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Rhenium and chalcophile elements in basaltic glasses from Ko'olau and Moloka'i volcanoes: Magmatic outgassing and composition of the Hawaiian plume

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Abstract—The behavior of chalcophile metals in volcanic environments is important for a variety of economic and environmental applications, and for understanding large-scale processes such as crustal recycling into the mantle. In order to better define the behavior of chalcophile metals in ocean island volcanoes, we measured the concentrations of Re, Cd, Bi, Cu, Pb, Zn, Pt, S, and a suite of major elements and lithophile trace elements in moderately evolved (6–7% MgO) tholeiitic glasses from Ko'olau and Moloka'i volcanoes. Correlated variations in the Re, Cd, and S contents of these glasses are consistent with loss of these elements as volatile species during magmatic outgassing. Bismuth also shows a good correlation with S in the Ko'olau glasses, but undegassed glasses from Moloka'i have unexpectedly low Bi contents. Rhenium appears to have been more volatile than either Cd or Bi in these magmas.

Undegassed glasses with 880–1400 ppm S have 1.2–1.5 ppb Re and 130–145 ppb Cd. In contrast, outgassed melts with low S (<200 ppm) are depleted in these elements by factors of 2–5. Key ratios such as Re/Yb and Cu/Re are fractionated significantly from mantle values. Copper, Pb, and Pt contents of these glasses show no correlation with S, ruling out segregation of an immiscible magmatic sulfide phase as the cause of these variations. Undegassed Hawaiian tholeiites have Re/Yb ratios significantly higher than those of MORB, and extend to values greater than that of the primitive mantle. Loss of Re during outgassing of ocean island volcanoes, may help resolve the apparent paradox of low Re/Os ratios in ocean island basalts with radiogenic Os isotopic compositions. Plume source regions with Re/Yb ratios greater than that of the primitive mantle may provide at least a partial solution to the “missing Re” problem in which one or more reservoirs with high Re/Yb are required to balance the low Re/Yb of MORB.

Lithophile trace element compositions of most Ko'olau and Moloka'i tholeiites are consistent with variable degrees of melting of fertile mantle peridotite. However, light rare earth element (LREE)-enriched glasses have trace element compositions more consistent with a garnet-rich source having a distinctive trace element composition. This provides additional evidence for a unique source component possibly related to recycled oceanic crust contributing to Ko'olau tholeiites. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

Chalcophile elements can exhibit moderately volatile behavior in magmatic systems, especially in oxidized, water-rich environments such as those associated with volcanic arcs (Gemmell, 1987; Symonds et al., 1987; Bernard et al., 1990). Magmatic gases and fluids carry a sizeable fraction of the flux of these elements into the shallow crust, hydrosphere, and atmosphere (Zoller et al., 1974; Lambert et al., 1988; Le Cloarec and Marty, 1991; Rubin, 1997; Hinkley et al., 1999). Transport of fluid-mobile elements in magmatic systems may contribute to economically important distributions of metals in the crust, locally acute environmental loadings, and to larger scale processes such as the generation of geochemical heterogeneity in the crust and mantle. For example, slab-derived fluids may contribute to the high but variable sulfur contents of arc magmas (Metrich et al., 1999) and Re-Os isotopic heterogeneity in the subarc mantle (Brandon et al., 1996; Widom et al., 2003).

The mobility of chalcophile metals in volcanic arc systems is well established, but less is known about the behavior of these

elements in other magmatic environments. Here we evaluate the mobility of Re, Cd, Bi, and a suite of other potentially volatile chalcophile elements during magmatic outgassing in an oceanic island volcanic setting through a comparison of metal abundances and sulfur contents in a suite of basaltic glasses from Ko'olau and Moloka'i volcanoes, Hawai'i. These data provide a direct measure of the extent to which these elements can be lost as volatile species from dry magmas, and present a useful comparison with compositions of atmospheric plumes and exhalations from active Hawaiian volcanoes (Crowe et al., 1987; Miller et al., 1990; Hinkley et al., 1994; Hinkley et al., 1999).

This study also provides a test of previous suggestions that the low Re contents of some ocean island basalts (OIB) are due to magmatic outgassing rather than source characteristics (Bennett et al., 2000; Lassiter, 2003). Ocean island basalts have, on average, lower Re contents than mid-ocean ridge basalt (MORB), a feature that has been thought to reflect primary compositional or mineralogical variations in the mantle (Martin, 1991; Hauri and Hart, 1997; Bennett et al., 2000). If significant Re loss occurs during subaerial eruptions, however, the low Re contents of OIB may be, at least in part, a result of outgassing of the lavas in near-surface environments rather

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Table 1. Major and trace element compositions of Ko'olau glasses. Oxides reported as wt%, elements as ppm.

Sample Lithology:	496-4 BB	496-5 BB	496-6 BB	496-8 BB	496-11-1 BB	496-11-2 BB	496-12 BB	497-5-1 BB	500-1 PP	500-3B BB	500-4A BB	500-5A BP	500-6 PP
SiO ₂	52.30	52.05	54.23	52.06	51.55	50.24	50.99	54.28	53.24	53.08	50.79	53.41	54.02
TiO ₂	2.38	2.43	2.48	2.53	2.50	3.65	2.49	2.02	1.90	2.20	3.32	2.13	2.31
Al ₂ O ₃	14.15	14.29	15.40	14.42	14.07	13.98	13.77	14.83	14.48	14.33	13.97	14.42	14.21
FeO _t	10.54	10.38	9.91	10.57	10.76	11.24	11.00	8.97	9.62	9.81	11.01	10.38	9.42
MgO	6.58	6.64	5.83	6.11	6.86	5.67	7.58	6.61	7.03	6.76	5.96	6.34	6.28
CaO	10.88	10.95	8.03	11.06	11.05	10.30	11.20	10.26	9.99	10.59	10.51	10.04	9.55
Na ₂ O	2.37	2.38	3.22	2.46	2.37	3.10	2.25	2.58	2.53	2.59	2.96	2.52	2.64
K ₂ O	0.41	0.44	0.57	0.39	0.48	0.83	0.35	0.35	0.45	0.32	0.74	0.49	0.58
P ₂ O ₅	0.23	0.23	0.27	0.25	0.24	0.51	0.21	0.22	0.22	0.17	0.42	0.25	0.31
Total	99.84	99.78	99.94	99.85	99.88	99.51	99.85	100.12	99.46	99.84	99.67	99.99	99.34
S ppm	189	137	79	152	56	102	139	144	894	183	73	1227	880
Sc	33.2	32.9	18.9	33.2	32.7	26.1	33.3	29.7	27.9	32.0	28.5	28.4	28.0
V	281	286	197	294	286	244	282	238	237	263	265	259	260
Cr	351	351	196	470	329	214	444	349	314	428	672	243	255
Ni	88	90	120	144	96	71	114	141	117	133	83	99	109
Rb	6.4	7.0	7.6	7.0	7.6	12.0	6.4	5.4	6.3	5.3	11.9	7.1	9.2
Sr	312	327	414	332	380	587	313	335	384	277	544	394	391
Y	26.1	26.7	24.3	28.2	26.3	28.1	24.9	22.6	21.2	24.3	28.5	23.7	26.8
Zr	144	153	165	155	164	258	143	127	126	122	242	143	178
Nb	11.5	12.2	11.0	13.0	13.0	24.2	13.7	8.3	8.4	10.2	22.2	9.4	13.1
Cs	0.062	0.064	0.074	0.073	0.080	0.130	0.064	0.046	0.066	0.052	0.124	0.071	0.139
Ba	76	83	97	81	96	171	73	67	85	61	160	95	117
La	10.4	11.4	11.4	11.4	12.1	21.0	10.7	9.4	9.7	8.6	19.8	10.9	14.0
Ce	26.1	28.4	28.6	28.4	30.3	50.9	27.0	23.6	24.1	21.8	47.9	27.0	34.4
Pr	3.69	3.97	4.00	4.02	4.27	6.98	3.80	3.35	3.40	3.08	6.56	3.81	4.78
Nd	18.5	19.8	20.6	20.2	21.4	33.6	19.1	16.8	17.2	15.7	32.1	19.3	23.8
Sm	5.19	5.34	5.74	5.67	5.82	8.74	5.28	4.77	4.66	4.54	8.27	5.33	6.38
Eu	1.82	1.89	2.01	2.00	2.01	2.92	1.86	1.68	1.67	1.66	2.76	1.85	2.09
Gd	5.73	5.86	6.07	6.21	6.12	8.29	5.74	5.12	4.86	5.27	8.08	5.51	6.42
Dy	5.24	5.35	5.12	5.71	5.43	6.30	5.15	4.62	4.38	4.93	6.27	4.88	5.58
Ho	1.04	1.04	0.95	1.13	1.03	1.10	1.01	0.89	0.84	0.96	1.12	0.94	1.07
Er	2.51	2.59	2.23	2.71	2.54	2.48	2.43	2.25	2.06	2.39	2.54	2.33	2.60
Yb	2.15	2.19	1.76	2.32	2.10	1.80	2.01	1.90	1.75	2.05	1.90	1.93	2.13
Lu	0.30	0.31	0.23	0.33	0.31	0.23	0.28	0.26	0.24	0.29	0.26	0.27	0.31
Hf	3.62	3.78	4.11	3.96	4.06	6.11	3.64	3.21	3.14	3.15	5.69	3.57	4.36
Ta	0.74	0.77	0.72	0.84	0.82	1.47	0.90	0.54	0.54	0.68	1.36	0.62	0.85
Pb	1.08	1.16	1.45	1.06	1.26	1.62	0.94	1.01	1.15	1.17	1.68	1.31	1.52
Th	0.72	0.80	0.74	0.81	0.85	1.56	0.79	0.56	0.56	0.61	1.44	0.65	0.92
U	0.22	0.23	0.21	0.26	0.27	0.48	0.25	0.16	0.17	0.19	0.46	0.19	0.28

Rock types: basaltic breccia (BB), picritic pillow lava (PP), basaltic pillow lava (BP). Total Fe reported as FeO_t.

than a primary magmatic feature. This would have implications for estimates of global Re and chalcophile element budgets, and fluxes of these elements to the atmosphere and hydrosphere. The goal of this work is to evaluate the effects of outgassing on the abundances of Re and other chalcophile metals in basaltic lavas, and to better characterize the primary abundances of these elements in OIB magmas. Submarine glasses from two Hawaiian volcanoes, Ko'olau and Moloka'i, having a broad range of S contents (56–1427 ppm) were analyzed, as the sulfur content of Hawaiian glasses is considered a good indicator of the extent of magmatic degassing (Moore and Fabbri, 1971; Swanson and Fabbri, 1973).

2. SAMPLES AND METHODS

Samples for this study were collected from Ko'olau and East Moloka'i volcanoes by the Shinkai 6500 manned submersible, operated by JAMSTEC, during a 1999 expedition. Samples were collected from the flanks of Ko'olau volcano at depths of 2800 to 3200 m (dives 496, 497, 500). The Moloka'i samples (dives 501 and 510) were collected from two landslide blocks 40 and 60 km north of the island that are part

of the Wailau slide (Yokose, 2002). Rock types included picritic and basaltic pillow basalts, and basaltic pillow breccias (Tables 1 and 2). The glasses were obtained from pillow rims and from glass clasts in the breccia. The outer margins of the glasses had thin manganese coatings and thin iddingsite rims (<1 mm). The interiors of these glasses are fresh, and were analyzed for this study. In addition to the Ko'olau and Moloka'i samples, the USGS basaltic glass standards BHVO-2G, BCR-2G, BIR-1G, and TB-1G, and glassy portions of a quenched sample of live lava collected from Kilauea on 10 May 1993 (KIL93-1489) were analyzed.

Major elements and S abundances (Tables 1 and 2) were measured by electron microprobe using the University of Hawai'i Cameca SX-50, five-spectrometer electron microprobe. Major element analyses were performed with a 15-kV accelerating voltage, 10-nA beam current, and a rastered beam over a 12 × 18 μm area. Peak counting times were 60 s for Ti, Al, Fe, and P; 50 s for Si and Mg; 40 s for Mn, Ca, Na, and K; and 120 s for S. Background counting times were half the peak time for each element. Natural glass and mineral standards were used for calibration. A PAP-ZAF matrix correction was applied to all analyses. Two-sigma precision based on counting statistics (Reed, 1993) is <1% for major elements, <5% for minor elements (K, Mn, P), and <10% for S. Reported analyses are the average of 4 to 15 spot analyses.

Table 2. Major and trace element compositions of Moloka'i glasses.

Sample	501-1	501-2	501-5b	501-7	510-1a	510-2a	510-4b	510-6c
SiO ₂	48.37	50.04	50.68	50.57	50.79	50.48	50.97	50.30
TiO ₂	2.72	2.19	2.51	2.20	2.62	2.50	2.94	2.89
Al ₂ O ₃	14.78	12.27	13.98	13.00	13.60	13.79	13.83	14.07
FeO	11.90	11.36	11.13	10.90	11.29	11.10	10.35	11.83
MgO	6.70	10.19	6.50	8.15	7.11	7.67	6.79	5.75
CaO	11.70	10.77	11.30	11.90	11.22	11.13	11.20	10.44
Na ₂ O	2.38	1.96	2.24	1.97	2.28	2.32	2.44	2.55
K ₂ O	0.34	0.30	0.33	0.27	0.38	0.37	0.46	0.52
P ₂ O ₅	0.23	0.19	0.23	0.19	0.22	0.22	0.27	0.33
Total	99.11	99.27	98.90	99.13	99.51	99.58	99.25	98.67
S ppm	1290	1050	1427	1230	230	170	170	1385
Sc	33.8	33.6	30.7	36.2	32.8	32.4	33.7	30.5
V	295	252	260	261	297	281	306	290
Cr	249	643	206	444	337	425	351	161
Ni	93	212	79	136	116	149	132	62
Rb	6.0	5.1	5.1	4.6	6.7	6.1	7.6	7.8
Sr	321	272	275	263	299	313	337	406
Y	30.4	25.4	25.5	24.3	28.0	24.9	28.1	28.5
Zr	167	152	143	132	159	148	171	178
Nb	14.7	13.1	12.6	11.4	13.7	13.4	16.6	14.3
Ba	69	58	58	52	78	72	94	101
La	11.9	10.7	10.3	9.20	11.10	10.90	13.7	13.5
Ce	30.3	27.3	26.1	23.6	28.4	27.6	33.8	34.3
Pr	4.41	3.99	3.82	3.47	4.24	4.07	4.94	5.00
Nd	21.5	19.1	18.2	16.8	20.7	19.3	23.1	24.0
Sm	5.92	5.23	5.12	4.79	5.74	5.36	6.11	6.53
Eu	2.16	1.84	1.78	1.72	2.02	1.86	2.20	2.23
Gd	6.68	5.80	5.56	5.37	6.43	5.84	6.88	6.86
Dy	6.17	5.21	5.20	5.02	5.91	5.32	5.92	5.93
Ho	1.16	1.00	0.98	0.96	1.11	0.99	1.15	1.14
Er	3.08	2.60	2.54	2.44	2.87	2.57	2.88	2.98
Yb	2.55	2.08	2.18	2.00	2.40	2.10	2.32	2.32
Lu	0.34	0.31	0.30	0.30	0.32	0.29	0.32	0.34
Hf	4.19	3.79	3.55	3.30	3.99	3.66	4.21	4.28
Ta	0.98	0.84	0.83	0.74	0.86	0.87	1.07	0.89
Pb	0.86	0.82	0.89	0.74	0.85	0.94	1.10	1.21
Th	0.88	0.80	0.76	0.70	0.82	0.82	0.99	0.84
U	0.30	0.26	0.24	0.21	0.26	0.25	0.31	0.28

Oxides reported as wt%, elements as ppm. All samples are basaltic breccias (BB) except 501-2 (PP).

Trace elements were measured by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) using a custom-built 193-nm excimer laser system (Eggs et al., 1998; Eggs and Shelley, 2002) and an Agilent 7500 quadrupole ICPMS operated in time-resolved mode using a dwell time of 20 ms per mass. A conventional suite of petrogenetic trace elements (Tables 1 and 2) was determined using a 65- μ m-diameter laser beam and a laser repetition rate of 4 Hz. The CaO content of each sample was used for internal normalization of the lithophile element analyses. Concentrations of Re, Cd, Bi, Cu, Zn, Pt, Y, Yb, and Hf (Table 3) were measured in separate sessions using a 225- μ m-diameter laser beam and a laser repetition rate of 20 Hz. Zirconium contents of the glasses determined by LA-ICPMS were used for internal normalization of the chalcophile element analyses. For all data, the NIST 612 glass was used for calibration of element sensitivity using values given in Tables 4 and 5 (Sylvester and Eggs, 1997; Pearce et al., 1997; Norman et al., 1996). Dry gas backgrounds were measured for 30–60 s before each ablation. Oxide production as measured by ThO/Th on the NIST glass was <0.5% for all sessions. Yb oxides that may interfere on ¹⁸⁷Re were monitored on masses 188, 189, and 190 during analysis of the NIST 612 glass, which is very low in Os (Sylvester and Eggs, 1997; Sun et al., 2003a,b). Yb-oxide production was found to be negligible (0.001–0.002%), corresponding to <1 cps on ¹⁸⁷Re. LA-ICPMS analyses of zircons indicated Hf-oxide production rates similar to those for Yb, or <1 cps on ¹⁹⁵Pt in the Ko'olau and Moloka'i glasses. Consequently, no corrections were made for YbO or HfO interferences on ¹⁸⁷Re and ¹⁹⁵Pt.

3. RESULTS

3.1. Standards and Reference Materials

Replicate LA-ICPMS analyses of the USGS basaltic glass standards BCR-2G, BHVO-2G, BIR-1G, and TB-1G run during this study demonstrate an external precision of ~1–3% (1 σ relative standard deviation) for most lithophile trace elements at abundances similar to those found in Hawaiian tholeiite glasses (Table 4). The accuracy and precision of these LA-ICPMS data are comparable to those obtainable by solution aspiration of dissolved whole rocks (see, e.g., Eggs et al., 1997; Norman et al., 1998; Yang et al., 2003). For the lithophile elements (Tables 1, 2, and 4), detection limits calculated according to the procedures of Longerich et al. (1996) were 2–5 ppb for La, Ce, Pr, Ho, Lu, Sr, Nb, Ba, and Ta; 5–10 ppb for Y, Eu, Th, and U; 10–50 ppb for Nd, Sm, Gd, Dy, Er, Yb, Sc, V, Co, Ga, Rb, Mo, Hf, and Pb; 50–100 ppb for Ni; and 500–700 ppb for Cr. Detection limits for Y, Yb, and Hf determined with the chalcophile elements (Tables 3 and 5) were significantly better (~0.1–0.2 ppb) due to the larger spot size and faster laser repetition rate used for these analyses.

Table 3. Chalcophile element data for Ko'olau and Moloka'i glasses.

Sample	Locality	Cu	Zn	Re	Cd	Bi	Pt	Y	Yb	Hf
496-4	Ko'olau	149	104	0.87	127	15.1	7.1	26.6	2.32	3.69
496-5	Ko'olau	124	95	0.87	105	11.6	4.4	26.1	2.24	3.85
496-6	Ko'olau	58	102	0.39	109	18.3	1.7	23.5	1.75	4.09
496-8	Ko'olau	120	97	0.64	111	14.2	5.4	27.8	2.36	3.89
496-11-1	Ko'olau	130	92	0.59	99	14.0	6.4	25.3	2.17	4.05
496-11-2	Ko'olau	106	116	0.42	99	9.6	3.7	27.7	1.83	6.16
496-12	Ko'olau	128	87	0.62	106	12.0	5.3	24.4	1.97	3.52
497-5-1	Ko'olau	141	86	0.69	124	18.0	4.1	22.9	1.96	3.23
500-1	Ko'olau	115	85	1.32	131	24.3	7.1	20.9	1.75	3.08
500-3b	Ko'olau	131	89	0.72	117	14.4	5.4	24.4	2.10	3.12
500-4a	Ko'olau	105	104	0.30	96	13.9	3.2	27.4	1.90	5.71
500-5a	Ko'olau	100	79	1.43	145		7.6	23.4	2.00	3.61
500-6	Ko'olau	133	87	1.54	143	26.7	4.7	26.6	2.19	4.34
501-1	Moloka'i	80	97	1.21	145	15.1	1.1	29.7	2.53	4.22
501-2	Moloka'i	157	96	1.28	129	15.5	7.5	24.4	2.13	3.73
501-5b	Moloka'i	94	78	1.18	143	13.2	1.4	24.7	2.12	3.63
501-7	Moloka'i	168	90	1.32	141	15.4	2.2	23.5	2.02	3.29
510-4b	Moloka'i	128	81	0.51	128		4.2	27.9	2.36	4.37

Cu, Zn, Y, Yb, and Hf data in ppm, all others in ppb.

Evaluation of the quality of the chalcophile element data is complicated by the lack of well-defined calibration standards (Eggins and Shelley, 2002), and the possibility of small-scale

natural variability in the samples. Sun et al. (2003b) demonstrated excellent correspondence between Re compositions of MORB glasses measured by isotope dilution ICPMS using

Table 4. Laser ablation ICP-MS data for USGS basaltic glass reference materials and calibration values for the NIST 612 glass.

	BCR-2G				BHVO-2G				BIR-1G				TB-1G			NIST 612 cal values
	avg	1 σ , n = 18	%RSD	PV	avg	1 σ , n = 4	rsd	PV	avg	1 σ , n = 4	rsd	PV	avg	1 σ , n = 4	rsd	
CaO (IS)	7.1	IS			11.4	IS			13.2	IS			6.9	IS		11.85
TiO ₂	2.35	0.02	1.0	2.28	2.81	0.01	0.2	2.82	0.99	0.01	0.4	1.01	0.86	0.01	0.48	41.5
Sc	33.9	0.2	0.7	33.8	31.9	0.3	0.9	31.8	43.8	0.2	0.5	43.8	21.8	0.1	0.57	40.8
V	380	2	0.6	379	286	2	0.6	285	296	1	0.4	286	163	1	0.35	33.2
Cr	17	3	16.2	15	307	2	0.7	292	420	3	0.8	412	58	1	0.64	36.9
Ni	12.4	0.3	2.5	12.8	128	1	1.1	120	196	2	0.8	175	17.0	0.2	1.34	36.8
Rb	44.8	0.8	1.7	46.9	9.1	0.2	2.1	9.1	0.19	0.02	10.5	0.20	139	1	0.70	26.7
Sr	334	2	0.7	340	390	1	0.3	396	108	1	0.0	108	1298	8	0.64	77.8
Y	34.1	0.4	1.1	34.3	24.6	0.1	0.5	24.9	14.8	0.1	0.4	14.4	24.7	0.2	0.78	41.0
Zr	191	2	0.8	193	173	1	0.6	175	14.8	0.2	1.5	14.1	248	1	0.22	41.9
Nb	13.0	0.2	1.2	12.7	19.0	0.1	0.7	18.8	0.55	0.02	2.8	0.54	29.7	0.1	0.34	40.8
Cs	1.17	0.03	2.7	1.18	0.103	0.003	2.7	0.100	<0.01	0.00	0.0	0.005	2.87	0.02	0.70	38.5
Ba	675	7	1.0	677	131	1	0.8	131	6.54	0.05	0.7	6.52	931	5	0.52	38.9
La	24.9	0.2	1.0	24.9	15.2	0.1	0.5	15.2	0.61	0.01	1.4	0.60	44.2	0.3	0.61	36.5
Ce	52.4	0.5	1.0	52.9	37.4	0.2	0.5	37.5	1.93	0.04	2.2	1.90	88.6	0.4	0.51	38.4
Pr	6.59	0.06	0.9	6.57	5.20	0.01	0.1	5.29	0.37	0.01	2.1	0.36	10.13	0.02	0.19	37.9
Nd	28.7	0.3	0.9	28.7	24.5	0.2	0.9	24.5	2.41	0.04	1.7	2.38	39.4	0.2	0.65	36.2
Sm	6.47	0.08	1.3	6.57	6.00	0.10	1.6	6.07	1.09	0.04	3.7	1.17	7.21	0.14	1.92	38.0
Eu	1.94	0.03	1.4	1.96	2.05	0.02	0.9	2.07	0.51	0.01	1.5	0.52	1.79	0.03	1.73	36.2
Gd	6.56	0.10	1.5	6.75	6.08	0.11	1.8	6.24	1.97	0.02	1.1	1.85	5.61	0.04	0.79	39.1
Dy	6.25	0.10	1.6	6.41	5.21	0.04	0.9	5.31	2.50	0.03	1.3	2.53	4.49	0.05	1.19	37.1
Ho	1.28	0.02	1.2	1.30	0.97	0.01	1.2	0.97	0.56	0.01	0.6	0.59	0.90	0.01	1.56	40.2
Er	3.62	0.05	1.3	3.66	2.51	0.03	1.0	2.54	1.67	0.04	2.2	1.60	2.58	0.04	1.73	40.1
Yb	3.36	0.06	1.7	3.38	1.98	0.07	3.6	2.00	1.63	0.02	1.3	1.65	2.50	0.09	3.47	40.2
Lu	0.50	0.01	2.5	0.52	0.275	0.014	5.1	0.274	0.249	0.005	1.9	0.247	0.390	0.003	0.83	39.6
Hf	4.71	0.06	1.3	4.90	4.20	0.11	2.6	4.22	0.55	0.02	4.5	0.56	5.49	0.05	0.95	37.3
Ta	0.80	0.01	1.8	0.81	1.15	0.01	1.3	1.20	0.038	0.006	14.9	0.041	1.52	0.02	1.48	41.4
Pb	10.9	0.3	2.7	10.3	2.11	0.15	6.9	2.10	3.75	0.05	1.4	2.97	16.8	0.1	0.71	36.9
Th	6.02	0.05	0.8	6.03	1.24	0.02	1.5	1.26	0.030	0.004	13.3	0.030	14.7	0.1	0.91	39.7
U	1.53	0.02	1.3	1.62	0.40	0.01	2.2	0.42	0.017	0.001	3.9	0.010	3.78	0.01	0.27	33.2

Oxides in wt%, all other data in ppm (all NIST 612 values in ppm). CaO used for internal normalization of each analysis. Preferred values (PV) are based on data for the corresponding rock powders (Raczek et al., 2001; Eggins et al., 1997; Robinson et al., 1999; Norman, unpublished data) and glasses (Norman et al., 1998).

Table 5. Laser ablation ICP-MS data for chalcophile elements in USGS glass standards and a quenched sample of 1993 Kilauea lava.

	BCR-2G				BHVO-2G				BIR-1G				KIL93-1489				NIST 612 cal values
	avg	n = 13	1 σ , %RSD	RV	avg	n = 8	1 σ , %RSD	RV	avg	n = 8	1 σ , %RSD	RV	avg	n = 14	1 σ , %RSD	RV	
Cu ppm	17	2	11.8	19	114	5	4.3	136	113	3	2.5	126	124	6	4.8	123	36.8
Zn ppm	134	8	6.0	130	103	1	1.2	105	70	1	1.4	71	103	4	3.6	104	34.9
Cd ppb	190	17	9.1	130	91	5	5.3	69	114	13	11.0	114	112	10	8.9	64	28.3
Re ppb	6.2	0.7	11.9	0.84	0.47	0.13	28.3	na	0.53	0.07	12.7	na	0.59	0.13	22.0	0.54	6.57
Pt ppb	778	604	77.6	2	456	94	20.6	2	922	60	6.5	2.8	5.7	0.9	15.5	4.68	2.59
Bi ppb	55	10	18.0	47	35	5	14.6	18	20	3	12.7	20	10.1	1.1	10.6	na	29.8
Y ppm	34.0	0.4	1.3	34.2	24.4	0.3	1.3	24.8	14.0	0.1	0.4	14.4	24.1	0.4	1.8	24.3	40.9
Yb ppm	3.45	0.05	1.3	3.38	2.02	0.01	0.5	2.02	1.62	0.03	1.6	1.65	2.05	0.03	1.2	1.97	40.2
Hf ppm	4.93	0.07	1.4	4.95	4.36	0.05	1.1	4.38	0.55	0.01	2.5	0.56	3.75	0.04	1.0	3.58	37.3

Reference values (RV) for BCR-1, BIR-1, and BHVO-1 are from Govindaraju (1994). Data for the 1993 Kilauea sample (KIL93-1489) are from Bennett et al. (2000). na = not available.

solution aspiration, and LA-ICPMS results obtained from the Research School of Earth Sciences laboratories. Similarly, the average Re concentration determined by LA-ICPMS on glassy portions of the KIL93 sample of quenched lava (Table 5) is within error of the whole rock composition of this sample determined by isotope dilution ICPMS (Bennett et al., 2000). Cu and Zn display excellent correspondence between the LA-ICPMS and reference values (Table 5). Cd and Bi values determined for BCR-2G, BHVO-2G, and KIL93 by LA-ICPMS tend to be higher than corresponding whole rock values, but there is good agreement for both of these elements in BIR-1G (Table 5). Cadmium values for undegassed samples of Ko'olau and Moloka'i glasses correspond well to isotope dilution data for Loihi basalts measured by multi-collector ICPMS (Yi et al., 2000), confirming the overall suitability of the NIST 612 Cd value used for calibration of the LA-ICPMS data. Time-resolved spectra of analyses of the USGS basaltic glass reference materials showed clear evidence for small-scale heterogeneity in Pt and Re, which is also apparent in the precision of replicate analyses (Table 5). The high levels of Pt clearly reflect contamination during preparation of these glasses by melting in Pt crucibles (S. Wilson, 1998, personal communication). The LA-ICPMS Pt data for KIL93 are ~20% higher than the whole rock value, possibly reflecting a bias in the calibration values used for the NIST 612 glass (Sylvester and Eggins, 1997; Sun et al., 2003b).

Typical detection limits were ~0.05 ppb for Re, ~2 ppb for Cd, ~0.05 ppb for Bi, ~0.2 ppb for Pt, and ~1–2 ppb for Cu and Zn (see Longerich et al., 1996, for details of the method used for calculating these detection limits). External precision on the chalcophile element data based on replicate analyses is conservatively estimated as <10% for Cu and Zn, and ~10–20% for Re, Cd, Bi, and Pt (Tables 4 and 5). Accuracy of the Re data is probably $\leq 10\%$ (Sun et al., 2003b), but there may be unrecognized systematic differences in the absolute concentrations of Cd, Bi, and Pt. Interpretation of the trends observed here would not be affected by minor systematic differences in calibration values. However, additional work is needed to establish well-calibrated chalcophile and siderophile standards for LA-ICPMS analysis.

3.2. Ko'olau and Moloka'i Glasses

3.2.1. Major elements

The Ko'olau submarine glasses studied here have major element compositions that are typical of shield lavas from this volcano (Jackson et al., 1999; Shinozaki et al., 2002; Haskins and Garcia, 2003). Subaerial Ko'olau lavas are noted for their relatively high SiO₂ contents, and the pillow lava samples and a few of the breccias are examples of this distinctive Hawaiian composition with SiO₂ contents extending to 54.3 wt.% (Fig. 1; Table 1). The other breccias have lower silica contents and major element compositions similar to the deeper portions of Ko'olau volcano that have been sampled in drill core and tunnels (Jackson et al., 1999; Haskins and Garcia, 2004). MgO contents of the submarine glasses range from 5.7 to 7.6 wt.%, which is typical of tholeiitic Hawaiian glasses (e.g., Garcia et al., 1995; Clague et al., 1995). These MgO contents are indicative of moderate quenching temperatures (1130 \pm 20°C) based on the MgO geothermometer of Helz and Thornber (1987).

The Ko'olau glasses can be subdivided into two groups based on their major element compositions. Samples 496-6, 496-11-2, and 500-4A have lower CaO and MgO, and higher Na₂O, K₂O, and TiO₂ than the main group of glasses (Fig. 1, Table 1); these three samples also have distinctive trace element compositions, as shown in the following sections. The Moloka'i glasses have compositions falling near the low-SiO₂ end of the main Ko'olau array (Fig. 1, Table 1). All of the glasses analyzed here are fresh, with K₂O/P₂O₅ ratios ≥ 1.4 (compared to typical values of 1.5–2.0 in Hawaiian tholeiitic basalts; Wright, 1971) and totals ≥ 98.9 wt.%, indicating negligible weathering or near-surface alteration.

3.2.2. Sulfur

Sulfur contents of the Ko'olau and Moloka'i glasses range from 56 ppm to 1427 ppm (Tables 1 and 2). Those samples with the highest S contents must be close to S-saturation (see, e.g., Fig. 4 of Davis et al., 2003), although sulfides were not observed petrographically in any of the samples studied here. Most of the Ko'olau glasses and one of the Moloka'i samples

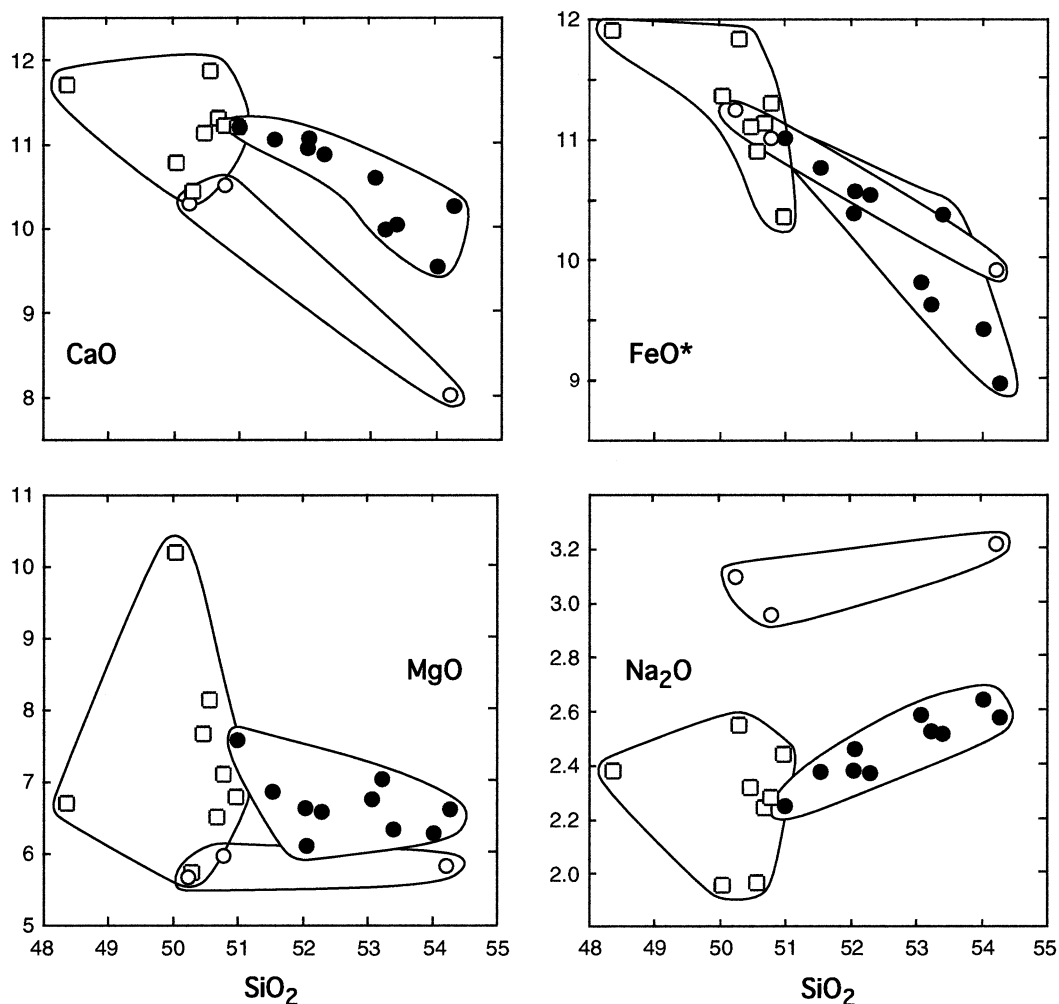


Fig. 1. Major element compositions of Ko'olau and Moloka'i glasses showing variation of CaO, FeO* (total Fe as FeO), MgO, and Na₂O vs. SiO₂. Main group of Ko'olau glasses (filled circles), LREE-enriched Ko'olau glasses (open circles), Moloka'i glasses (open squares). All data in wt.%.

have <200 ppm S, consistent with substantial degassing of the magmas in shallow chambers or at the surface (Moore and Fabbi, 1971; Swanson and Fabbi, 1973; Davis et al., 2003). Other glasses from both Ko'olau and Moloka'i have high S contents (880–1427 ppm; Tables 1 and 2), similar to undegassed Hawaiian magmas (Moore and Fabbi, 1971; Davis et al., 2003). The three Ko'olau glasses with unusual major element compositions (496-6, 496-11-2, 500-4A) have among the lowest S contents observed in this study, but there is no correlation of S content with major element compositions in either the Ko'olau or Moloka'i samples (Fig. 2). The only other previously reported S data for Ko'olau tholeiites are from a study of olivine-hosted melt inclusions in two subaerial lavas, which found S contents of 150 to 822 ppm (Hauri, 2002).

3.2.3. Lithophile trace elements

Incompatible lithophile trace elements in the Ko'olau and Moloka'i glasses span a broad range of concentrations, with many elements varying by factors of 2–3 (Tables 1 and 2, Fig.

3). There is a general trend of increasing incompatible element concentration with decreasing MgO, which is mainly controlled by the relatively low trace element concentrations in the Moloka'i glasses, and the atypically high concentrations in the three low-MgO Ko'olau glasses (Fig. 3). This cannot be simply the result of closed-system crystallization of a common parental magma composition, however, as shown by the large range of La/Yb and Lu/Hf ratios in these glasses (Figs. 3 and 4). Zr/Nb and Ce/Pb ratios show surprisingly good correlations with SiO₂, FeO*, and TiO₂ (Fig. 5). Zr/Nb ratios in whole rock samples of submarine Ko'olau tholeiites are correlated with their Sr, Nd, and Pb isotopic compositions (Tanaka et al., 2002), which is consistent with contributions from compositionally distinct plume source components to these glasses.

3.2.4. Chalcophile trace elements

A subset of the Ko'olau and Moloka'i glasses representing the range of S contents was selected for chalcophile element (Re, Cd, Bi, Cu, Zn, and Pt) analysis by LA-ICPMS (Table 3).

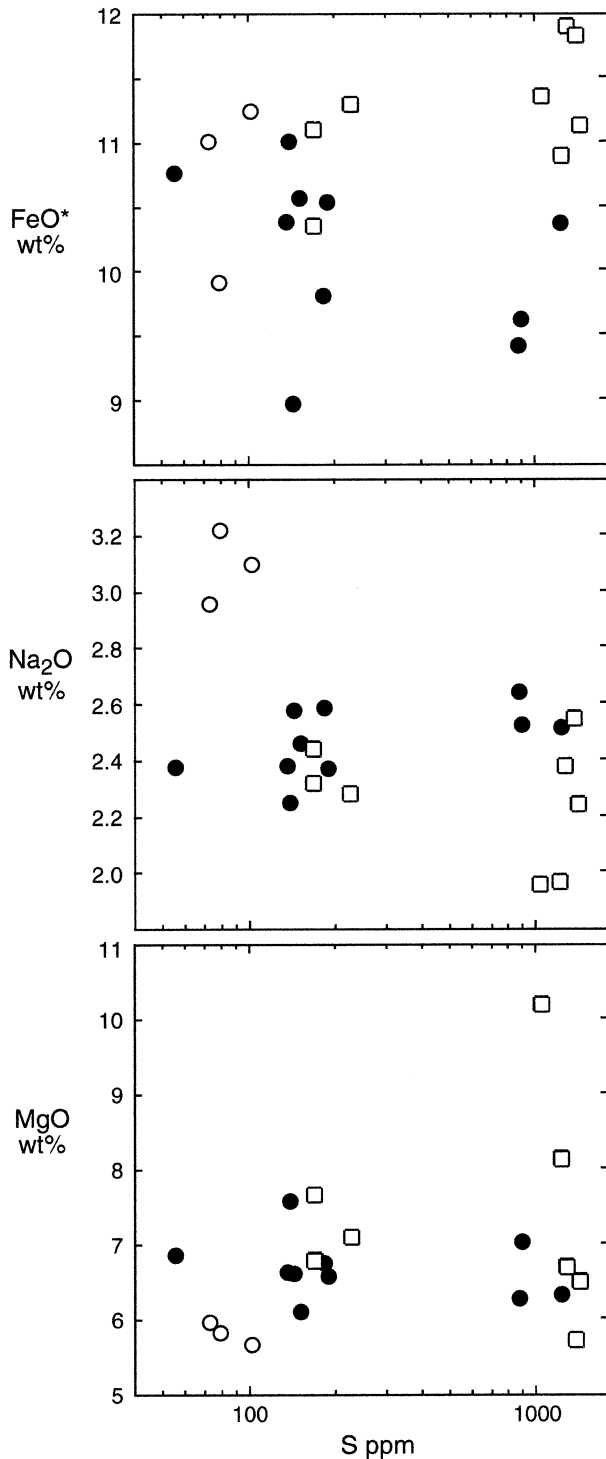


Fig. 2. FeO*, Na₂O, and MgO vs. S content of the Ko'olau and Moloka'i glasses illustrating lack of variation of S with major element composition. Symbols same as Figure 1.

Concentrations of Re and Cd are positively correlated with S contents (Fig. 6). Undegassed glasses with 880–1430 ppm S have 1.2 to 1.5 ppb Re and 130–145 ppb Cd. These Cd concentrations are similar to those found by Yi et al. (2000) for 10 samples from the Loihi seamount (135 ± 18 ppb). In

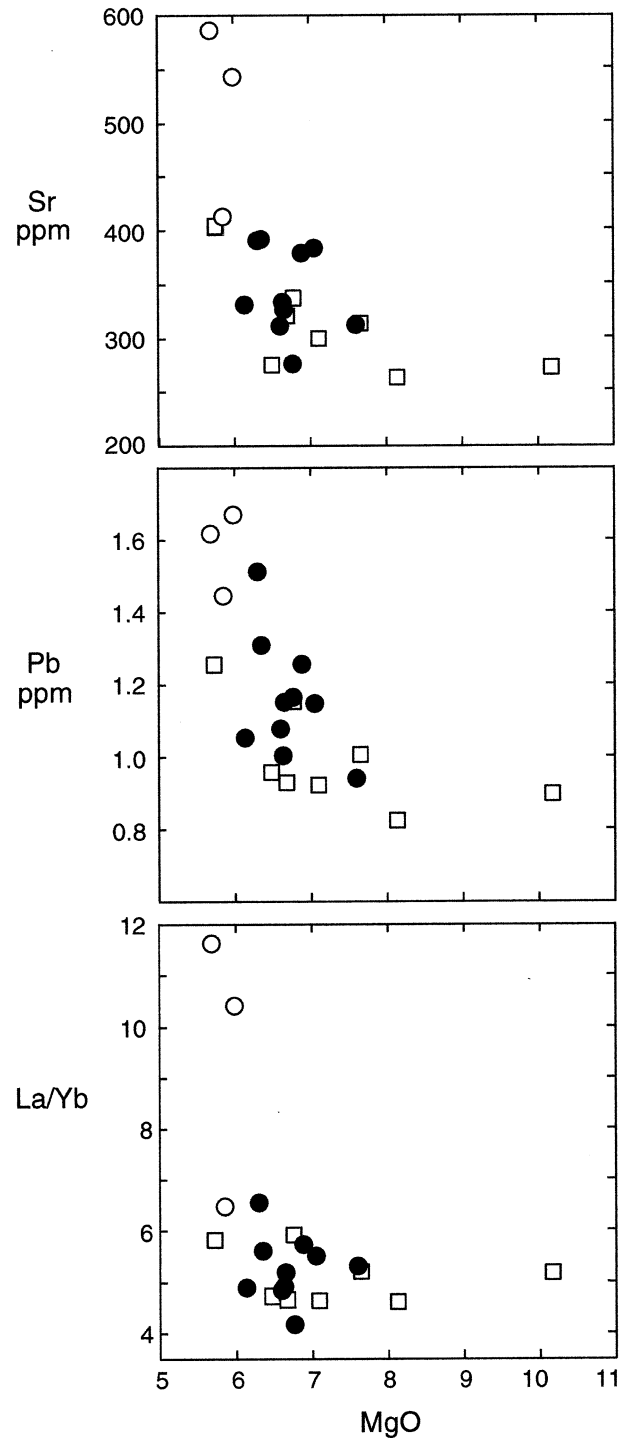


Fig. 3. Variation of Sr, Pb, and La/Yb with MgO concentration in the Ko'olau and Moloka'i glasses. Symbols same as Figure 1.

contrast, outgassed magmas with lower S contents (<200 ppm) are depleted by up to factors of 5–6 in Re (0.24–0.87 ppb) and by ~10–40% in Cd relative to the least degassed samples (Table 3, Fig. 6). Bismuth also appears to correlate with Cd and S in the Ko'olau glasses (Figs. 6 and 7), but the undegassed Moloka'i glasses have about the same Bi content as the degassed Ko'olau glasses. Key trace element ratios such as Re/

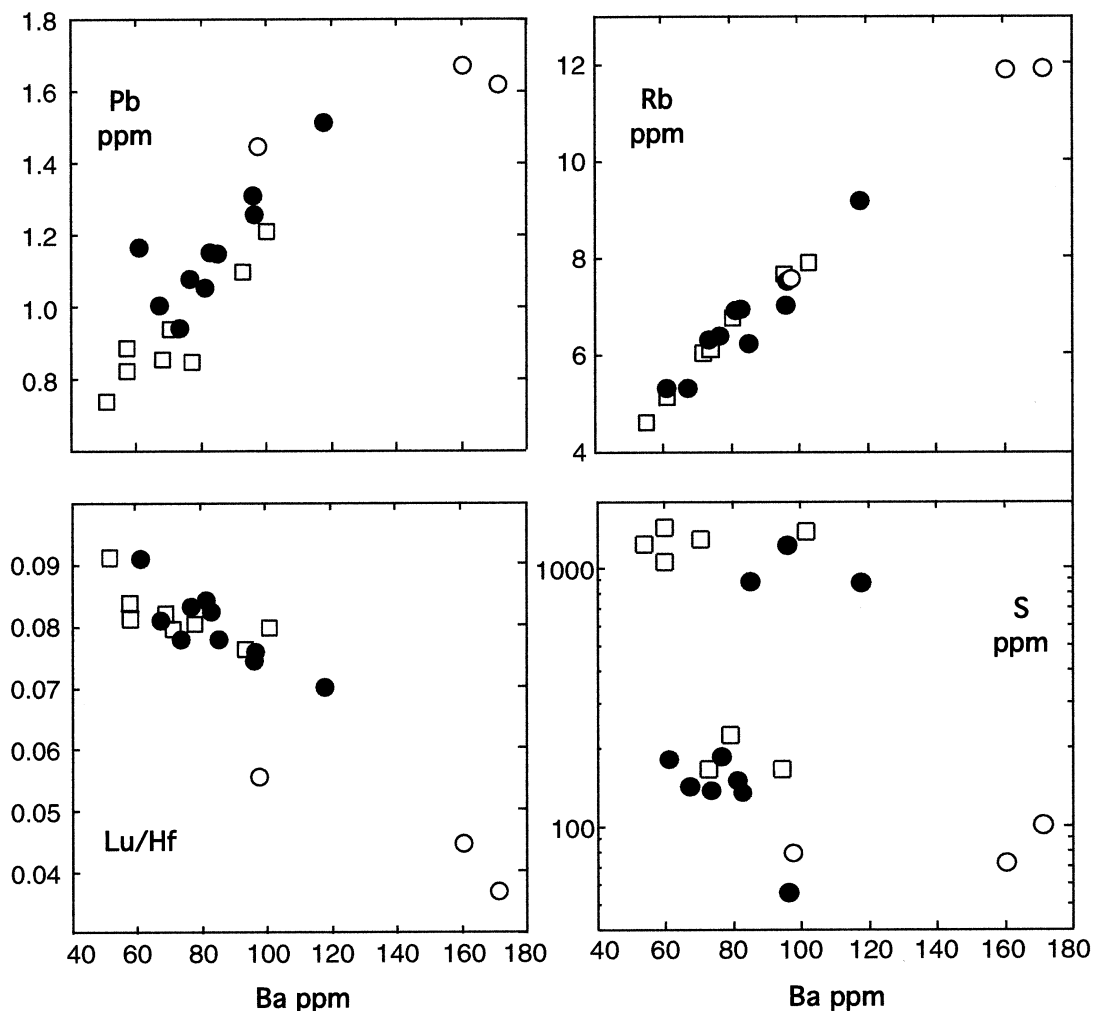


Fig. 4. Variation of Pb, Rb, S, and Lu/Hf with Ba concentration in the Ko'olau and Moloka'i glasses. Symbols same as Figure 1.

Yb, Cu/Re, and Cd/Dy, which are relatively constant in MORB (Hauri and Hart, 1997; Yi et al., 2000), are close to primitive mantle values in the undegassed glasses, and strongly fractionated in the degassed lavas (Fig. 8).

Other potentially volatile chalcophile elements such as Cu, Zn, and Pb show no obvious trends that could be related to magmatic outgassing (Fig. 9). Lead apparently behaved more like an incompatible lithophile element, with higher values in the three light rare earth element (LREE)-enriched Ko'olau glasses and lower values in the Moloka'i glasses (Fig. 4). Zinc and Cu concentrations in these glasses show relatively modest ranges in concentrations and poor correlations with either S (Fig. 9) or other lithophile and chalcophile elements. The three LREE-enriched Ko'olau glasses have somewhat higher Zn contents compared to the other glasses (Fig. 9).

Platinum concentrations in the Ko'olau and Moloka'i glasses are highly variable (1.5–7.5 ppm) but there is no obvious correlation with indicators of outgassing, source composition, melting, or fractionation. Among the Ko'olau glasses, the three trace element-enriched samples have among the lowest Pt and Re contents, but some of the undegassed Moloka'i glasses also

have very low Pt concentrations. One analysis of Moloka'i sample 501-5b showed a remarkable excursion of Cu and Pt during the run that may be indicating the presence of sulfide inclusions in this sample (Fig. 10). Other analyses of this sample gave among the lowest Pt concentration of any sample analyzed for this study (1.5 ppb; Table 3). Note that the Re signal was only modestly affected by the presence of the inclusion, if at all. A detailed evaluation of sulfide immiscibility in these lavas will not be pursued here, but these data raise the possibility that the highly siderophile element compositions of Hawaiian tholeiites may reflect a complex interplay between the timing of sulfide saturation vs. oxidation and outgassing of S from the magma.

4. DISCUSSION

4.1. Magmatic Outgassing

Correlations between S, Re, and Cd contents in the Ko'olau and Moloka'i glasses are consistent with loss of these elements during magmatic outgassing. Bismuth also appears to have

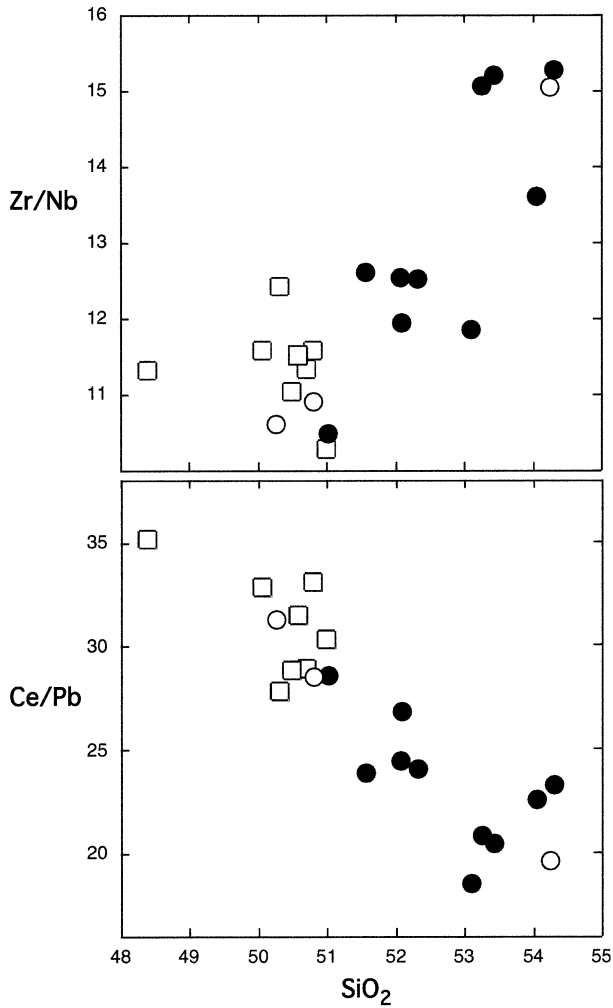


Fig. 5. Variation of Zr/Nb and Ce/Pb with SiO₂ in the Ko'olau and Moloka'i glasses. Symbols same as Figure 1.

been lost from the Ko'olau magma, but additional work is required to explain the differences in Bi content between undegassed magmas from Ko'olau and Moloka'i volcanoes. A comparison of the extent of depletion of chalcophile elements in the Ko'olau and Moloka'i glasses shows that Re was less volatile than S, but more volatile than either Cd or Bi. In contrast, Cu, Zn, Pb, and Pt concentrations in these glasses are not related to S contents, indicating limited depletion of these elements during outgassing, and negating segregation of an immiscible sulfide melt as the cause of the compositional variations in S, Re, Cd, and Bi.

Rhenium concentrations in the undegassed Ko'olau glasses (1.3–1.5 ppb) are significantly higher than those of most subaerial Ko'olau lavas, which have Re contents similar to those of the degassed glasses (0.2–0.5 ppb; Lassiter and Hauri, 1998; Bennett et al., 2000). The low Re/Yb and high Cu/Re ratios of the degassed Ko'olau and Moloka'i glasses are also similar to those of subaerial picritic tholeiites from both Ko'olau and Kilauea that were identified previously as having anomalously low Re contents (Bennett et al., 2000). The low Re contents of many Ko'olau tholeiites are most likely a secondary feature

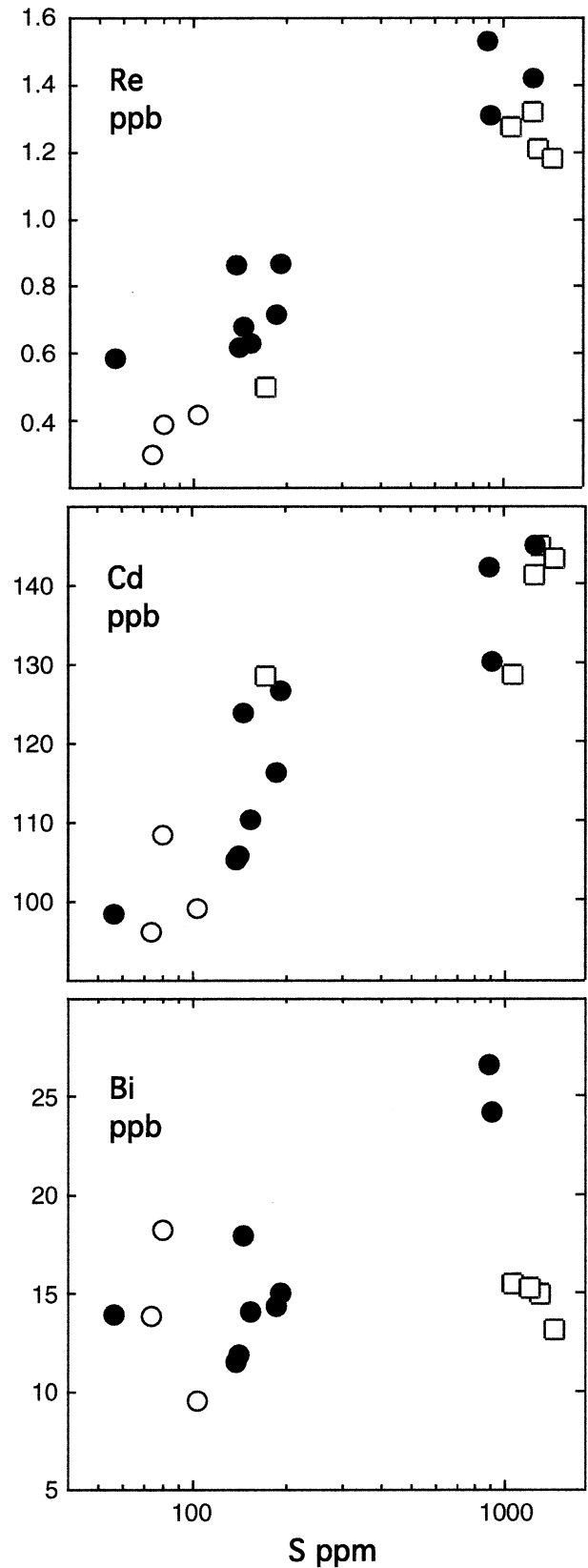


Fig. 6. Variation of Re, Cd, and Bi with S concentration in the Ko'olau and Moloka'i glasses. Symbols same as Figure 1.

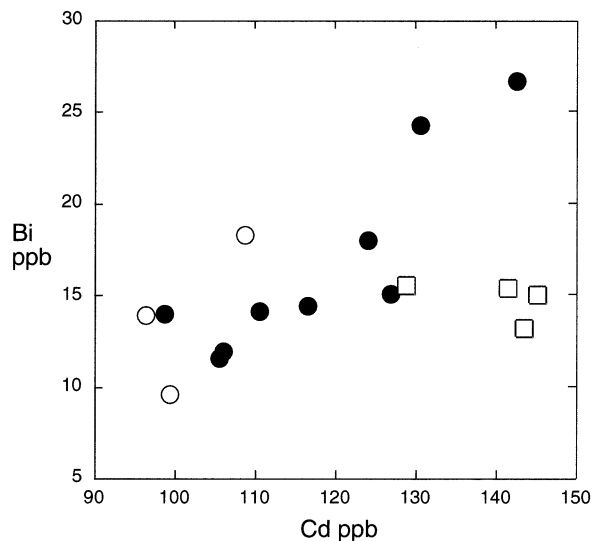


Fig. 7. Variation of Cd vs. Bi concentrations in the Ko'olau and Moloka'i glasses. Symbols same as Figure 1.

related to near-surface degassing rather than a primary, source-related feature. Primitive Ko'olau magmas probably had Re concentrations and Re/Yb or Cu/Re ratios comparable to those of undegassed lavas from other Hawaiian volcanoes (Fig. 11). Degassing and loss of S and Re also affected subaerial or shallow submarine picritic lavas from other Hawaiian volcanoes, producing compositional trends like those in the Ko'olau and Moloka'i glasses (Fig. 11). Lassiter (2003) showed that Mauna Kea lavas sampled by the Hawaiian Scientific Drilling Program (HSDP) core vary systematically with emplacement depth, such that subaerial lavas are systematically depleted in Re relative to submarine lavas. We conclude that substantial Re can be lost from Hawaiian magmas during outgassing, and that this is likely to be a common process affecting ocean island and continental flood basalts in general.

The Ko'olau glass compositions provide a direct measure of the emanation coefficients (ϵ) for volatile elements, which defines the extent of magmatic outgassing. Emanation coefficients have been defined as: $\epsilon = (C_i - C_f)/C_i$, where C_i = the initial concentration of an element in the magma, and C_f = the concentration of that element in the magma after degassing (Gill et al., 1985; Lambert et al., 1986; Pennisi et al., 1988), such that $\epsilon = 1$ for gases, and zero for nonvolatile elements. Previous estimates of ϵ have been inferred indirectly from measurement of trace element concentrations or radioactive disequilibrium within volcanic emissions (Lambert et al., 1986; Pennisi et al., 1988; Le Cloarec et al., 1992).

Emanation coefficients for S (0.86–0.92), Re (0.50–0.74), Bi (0.44–0.45), and Cd (0.19–0.27) can be calculated from the Ko'olau glass compositions presented here, assuming C_i = the average composition of undegassed glasses 500-5A, 500-6, and 500-1, and C_f = the average composition of either the seven samples of degassed ($S < 200$ ppm) main group glasses, or the three LREE-enriched glasses, respectively (Tables 1 and 3). These values for ϵ_{Cd} and ϵ_{Bi} are in reasonably good agreement with data compiled by Rubin (1997) for mafic eruptions worldwide ($\epsilon_{Bi} = 0.31$, $\epsilon_{Cd} = 0.26$), but they imply that Re was

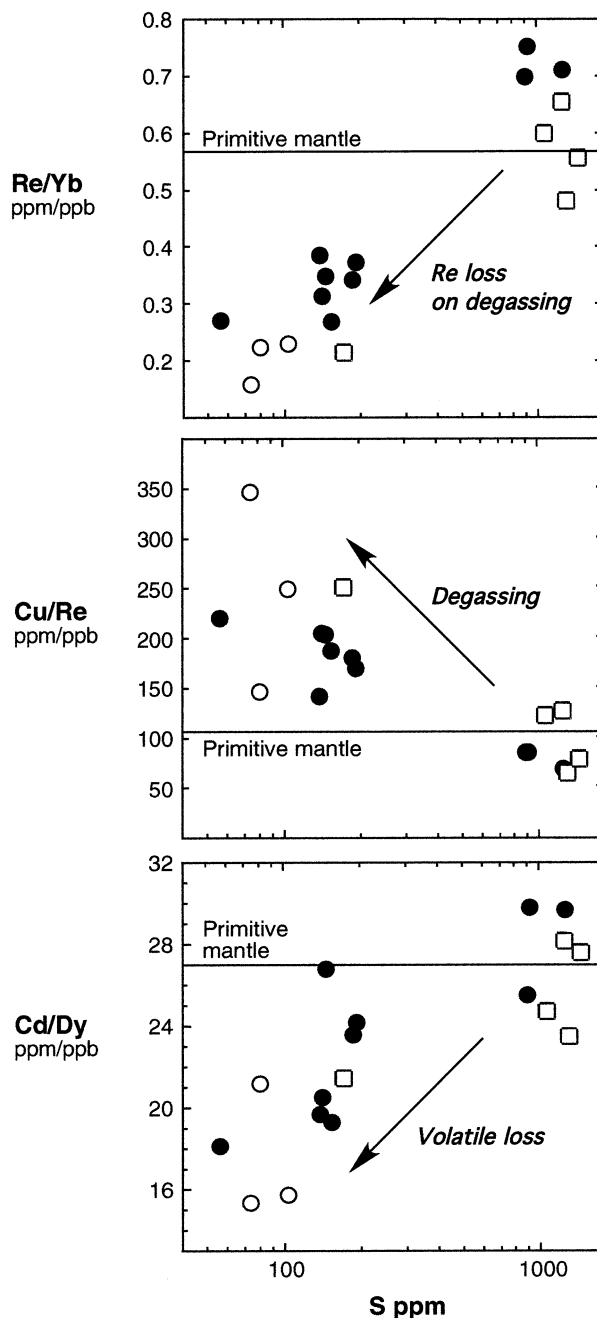


Fig. 8. Variation of Re/Yb, Cu/Re, and Cd/Dy vs. S concentrations in the Ko'olau and Moloka'i glasses. Line labeled "Primitive mantle" shows the primitive mantle value of the trace element ratios (from McDonough and Sun, 1995; Yi et al., 2000). Symbols same as Figure 1.

much more volatile during eruption of Ko'olau than would be expected based on previous estimates (cf. $\epsilon_{Re} = 0.12$ compiled by Rubin, 1997). At least for Ko'olau, and probably for other Hawaiian volcanoes, Re appears to be the most volatile of the chalcophile metals (Fig. 12). Because of their relatively low concentrations in most rocks, highly volatile chalcophile metals (e.g., Re, Cd, Bi, Se) may provide the clearest signature of a magmatic input to hydrothermal systems (Symonds et al.,

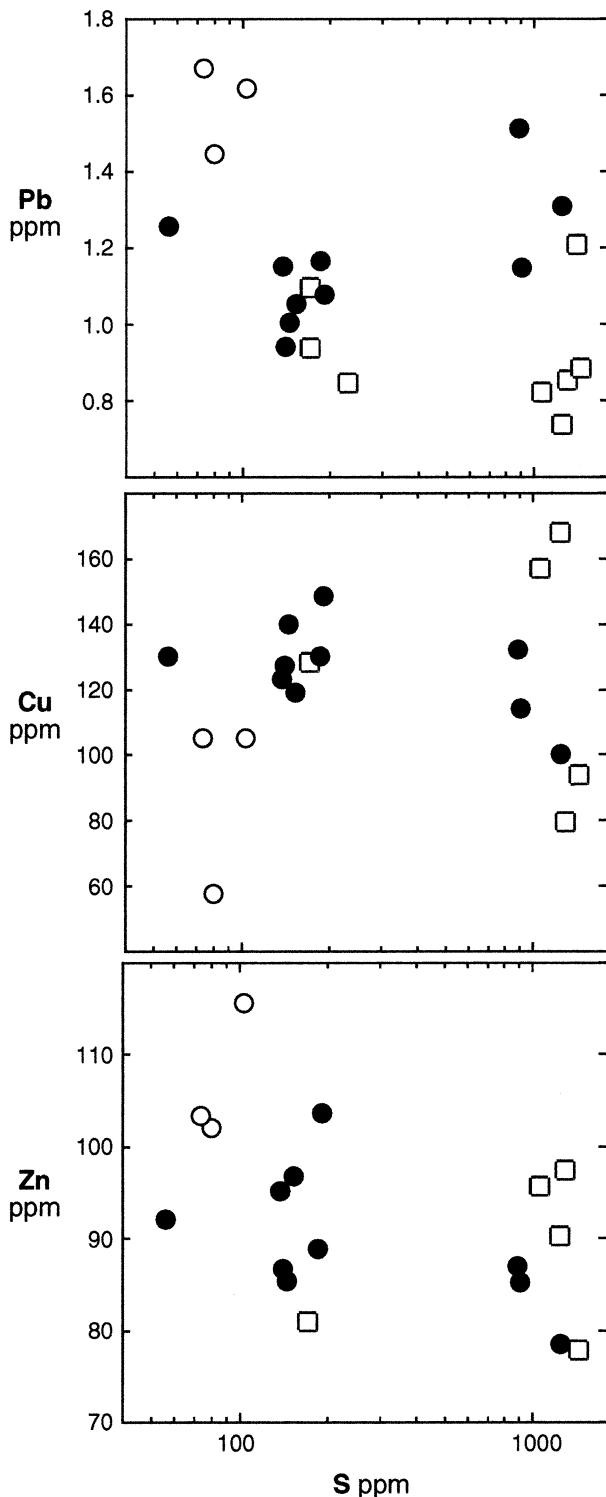


Fig. 9. Variation of Pb, Cu, and Zn with S concentrations in the Ko'olau and Moloka'i glasses. Symbols same as Figure 1.

1987), and as environmental tracers of large mafic eruptions such as formation of oceanic plateaux (Rubin, 1997).

Support for our interpretation that significant fractions of some chalcophile metals can be lost as volatile species during outgassing of Hawaiian magmas is found in the composition of

fumes collected from active vents on Kilauea (Crowe et al., 1987; Miller et al., 1990; Hinkley et al., 1999). These studies demonstrated extreme (10^5 – 10^7) enrichments of Re, Cd, Se, As, and Au in samples of volcanic gases and associated particulates relative to outgassed lava. Concentrations of Re, Cd, Cl, and S in the fumes are strongly correlated, but this probably reflects changes in plume density during dilution in the atmosphere (Crowe et al., 1987) rather than an indication of the type of volatile species present. Although Cu, Pb, and Zn are among the most abundant metals in volcanic plumes by mass (Hinkley et al., 1999), this is primarily due to their comparatively high abundance in the magma. The fraction of these elements lost from the magma as volatiles is actually quite small (e.g., $\epsilon_{\text{Pb}} = 0.015$, $\epsilon_{\text{Cu}} = 0.010$, $\epsilon_{\text{Zn}} = 0.0026$; Rubin, 1997), and changes in melt composition due to volatile loss of these elements would be within the analytical error of our measurements.

Outgassing of active volcanoes provides a significant load of sulfur and metals to the hydrosphere and atmosphere. Recent measurements of volcanic fumes from the Pu'u O'o and Halemaumau vents of Kilauea indicate ~ 1000 – 2500 tonnes/d of SO_2 are produced from $\sim 3.5 \times 10^5 \text{ m}^3$ of magma (Hinkley et al., 1999; Sutton et al., 2001). This is consistent with the efficient ($\geq 90\%$) loss of S from Hawaiian magmas inferred from the compositions of Hawaiian glasses (Swanson and Fabbri, 1973; Davis et al., 2003). Assuming mass loss fractions given by the emanation coefficients calculated for the Ko'olau glasses (Re = 0.50–0.75; Bi = 0.45; Cd = 0.19–0.27), original magmatic concentrations of chalcophile metals similar to those found in the undegassed Ko'olau glasses (Re 1.4 ppb, Cd 140 ppb, Bi 25 ppb), and outgassing of $3.5 \times 10^5 \text{ m}^3$ of new magma per day during sustained eruptions, environmental loadings of 9–13 tonnes/yr of Cd, 4 tonnes/yr of Bi, and 0.2–0.4 tonnes/yr of Re can be calculated for the Ko'olau eruptions represented by the glasses. These loadings are considerably less than those estimated for quiescent degassing of Kilauea during 1991 and 1996 (Cd 33 tonnes/yr; Bi 95 tonnes/yr), and would be relatively minor compared to the annual contributions of volatile metals from arc volcanoes (Hinkley et al., 1999). However, these estimates are highly uncertain due to observed fluctuations in production of S and metals in volcanic plumes from active Hawaiian volcanoes (Sutton et al., 2001; Crowe et al., 1987; Hinkley et al., 1999), and our assumption regarding the volume of magma that was degassed at Ko'olau.

4.2. Source Characteristics of Ko'olau and Moloka'i Magmas

The new major and trace element data for Ko'olau and Moloka'i glasses provide additional insight into the nature of the mantle source region that produced these magmas. Ko'olau is of particular interest due to the distinctive major element, trace element, and isotopic characteristics of its exposed sub-aerial lavas (Frey et al., 1994; Hauri, 1996). A unique source region for Ko'olau tholeiites appears to be necessary, but the nature of this source is controversial with contributions from recycled oceanic crust or shallow lithosphere components being frequently invoked (Hauri, 1996; Jackson et al., 1999; Blichert-Toft et al., 1999; Norman et al., 2002; Haskins and Garcia, 2004).

Strongly correlated variations between major element com-

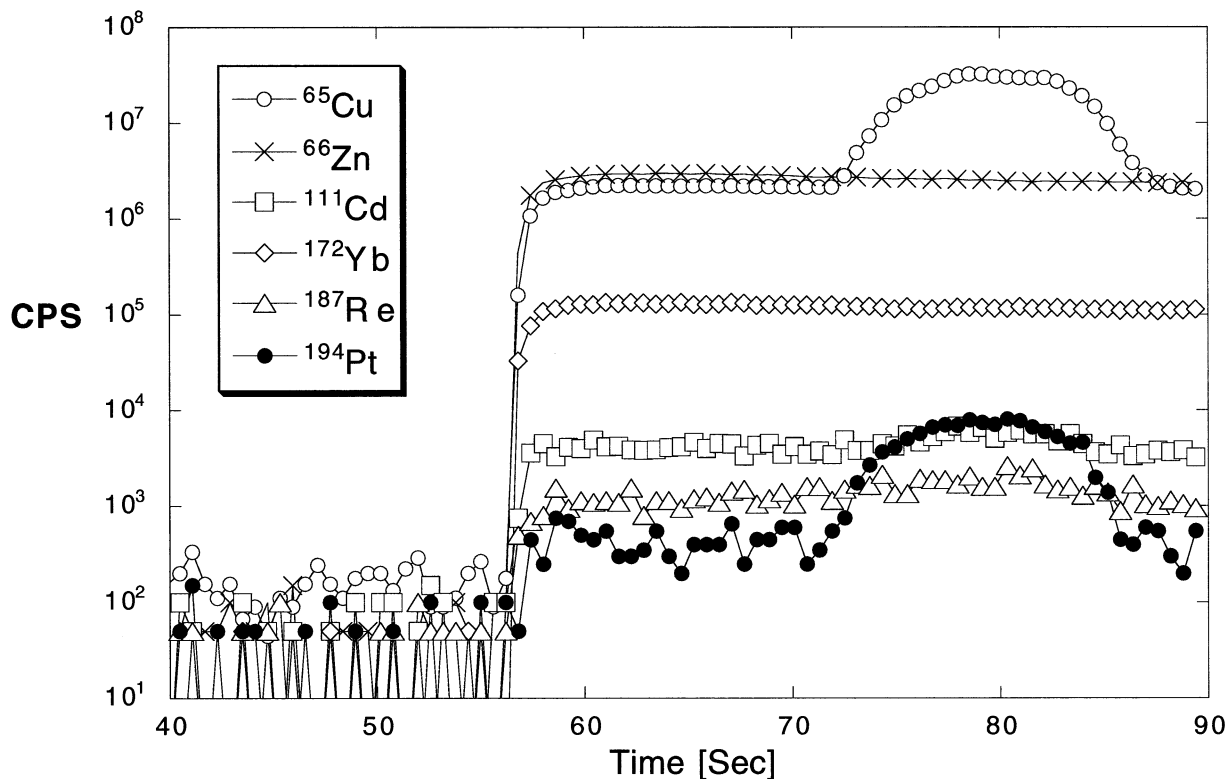


Fig. 10. Time-resolved plot of a laser ablation ICPMS analysis of Moloka'i glass 501-5b showing signal intensity in counts per second (cps) vs. time (sec). The steep rise in signal intensity at ~ 56 s marks the beginning of ablation. The analysis apparently intersected a sulfide inclusion at ~ 70 s as shown by the excursion of Cu and Pt to higher count rates. Re and Cd were only modestly affected by the inclusion. The low count rates before ablation are the dry gas background. This analysis was not used for determination of chalcophile elements in this sample.

positions (e.g., SiO_2 , FeO^* , and TiO_2) and trace element ratios that are known to vary with isotopic composition in Hawaiian magmas (e.g., Zr/Nb, Ce/Pb) are consistent with the contribution of isotopically diverse source components to these Ko'olau and Moloka'i magmas (Tanaka et al., 2002). Zr/Nb ratios in the Ko'olau glasses span nearly the entire range known for Hawaiian tholeiites from all volcanoes, confirming the extreme compositional diversity of Ko'olau compared to other Hawaiian shield volcanoes (Tanaka et al., 2002; Haskins and Garcia, 2004). The systematic variation of Ce/Pb with major element composition seen in the Ko'olau and Moloka'i glasses (Fig. 5) has not been observed for any other Hawaiian volcano.

Other trace element characteristics such as La/Yb and Lu/Hf are sensitive to extent of melting and source mineralogy. A simple melting model shows that much of the variation in La/Yb and Lu/Hf in these lavas can be accounted for by variable degrees of melting of a peridotite source having modest amounts of residual garnet (3.5%) and trace element abundances similar to those of primitive mantle (Fig. 13). Norman and Garcia (1999) used a source with similar mineralogy and trace element characteristics to model the trace element compositions of primitive picritic lavas from a variety of Hawaiian volcanoes. Compositions of the main group of Ko'olau and Moloka'i glasses studied here (Tables 1 and 2), glasses recovered by the Ko'olau Scientific Drilling Program KSDP; (Haskins and Garcia, 2004), lavas from the Trans-Ko'olau tunnel (Jackson et al., 1999), and submarine landslide samples

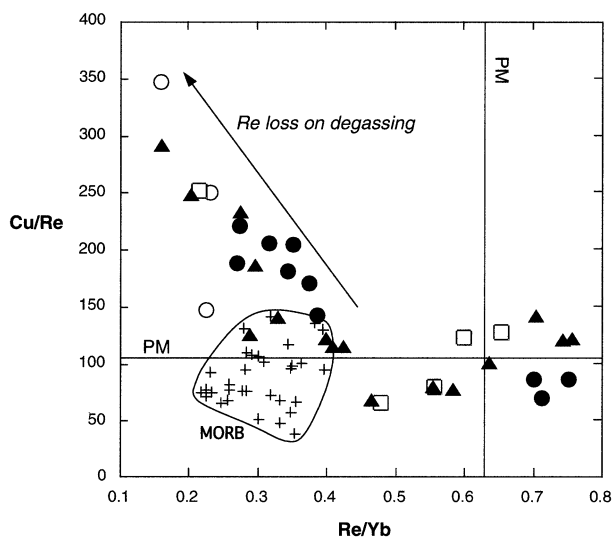


Fig. 11. Variation of Re/Yb and Cu/Re in Ko'olau and Moloka'i glasses, and Hawaiian picrites (data from Bennett et al., 2000) compared with MORB glasses (+, data from Sun et al., 2003b). Undegassed Hawaiian lavas have Cu/Re values similar to primitive mantle (PM) values, and Re/Yb equal to or greater than the primitive mantle. Re loss by degassing produces a trend to lower Re/Yb and higher Cu/Re. Undegassed Hawaiian tholeiites have Re/Yb ratios significantly higher than MORB.

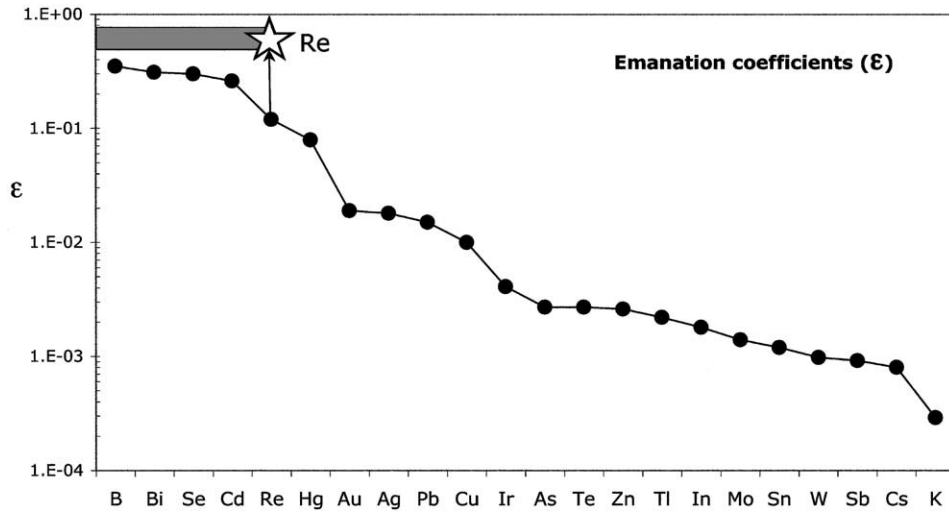


Fig. 12. Emanation coefficients for volatile chalcophile and lithophile elements in basaltic magmas. Data from Rubin (1997) except Re (star) from this study. Re appears to be the most volatile chalcophile metal in Hawaiian shield volcanoes.

(Tanaka et al., 2002) are all consistent with such a model, implying a common source composition for these suites of lavas.

The LREE-enriched Ko’olau glasses, on the other hand,

apparently require a distinctive petrogenesis, as the high La/Yb, low Lu/Hf, and incompatible trace element abundances of the glasses cannot be reproduced by melting of a source similar to that described above, even taking relatively wide variations in

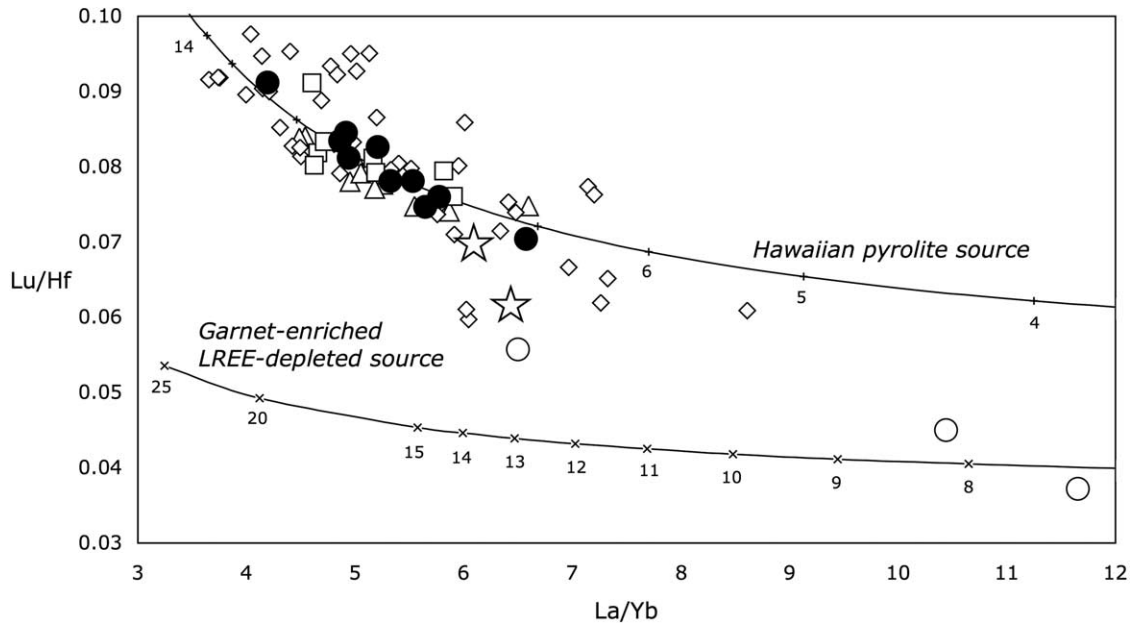


Fig. 13. A comparison of the La/Yb vs. Lu/Hf composition of Ko’olau and Moloka’i tholeiites with trends predicted by two melting models. The line labeled “Hawaiian pyrolite” indicates melt compositions predicted for accumulated fractional melting of fertile peridotite. The source composition was similar to that used by Norman and Garcia (1999) to model the composition of Hawaiian picrites. Trace element abundances approximate those of a primitive source (La 0.70 ppm, Hf 0.31 ppm, Yb 0.49 ppm, Lu 0.73 ppm). Mineral mode contains a modest amount of residual garnet (olivine + opx 87%, cpx 10%, garnet 3.5%). The lower line indicates melt compositions predicted for a source having greater amounts of residual garnet (olivine + opx 60%, cpx 10%, garnet 30%), and trace element abundances similar to those of recycled MORB (La 1.6 ppm, Hf 1.8 ppm, Yb 3.7 ppm, Lu 0.5 ppm). Distribution coefficients: ol + opx (La 0.001, Hf 0.015, Yb 0.03, Lu 0.05), cpx (La 0.055, Hf 0.30, Yb 0.45, Lu 0.42), garnet (La 0.02, Hf 0.80, Yb 6.5, Lu 7.0). Symbols: filled circles: normal Ko’olau Shinkai glasses (this study); open circles: LREE-enriched Ko’olau Shinkai glasses (this study); open triangles: Ko’olau KSDP glasses (Haskins and Garcia, 2004); open diamonds: Ko’olau tholeiites (Jackson et al., 1999; Tanaka et al., 2002); open stars: Ko’olau picrites (Norman and Garcia, 1999); open squares: Moloka’i glasses (this study).

mineralogy and trace element composition into account. Instead the compositions of these glasses are better reproduced by a source with greater amounts of residual garnet, a strongly LREE-depleted trace element pattern, and trace element abundances similar to MORB (Fig. 13). This provides additional evidence for a unique and physically discrete source component contributing to Ko'olau magmas (Hauri, 1996; Norman and Garcia, 1999; Jackson et al., 1999; Tanaka et al., 2002; Norman et al., 2002), and may lend support to the idea that the source of Ko'olau tholeiites contains recycled oceanic crust (Blichert-Toft et al., 1999; Brandon et al., 1999). A garnet-rich source for Ko'olau has been inferred previously based on trace element characteristics (Jackson et al., 1999), and it may be significant that the compositions of some Ko'olau tholeiites appear to extend toward the low-MgO glasses, which have the most extreme La/Yb and Lu/Hf yet reported for tholeiitic lavas from this volcano (Fig. 13).

Although it is probably coincidental, we note that the LREE-enriched Ko'olau glasses also have among the lowest Re, Cd, and S contents measured in this study (Fig. 14). While the low S and chalcophile element contents of these glasses most likely result from outgassing during the low-pressure evolution of these magmas, the possibility that the garnet-enriched component is intrinsically depleted in Re, S, and other chalcophiles may need to be considered. If this component does in fact reflect recycled oceanic crust in the Hawaiian plume, the low S and Re contents might have been produced by devolatilization in a subducted slab (Metrich et al., 1999; Becker, 2000), or during hydrothermal alteration of oceanic crust (Ravizza et al., 1996; Cave et al., 2003, but see Peucker-Ehrenbrink et al., 2003, for an alternative opinion).

4.3. Implications for OIB Source Regions

The volatile behavior of Re in basaltic systems carries implications for the global Re cycle and the crust-mantle system. For example, volatility-related losses likely lead to an underestimate of primary Re concentrations in OIB, as most of the previously analyzed samples were subaerial lavas (see summary by Hauri and Hart, 1997). While the compiled global average abundance of Re in OIB is substantially lower than that of average MORB (0.35 ± 0.16 ppb vs. 0.93 ± 0.34 ppb, respectively; Hauri and Hart, 1997), the clear evidence for Re loss in Hawaiian lavas shows that this is likely to be a secondary feature acquired during outgassing of crustal magma chambers rather than a primary compositional difference in MORB vs. OIB mantle source regions, or an effect of partitioning of Re into residual sulfide or garnet during mantle melting as proposed previously (Hauri and Hart, 1997; Righter and Hauri, 1998; Bennett et al., 2000). Righter and Hauri (1998) noted that many subaerial flood basalts (e.g., Karoo, Siberia) also have low bulk Re contents, which are difficult to explain by the presence of residual sulfide during melting. However, it is likely that those lavas also lost Re and possibly other chalcophile metals as a result of magmatic outgassing, so they cannot be used to define either the Re content of mantle plumes or the behavior of Re during mantle melting.

The fact that undegassed Hawaiian lavas have Re/Yb ratios extending to values greater than that of the primitive mantle suggests that OIB source regions probably have higher Re

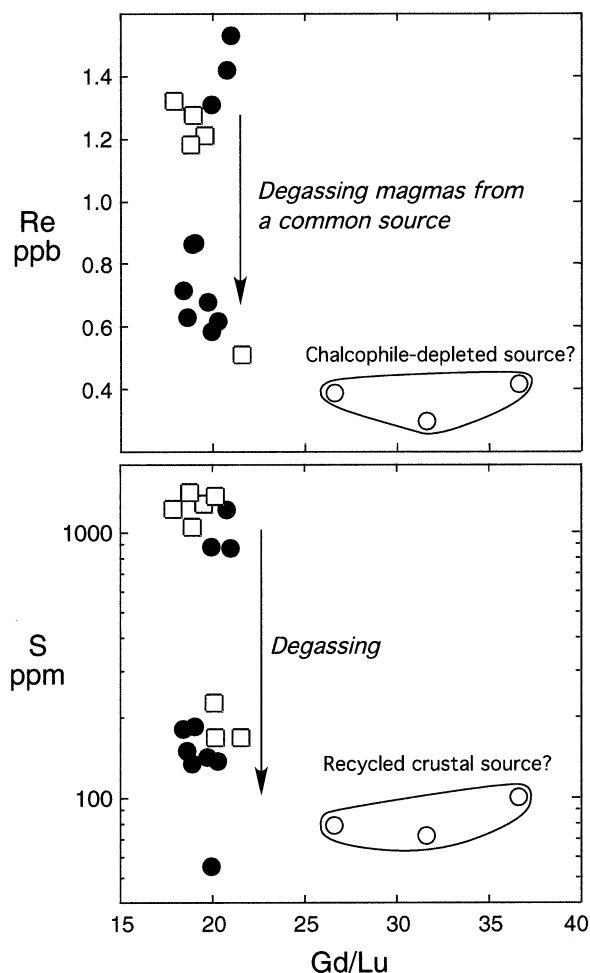


Fig. 14. Variation of Re and S with Gd/Lu in the Ko'olau and Moloka'i glasses. Variable Re and S content at a relatively constant Gd/Lu in the main group of Ko'olau and Moloka'i glasses is interpreted to represent variable outgassing of lavas produced from a common source. The higher Gd/Lu of the three unusual Ko'olau glasses may indicate a distinctive garnet-rich source (see Fig. 13). The low Re and S contents of the three glasses with high Gd/Lu may reflect a source effect as well as outgassing. Symbols same as Figure 1.

contents and higher Re/Yb ratios than previously thought. The Ko'olau and Moloka'i glasses with >800 ppm S, and six submarine picrites from Kilauea and Loihi (data from Bennett et al., 2000) give an average Re concentration of 1.09 ± 0.29 ppb Re. This is within error of previously reported values of 0.93 ± 0.34 ppb (Hauri and Hart, 1997) and 0.98 ± 0.19 ppb (Sun et al., 2003b) for average MORB. Undegassed glasses from Ko'olau and Moloka'i have Re/Yb ratios that extend to values as high as ~ 0.8 (Fig. 11), similar to the deepest Mauna Kea lavas in the HSDP drill core (Lassiter, 2003). The undegassed Hawaiian glasses and submarine picrites have an average Re/Yb of 0.65 ± 0.09 (ppb/ppm), which is identical to the primitive mantle value of 0.63 (McDonough and Sun, 1995) and about a factor of two greater than typical MORB compositions (0.2–0.4; Hauri and Hart, 1997; Sun et al., 2003b; Fig. 11). Cu/Re ratios of these undegassed Hawaiian tholeiites average 100 ± 25 , which is also very close to the primitive mantle value (107 ppm/ppb; McDonough and Sun, 1995).

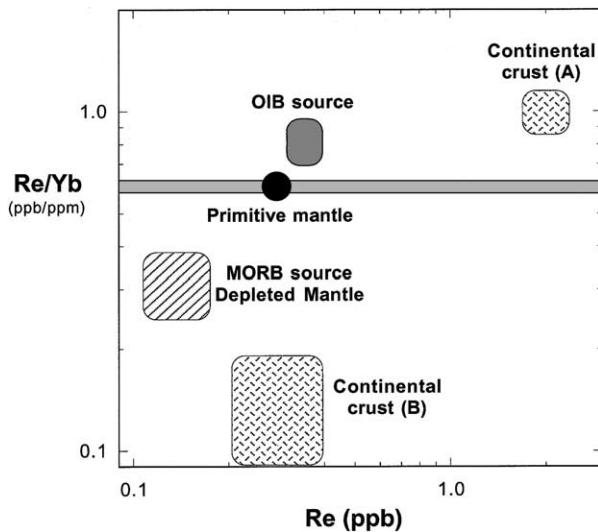


Fig. 15. A schematic representation of Re (ppb) vs. Re/Yb (ppb/ppm) in major mantle and crustal reservoirs. The primitive mantle composition (filled circle) can be accounted for by a combination of MORB and OIB mantle sources. Previous estimates may have underestimated both the Re and the Re/Yb of the OIB source due to volatile loss of Re from subaerial lavas. The OIB source (dark stippled field) is assumed to have Re/Yb ~ 0.8 as given by the upper limit on undegassed Hawaiian lava compositions (Lassiter, 2003; this study). The depleted mantle (diagonal stripes) is assumed to have Re/Yb ~ 0.3 as indicated by the compositions of MORB glasses (Sun et al., 2003b). A value of 0.45 ppm for Yb (McDonough and Sun, 1995) is assumed for both the OIB and the MORB source. Estimates of continental crust composition (hatched symbols) from (A) Sun et al. (2003a) and (B) Esser and Turekian (1993), Peucker-Ehrenbrink and Jahn (2001), with Yb from Taylor and McLennan (1985).

Mantle plumes with Re/Yb ratios greater than those of the primitive mantle have not previously been considered in mass balance models for Re in the silicate Earth, which have invoked a missing component with high Re/Yb. Hauri and Hart (1997) inferred the existence of a cryptic Re-rich reservoir based on the observation that all major geochemical reservoirs including the continental crust, depleted mantle (MORB source), and OIB sources apparently had Re/Yb ratios less than that of the primitive mantle (Re and Yb have similar bulk partition coefficients during melting of the mantle such that Re/Yb ratios remain relatively constant in a variety of basaltic systems). This would imply the existence of a hidden reservoir with high Re/Yb to balance the global budget. An additional problem has been accounting for the radiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotopic compositions that are characteristic of OIB. That is, if OIB source regions are typified by low Re/Os ratios compared with the MORB source, why do they have higher $^{187}\text{Os}/^{188}\text{Os}$? The conclusion that substantial Re can be lost from basaltic magmas during outgassing may contribute to at least a partial resolution of these issues.

The Re/Yb relations (Fig. 15) allow basic constraints to be placed on the relative size of MORB and OIB source regions. Assuming that an OIB source with Re/Yb (ppb/ppm) of ~ 0.8 , as given by the upper limit for undegassed Hawaiian tholeiites (Fig. 11; Lassiter, 2003), best represents the plume composition and is the only complement to the depleted mantle (Re/Yb ~ 0.3 as given by MORB), and that both sources have the same

Yb content, then the OIB source region must be equal to 30% to 40% by mass of the depleted mantle to sum to a primitive mantle Re/Yb. Such a large OIB source may be incompatible with models calling upon preservation of significant amounts of primitive mantle, but it would be in concert with some models of deep mantle structure in which the lower mantle is complex in both structure and composition (e.g., Van der Hilst and Karason, 1999). Potential explanations for generating Re enrichments in OIB source regions include subduction of anoxic or suboxic oceanic sediments, which can have extremely high Re concentrations (10's to 100's of ppb; e.g., Ravizza and Turekian, 1989; Crusius et al., 1996; Morford and Emerson, 1999), and/or addition of small amounts (<0.5 wt.%) of outer core material to the plume source (e.g., Brandon et al., 1999). This is likely to be an upper limit to the size of the OIB source, however, as recent work suggests that the continental crust may also have higher Re/Yb than previously considered (Sun et al., 2003a) (Fig. 15).

5. CONCLUSIONS

Glasses from Ko'olau and Moloka'i volcanoes show clear correlations of S, Re, Cd, and possibly Bi contents. These correlations are consistent with loss of these elements from the magma during outgassing. Rhenium appears to be considerably more volatile during outgassing of basaltic volcanoes than previously thought, with an emanation coefficient of 0.50–0.74, making it the most volatile chalcophile metal in ocean island magmatic systems. Undegassed Ko'olau and Moloka'i glasses and submarine picrites from Kilauea and Loihi have an average Re content of 1.1 ± 0.3 ppb, similar to MORB, and Re/Yb ratios that extend to values greater than that of the primitive mantle. The low bulk Re contents of many OIB and subaerial flood basalts may be due to at least in part to Re loss as a volatile species during outgassing of the magmas. This mechanism may help explain the surprising combination of radiogenic Os isotopic compositions and low Re/Os ratios in some OIB. Plume source regions with high Re/Yb ratios may provide at least a partial complement to the depleted mantle.

Lithophile trace element compositions of most Ko'olau and Moloka'i tholeiites are consistent with variable degrees of melting of fertile mantle peridotite. However, rare glasses with high La/Yb and low Lu/Hf are difficult to explain by this type of process and are better described by melting of a garnet-rich source with distinctive trace element characteristics. This provides additional evidence for a unique petrogenesis of Ko'olau tholeiites in the context of Hawaiian shield volcanism.

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