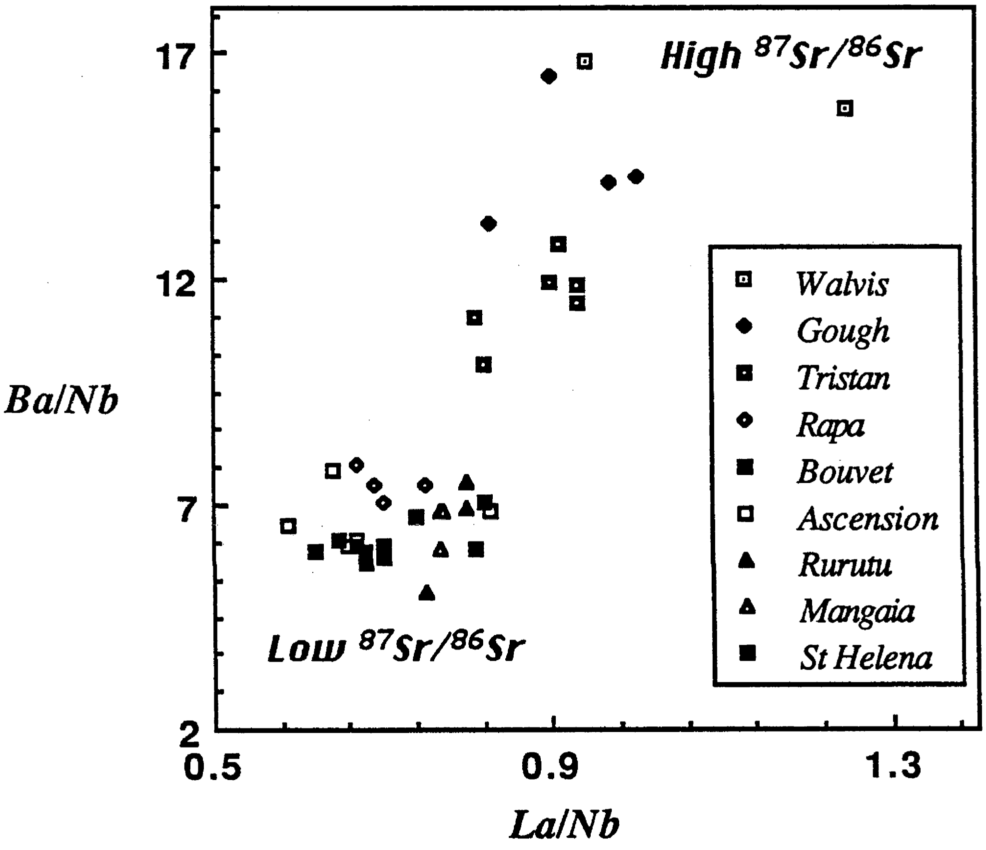

High $^{87}Sr/^{86}Sr$
Low $^{87}Sr/^{86}Sr$
Ba/Nb
La/Nb
17
12
7
2
0.5
0.9
1.3
Walvis
Gough
Tristan
Rapa
Bouvet
Ascension
Rurutu
Mangaia
St Helena

Figure 4

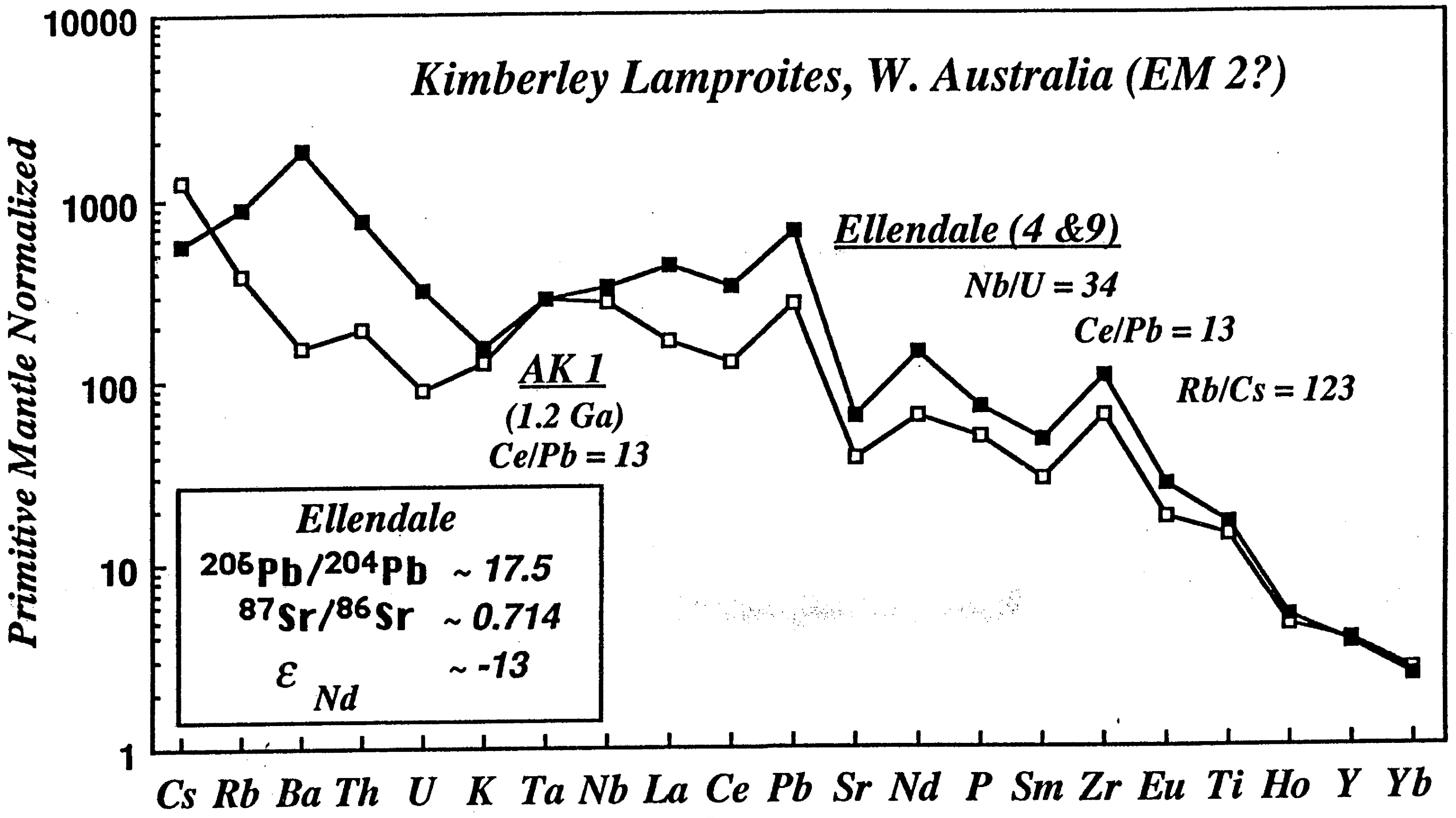

Kimberley Lamproites, W. Australia (EM 2?)
Primitive Mantle Normalized
10000
1000
100
10
1
Cs Rb Ba Th U K Ta Nb La Ce Pb Sr Nd P Sm Zr Eu Ti Ho Y Yb
Ellendale (4 &9)
Nb/U = 34
Ce/Pb = 13
Rb/Cs = 123
AK 1
(1.2 Ga)
Ce/Pb = 13
Ellendale
$^{206}Pb/^{204}Pb$ ~ 17.5
$^{87}Sr/^{86}Sr$ ~ 0.714
ε_{Nd} ~ -13

Fig 5

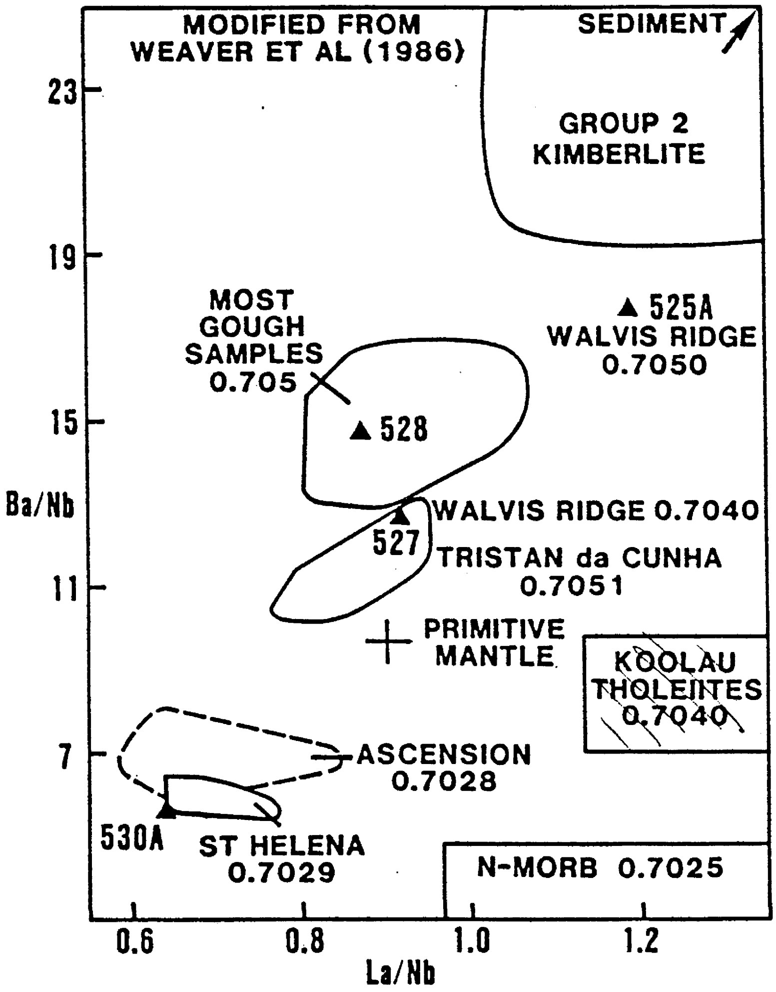

MODIFIED FROM
WEAVER ET AL (1986)
SEDIMENT
GROUP 2
KIMBERLITE
23
19
15
11
7
Ba/Nb
MOST
GOUGH
SAMPLES
0.705
525A
WALVIS RIDGE
0.7050
528
WALVIS RIDGE 0.7040
527
TRISTAN da CUNHA
0.7051
PRIMITIVE
MANTLE
KOOLAU
THOLEIITES
0.7040
ASCENSION
0.7028
530A
ST HELENA
0.7029
N-MORB 0.7025
0.6
0.8
1.0
1.2
La/Nb

Fig 6

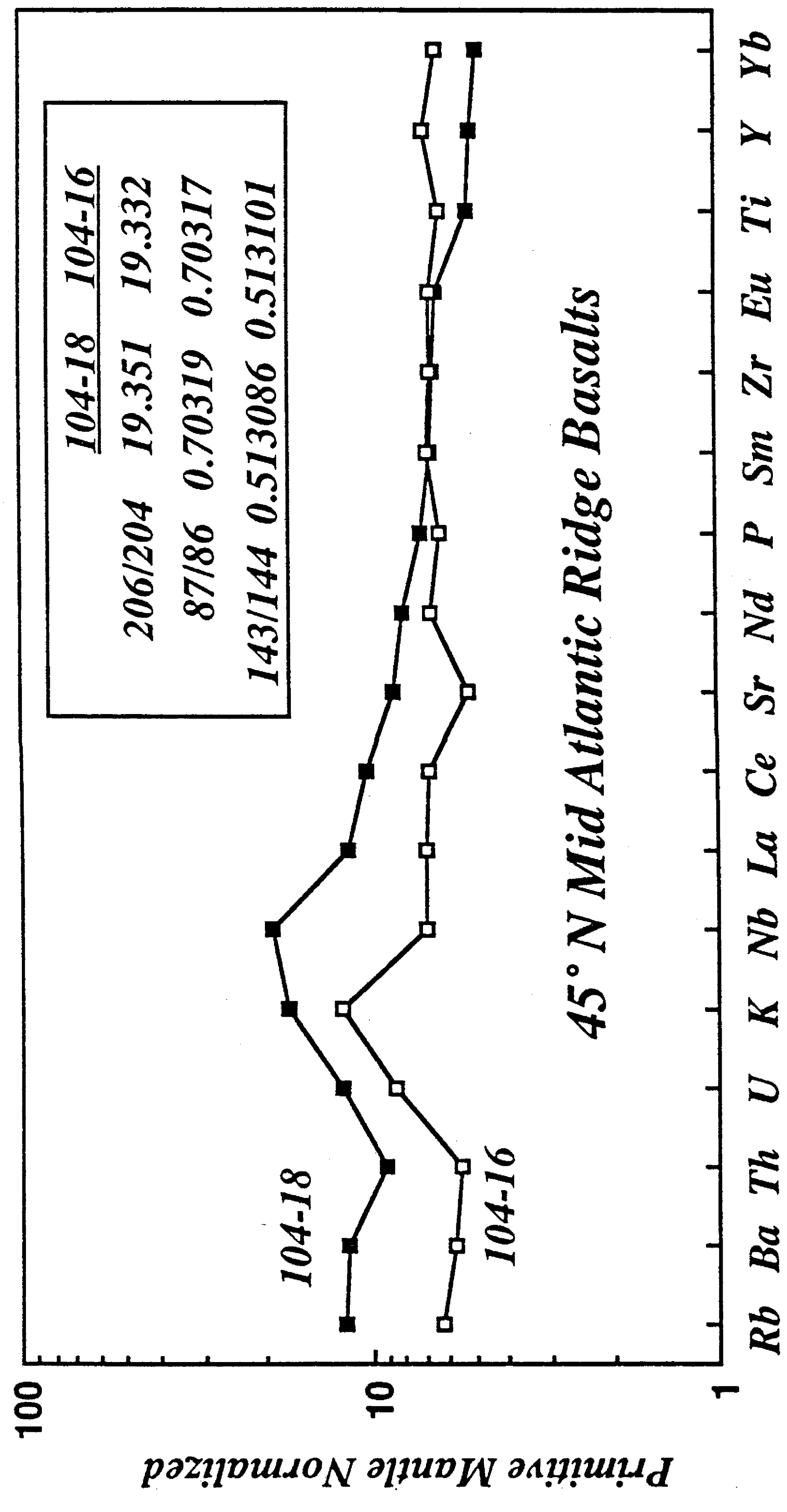
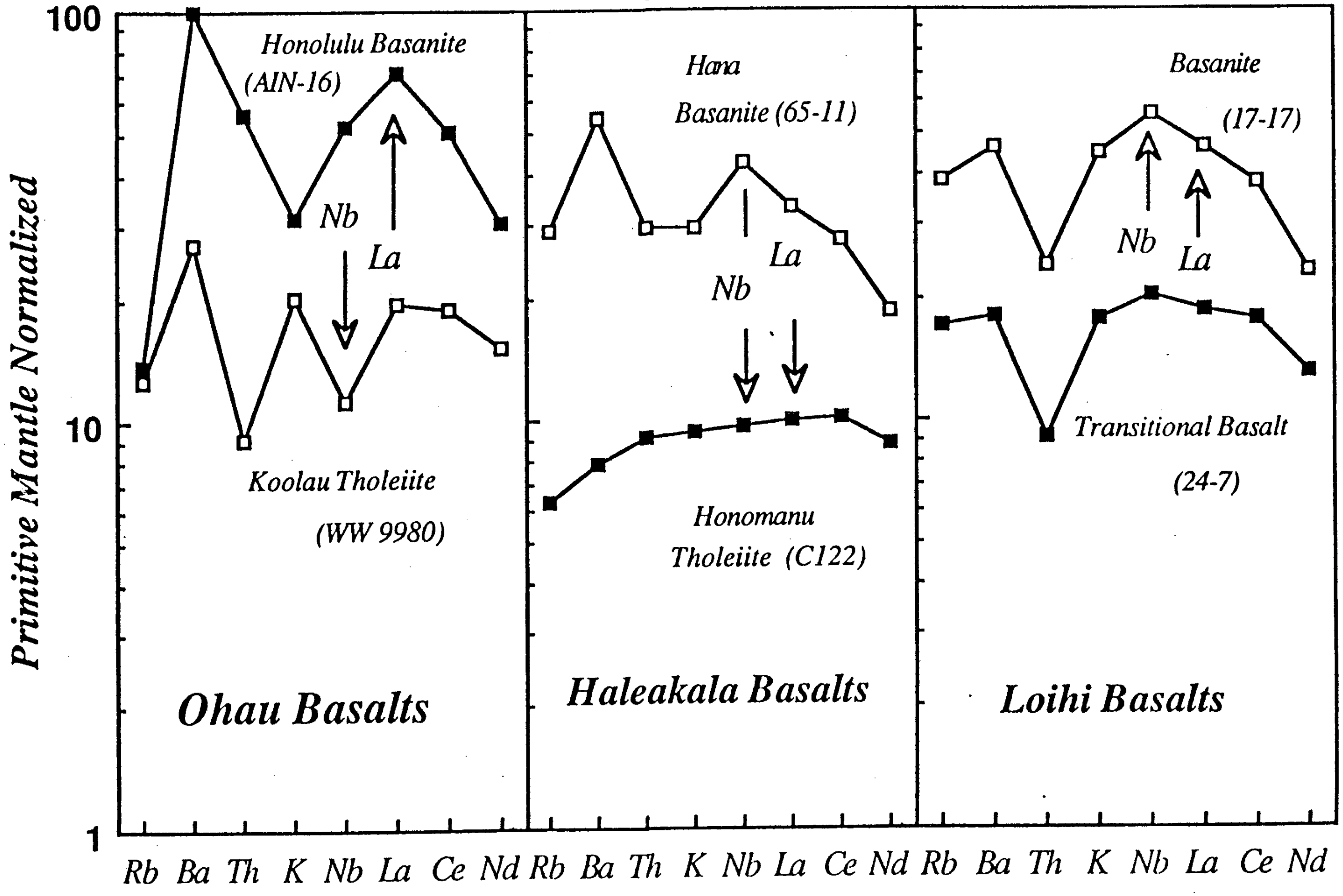
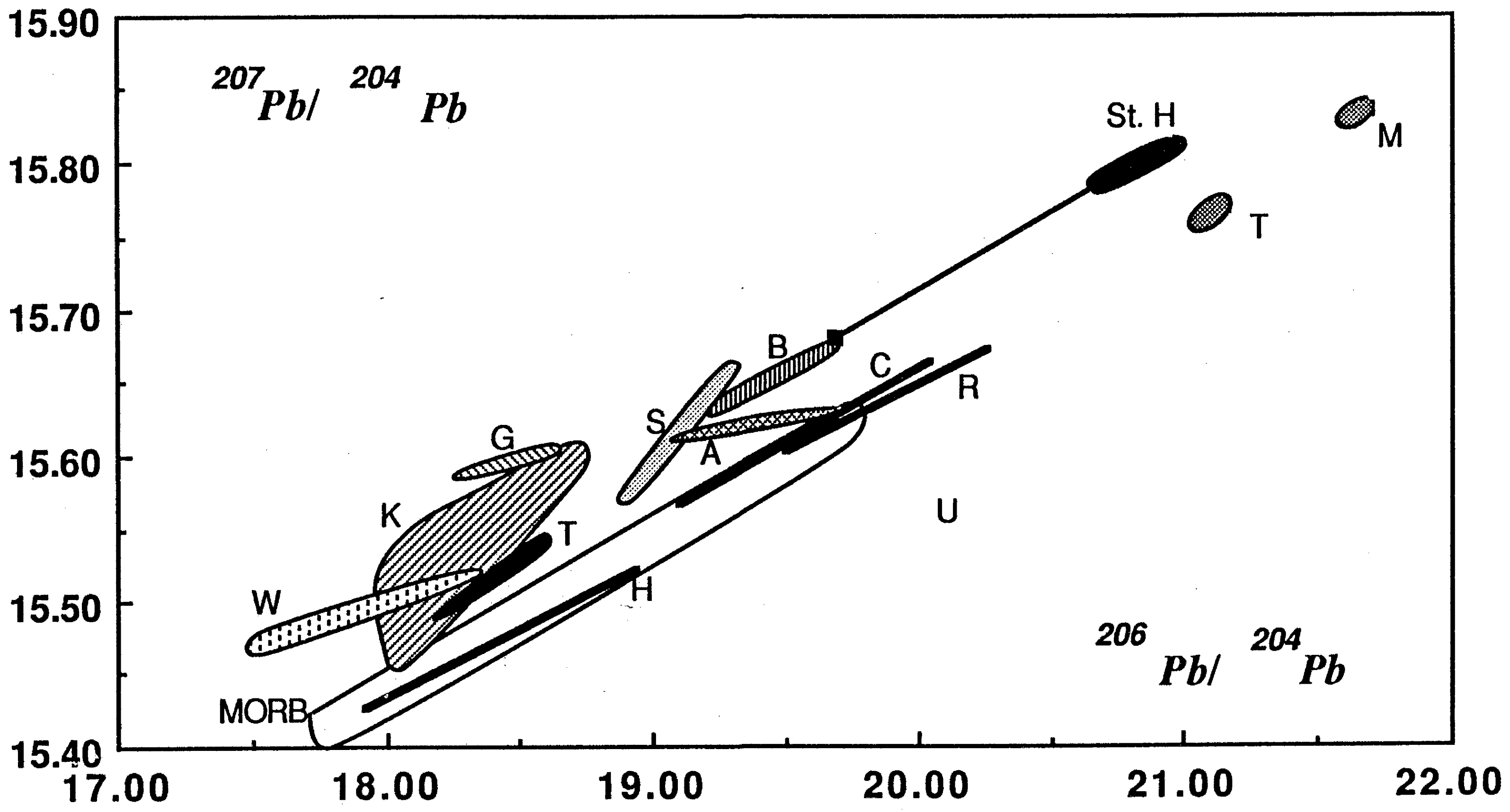

45° N Mid Atlantic Ridge Basalts
104-18
104-16
206/204 19.351 19.332
87/86 0.70319 0.70317
143/144 0.513086 0.513101
Primitive Mantle Normalized
100
10
1
Rb
Ba
Th
U
K
Nb
La
Ce
Sr
Nd
P
Sm
Zr
Eu
Ti
Y
Yb

Fig 7

Fig 8


Primitive Mantle Normalized
100
10
1
Honolulu Basanite
(AIN-16)
Nb
La
Koolau Tholeiite
(WW 9980)
Ohau Basalts
Hana
Basanite (65-11)
La
Nb
Honomanu
Tholeiite (C122)
Haleakala Basalts
Basanite
(17-17)
Nb
La
Transitional Basalt
(24-7)
Loihi Basalts
Rb Ba Th K Nb La Ce Nd Rb Ba Th K Nb La Ce Nd Rb Ba Th K Nb La Ce Nd



$^{207}Pb/^{204}Pb$
15.90
15.80
15.70
15.60
15.50
15.40
17.00
18.00
19.00
20.00
21.00
22.00
$^{206}Pb/^{204}Pb$
St. H
M
T
B
C
R
S
A
G
K
T
U
W
H
MORB

Figure 9

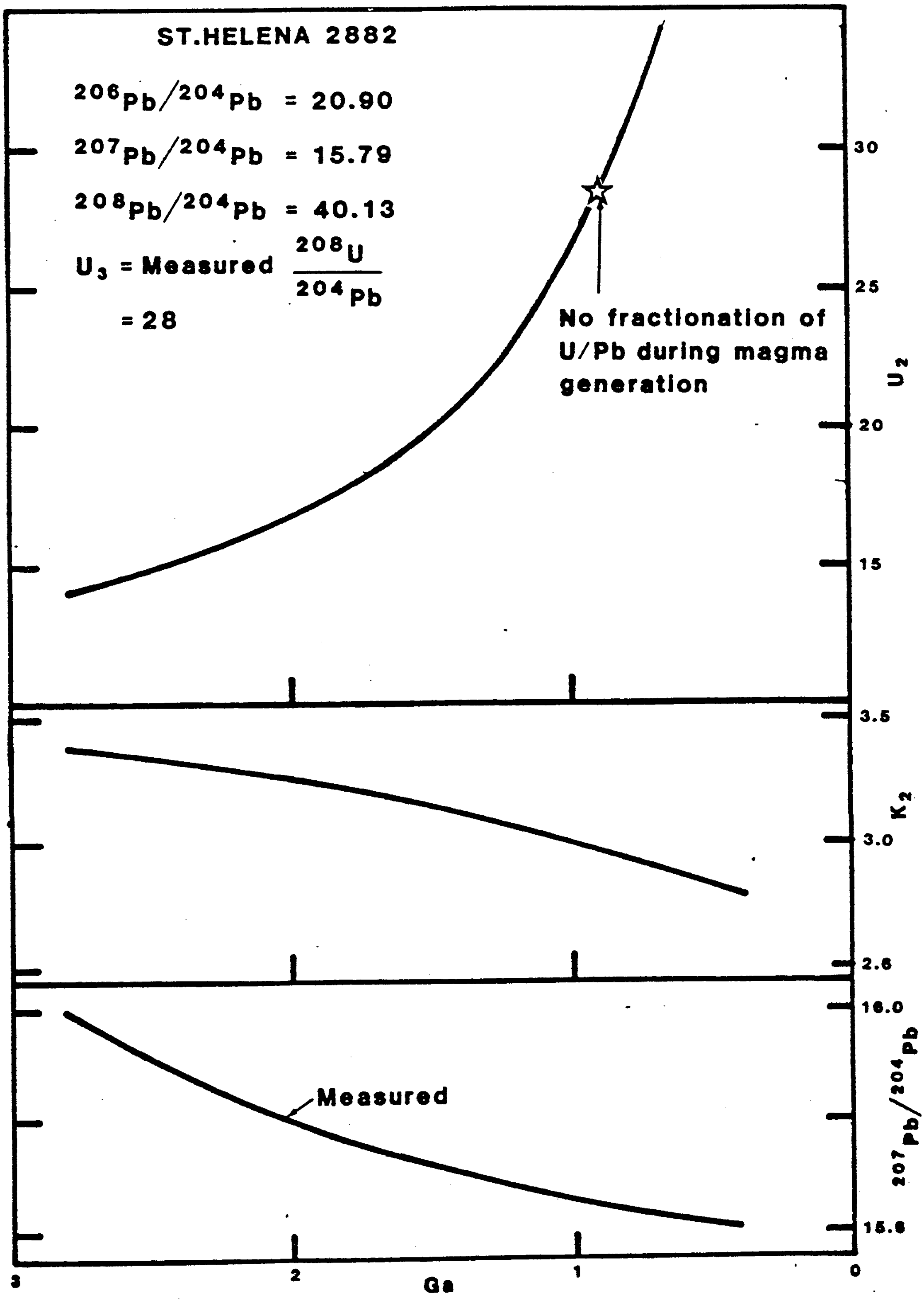

ST.HELENA 2882
$^{206}Pb/^{204}Pb = 20.90$
$^{207}Pb/^{204}Pb = 15.79$
$^{208}Pb/^{204}Pb = 40.13$
U_3 = Measured $\frac{^{208}U}{^{204}Pb}$ = 28
No fractionation of U/Pb during magma generation
30
25
20
15
U_2
3.5
3.0
2.6
K_2
16.0
15.8
$^{207}Pb/^{204}Pb$
Measured
3
2
1
0
Ga

Fig. 10

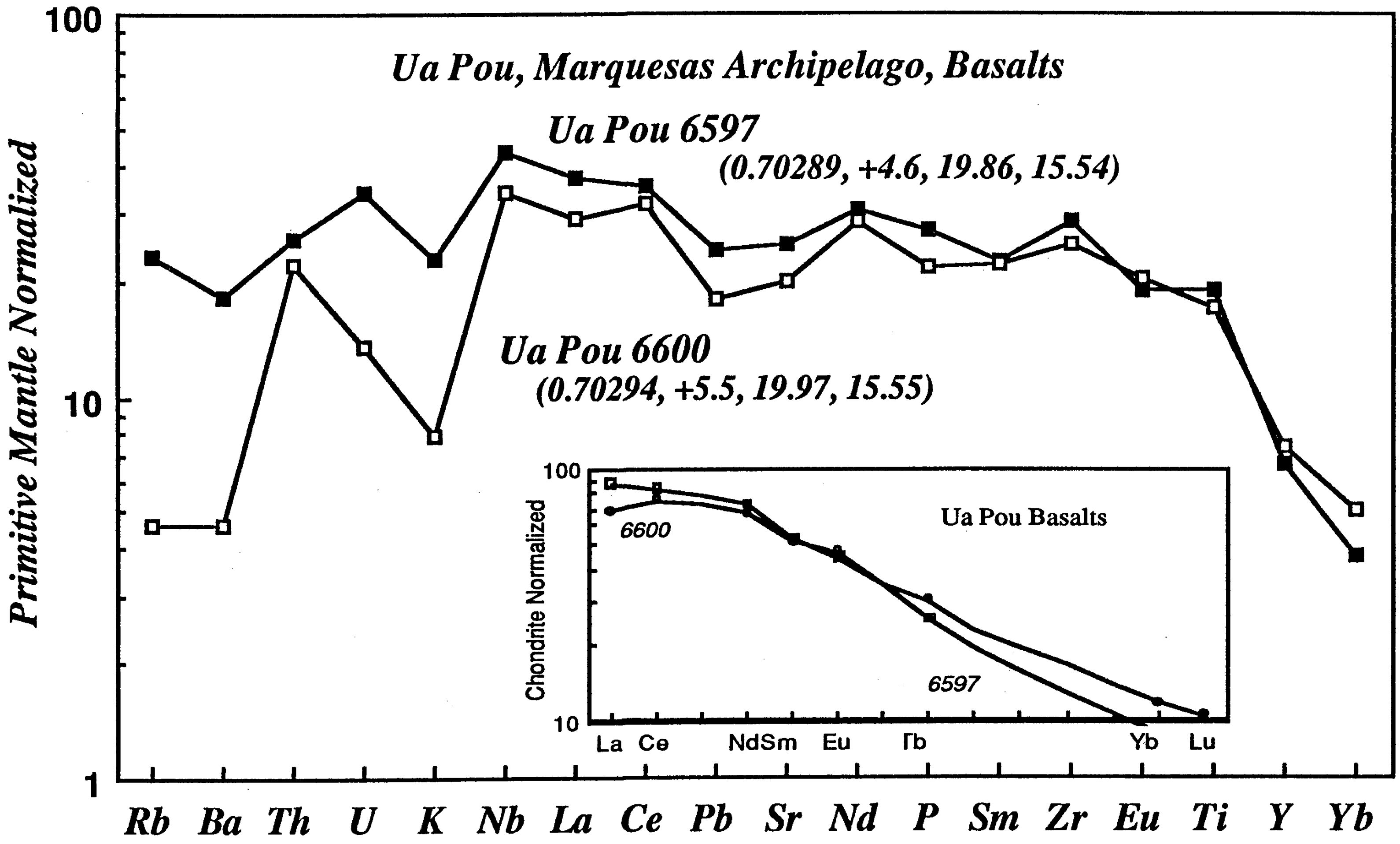

Ua Pou, Marquesas Archipelago, Basalts
Ua Pou 6597
(0.70289, +4.6, 19.86, 15.54)
Ua Pou 6600
(0.70294, +5.5, 19.97, 15.55)
Primitive Mantle Normalized
100
10
1
Rb
Ba
Th
U
K
Nb
La
Ce
Pb
Sr
Nd
P
Sm
Zr
Eu
Ti
Y
Yb
Ua Pou Basalts
Chondrite Normalized
100
10
6600
6597
La
Ce
NdSm
Eu
Tb
Yb
Lu

Figure 11

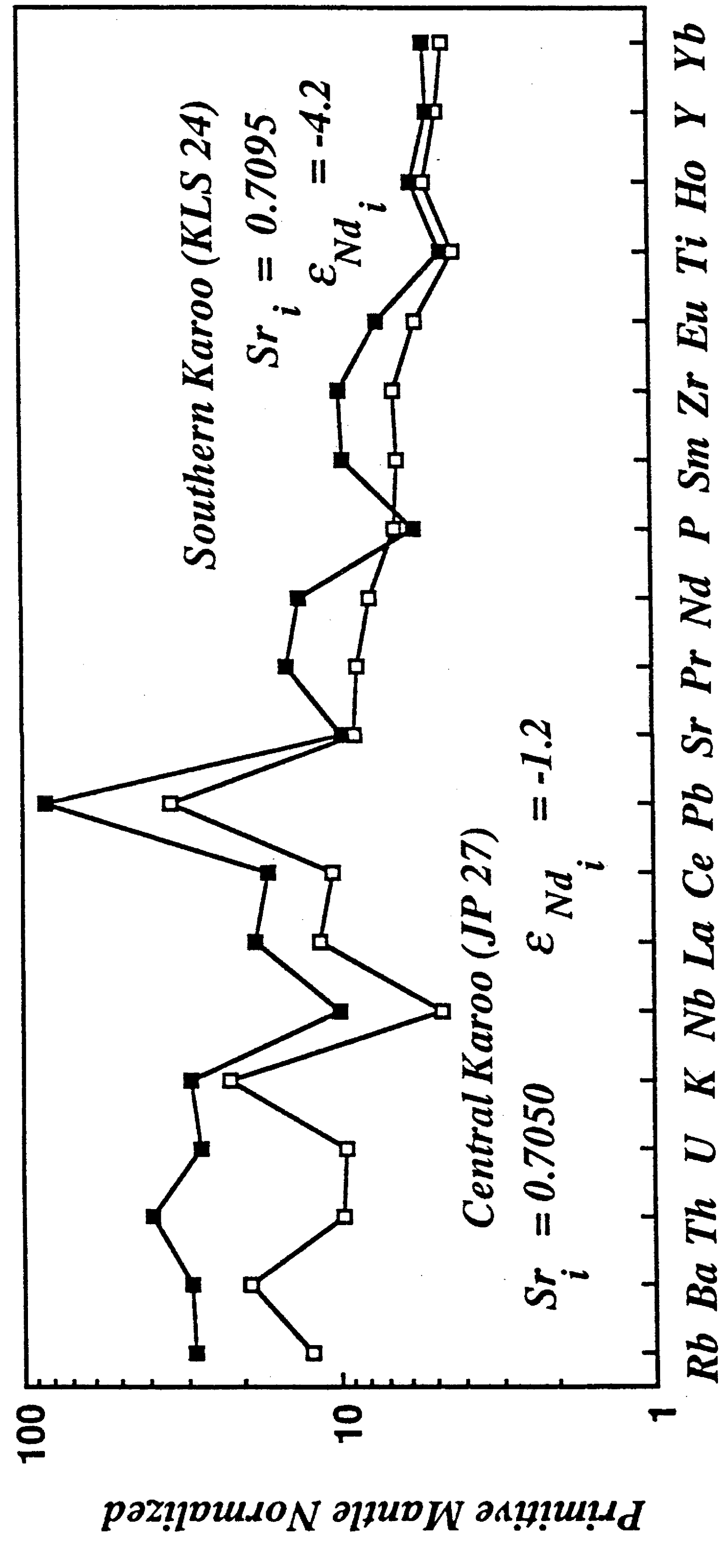

Southern Karoo (KLS 24)
$Sr_i = 0.7095$
$\varepsilon_{Nd_i} = -4.2$
Central Karoo (JP 27)
$Sr_i = 0.7050$
$\varepsilon_{Nd_i} = -1.2$
Primitive Mantle Normalized
100
10
1
Rb Ba Th U K Nb La Ce Pb Sr Pr Nd P Sm Zr Eu Ti Ho Y Yb

Fig 12

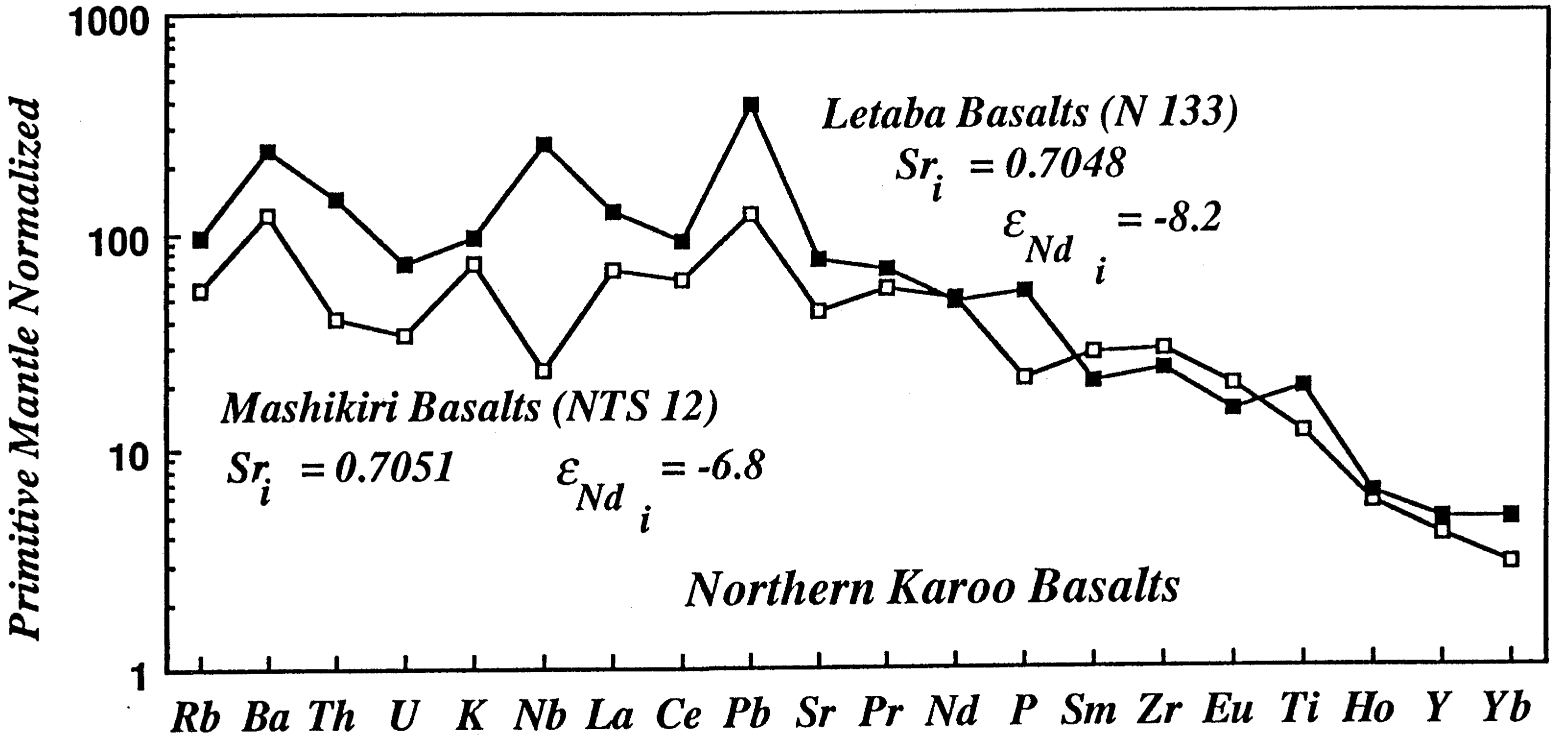

Primitive Mantle Normalized
1000
100
10
1
Rb Ba Th U K Nb La Ce Pb Sr Pr Nd P Sm Zr Eu Ti Ho Y Yb
Letaba Basalts (N 133)
$Sr_i = 0.7048$
$\varepsilon_{Nd\ i} = -8.2$
Mashikiri Basalts (NTS 12)
$Sr_i = 0.7051$
$\varepsilon_{Nd\ i} = -6.8$
Northern Karoo Basalts

Fig 13

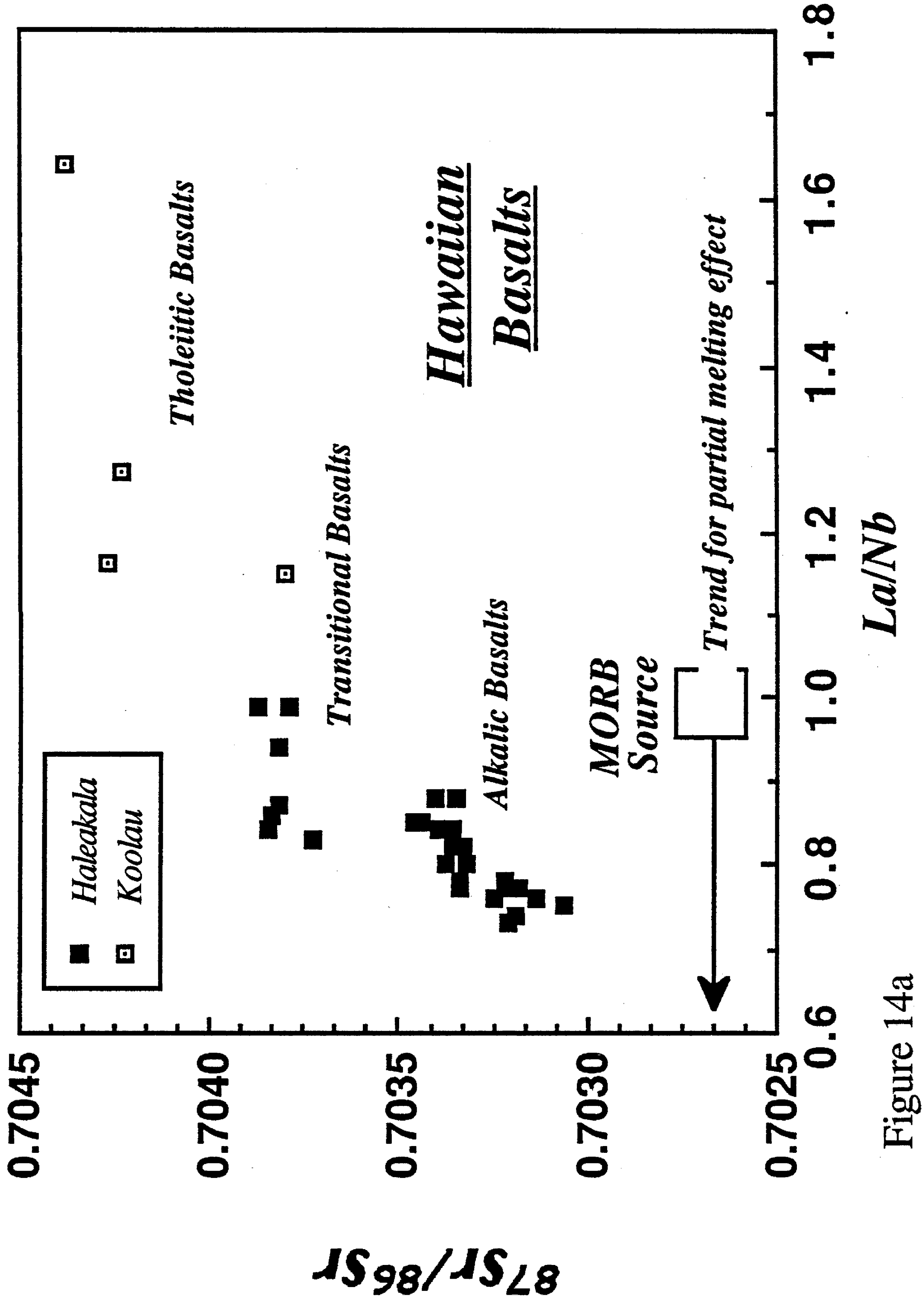

Hawaiian Basalts
Haleakala
Koolau
Tholeiitic Basalts
Transitional Basalts
Alkalic Basalts
MORB Source
Trend for partial melting effect
La/Nb
0.6
0.8
1.0
1.2
1.4
1.6
1.8
$^{87}Sr/^{86}Sr$
0.7025
0.7030
0.7035
0.7040
0.7045

Figure 14a

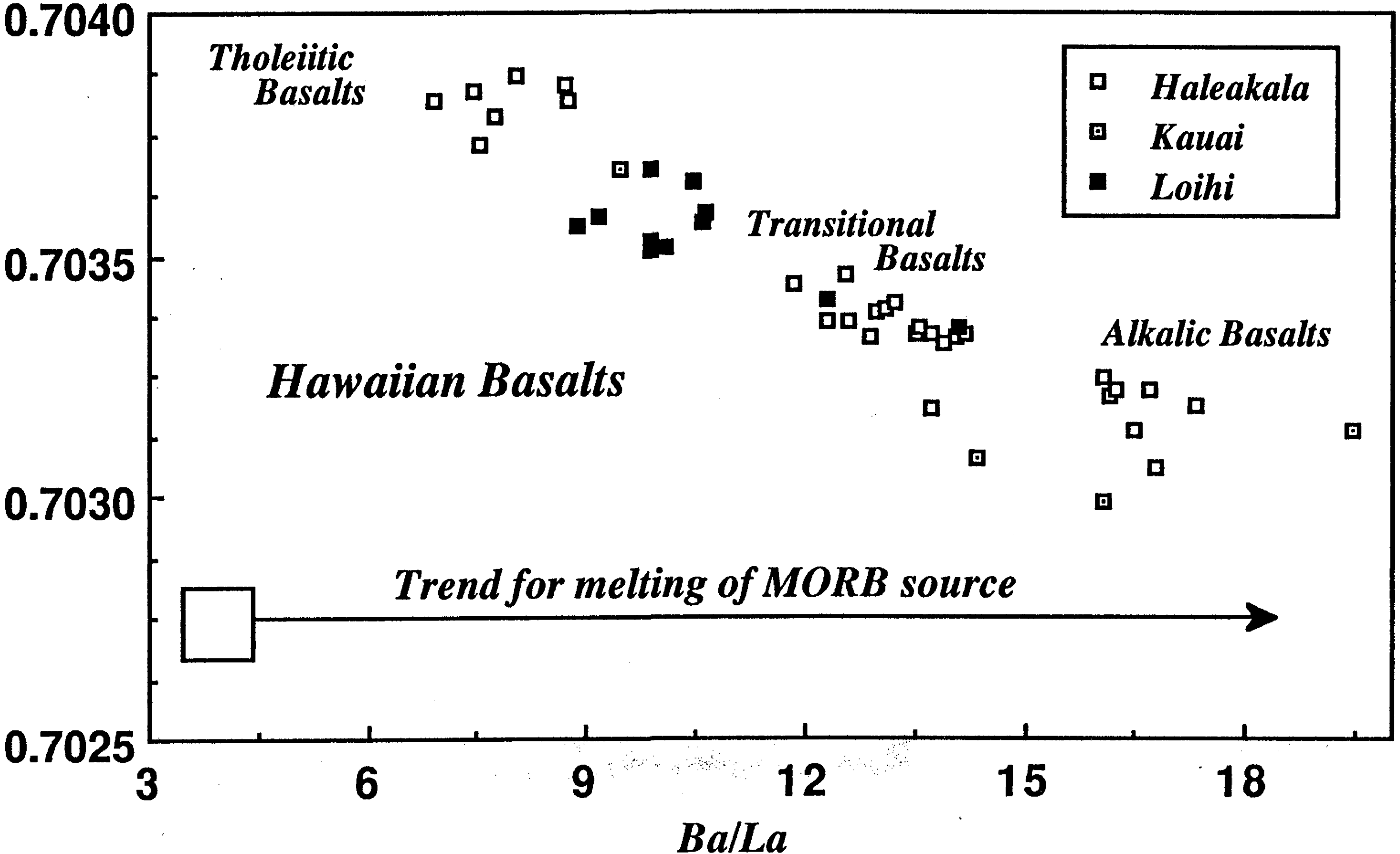

0.7040
0.7035
0.7030
0.7025
3
6
9
12
15
18
Ba/La
Tholeiitic Basalts
Transitional Basalts
Alkalic Basalts
Hawaiian Basalts
Trend for melting of MORB source
Haleakala
Kauai
Loihi

Figure 14b

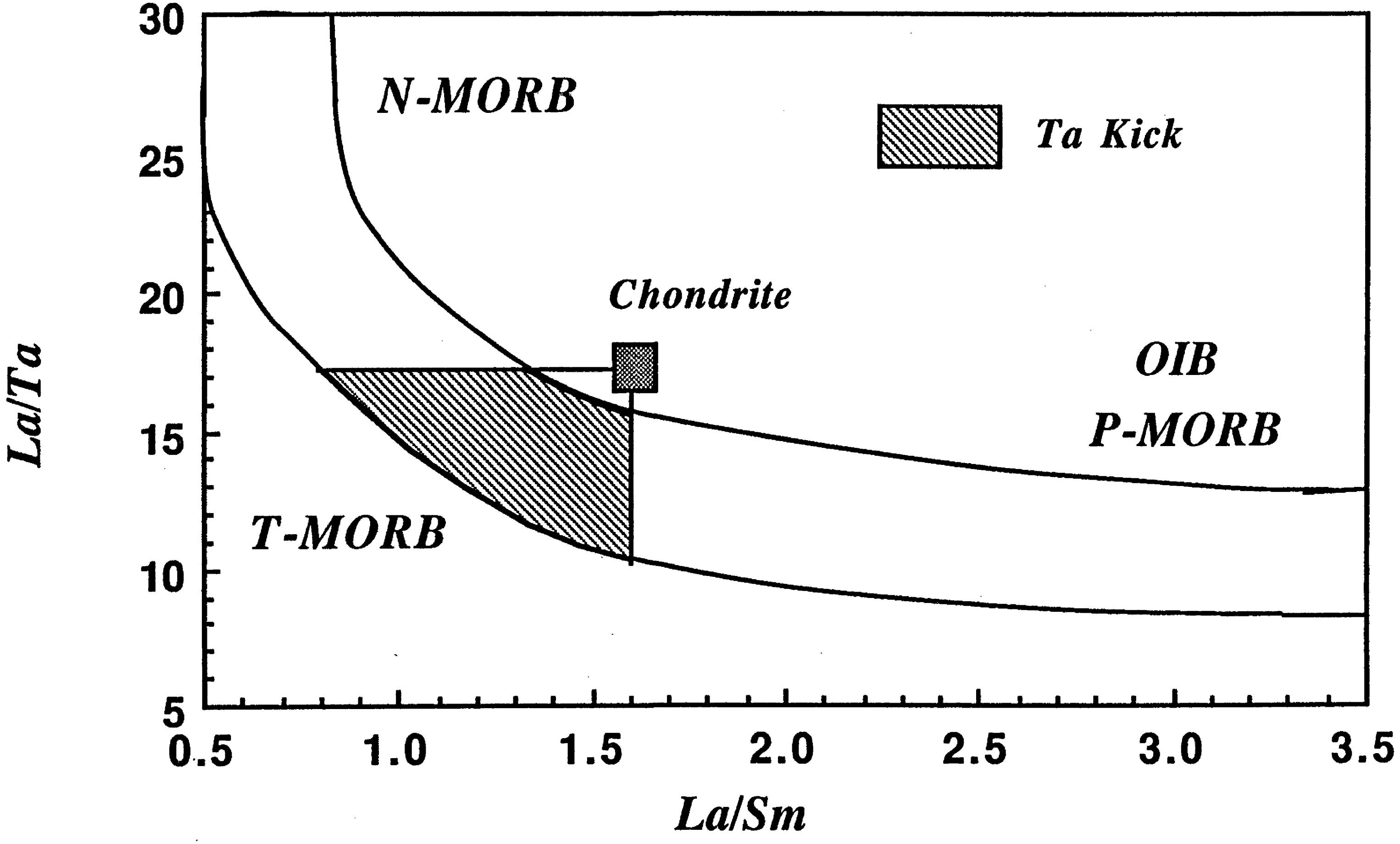

30
25
20
15
10
5
La/Ta
N-MORB
Ta Kick
Chondrite
OIB
P-MORB
T-MORB
0.5
1.0
1.5
2.0
2.5
3.0
3.5
La/Sm

Figure 15

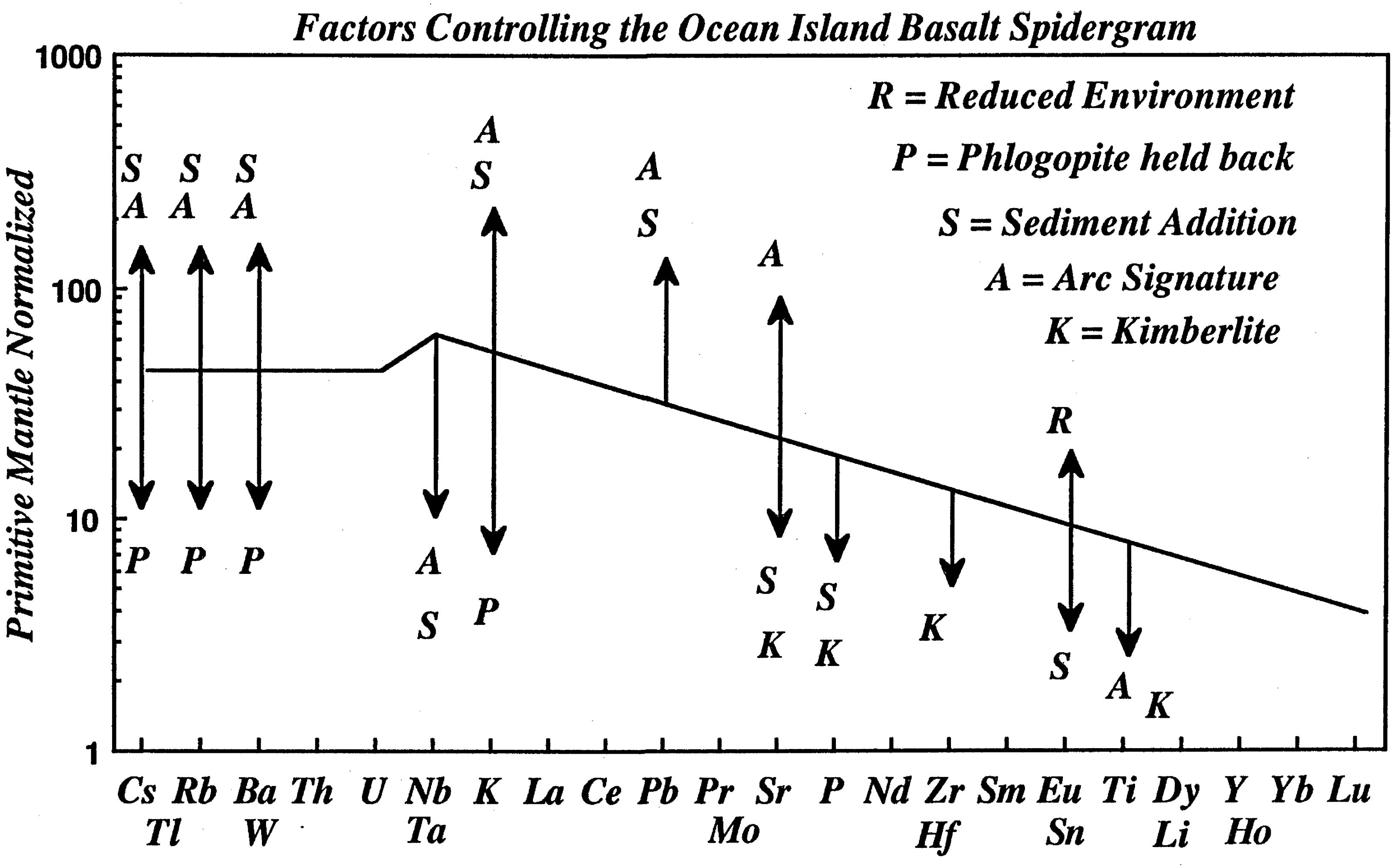

Factors Controlling the Ocean Island Basalt Spidergram
Primitive Mantle Normalized
1000
100
10
1
R = Reduced Environment
P = Phlogopite held back
S = Sediment Addition
A = Arc Signature
K = Kimberlite
S A P
S A P
S A P
A S P
A S
A S
A S K
S K
K
R S
A K
Cs Tl
Rb
Ba W
Th
U
Nb Ta
K
La
Ce
Pb
Pr Mo
Sr
P
Nd
Zr Hf
Sm
Eu Sn
Ti
Dy Li
Y Ho
Yb
Lu

Fig 16

Table 1. Element Concentrations in CI Chondrite, Primitive Mantle, E-Type MORB, N-Type MORB and OIB

Element	CI Chondrite	Primitive Mantle	N-type MORB	E-type MORB	OIB
Cs	0.188	0.033	0.0065	0.060	0.360
Tl	0.142	0.010	0.0013	0.012	0.07
Rb	2.32	0.650	0.53	4.75	29.0
Ba	2.41	7.230	6.30	57	350
W	0.095	0.021	0.010	0.092	0.560
Th	0.029	0.092	0.130	0.60	4.00
U	0.008	0.022	0.052	0.18	1.02
Nb	0.246	0.738	2.60	8.30	48.0
Ta	0.014	0.042	0.148	0.47	2.70
K	545	230	650	2100	12000
La	0.244	0.732	2.50	6.30	37.0
Ce	0.632	1.896	7.50	15.0	80.0
Pb	2.47	0.200	0.30	0.60	3.20
Pr	0.093	0.279	1.32	2.05	9.70
Mo	0.92	0.065	0.31	0.47	2.40
Sr	7.26	21.8	90	155	660
P	1220	92	525	620	2700
Nd	0.471	1.413	7.30	9.00	38.5
F	60.7	26	210	250	1150
Zr	3.85	11.6	74	73	280
Hf	0.107	0.320	2.05	2.03	7.80
Sm	0.152	0.456	2.63	2.60	10.0
Eu	0.0573	0.172	1.02	0.91	3.00
Sn	1.72	0.175	1.1	0.8	2.7
Sb	0.16	0.005	0.10	0.07	0.24
Ti	440	1300	7600	6000	17200
Gd	0.203	0.610	3.68	2.95	7.60
Tb	0.033	0.098	0.59	0.47	0.97
Dy	0.252	0.756	4.57	3.54	5.55
Li	1.57	1.600	4.3	3.5	5.6
Y	1.57	4.700	28	22	29
Ho	0.056	0.167	1.01	0.79	1.02
Er	0.165	0.495	3.00	2.32	2.64
Tm	0.025	0.075	0.45	0.35	0.35
Yb	0.166	0.498	3.00	2.40	2.16
Lu	0.0254	0.076	0.46	0.36	0.30

Table 3. Contrasts of some element ratios observed in HIMU type and EM type OIB

	Nb/Pb	Ce/Pb	Nb/U	K/U	K/Nb	Rb/Cs	Nb/Th
		(1) N-Type MORB		0.7025			
MORB	7.5	25	50	12700	260	80	20
		(2) St. Helena Type		0.7029			
St Helena	23	33	48	8000	180	100	13.3
Rurutu	18	~30	–	7000	180	–	12.5
Mangaia	18	29	–	6000	160	–	10
Dunedin	20	~30	~45	7000	170	–	17
Ua Pou (th)	19	38	43	8000	180	–	13
		(3) EM Type OIB		0.705 - 0.706			
Gough	10.4	20	43	18000	430	70	9.3
Kerguelen	8.5	14.5	43	(8000)*	270	–	11.5
Aitutaki	8.3	16	–	(5600)	(170)	–	6.3
Upolu	12.1	31	–	(9700)	(200)	–	–
Tutuila	12.2	~25	–	(8300)	(250)	–	9.1
Tristan	15.9	24	41	11500	270	85	9.1
Sao Miguel	–	–	40	13700	340	90	9.2

*low K/La suggesting K has been held back? Data sources: Hofmann et al (1986); Newsom et al (1986); Palacz and Saunders (1986), White et al (1979); Sun and Hanson (1975a); Weaver et al (1986), Hofmann and White (1983) and this paper.

Table 2. Generalization of Primitive Mantle Normalized abundances ratios (alkali basalt with $^{87}Sr/^{86}Sr \sim 0.7035$ -----> Group I kimberlites)

La (ppm)	Nb/La	K/La	Sr/Pr	Sr/Nd	P/Nd	Zr/Hf/Sm	Ti/Eu
30	1.2 - 1.5	0.7 - 1.0	~1.0	~1.0	1.0	1.0	~0.9
50-100	(1.5) - 2.0	~0.4	(0.8) -1.0	~1.0	1.0	(0.7) -1.0	~0.9
≥200*	1.2 - 2.0	≤0.2	~0.6	≤0.6	~0.5	≥0.5	0.2 - 0.5

* in general we are not sure that at low degrees of partial melting whether these ratios are reflecting source mineralogy or subsequent lower pressure fractionation effects

Table 4. Mass balance calculation assuming complimentary relationship between the bulk continental crust and MORB source (upper mantle).

(a)	Rb	U	Nb	La	Ce	Pb	Nd	Sr	Sm	Al	Ca%
Bulk Crust[§] (0.6%)	32	0.91	8*	16	33	8	16	260	3.5	8.4	5.3
Primitive Mantle	0.65	0.022	0.74	0.71	1.84	0.20	1.40	21.8	0.46	2.28	2.50
% bulk Mantle	30	25	6.5	13.5	10.8	24	6.9	7.2	4.6	2.2	1.3
% upper Mantle[†]	100	83	21.6	45.1	36.9	80	22.9	23.9	15.2	7.6	4.2
depleted U mantle after crust extraction	0.0	0.0039	0.59	0.40	1.20	0.041	1.10	16.9	0.40	2.16	2.44

(b)	La/Nb	La/Sm	Sm/Nd	Ce/Pb	Nb/U
Calculated for UM after crust extraction	0.68	1.0	0.36	30	152
observed in MORB	0.97	0.96	0.36	25±5	47±10

* a value of La/Nb = 2.0 is used for crustal abundance ratio. [†]30% of the total mantle.

[§] Bulk Crust = 0.4% Bulk Earth *and* Bulk Crust = 0.6% of the Bulk Silicate Earth.