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Oceanic Island Volcanism II: Mantle Processes

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Résumé de l'article

L'étude des basaltes d'îles océaniques (BÎOs, ou OIBs en anglais) s'est avéré essentielle pour la compréhension de l'évolution de la Terre et de son manteau, et cela, de par l'isolement de ces îles dans les bassins océaniques, ce qui limite les possibilités de contamination par des matériaux de la croûte continentale. Les mécanismes de fusion (le pour-centage de fusion par ex.) délimitent la composition chimique des BÎOs, mais les ratios isotopiques et des éléments traces permettent d'obtenir des indications sur la composition des sources mantelliques. Ils indiquent que les sources mantelliques des BÎOs sont des mélanges de basaltes de dorsales océaniques (BDOs ou MORBs en anglais) de quatre autres composantes du manteau, soit des EM1 (enriched mantle), EM2, HIMU (ratio élevé de U/Pb= Hi μ), et FOZO (FOcal ZOne). Les études des bilans massiques et des gaz nobles indiquent que la plus grande partie du manteau a subit un appauvrissement, mais les isotopes He et Ne, ainsi que la convergence des ensembles isotopiques Sr-Nd-Pb portent à penser que la composante FOZO serait de composition à peu près primitive (n'aurait pas subit de fusion) qui serait commune à toutes les sources de basaltes océaniques. Les autres composantes renferment des" matériaux " issus de plancher océanique basaltique (HIMU), de sédiments pélagiques (EM1), de plateaux océaniques (EM1), de lithosphère souscontinentale (EM1 et EM2), de sédiments terrigènes ou de croûtes continentales enfouies (EM2) et qui ont été recyclés par des mécanismes de subduction et réinjecté dans les matériaux appauvris du manteau. La façon dont ces composantes sont recyclées dans le manteau fait l'objet de discussions serrées et on observe la présence d'hétérogénéité à toute échelle. Une des écoles de pensée soutient que les îles océaniques se forment au-dessus de cellules de convection de panaches mantelliques qui apportent des composantes recyclées et de la FOZO (manteau inférieur?) et les mélangent avec les couches supérieures appauvries du manteau. D'autres croient plutôt que ce sont des fissures de la croûte qui permettent la formation des îles océaniques, qu'il n'y pas de panaches, que les couches inférieures et supérieures du manteau sont isolées et appauvries et que les BÎO et les BDO sont formés à partir des matériaux des même couches supérieures. Les BÎO seraient le reflet de fusions d'hétérogénéités locales à faibles températures de fusion, alors que les BDO seraient le résultat de fusions à grande échelle expliquant une composition correspondant à la moyenne de toutes les hétérogénéités. L'existence de points de vue si radicalement opposés sur la structure et la composition du manteau démontrent que les BÎOs seront encore l'objet d'études sur l'évolution de la Terre.

SERIES

Igneous Rock Associations 5. Oceanic Island Volcanism II: Mantle Processes

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SUMMARY

Oceanic island basalts (OIBs) have been central to understanding evolution of the Earth and mantle because their isolated positions in ocean basins limit the potential for magma contamination by continental crust. Melting processes (e.g., percentage melting) affect OIB chemistry but isotopic and trace-element ratios provide information on mantle-source compositions. They indicate that OIB mantle sources represent mixtures between mid-ocean ridge basalt (MORB) mantle and four other mantle components: EM1 (enriched mantle 1), EM2, HIMU (High U/Pb = Hi μ) and FOZO (FOcal ZOne). Mass-balance and noble-gas arguments indicate that most of the mantle is depleted but He and Ne isotopes, and convergence of Sr-Nd-Pb isotopic arrays suggest that FOZO is a somewhat primitive (unmelted) component common to all oceanic basalt sources. The other components contain "materials" such as basaltic ocean floor (HIMU), pelagic sediments (EM1), oceanic plateaus (EM1), subcontinental lithosphere (EM1, EM2), terrigenous sediments or subducted continental crust (EM2), which have been recycled by subduction processes, and mixed back into the depleted mantle. How these components cycle through the mantle is debated but heterogeneities occur on all length-scales. One school argues that oceanic islands develop above mantle plume convection cells that deliver recycled components and FOZO (lower mantle?) for mixing with depleted upper mantle. Others contend that propagating cracks in the lithosphere create oceanic islands, that plumes do not exist, that the upper and lower mantle are isolated and depleted, and that MORB and OIB form from the same upper-mantle reservoir. Small-scale melting allows OIB to sample local, low-melting-point heterogeneities that are averaged-out by the large-scale melting that forms MORB. These radically different views of mantle structure and composition indicate that OIB will continue to be a focal point in studies of Earth's evolution.

SUMMAIRE

L'étude des basaltes d'îles océaniques (BÎOs, ou OIBs en anglais) s'est avéré essentielle pour la compréhension de l'évolution de la Terre et de son manteau, et cela, de par l'isolement de ces îles dans les bassins océaniques, ce qui limite les possibilités de contamination par des matériaux de la croûte continentale. Les mécanismes de fusion (le pourcentage de fusion par ex.) délimitent la composition chimique des BÎOs, mais les ratios isotopiques et des éléments traces permettent d'obtenir des indications sur la composition des sources mantelliques. Ils indiquent que les sources mantelliques des BÎOs sont des mélanges de basaltes de dorsales océaniques (BDOs ou MORBs en anglais) de quatre autres composantes du manteau, soit des EM1 (enriched mantle), EM2, HIMU (ratio élevé de U/Pb = Hi μ), et FOZO (FOcal ZOne). Les études des bilans massiques et des gaz nobles indiquent que la plus grande partie du manteau a subit un appauvrissement, mais les isotopes He et Ne, ainsi que la convergence des ensembles isotopiques Sr-Nd-Pb portent à penser que la composante FOZO serait de composition à peu près primitive (n'aurait pas subit de fusion) qui serait commune à toutes les sources de basaltes océaniques. Les autres composantes renferment des " matériaux " issus de plancher océanique basaltique (HIMU), de sédiments pélagiques (EM1), de plateaux océaniques (EM1), de lithosphère sous-continentale (EM1 et EM2), de sédiments terrigènes ou de croûtes continentales enfouies (EM2) et qui ont été recyclés par des mécanismes de subduction et réinjecté dans les matériaux appauvris du manteau. La façon dont ces composantes sont recyclées dans le manteau fait l'objet de discussions serrées et on observe la présence d'hétérogénéité à toute échelle. Une des écoles de pensée soutient que les îles océaniques se forment au-dessus de cellules de convection de panaches mantelliques qui apportent des composantes recyclées et de la

FOZO (manteau inférieur?) et les mélangent avec les couches supérieures appauvries du manteau. D'autres croient plutôt que ce sont des fissures de la croûte qui permettent la formation des îles océaniques, qu'il n'y pas de panaches, que les couches inférieures et supérieures du manteau sont isolées et appauvries et que les BÎO et les BDO sont formés à partir des matériaux des même couches supérieures. Les BÎO seraient le reflet de fusions d'hétérogénéités locales à faibles températures de fusion, alors que les BDO seraient le résultat de fusions à grande échelle expliquant une composition correspondant à la moyenne de toutes les hétérogénéités. L'existence de points de vue si radicalement opposés sur la structure et la composition du manteau démontrent que les BÎOs seront encore l'objet d'études sur l'évolution de la Terre.

INTRODUCTION

Oceanic islands represent a small proportion of the Earth's surface yet their volcanic rocks are amongst the most studied; this is because they occur far from continental crust that might contaminate rising magma, and they are unaffected by orogenic, metamorphic and tectonic processes (Basaltic Volcanism Study Project = BVSP, 1981, p. 161). Thus, oceanic island basalts (OIBs) provide important chemical evidence regarding mantle composition, magma formation processes and magma evolution. Perhaps reflecting the availability and accuracy of major element, trace element and isotopic analyses, the emphasis of studies on OIB has shifted over 40 years from the effects of differentiation, to the impact of melting processes on magmas, to studying what magma chemistry can tell us about mantle-source compositions. Today, based mostly on isotopic data from OIB and mid-ocean ridge basalt (MORB), five types of mantle-source regions, or components, are recognized (Zindler and Hart, 1986; Hofmann, 2003). These appear to reflect variable melt-extraction and subduction-related recycling of materials back into the mantle over Earth history, although the specifics of how each "component" formed are debated.

Models for the distribution, scale and melting behaviour of these components are even more contentious and lead to very different hypotheses for chemical structure and convection patterns in the mantle. One school sees some amount of plume-related(?) exchange between primitive (relatively unmelted) lower mantle and "depleted" (previously melted) upper mantle (e.g., Allègre, 2002; Hofmann, 2003). The other sees the entire mantle as convecting and depleted; the lower mantle is separated from the upper mantle that is locally enriched in subduction-recycled components (Anderson, 1999; Hamilton, 2003). Mantle plumes may not exist (Anderson, 2000). Thus a healthy, and at present unresolved, debate has emerged that reflects fundamental views of how planet Earth works, and OIBs are front and centre in the discussion.

This paper looks at how OIB compositions (Table 1) reflect source region compositions and mantle melting processes (e.g., pressure effects, impact of fluids, melting percentage). Hypotheses for the origin of mantle heterogeneity (the mantle components), evidence for the survival of primitive mantle, and models for chemical structure in the Earth are then reviewed. This manuscript complements Greenough et al., (2005) that covers the mineralogy, petrology and differentiation of oceanic island basalts.

SOURCE-REGION MELTING

Controls on Major-Element Compositions

A recurring theme in petrology is whether a basalt has experienced differentiation or is "primary" and derived directly from the mantle. Although debated, primary magmas are thought to have Mg# values of about 0.72 as a result of equilibration with Fo_{92} olivine that is found in most mantle lherzolite xenoliths (Roeder and Emslie, 1970). At least a few aphyric basalts on most oceanic islands have Mg# values around 0.72, which is consistent with this hypothesis. Olivine partitioning data indicate that primary basaltic magmas should have Ni/MgO ratios (ppm/wt.% oxide) between 22 and 50 with Ni = 200 to 1000 ppm (Basaltic Volcanism Study Project, 1981, p. 424). A review of the Ni, Cr, Co and Sc contents in approximately 200 "primary" basalts (Mg# values of 0.72) from French Polynesia, using regression analysis, gives concentration ranges of 350-550, 650-930, 70-80 and 20-40 ppm, respectively.

Figure 1a illustrates the pressure effects on the beginning-of-melting point in a synthetic ternary system modelling lherzolite. Points I_0, I_1, I_2, I_3 show that magmas become increasingly silica-undersaturated, and Ne normative, with increasing pressure (1 atmosphere, 10, 20, and 30 kbar, respectively). Experiments on an anhydrous spinel lherzolite indicate that magmas change from Ne normative (alkaline) to Hy normative (tholeiitic) as melting percentages increase, and the Ne component increases as pressure increases (Fig. 1a). As Haase (1996) emphasized, the silica content of magmas is very sensitive to pressure. Melting experiments also show that CO_2 leads to undersaturated magmas, whereas H_2O produces more silica-rich magmas (Fig. 1b). These generalizations suggest that relative to tholeiites, oceanic island alkaline magmas reflect small percentages of melting of CO_2-rich lherzolite at high pressures.

Metasomatism

Metasomatism is the process whereby migration of CO_2- and H_2O-rich fluids (or melts), through the mantle, leads to local incompatible element enrichment prior to magma formation. Alkaline OIBs commonly contain too much Rb for their observed $^{87}Sr/^{86}Sr$ ratios. This suggests that metasomatic fluids or melts carry large ion lithophile elements to their sources a short time prior to melt extraction. Metasomatism may also occur long before magma genesis. Many experiments suggest that ancient subduction-related metasomatism affected OIB mantle sources long before island magmatism. Clearly, metasomatism coincident with magmatism is important, but it cannot yield the large variations in daughter radiogenic isotopes observed among islands because they require millions or billions of years to develop from parent isotopes having long half-lives. However, Kamber and Collerson (1999) proposed that OIB Pb isotope variations partly reflect metasomatism by melts derived from the lower mantle only 150 million years ago. Halliday et al. (1995) argued that melt metasomatism during lithosphere formation at the ocean ridges produces high U/Pb ratios (high μ = high "mu") that

Table 1: Average whole-rock major element, trace element and isotopic data for selected oceanic islands.

Island	Gough	Sao Miquel	Easter Is.	Tristan	Isabela	Tutuila	St. Helena	Iceland	Tahiti	Aitutaki	Mangaia	Tubuai
Series	Alkaline	Alkaline	Alkaline	S. Alkaline	Tholeiitic	Alkaline	Alkaline	Tholeiitic	Alkaline	S. Alkaline	Alkaline	S. Alkaline
Type	EM1	EM2	DM	EM1	DM	EM2	HIMU	DM	EM2	EM1	HIMU	HIMU
SiO_2	49.53	47.42	48.67	46.31	49.11	46.84	46.55	48.85	45.33	43.01	45.19	44.04
TiO_2	3.1	3.45	3.71	3.31	3.34	3.94	3.09	1.4	3.62	2.53	2.97	2.93
Al_2O_3	14.27	13.82	16.04	15.57	14	12.68	14.98	15.05	13.21	12.01	13.29	13.32
FeO	10.4	10.87	10.77	11.38	12.88	12.49	12.15	10.59	12.35	12.03	12.99	13.48
CaO	8.21	10.09	9.79	10.21	10.43	9.42	10.6	12.19	10.94	12.11	12.2	11.68
MgO	8.02	8.74	6.34	6.54	5.94	9.95	7.73	9.31	9.89	11.57	8.94	9.16
MnO	0.15	0.17	0.17	0.18	0.2	0.18	0.19	0.18	0.18	0.2	0.21	0.24
K_2O	2.46	2	0.81	2.21	0.58	1.09	1.11	0.22	1.24	1.52	0.88	1.04
Na_2O	3.22	2.9	3.27	3.57	3.14	2.91	3.05	2.02	2.6	4.02	2.87	3.49
P_2O_5	0.65	0.55	0.43	0.73	0.38	0.51	0.56	0.17	0.63	1.01	0.46	0.63
Mg#	0.58	0.61	0.53	0.52	0.47	0.61	0.54	0.63	0.59	0.65	0.55	0.56
Li					5.6				6.4	13.7	8.8	6.6
Cs	0.23	0.46	0.088	0.87	4.8		0.15	0.15			0.29	0.27
Rb	48	46	19	54	11	36	27	6	36	43	18	28
Sr	769	670	406	1059	317	526	596	180	662	1148	508	699
Ba	726	584	214	666	120	221	338	62	430	843	278	355
La	66.4	50.3	28.6	56.7	25.6	24.1	50.7	7.6	43.3	71.8	38.9	62.8
Ce	96.7	105	57.3	124.4	55.9	56.8	102	18.9	99.9	131.8	81.3	129.2
Pr	10.8	13.1	5.3	14.3	6.3		10.5	1.6	12.2		9.3	14.3
Nd	51.8	47.7	35.6	65	33.2	39.6	43.3	12.1	48.8	59.9	38.5	55
Sm	9.85	9.34	8.03	10.7	8.53	9.57	8.61	3.25	9.88	11.41	8.09	9.57
Eu	3.38	3.12	2.33	3.17	2.58	2.76	2.68	1.16	3.22	3.52	2.52	2.99
Gd		8.68	6.95	7.74	8.79	9.51	7.78	2.96	8.99		7.07	8.25
Tb	1.01	1.21	1.11	0.98	1.46	1.15	1.2	0.65	1.33	1.44	1.03	1.02
Dy		6.32	6.34	5.83	7.61	4.6	5.85	3.24	6.82		5.44	6.28
Ho			1.19	1.02	1.52		1.28	0.69	1.19		1.03	0.98
Er		2.88	3.31	2.82	4		2.82	2.01	2.82		2.6	2.82
Tm			0.496	0.44	0.549		0.4	2.41	0.381		0.331	0.322
Yb		2.35	3.19	2.1	3.89	2.12	2.73	2.18	2.14	1.9	2.06	2.09
Lu		0.333	0.465	0.288	0.579	0.25	0.406	0.327	0.295	0.256	0.298	0.293
Y	28.9	30.9	32.8	27.2	39	32	32.6	24	31.5	31	28.5	29.3
Zr	309	290	247	281	328	234	245	92	305	284	223	271
Hf	8.21	7.99	6.58	7.73	7.17	5.77	5.62	3.83	7.64	4.73	4.98	7.14
Nb	50.5	60.1	34.7	72.2	28.7	33.5	64.9	9.9	47.9	71.5	51.1	78.8
Ta	3.56	4.32	2.63	4.54	2.16	2.19	3.48	1.19	3.54	4.53	3.4	5.54
Th	5.42	5.23	3.02	6.97	2.76	3.34	3.72	1.03	5.44	12.97	4.17	8.02
U	1.33	1.37	0.95	1.72	0.78	0.66	1.21	0.36	1.49	2.59	1.12	2.06
Ga	21.3	22			22.7			17.2			20.4	18.2
V	185	264	248	282	332	280	229	266	287		300	263
Sc	20.6	22.4	25.9	21.6	27.6	29	30	38.7	22.9		31.3	26.2
Cr	217	357	143	133	121	364	299	366	397	173	464	361
Co	46.8	43.7	34.3	49.3	48.3	42	65.1	51.8	57.3		61.9	53.6
Ni	194	179	76	72	52	229	136	157	209	133	169	164
Cu	33.5	61.2	52.5	43.7	82.9		54	122.6	79.1		116.7	102.3
Pb		4.3	1.53	4.48	1.62	3.2	2.48	1.61	3.62	7.9	2.4	4
Zn	108	115	101	100	120		109	89	115		120	111
Mo				4.73			4.44	0.88				
Cd			114	98				87				
Sn	3.09	3.46		3.43	1.94		2.39		3.08			4.54
Sb	0.217	0.29		0.344			0.247		0.152			0.332
Te			0.29	0.55				0.93				
W				1.25			0.87					
Re	90.2	392.3			455.4	209	146.8	479		51	325	398
Os	30.6	63.4				38.8	17.9	122		27.4	274	351
$^{143}Nd/^{144}Nd$	0.512574	0.512803	0.5129694	0.5125603	0.5129837	0.5127315	0.51288	0.5130465	0.5128357	0.5127642	0.5128875	0.512896
$^{87}Sr/^{86}Sr$	0.70532	0.7044491	0.7031304	0.7049259	0.7030976	0.7058075	0.7029127	0.703183	0.7043635	0.7047786	0.7028407	0.7028247
$^{206}Pb/^{204}Pb$	18.4235	19.74831	19.512556	18.610522	19.138839	19.095529	20.690347	18.690463	19.063913	19.018375	21.658163	21.07552
$^{207}Pb/^{204}Pb$	15.608	15.686621	15.611	15.547087	15.573037	15.608588	15.767774	15.476551	15.557	15.71375	15.888395	15.75992
$^{208}Pb/^{204}Pb$	38.892	39.84669	39.197	39.066913	38.763392	39.290706	39.717754	38.043333	38.676696	38.951	40.540674	40.3344
$^{187}Os/^{188}Os$		0.140293						0.132117		0.137	0.1768	
$^{176}Hf/^{177}Hf$					0.2830689		0.282888	0.2832239				0.2829436

Notes: Island = Island or area where data came from. Series = whether rocks are tholeiitic, alkaline or strongly alkaline (S. Alkaline) based on total alkalis versus silica diagram. Type = mantle source type where EM1 = enriched mantle 1, EM2 = enriched mantle 2; HIMU = High μ = High U/Pb; DM = depleted mantle. Columns represent averages. Major element oxides in wt. % recalculated to 100% volatile free with total Fe as FeO. Mg# = Mg/(Mg+0.9Fe) atomic. Trace element concentrations in ppm except Re and Os in ppt and Au, Pd, Pt, Ru, and Ir in ppb.

Radiogenic isotopes (Nd, Sr, Pb, Os, Hf) represent initial ratios (corrected for age if necessary).

Averages for more islands, the number of samples averaged, standard deviations, data sources and data reduction procedures appear with the supplementary materials.

with aging (~10^8 years) can explain the high ^{206}Pb/^{204}Pb ratios of HIMU oceanic islands (see Isotopes section below).

Percentage of Melting

The percentage of melting affects trace-element concentrations as illustrated by chondrite-normalized rare-earth-element (REE) diagrams (Fig. 2; Table 1). Highly alkaline magmas (e.g., Aitutaki; low % melting) show steep slopes and tholeiites low slopes (e.g., Iceland; high % melting). La (largest REE cation) is substantially more incompatible in mantle minerals than Lu (smallest REE). Nearly all La enters the first drops of magma yielding high concentrations in alkaline magmas. Concentrations fall rapidly as the percentage of melting increases. Lu is less incompatible, so magma concentrations are low and change slowly, causing La/Lu ratios to decrease as melting increases. Ratios reflecting relative percentages of melting are calculated from elements $\geq$ 10 elements apart in the Sun and McDonough (1989) incompatibility list (Table 2, notes). Thus, Nb/Y (23 elements apart) is an excellent chemical separator of alkaline (ratios > 1) and tholeiitic (< 1) magmas and provides a continuous measure of "alkalinity". The correlation in Figure 3 shows that as the depth/pressure of melting increases (reflected by SiO_2; Haase, 1996), the percentage of melting (monitored by Nb/Y) decreases. The depth and pressure of melting correlate with the age (Haase, 1996) and thickness (Watson and McKenzie, 1991) of the lithosphere. Thus, strongly alkaline magmas form where the lithosphere is old, cold and thick, and this causes melting to occur at the greatest depths, where the percentage of melting is apparently low.

The percentage of melting correlates with, and appears responsible for, excesses in the U-series ratios (^{230}Th/^{238}U), (^{226}Ra/^{230}Th), and (^{231}Pa/^{235}U) (brackets = activity ratios), which increase between tholeiites (high % melting) and alkali basalts (Bourdon and Sims, 2003; see brief introduction to U-series dating in Oceanic Island Volcanism I: Mineralogy and Petrology, Greenough et al., 2005). Apparently, magma is enriched in more-incompatible daughter isotopes (^{230}Th, ^{226}Ra, ^{231}Pa) during melting and the process of melt formation and extraction occurs rapidly enough that daughter excesses are not erased (equilibrium is not re-established). Plume models for Hawaiian volcanism indicate that excesses are negatively correlated with mantle upwelling velocity; both upwelling velocity and melting percentage (faster = higher % melting) decrease away from the axis of the plume.

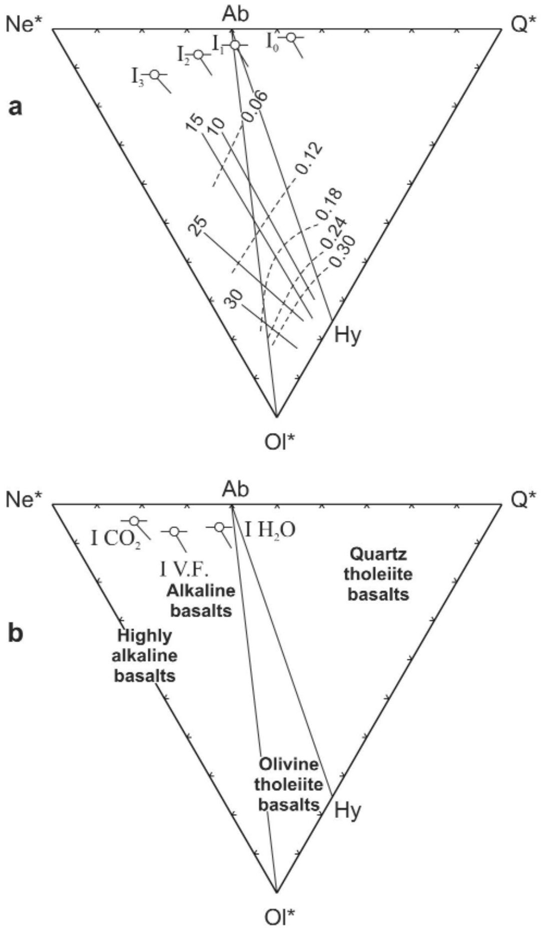

Figure 1. Schematic diagrams showing the effect of pressure and percentage of melting and volatile composition on the composition of magmas. a) The points I_0, I_1, I_2, and I_3 refer to the beginning-of-melting invariant points at pressures of 1 atmosphere, 10, 20, and 30 kbar in the synthetic ternary system Mg_2SiO_4-SiO_2-$NaAlSiO_4$ (Kushiro, 1968; re-plotted as wt.% normative Ol*, Q* and Ne*). Results of experiments on an anhydrous spinel lherzolite (Hirose and Kushiro, 1993) are shown by solid lines that give melt compositions formed at various pressures (in kbar, labelled 10, 15, 25, and 30) and melt fractions (dashed lines labeled 0.30, 0.24 etc., which denote 30% and 24 % melting). b) Diagram showing that beginning-of-melting invariant points move toward greater silica undersaturation between water- (I H_2O) and CO_2-saturated (I CO_2) conditions (P = 20 kbar) in a synthetic system. V.F. = volatile free invariant point. From Eggler and Holloway (1977).

Residual Minor Phases

The phases that are left behind after magma extraction from the mantle can be inferred from trace-element data. For example, most "undifferentiated" OIBs exhibit low chondrite-normalized heavy REE (Yb, Lu) concentrations (6 - 9 times chondrites) that change little between alkaline (e.g., Kauai) and tholeiitic (Kilauea) magmas (Fig. 2). A persistent phase creates a bulk crystal/liquid partitioning coefficient for these elements close to 1. Garnet shows high partition coefficients for the heavy REE (e.g., Rollinson, 1993; p. 108). Apparently most OIBs form at pressures great enough for garnet stability, and the mineral forms a residual phase over a wide range of melting percentages. Excesses in the activity of (^{230}Th) over (^{238}U) are commonly ascribed to the presence of residual garnet in oceanic island sources (Bourdon and Sims, 2003).

Highly alkaline rocks (La > 50 ppm) show lower element/La ratios for Rb, K, Sr, Th, Zr, Nb and Ta indicating residual minor phases in their sources (Sun and McDonough, 1989). In single-locality suites of primitive (Mg# = 0.67-0.75) basalts, rocks with the highest Sr show intermediate Rb concentrations, those with highest Rb have intermediate Sr, and the lowest Rb and Sr occur together (Greenough, 1988). This may reflect retention of Rb in phlogopite at low percentages of melting (highest Sr rocks). As phlogopite melts, magma Rb concentrations rise, and they peak just as it is entirely consumed. With more melting, both Rb and Sr decrease because of dilution. A similar "arrow-shaped" pattern for Ti versus Sr suggests a residual titanate mineral or Ti-phlogopite at low-percentages of melting. Highly alkaline magmas also have somewhat low Nb, Ta, Zr and Hf (relative to Ba, La) supporting residual rutile or ilmenite although the Sr-Ti relationship favours phlogopite (Greenough, 1988). Halliday et al. (1995) argued that OIB sources with high U/Pb ratios (HIMU) result from migration of small percentage melts that equilibrated with minor amphibole, sulfide and phlogopite. In summary, minor minerals probably play a major role in controlling the chemistry of some OIB source region types and their alkaline magmas.

ISOTOPES AND SOURCE REGION COMPOSITIONS

Lithophile and Siderophile Isotopes

Since the pioneering work of Gast, Tilton and Hedge in the 1960s, isotopic ratios have been the cornerstone of mantle composition studies. This is because, unlike element concentrations, these ratios are generally thought to be unaffected by melting percentages (but see Os discussion below). Variations in $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$, $^{187}Os/^{188}Os$ and $^{176}Hf/^{177}Hf$ reflect long-lived fractionation of parent isotopes ($^{87}Rb/^{86}Sr$, $^{147}Sm/^{144}Nd$, $^{238}U/^{204}Pb$, $^{235}U/^{204}Pb$, $^{232}Th/^{204}Pb$, $^{187}Re/^{188}Os$, $^{176}Lu/^{177}Hf$, respectively) from fore-listed daughter isotopes. For example, Rb is more incompatible in mantle minerals than Sr during melting. Magma removal to form oceanic crust results in mantle residue that is depleted in Rb relative to Sr, and the crust is Rb-enriched. Because ^{87}Rb decays to ^{87}Sr with time, the crust develops a high $^{87}Sr/^{86}Sr$ ratio relative to unmelted mantle, but this ratio in the residue increases slowly (is low today) because of being depleted in ^{87}Rb (see Faure, 2001).

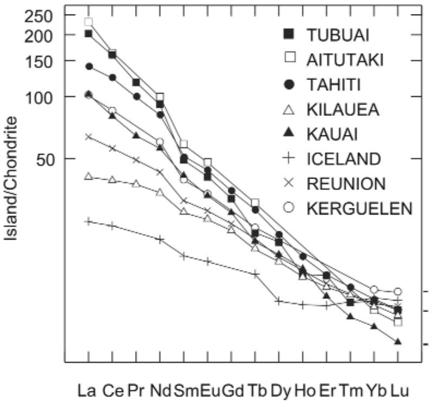

Figure 2. Chondrite-normalized rare earth element diagrams for basalts (averaged data) from selected oceanic islands. Steep patterns (Aitutaki and Tubuai) are typical of strongly alkaline OIBs. Lower slopes for Kilauea and Iceland are representative of tholeiites. Normalizing values of Boynton from Rollinson (1993, p. 134). Data sources in supplementary materials [see http://www.gac.ca/JOURNALS/geocan.html].

Isotopes are used to identify four end-member types of mantle formed by previous melt extraction and recycling of materials (e.g., crust) by subduction (Zindler and Hart, 1986; Hofmann, 2003). The component (type) sampled by MORB has low incompatible element concentrations, low $^{87}Sr/^{86}Sr$, and high $^{143}Nd/^{144}Nd$, reflecting previous (ancient) melt extraction (Fig. 4). This depleted MORB mantle (DMM) is not well represented by OIB (see Iceland debate; Hanan et al., 2000; Fitton et al., 2003), but less-extreme depleted mantle (DM) underlies some islands (e.g., Easter). High Pb isotopic ratios in OIB (e.g., St. Helena, Fig. 4) reflect high mantle U/Pb and Th/Pb ratios in the HIMU component (= high μ = high $^{238}U/^{204}Pb$). The enriched mantle (EM) components have high incompatible element concentrations relative to hypothetical primitive (unmelted) mantle. The EM1 islands show the lowest $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$ ratios and high $^{87}Sr/^{86}Sr$ (e.g., Gough, Fig. 4) and EM2 islands have the highest $^{87}Sr/^{86}Sr$ ratios (e.g., Tutuila). Most OIBs have intermediate compositions explained by convective mixing between components (Zindler and Hart, 1986). Three-dimensional graphs of isotopic ratios (e.g., Pb, Sr, Nd) show that islands plot close to a mixing plane, determined by regression analysis (Fig. 5; Zindler and Hart, 1986). These simple isotopic relationships are easier to explain if the components formed at particular times by specific processes. Thus they may reflect major events in Earth's evolution.

The Nd-Sr isotopic array (Fig. 4a) might be explained by mixing between depleted MORB mantle (depleted to form continental crust) and primordial (unmelted) mantle but EM1 and EM2 islands plot off the array and Pb isotope variations are unaccounted for (e.g., HIMU; Fig. 5a). Thus this simple model advocating unidirectional movement of incompatible elements into the crust is not tenable.

A plot of $^{206}Pb/^{204}Pb$ versus $^{207}Pb/^{204}Pb$ sheds light on mantle evolution (Fig. 4c). The ratio of $^{235}U/^{238}U$ has changed throughout Earth history because the two isotopes have different decay rates, but at any one time the ratio was everywhere the same. This allows the calculation of model ages. Any mantle fractionation process that creates variable U/Pb ratios and a single set of $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios will, with time, evolve sets of Pb isotopic ratios that define a linear array dating the disturbance (see Faure, 2001). The Geochron dates the Earth (Fig.4c). Most OIBs and MORBs plot to the right of the Geochron (Fig. 4c) and this is referred to as the Pb paradox. It implies that U was added or Pb removed from the mantle sources of all oceanic basalts in the ancient past. MORB basalts are mildly enriched in U (and Th), relative to Pb during mantle melting and the residue should have a low U/Pb ratio. However, MORBs have high $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios, requiring a long-term high U/Pb ratio. To explain the Pb paradox, it has been suggested that fluids efficiently and permanently delivered Pb from oceanic lithosphere to the continental crust during ancient subduction events, whereas U was more effectively recycled back into the mantle (Hofmann, 1997; 2003).

Given the importance of subduction, it is reasonable to expect that OIB magma compositions might hold evidence for recycling of oceanic lithosphere. HIMU basalts are commonly ascribed to melting of mantle containing recycled oceanic crust (Zindler and Hart, 1986; Hofmann, 1997). Mixing between this reservoir and depleted mantle can explain first-order correlations between Pb isotopes (Fig. 4c, 4d). If so, the slope on the line (model Pb age) has no age significance. However, HIMU sources with the highest ^{206}Pb/^{204}Pb ratios could be 2 billion years old (Hofmann, 1997). Kamber and Collerson (1999) suggested that mixing between depleted MORB mantle and melts from EM1-type mantle can produce HIMU-type sources. HIMU Pb isotopic ratios are produced after only 150 Ma. Lithium isotopes (^{7}Li/^{6}Li reported as δ^7Li), appear to be primarily fractionated by low- (surface) and medium-temperature (crust and lithosphere) processes. There is a significant range in OIB δ^7Li ratios and this supports widespread distribution of recycled materials in the mantle (see review, Elliott et al., 2004). However, HIMU sources appear enriched in the heavy ^{7}Li isotope. This is the opposite of what is predicted for mantle with basaltic ocean floor that has been "processed" during subduction. Thus, Li may place new constraints on HIMU formation and is potentially more useful than other stable isotopes for monitoring recycling processes.

EM1 and EM2 cannot be explained by mixing between depleted mantle and HIMU components (Fig. 4a, 4b; Hofmann, 1997). The Sr, Nd, Hf and Pb isotopes of EM1-sourced OIBs resemble lower continental crust but Pb/Zr ratios are low. A "primitive" mantle explanation for the enriched nature of EM1 is inconsistent with low ^{3}He/^{4}He ratios that imply previous and extensive outgassing and melting. Gasparini et al. (2000) proposed that EM1 basalts form by melting subducted (recycled) oceanic plateaux containing enriched basalts produced by an ancient plume head. Alternatively, EM1 sources may bear an imprint from subducted pelagic sediment subduction (Weaver, 1991) or represent subcontinental lithospheric mantle scraped from beneath continents (e.g., Milner and le Roex, 1996). Enriched mantle sources are more common in a globe-encircling band possibly related to the detachment of African and South American subcontinental lithosphere during the assembly and breakup of Gondwana. EM1 may be delaminated Archean subcontinental lithosphere, given that the most extreme isotopic examples come from some Cenozoic, cratonic mafic magmas (Greenough and Kyser, 2003). Diamonds are most commonly associated with Archean subcontinental lithosphere but nanodiamonds were recently reported from mantle xenoliths in EM1-like Hawaiian basalts (Wirth and Rocholl, 2003). Tatsumi (2000) showed that EM1 Sr-Nd-Pb isotopic compositions are consistent with melting Archean pyroxenite from the subcontinental lithosphere, and the ^{206}Pb/^{204}Pb versus ^{207}Pb/^{204}Pb model age from EM1 sources supports an Archean age (Fig. 4c).

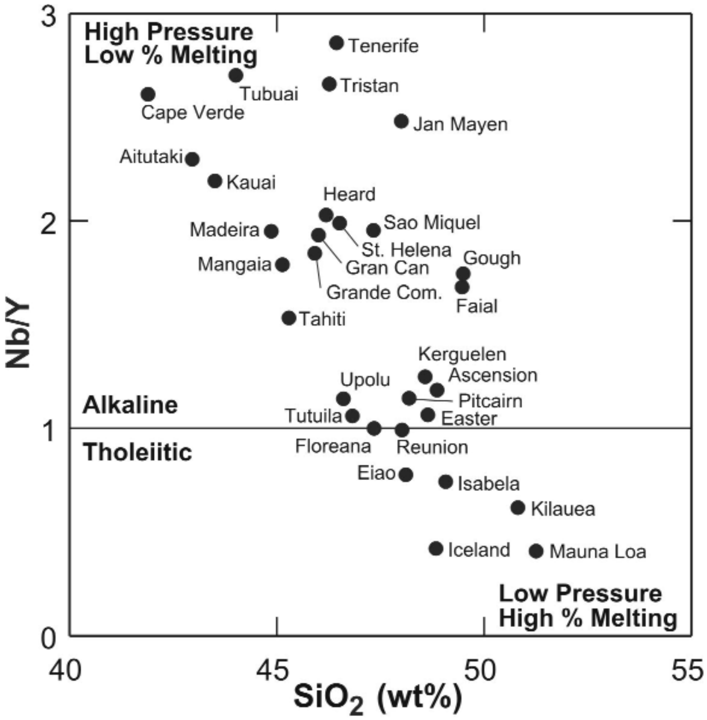

Figure 3. Plot of average SiO_2 versus Nb/Y in oceanic island basalts. Highly alkaline magmas are products of low percentages of melting (high Nb/Y) at great depths (low SiO_2) below old, cold and thick lithosphere. Tholeiites form under opposite conditions. The left edge of the data cluster shows a strong negative correlation. Differentiation tends to increase SiO_2, thus moving the points to the right. Compare this Nb/Y-based classification with classifications based on total alkalis ($Na_2O + K_2O$) versus silica (SiO_2) or normative mineralogy (calculated mineralogy from major element analyses) in Greenough et al. (2005; this series). Abbreviation: Gran Can = Gran Cararia, Canaries. Data for selected islands given in Table 1. Complete data set and references appear in the supplementary materials on the GAC website at http://www.gac.ca/JOURNALS/geocan.html.

The high ^{207}Pb/^{204}Pb and ^{87}Sr/^{86}Sr of EM2 sources (Figs.4 and 5) suggest that they contain recycled (subducted) terrigenous sediments or pelagic sediments having a continental signature (Weaver, 1991). Elevated oxygen isotopic ratios (δ^{18}O), reflecting near-surface, low-temperature, fractionation processes, support the subducted sediment model (Eiler et al., 1997). EM2 may also represent delaminated, post-Archean, subcontinental lithosphere (Greenough and Kyser, 2003).

The ^{187}Re - ^{187}Os system provides insights into the origin and distribution of mantle components. Compared to lithophile isotopic systems (e.g., Rb-Sr) that behave incompatibly during mantle melting, Os is compatible and Re is incompatible; their chalcophyic/siderophilic geochemistry suggests they are mostly stored in the core (Hauri, 2002). Basalts are enriched in Re

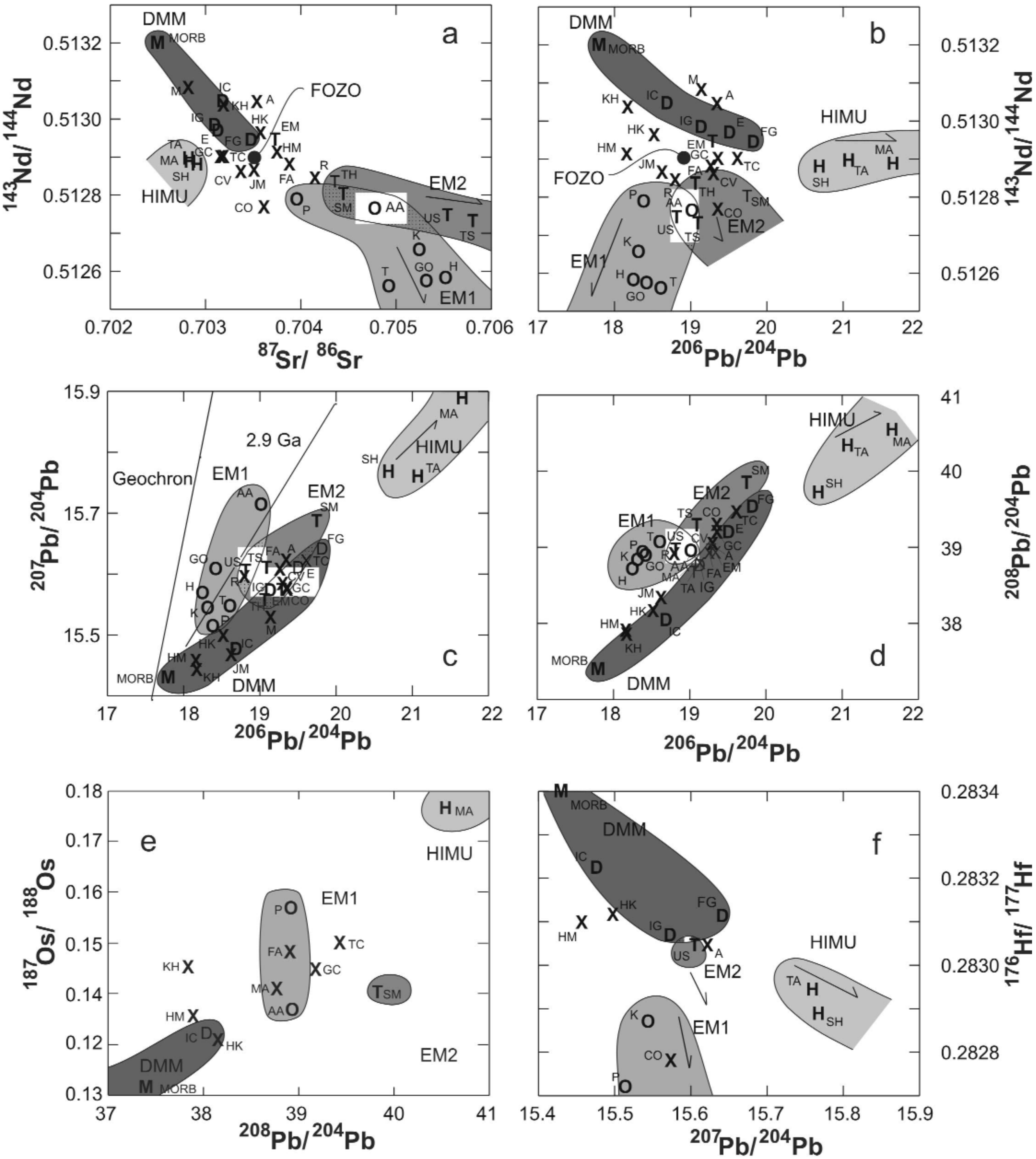

Figure 4. Plots of isotopic ratios in oceanic island basalts. Hand-drawn fields outline areas dominated by each mantle component. Arrows point toward extreme (hypothetical) mantle component compositions. Diagram c) shows the Geochron and a least-squares line through EM1 data that gives a model age of 2.9 Ga. Sample symbols (O = EM1; T = EM2; H = HIMU; D = Depleted Mantle) reflect commonly assigned tendencies for islands, with X's not categorized or intermediate. Composition of FOZO (= Focal Zone) from Hilton et al. (1999) based on samples with high ^{3}He/^{4}He. Island abbreviations: A = Ascension; AA = Aitutaki, Austral-Cook Islands; CO = Grande Comore, Comoros; CV = CapeVerde; E= Easter Island; EM = Eiao, Marquesas; FA= Faial, Azores; FG = Floreana, Galapagos; GC = Gran Canaria, Canaries; GO = Gough; H = Heard Island; HK = Kilauea Volcano, Hawaii; HM = Mauna Loa Volcano, Hawaii; IC = Iceland; IG = Isabela, Galapagos; JM = Jan Mayen ; K = Kergulen; KH = Kauai, Hawaii; M= Madeira; MA = Mangaia, Austral-Cook Islands; P = Pitcairn; R= Reunion; SH = St. Helena; SM = Sao Miquel, Azores; T = Tristan da Cunha; TA = Tubuai, Austral-Cook Islands; TC = Tenerife, Canaries; TH = Tahiti, Societies; TS = Tutuila, Samoa; US = Upolu, Samoa.

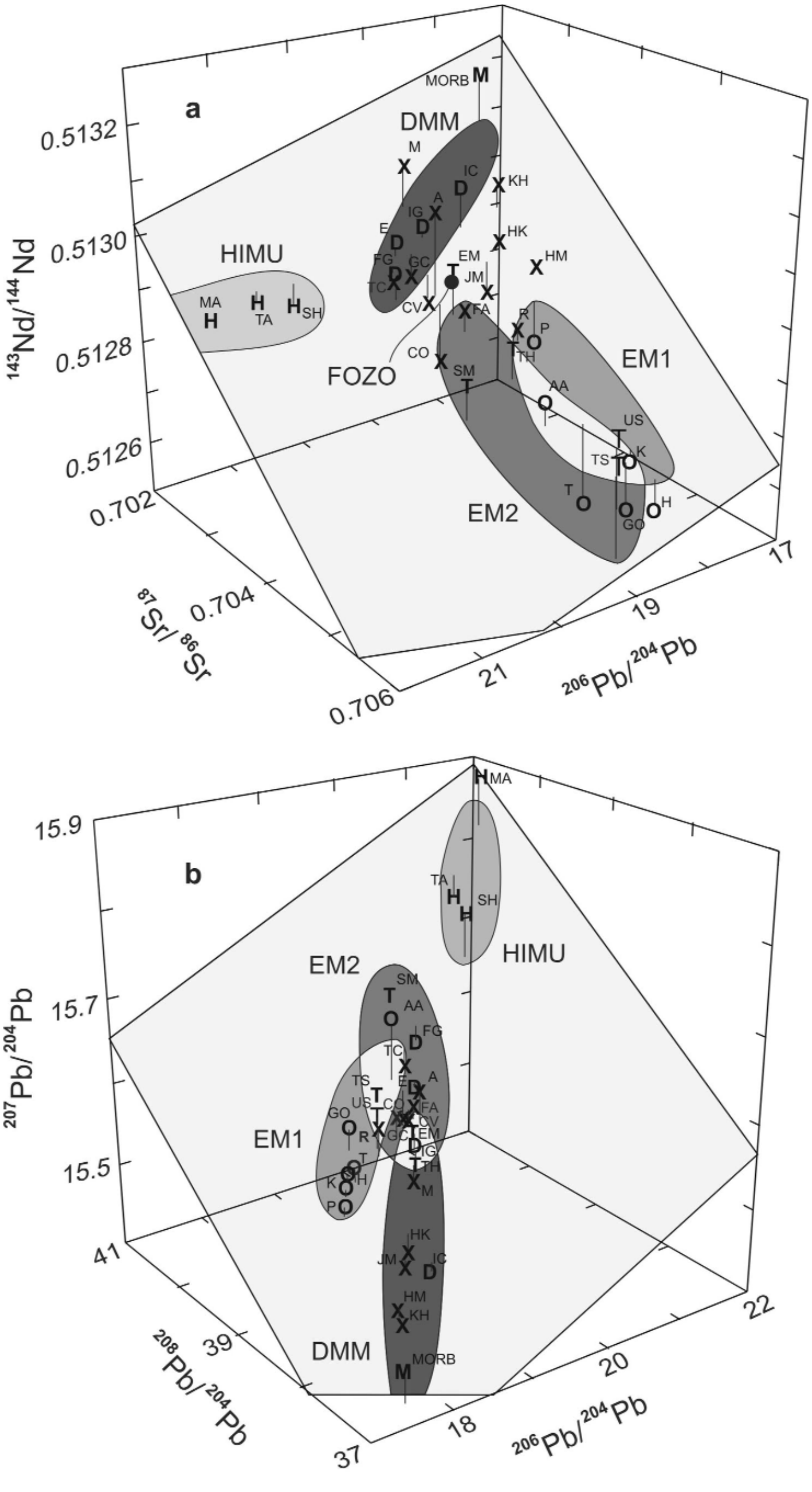

Figure 5. Plots of isotopic ratios in oceanic island basalts portrayed in 3-dimensional isotopic space. a) ^{206}Pb/^{204}Pb - ^{143}Nd/^{144}Nd - ^{87}Sr/^{86}Sr and b) ^{206}Pb/^{204}Pb - ^{207}Pb/^{204}Pb - ^{208}Pb/^{204}Pb. Shading shows the best-fit regression plane through the data. "Sticks" drawn from the plane indicate how far above (sample symbol sits atop the stick) or below (symbol at bottom of stick) the plane a sample occurs. Mantle component fields are drawn on the regression plane. Island symbols from Figure 4. Sample symbols: O = EM1; T = EM2; H = HIMU; D = Depleted mantle; X = not categorized or transitional; FOZO = Focal Zone composition of Hilton et al. (1999).

over Os, and they develop high ^{187}Os/^{188}Os ratios over time, which should identify recycled ocean crust in the mantle. Indeed, Os isotopes suggest that most OIB sources contain > 10% recycled basalt and HIMU sources are even higher (i.e., high ^{187}Os/^{188}Os; Fig. 4e) (Hauri, 2002).

The geochemistry of Os is not well understood. Mantle minerals holding Os include sulphides, chromite and metal alloys; their distribution and melting behaviour are not well known. Silicate phases hosting Re may melt before Os-rich phases, resulting in magmas with high ^{187}Os/^{188}Os ratios (from Re decay) out of equilibrium with the bulk source composition; thus magmas may not reflect average mantle Os compositions (Becker, 2000; Hofmann, 2003). Walker et al. (1999) cautioned against using Os to estimate the percentage of recycled ocean floor in OIB sources. Although examples of correlations between Os and lithophile isotopes exist (Shiano et al., 2001), they are "disconnected" in most OIBs. The EM1 basalts, which show both high and low Os ratios, illustrate this well (Fig. 4e). An alternative to disequilibrium melting is that Os isotopes reflect the proportion of peridotite to recycled oceanic crust, whereas other isotopes are controlled by the amount of recycled sediment (Eisele et al., 2002). Possibly OIB Os isotopes, along with platinum-group-element concentrations are controlled by mantle-outer core (high ^{187}Os/^{188}Os? ratios) interaction, or the distribution of late-bombardment meteorite material (high Pt, Os etc.) in the mantle (Fryer and Greenough, 1992; Walker et al., 1999). There is much yet to learn about and from Os isotopes.

Hafnium and Nd isotopes support the presence of recycled ocean floor in the mantle. In a plot of ^{143}Nd/^{144}Nd versus ^{176}Hf/^{177}Hf, a regression line passed through depleted mantle, OIB and continental crust does not pass through bulk silicate Earth. This suggests there is a "hidden" mantle reservoir with prolonged, high Sm/Nd and low Lu/Hf (time-integrated high ^{143}Nd/^{144}Nd and low ^{176}Hf/^{177}Hf) similar to that predicted for extreme HIMU sources (Bizzarro et al., 2002; Pearson and Nowell, 2002). Modern MORB contains the requisite trace-element ratios for such a hidden reservoir. The Sm/Nd ratio is high reflecting previous melt extraction whereas the incompatibility of Hf, relative to Lu during melting, results in low Lu/Hf ratios. Thus, there may be a "hidden", extreme, HIMU-like mantle reservoir containing basaltic crust that represents 1 to 15% of the silicate Earth.

Noble Gas Isotopes

Noble gas isotopes (e.g., ^{3}He/^{4}He, ^{20}Ne/^{22}Ne, ^{21}Ne/^{22}Ne, ^{40}Ar/^{36}Ar, ^{129}Xe/^{130}Xe) are central to some heated debates on the composition and structure of the mantle (Hilton and Porcelli, 2003; McDougall and Honda, 1998). Some isotopes are radiogenic (^{4}He and ^{21}Ne from U and Th decay, ^{40}Ar from ^{40}K, ^{129}Xe from ^{129}I), and exceptionally high ratios in mantle reservoirs (e.g., MORB ^{40}Ar/^{36}Ar > 20,000 compared to 295.5 in atmosphere) reflect major enrichment in the radiogenic, relative to the primordial (unradioactive and unradiogenic) isotopes. Apparently the Earth underwent massive degassing so that mantle gases are now dominated by the radiogenic isotopes. High ^{129}Xe/^{130}Xe ratios in MORBs compared to the atmosphere indicate that the catastrophic degassing occurred during the first 100 Ma of Earth history (McDougall and Honda, 1998) because ^{129}Xe is produced by the radioactive decay of short-lived ^{129}I (½ life = 17 Ma). Lower atmospheric ^{129}Xe/^{130}Xe ratios indicate that the degassing occurred before most ^{129}I had decayed.

MORB sources show low, uniform ^{3}He/^{4}He ratios whereas OIB sources are variable. The highest ratios occur in some Hawaiian and Icelandic basalts (Hilton et al., 1999). High ^{3}He (relative to ^{4}He) implies formation from less-degassed or undegassed primordial mantle. Supporting this, these basalts have FOZO isotopic compositions (Hilton et al., 1999). Arrays can be drawn, in Sr-Nd-Pb isotopic space, from the mantle components to a common point called FOZO for focal zone (Hart et al., 1992; Figs.4a, 4b and 5a). FOZO is regarded by some as a fifth mantle component of possibly primordial origin and common to (involved in mixing to form) all OIB.

An alternative explanation for high ^{3}He/^{4}He ratios in specific OIB samples is that small-scale melting leads to localized sampling of highly depleted (low U+Th) sources that produced little ^{4}He – the opposite of the primordial mantle hypothesis (Anderson, 1999; 2001; Meibom et al., 2003)! In this model, low but uniform ^{3}He/^{4}He in MORB reflects a source having localized domains of depleted and enriched mantle, the latter containing recycled materials (e.g., ancient subducted crust) with high (U+Th)/He (high radiogenic ^{4}He) and low ^{3}He/^{4}He ratios. The large-scale melting that yields MORB homogenizes the isotopic signature from these domains but it is dominated by radiogenic He from enriched mantle. Slow-spreading ridges that have reduced melt production, and more localized melting, should have more variable ^{3}He/^{4}He ratios (Anderson, 2001) but Georgen et al. (2003) present evidence that the slow-spreading Southwest Indian Ridge shows uniform ^{3}He/^{4}He ratios. Another issue is that the Iceland samples with the highest ^{3}He/^{4}He ratios on Earth have elevated ^{87}Sr/^{86}Sr and lower ^{143}Nd/^{144}Nd ratios relative to other Iceland basalts indicating they are not coming from a highly depleted source (Hilton et al., 1999).

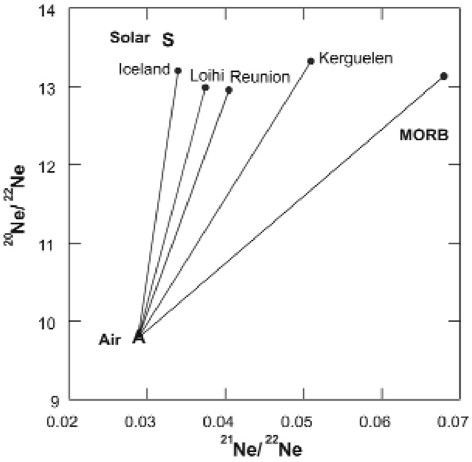

Figure 6. Three-isotope neon plot showing regression lines through Ne isotope data for various locations (labeled) as well as the isotopic compositions of Solar (S) and Air (A; atmospheric) neon. The ends of the lines give the highest ^{20}Ne/^{22}Ne values recorded for each locality. Modified from Hilton and Porcelli (2003).

Ne isotopes provide support for relatively undegassed domains in the mantle. Plots of ^{20}Ne/^{22}Ne versus ^{21}Ne/^{22}Ne show that basalts from the various localities define linear trends (e.g., MORB, Iceland and Loihi, Hawaii, Fig. 6; Hilton and Porcelli, 2003). Rare samples from each place have high ^{20}Ne/^{22}Ne ratios that approach solar values. Because ^{20}Ne and ^{22}Ne are primordial (nonradiogenic or radioactive), it appears the mantle's original Ne composition was "solar". Each location has different maximum ^{21}Ne/^{22}Ne ratios reflecting variable impact of nucleogenic ^{21}Ne on mantle Ne isotopic ratios. The linear trends (Fig. 6) result from mixing between "Air" and mantle Ne (McDougal and Honda, 1998) and most basalts are contaminated by atmospheric Ne derived from seawater or air. The Iceland and Loihi samples with the highest ^{20}Ne/^{22}Ne ratios also have near-solar ^{21}Ne/^{22}Ne ratios (e.g., Trieloff et al., 2000; 2003). Their primordial mantle Ne concentrations are apparently so high (un-degassed?) that nucleogenic production of ^{21}Ne has not been able to substantially modify the ^{21}Ne/^{22}Ne ratios from the solar values (Dixon et al., 2000; Moreira et al., 2001).

Most of the mantle may be substantially degassed/depleted (Anderson, 1999; Davies, 1999). Modeling by Coltice and Ricard (2002) suggests that the Loihi source contains < 3% primitive mantle, but these small amounts, perhaps as partially degassed peridotite, create the "primordial" noble gas signature. Consistent with this, Hanyu et al. (2001) report primitive Ne and Ar from Reunion, but lithophile isotopes (e.g., ^{87}Sr/^{86}Sr) are unlike Iceland or Hawaii. There may be several types of relatively undegassed mantle sources with different evolutionary histories.

TRACE-ELEMENT RATIOS AND MANTLE COMPOSITIONS

Isotopes are used to identify the mantle components but they do not provide a clear chemical picture of what these components are, or how they are formed. Trace elements help but concentrations in flows reflect melting processes as well as source compositions. This problem is ameliorated by using the ratios of similarly incompatible elements. Two elements with similar incompatibility have comparable bulk distribution coefficients during melting. Their ratios in magmas are not overly affected by the percentage of melting and approach source ratios. Ratio differences between rocks will reflect variations in mantle composition, providing the elements used in the ratios are separated by ≤ 10 elements in the Sun and McDonough (1989) incompatibility list (Table 2, notes; Greenough et al., unpublished data). The pioneering work of Allègre et al. (1995) showed that the same mantle components identified using isotopes are delimited in multidimensional trace-element ratio space.

Figure 7 and Table 2 show selected, similarly incompatible-element-ratios that distinguish mantle components. All ratios have the slightly more incompatible element in the numerator. Thus, all normal - MORB ratios are lower than in OIB implying a highly depleted source for the former (Table 2). Even the average OIB depleted mantle (DM) has not experienced as much former melt extraction as MORB sources (Table 2) although Figure 6 illustrates their similarity.

HIMU shows high U/X, Nb/X, Ta/X and light REE/X ratios but low Rb/X, K/X, Pb/X and (commonly) Ba/X ratios where X represents various elements having similar but slightly lower incompatibility than the numerator element. This indicates HIMU is enriched in U, Nb, Ta and the light REE but depleted in K, Rb, Ba and Pb. It relates the low $^{87}Sr/^{86}Sr$ ratio of HIMU to ancient Rb depletion and high $^{206}Pb/^{204}Pb$ to U enrichment and/or Pb depletion. The data pattern supports the idea that HIMU sources contain ancient, recycled basaltic ocean crust (Zindler and Hart, 1986; Hofmann, 1997). Processing in ancient subduction zones removed elements soluble in water-rich metasomatic fluids and concentrated insoluble high-field-strength elements (e.g., U, Nb, Ta; Weaver, 1991) by stabilizing oxide phases in an oxidizing environment. Possibly Nb is not enriched in HIMU sources (Niu and O'Hara , 2003) but this is not supported by Table 2, and other reviews. Kamber and Collerson (2000) proposed that correlated Zr and Nb concentrations in oceanic basalts indicate mixing between MORB mantle and sources (components) variably affected by metasomatic partial melts.

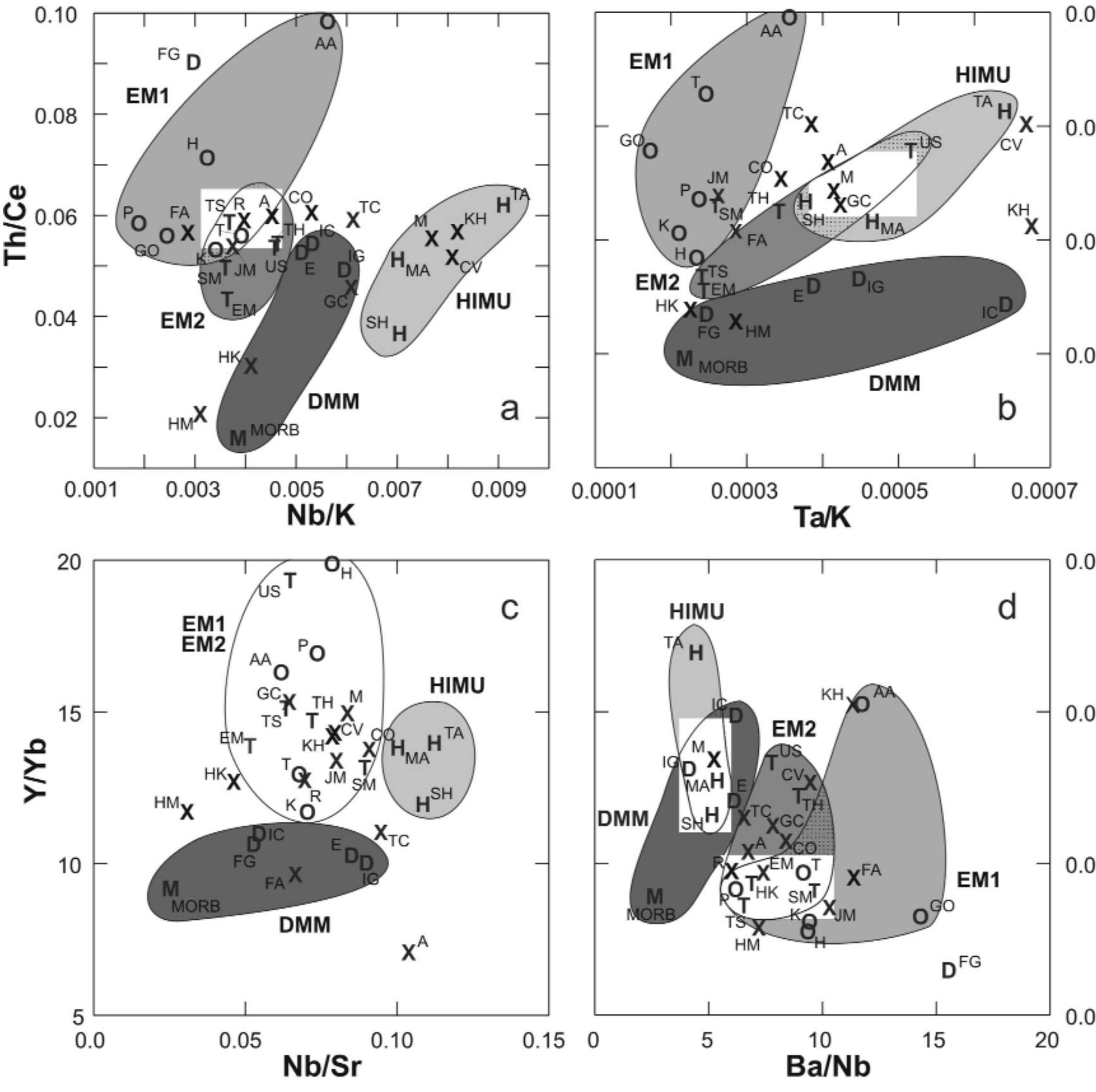

Figure 7. Plots of element ratios in oceanic island basalts. Hand-drawn fields outline areas dominated by source region types (O = EM1; T = EM2; H = HIMU; D = DM; X = not categorized or transitional) based on isotopic studies in the literature. Island symbols as in Figure 4.

Similarly, Halliday et al. (1995) argued that high U/Pb, low K/U and moderate Ba/Ce support HIMU formation at ocean ridges by metasomatism of small percentage melts that equilibrated with phlogopite, amphibole, and sulfides.

The EM2 sources show the highest Rb/X and lowest Sr/X ratios in the ocean basins (Table 2; X defined previous paragraph) which explains why they have the highest ^{87}Sr/^{86}Sr ratios. Moderate enrichment in other large ion lithophile elements (Ba, K) and strong Nb depletion are consistent with several percent of subducted terrigenous sediment in the source (Weaver, 1991).

Many highly incompatible elements are more enriched in EM1 than EM2. The EM1 ratios involving Ba, Th, and K (in numerator) are the highest, and U, Nb and Ta are the lowest in the ocean basins, and comparing OIB only, HIMU is the reverse of EM1 (Table 2). For elements more compatible than Pb, (below Pb/P, Table 2), EM1 and EM2 form opposite extremes. The EM1 has the highest Sr/X, P/X, Zr/X, Hf/X, middle REE (Nd, Sm, Eu)/X ratios in OIB whereas EM2 ratios are mostly the lowest. The EM1 characteristics, particularly high Ba/X values, have been ascribed to ancient pelagic sediment (Weaver, 1991). Dostal et al. (1998) modeled EM1 by adding pelagic sediment to a HIMU-type source. Predicted large-ion lithophile-element concentrations were too high indicating that, in nature, these elements are partially lost from sediment during subduction; EM1 and EM2 may contain delaminated subcontinental lithospheric mantle. Continental basalts that melted Archean subcontinental lithosphere show the same pattern of high- or low-element ratios (relative to non-EM1 mantle components) as exhibited by EM1 (Table 2), but ratios are more extreme than in EM1 (Greenough et al., unpublished data).

Few trace-element ratio constraints can be placed on the primordial mantle – deep mantle – FOZO component common to all oceanic basalts. Allègre et al. (1995) showed that Hawaii (representing FOZO) is distinctive, in multi-trace element ratio space, relative to MORB, EM1, EM2 and HIMU. Baksi (2001) argued that FOZO can be identified using Nb/Y and Zr/Y ratios.

CHEMICAL STRUCTURE OF THE MANTLE

Variations in OIB and MORB geochemistry lead to models for chemical structure in the mantle. Most mantle heterogeneity appears related to melt extraction to form continental and oceanic crust, and recycling of oceanic and continental lithosphere back into the mantle. Compositional variability exists at all scales in the mantle (Zindler and Hart, 1986). Xenoliths document heterogeneity at the mineral scale. Individual flows on volcanoes indicate heterogeneity at the km-scale in the source region. High ^{187}Os/^{188}Os ratios in some Hawaiian flows are consistent with low-temperature mantle melting of pyroxenite "blobs" or veins (Lassiter et al., 2000). Melting experiments on peridotite-basalt-peridotite "sandwiches" confirm that low-temperature rocks (basalt as eclogite) melt first (Takahashi and Nakajima, 2002). The volume of stratigraphic units (Makapuu stage of Koolau, Hawaii) ascribed to eclogite melting suggests the presence of 10^3 km^3 blocks in the underlying mantle. Similarly, early-formed seamounts along island chains show more extreme trace element and isotopic compositions than islands indicating that components (e.g., EM1) have lower melting temperatures, melt first, and form distinct, localized, rock masses in the mantle (Devey et al., 2003). Niu et al. (2002) came to similar conclusions on the scale and melting behaviour of mantle domains underlying seamounts near the East Pacific Rise. At larger scales, individual islands, island chains and ocean basins (e.g., Indian Ocean) exhibit distinct signatures (Allègre, 2002). Pb isotope maps show anomalous mantle between 30° and 40° S latitude encircling much of the planet (Dupal anomaly; Zindler and Hart, 1986).

Opinions differ on how chemical heterogeneities are cycled through the mantle (e.g., Allègre, 2002; Hofmann, 2003; Van Keken et al., 2003). Mass balance calculations originally indicated that melting of primitive upper mantle pro-

Table 2: Ratios of similarly incompatible elements in end-member oceanic island basalts.

	HIMU	EM2	EM1	DM	MORB
Rb/Ba1	*0.074*	**0.104**	0.077	0.084	0.089
Ba/Nb4	*5*	8	**10.1**	8.1	2.7
Th/Ce6	*0.05*	0.052	**0.066**	0.062	0.016
U/K3	**0.000175**	0.000111	*0.000094*	0.000133	0.000078
U/Pb6	**0.49**	0.34	*0.34*	0.35	0.16
Nb/K2	**0.0077**	0.004	**0.0034**	0.0049	0.0039
Nb/Sr8	**0.107**	*0.069*	0.07	0.071	0.026
Ta/K1	**0.0005**	0.00032	*0.00024*	0.00043	0.00022
K/La1	*168*	277	**356**	259	240
Ce/Pb1	**36**	29	*23*	24	25
Ce/P5	**0.043**	0.039	0.033	*0.029*	0.015
Pb/P4	*0.0012*	0.0015	0.0015	**0.0015**	0.0006
Sr/Zr6	2.4	*2.2*	**2.8**	2.2	1.2
P/Zr5	9.7	8.8	**10.6**	*8.6*	6.9
Nd/Ti8	0.0025	0.0021	**0.0027**	*0.0015*	0.001
Zr/Ti5	0.014	*0.012*	**0.015**	0.012	0.01
Hf/Ti4	0.00033	*0.00031*	**0.00036**	0.00033	0.00027
Ti/Y5	598	**680**	638	*489*	271
Y/Yb4	13	15	**16**	*10*	9

Notes: Bold = highest ratio in OIB; underlined italics = lowest ratio in OIB. Trace element ratios were calculated from average element concentrations (ppm of cations) for each oceanic island listed below. These ratios were then averaged. All ratios have the more incompatible element in the numerator and the number following the ratio (e.g. Ta/K1) shows how far apart the elements are in the Sun and McDonough (1989) incompatibility list (most incompatible Cs, Tl, Rb, Ba, W, Th, U, Nb, Ta, K, La, Ce, Pb, Pr, Mo, Sr, P, Nd, F, Sm, Zr, Hf, Eu, Sn, Sb, Ti, Gd, Tb, Dy, Li, Y, Ho, Er. Tm, Yb, Lu; least incompatible).
Ratios are organized according to the incompatibility of numerator cations (e.g. Rb most incompatible, Ba somewhat less incompatible, etc.). HIMU = 3 islands (St. Helena, Mangaia (Austral-Cook), Tubuai (Austral-Cook)); EM2 = 5 islands (Sao Miguel (Azores), Tutuila (Samoa), Upolu (Samoa), Tahiti (Society), Eiao (Marquesas)); EM1 = 5 islands (Gough, Kergulen, Pitcairn, Tristan da Cunha, Aitutaki (Austral-Cook)); DM = 4 islands (Easter Island, Floreana (Galapagos), Isabela (Galapagos), Iceland); MORB = Ratios from average N-MORB, in Sun and McDonough (1989).

duced the continental crust. The residue forms present-day depleted MORB mantle. The percentage of depleted mantle (30%; more recent estimates higher) resembled the amount of mantle above the 670 km seismic discontinuity suggesting a depleted upper mantle, a primitive lower mantle, and little or no exchange between the two (Hofmann, 2003; Bennett; 2003). The discovery of high ^{3}He/^{4}He ratios in some OIBs (and solar Ne isotopes) was attributed to small amounts of primitive, noble-gas-rich lower mantle being entrained by mantle plumes rising from the 670 km boundary. Plumes were also seen as the carriers of recycled material (components) seen in OIB geochemistry (Hofmann, 1997). When seismic tomography showed subducted oceanic lithosphere penetrating the lower mantle, and plumes rising from the core-mantle boundary, an isolated lower mantle seemed impossible (Van Keken et al., 2003). Nevertheless, others argued that whole-mantle convection has been episodic or is a recent phenomenon (Allègre, 2002; Hofmann, 2003).

Some models suggest that primitive/un-degassed mantle does not exist (e.g., Davies, 1999; Anderson, 1999; Coltice and Ricard, 2002; Hamilton, 2003). None of the mantle components, including FOZO (which is actually "depleted") with high ^{3}He/^{4}He ratios and solar Ne, have lithophile isotopic compositions requisite of primitive mantle (Bennett, 2003). Most arguments for large amounts of un-degassed primitive mantle account for the ^{40}Ar budget by estimating Earth's ^{40}K content from K/U ratios (Davies, 1999; Allègre, 2002). If the K content has been overestimated, primitive lower-mantle storing ^{40}Ar is not required.

There is an "alternative" model for the Earth (e.g., Anderson, 1999, 2000; Hamilton, 2002, 2003). The entire mantle has been processed, melted and depleted, much of it during the Earth's earliest history (see Bennett, 2003). It is layered and there is no mass transfer across the 670 km boundary (seismic tomography results are wrong!). Mantle plumes do not exist and hot-spot trails are seen as the result of propagating cracks in the lithosphere. Ocean basin heat flow implies that most radioactivity occurs in the upper mantle, which has been progressively enriched in radioactive K and U by recycling of crustal materials back into the mantle. Both MORB and OIB are derived from the same upper mantle source containing recycled materials. MORB magmas are more homogenous because of larger percentages and volumes of melting. The high ^{3}He/^{4}He ratios of a few OIBs reflect melting of small pockets of highly depleted mantle (low U + Th) (Anderson, 2001). Central to testing this model is whether differences in sampling scale (MORB large, OIB small) and melting process (OIB preferentially sample low-melting point domains) can explain the major compositional differences (Allègre et al., 1995; Allègre, 2002) between OIB and MORB or whether their sources are truly different. Non-conclusive numerical modeling of heterogeneity development in the mantle suggests that melting process may account for the differences (Kellogg et al., 2002).

FUTURE RESEARCH DIRECTIONS

Many hypotheses for the origin of the mantle components show that there is much left to learn about their composition and significance. Possibly new isotopic systems such as Li, or further work with trace-element ratios will help clarify these issues. How components (heterogeneities) cycle through the mantle is also problematic. Whether they reflect plume-entrained material brought from the lower mantle, the 670 km discontinuity, or simply the scale and process of melting requires further work. Information is needed on 1) what the components are, 2) how they melt, 3) the length-scales of heterogeneities, and 4) whether seismic tomography results really confirm the existence of complete mantle convection. Clearly, OIBs will continue to play an important role in understanding the evolution of the mantle and the Earth.

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SUPPLEMENTARY MATERIAL

Supplementary material, including references and notes on whole-rock data, can be viewed at the following location: http://www.gac.ca/JOURNALS/geocan.html.

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