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Carbonatite and silicate melt metasomatism of the mantle surrounding the Hawaiian plume: Evidence from volatiles, trace elements, and radiogenic isotopes in rejuvenated-stage lavas from Niihau, Hawaii

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[1] We present new volatile, trace element, and radiogenic isotopic compositions for rejuvenated-stage lavas erupted on Niihau and its submarine northwest flank. Niihau rejuvenated-stage Kiekie Basalt lavas are mildly alkalic and are isotopically similar to, though shifted to higher $^{87}\text{Sr}/^{86}\text{Sr}$ and lower $^{206}\text{Pb}/^{204}\text{Pb}$ than, rejuvenated-stage lavas erupted on other islands and marginal seafloor settings. Kiekie lavas display trace element heterogeneity greater than that of other rejuvenated-stage lavas, with enrichments in Ba, Sr, and light-rare earth elements resulting in high and highly variable Ba/Th and Sr/Ce. The high Ba/Th lavas are among the least silica-undersaturated of the rejuvenated-stage suite, implying that the greatest enrichments are associated with the largest extents of melting. Kiekie lavas also have high and variable $\text{H}_2\text{O}/\text{Ce}$ and Cl/La , up to 620 and 39, respectively. We model the trace element concentrations of most rejuvenated-stage lavas by small degrees ($\sim 1\%$ to 9%) of melting of depleted peridotite recently metasomatized by a few percent of an enriched incipient melt (0.5% melting) of the Hawaiian plume. Kiekie lavas are best explained by 4% to 13% partial melting of a peridotite source metasomatized by up to 0.2% carbonatite, similar in composition to oceanic carbonatites from the Canary and Cape Verde Islands, with lower proportion of incipient melt than that for other rejuvenated-stage lavas. Primary H_2O and Cl of the carbonatite component must be high, but variability in the volatile data may be caused by heterogeneity in the carbonatite composition and/or interaction with seawater. Our model is consistent with predictions based on carbonated eclogite and peridotite melting experiments in which (1) carbonated eclogite and peridotite within the Hawaiian plume are the first to melt during plume ascent; (2) carbonatite melt metasomatizes plume and surrounding depleted peridotite; (3) as the plume rises, silica-undersaturated silicate melts are also produced and contribute to the metasomatic signature. The metasomatic component

is best preserved at the margins of the plume, where low extents of melting of the metasomatized depleted mantle surrounding the plume are sampled during flexural uplift. Formation of carbonatite melts may provide a mechanism to transfer plume He to the margins of the plume.

Components: 21,917 words, 17 figures, 11 tables.

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1. Introduction

[2] Hawaiian volcanoes, dominantly shields of tholeiitic basalt, form as the Pacific plate migrates over a melting anomaly in the mantle, hereafter referred to as the Hawaiian plume. As these shields migrate away from the plume, strongly alkalic lavas, forming the rejuvenated-stage of volcanism, may erupt from vents scattered on the tholeiitic shields after an interval of erosion lasting for 0.25–2.5 million years [e.g., Ozawa *et al.*, 2005; Clague, 1987, and references therein]. These lavas occur on the shields of West Maui (Lahaina Basalt), East Molokai (Kalaupapa Basalt), Koolau (Honolulu Volcanics), Kauai (Koloa Volcanics), and Niihau (Kiekie Basalt), with compositions including alkali olivine basalt, basanite, nephelinite, and nepheline melilitite [e.g., Clague and Frey, 1982; Feigenson, 1984; Garcia *et al.*, 1986; Chen and Frey, 1983, 1985; Clague, 1987; Clague and Dalrymple, 1988; Maaløe *et al.*, 1992; Bergmanis *et al.*, 2000; Fekiacova *et al.*, 2007]. In addition to the subaerially erupted, rejuvenated-stage lavas, submarine lavas with similar characteristics have been collected on the seafloor surrounding the islands (peripheral lavas) [e.g., Lipman *et al.*, 1989; Clague and Dalrymple, 1989; Clague *et al.*, 1990, 2006; Dixon *et al.*, 1997; Frey *et al.*, 2000; Hanyu *et al.*, 2005], including volcanics erupted upstream of the plume (preshield or precursory-stage eruptions).

[3] These alkalic lavas are generated by small extents of partial melting resulting from decompression during lithospheric flexural uplift as the oceanic plate (precursory and peripheral) or shield (rejuvenated-stage) passes over the flexural arch, which occurs ~200 km from the center of loading

by the growth of the Hawaiian Islands [e.g., Clague and Dalrymple, 1987; Lipman *et al.*, 1989; ten Brink, 1991; Ribe and Christensen, 1999; Ozawa *et al.*, 2005; Bianco *et al.*, 2005]. Because precursory, peripheral, and rejuvenated-stage lavas are generated by the same mechanism, we use rejuvenated-stage to refer to lavas erupted in all three settings.

[4] Radiogenic isotopic compositions of rejuvenated-stage lavas are consistent with mixing between the Hawaiian plume and a depleted mantle component [e.g., Yang *et al.*, 2003]. Though a variety of models have been proposed [e.g., Chen and Frey, 1983, 1985; Sims *et al.*, 1995; Frey *et al.*, 2000; Reiners, 2002], the enrichment of incompatible elements coupled with low $^{87}\text{Sr}/^{86}\text{Sr}$ and high $^{143}\text{Nd}/^{144}\text{Nd}$ relative to bulk Earth is best explained by melting of depleted mantle recently metasomatized by enriched incipient melt (<2% melting) from the Hawaiian plume [Yang *et al.*, 2003]. Recent radiogenic isotopic studies [Bizimis *et al.*, 2005; Frey *et al.*, 2005; Salters *et al.*, 2006; Fekiacova *et al.*, 2007] support this model by showing the depleted component is most likely derived from depleted mantle thermally entrained by the upwelling Hawaiian plume and not from the Pacific lithosphere.

[5] In this paper, we present new compositional data for rejuvenated-stage lavas from Niihau, the Kiekie Basalt, including submarine lavas erupted on the northwest flank. These lavas provide a unique opportunity to study temporal and spatial variations in magma generation processes associated with Hawaiian volcanism. In particular, the submarine lavas allow us to investigate magmatic variations with respect to water and carbon dioxide, which are partially to mostly retained in quenched glassy rinds. We will show that trace

Figure 1. Location map showing Geological Long-Range Inclined Asdic (GLORIA) acoustic imagery of the sea floor around Niihau. Black rectangle in upper right corner shows general location of Hawaiian Islands. Bright areas are young volcanics with high backscatter, in contrast to dark, low-backscatter sediment-covered sea floor. Red rectangles show areas enlarged in Figures 2 and 3.

element compositions of the lavas are best explained by the presence of carbonate in the Hawaiian plume and the occurrence of carbonatitic, as well as silicate, melt metasomatism of the mantle source for rejuvenated-stage Hawaiian magmas.

2. Samples

[6] The location of Niihau within the Hawaiian chain is shown in Figure 1. Locations of subaerial Kiekie lavas are shown on Figure 2. Subaerial rejuvenated-stage Kiekie Basalt on the island of Niihau are alkalic basalts erupted 0.3 to 3.5 million years ago [Clague and Dalrymple, 1987] and make up more than half of the subaerial lavas [Stearns and Macdonald, 1947; Clague, 1987]. Samples of young lava flows and volcanic cones on the submarine northwest flank of Niihau Island were collected during four dives of the remote operated vehicle (ROV) *Tiburon* on the Monterey Bay

Aquarium Research Institute (MBARI) R/V *Western Flyer* in 2001 (dives T317, T318, T322, and T323; Figure 3). The ages of the Niihau cones are estimated to be <1 Ma based on the thickness of Mn-oxide coating on the rocks [Moore and Clague, 2004].

[7] Compositions of the Kiekie lavas will be compared to those of other rejuvenated-stage lavas, as well as to compositions of lavas from various Hawaiian shields. Data sources are listed in Table 1. The data set used is internally consistent; trace element data are all analyzed in the same laboratory using ICP-MS. Only samples with MgO > 6 wt% are plotted to avoid samples that have undergone multiphase fractionation. Shield lavas include Kilauea Puna Ridge, South Kona Landslide, Kohala, Molokai, Kahoolawe, Lanai, the Waianae Landslide, Mahukona Terrace, and the Niihau Paniau Shield. Lavas with compositions representative of the main rejuvenated-stage trend (blue diamonds on all figures) include lavas from the North Arch, Kauai-Oahu Channel, West Maui (Lahaina Basalt), East Molokai (Kalaupapa Basalt), and Kauai (Koloa Volcanics). Other rejuvenated-stage lavas highlighted with separate symbols include those from Niihau (this study), the South

Figure 2. Map of the island of Niihau with topography displayed as Sun-illuminated from the southeast. Locations (red circles) and sample numbers of the subaerial vents comprising the Kiekie Volcanics are superposed.

Figure 3. Locations of dives on the northwest flank of Niihau by Monterey Bay Aquarium Research Institute (MBARI) R/V *Western Flyer* and remote operated vehicle *Tiburon* in 2001. Bathymetry from MBARI Hawaiian submarine mapping project using Simrad EM300 multibeam data.

Arch, Oahu (Honolulu Volcanics), and Kaula Island (nephelinites).

3. Analytical Techniques

[8] Fresh glasses from rinds on lava were analyzed by electron microprobe with a JEOL Superprobe at the U.S. Geological Survey in Menlo Park using natural and synthetic standards (Table 2). Methods and analytical precision and accuracy are described by *Davis et al.* [1994].

[9] Nineteen whole-rock submarine lava samples from dives T317, T318, T322, and T323 were analyzed for major and trace elements using a combination of X-ray fluorescence (XRF) and inductively coupled plasma-mass spectrometry (ICP-MS) techniques at the GeoAnalytical Laboratory at Washington State University (Tables 3a and 3b), using techniques described by *Knaack et al.* [1994]. An additional seven glass samples were analyzed by ICP-MS at the GeoAnalytical Laboratory (also in Tables 3a and 3b). Major element analyses for 26 subaerial Kiekie Basalt samples were analyzed at laboratories of the U. S. Geolog-

ical Survey in Denver, Colorado using wet chemistry [*Jackson et al.*, 1987]. Trace elements for the subaerial samples were analyzed using a combination of ICP-MS at GeoAnalytical Laboratory and X-ray fluorescence spectrometry (XRF) at the University of Massachusetts.

[10] Concentrations of dissolved water and carbon dioxide were measured in submarine glasses using

Table 1. Sources of Data and Group Classification of Hawaiian Shield and Rejuvenated-Stage Lavas

Classification	Source
<i>Shield Lavas (Gray Circles on All Figures)</i>	
Kilauea Puna Ridge	
South Kona Landslide	
Kohala	
Molokai	
Kahoolawe	
Lanai	
Waianae Landslide	
Mahukona Terrace	
Niihau Paniau Shield	
<i>Representative Rejuvenated-Stage Trend (Blue Diamonds on All Figures)</i>	
Kauai-Oahu Channel	<i>Dixon and Clague</i> [2001]; <i>D. Clague et al.</i> (manuscript in preparation, 2008)
West Maui	lava LA35; <i>Gaffney et al.</i> [2004]
North Arch	<i>Clague et al.</i> [1990] <i>Dixon et al.</i> [1997] <i>Frey et al.</i> [2000] <i>Yang et al.</i> [2003] <i>Hanyu et al.</i> [2005] <i>Davis et al.</i> [1994]
Molokai	<i>Clague and Frey</i> [1982] <i>Clague and Moore</i> [2002] <i>Xu et al.</i> [2005]
Koloa Volcanics from Kauai	<i>Clague and Dalrymple</i> [1988] <i>Maaløe et al.</i> [1992] <i>Reiners and Nelson</i> [1998]
<i>Other Rejuvenated-Stage Lavas (Separate Symbols)</i>	
Niihau	this study
South Arch	<i>Lipman et al.</i> [1989] <i>Sims et al.</i> [1995] <i>Dixon and Clague</i> [2001] <i>Clague et al.</i> (manuscript in preparation, 2008) <i>Clague and Frey</i> [1982]
Honolulu Series on Oahu	<i>Yang et al.</i> [2003]
Kaula nephelinites	<i>Garcia et al.</i> [1986]

Table 2. Microprobe Analyses of Submarine Kiekie Basalt Glasses^a

Sample	Number ^b	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S	Cl	Total
T317-R01	6	47.77	1.57	16.08	11.29	0.19	6.89	11.83	3.13	0.36	0.29	0.139	0.026	99.57
T317-R01 R	9	47.85	1.56	15.96	11.74	0.18	6.78	11.86	3.07	0.36	0.30	0.132	0.027	99.83
T317-R02	5	47.76	1.48	16.42	11.46	0.18	7.26	11.58	2.98	0.35	0.32	0.124	0.021	99.93
T317-R03	5	47.73	1.55	15.99	11.46	0.19	6.92	11.84	3.15	0.36	0.29	0.126	0.028	99.65
T317-R03 R	6	48.05	1.55	15.90	11.65	0.18	6.81	11.62	3.09	0.36	0.29	0.132	0.027	99.67
T317-R04A	6	46.68	1.42	16.39	12.18	0.17	7.80	11.55	2.83	0.32	0.16	0.064	0.032	99.60
T317-R08	6	47.81	1.60	16.10	11.44	0.21	6.87	11.84	3.20	0.37	0.30	0.132	0.028	99.88
T317-R10	5	45.73	1.96	16.06	12.02	0.19	6.64	12.65	3.20	0.60	0.33	0.172	0.034	99.60
T317-R12	13	47.03	1.40	16.61	11.97	0.16	7.86	11.64	2.93	0.31	0.17	0.076	0.021	100.18
T317-R13	6	47.68	1.48	16.52	11.29	0.17	7.21	11.80	3.03	0.34	0.28	0.127	0.019	99.96
T317-R14	6	46.62	1.47	16.82	11.81	0.17	7.48	11.84	2.98	0.36	0.20	0.108	0.018	99.88
T317-R15	6	47.78	1.47	16.42	11.08	0.19	7.24	11.77	3.02	0.34	0.29	0.126	0.021	99.75
T317-R15 R	6	48.00	1.48	16.32	11.34	0.17	7.19	11.65	2.97	0.34	0.28	0.127	0.021	99.89
T317-R16	6	47.58	1.48	16.37	11.31	0.18	7.24	11.82	3.02	0.35	0.29	0.127	0.022	99.78
T317-R18	6	44.95	2.24	15.98	12.04	0.20	6.28	12.99	3.40	0.74	0.40	0.186	0.044	99.45
T317-R18 R	6	45.28	2.26	16.12	12.27	0.19	6.31	12.90	3.34	0.73	0.42	0.186	0.042	100.04
T318-R01	5	46.21	1.40	16.85	11.76	0.18	7.63	12.19	2.97	0.33	0.15	0.109	0.019	99.80
T318-R02	6	46.24	1.32	16.94	11.78	0.20	7.53	12.10	2.95	0.33	0.16	0.107	0.021	99.66
T318-R03	6	46.44	1.30	16.99	11.63	0.20	7.39	12.24	2.99	0.33	0.17	0.109	0.022	99.80
T318-R04	6	46.26	1.32	16.92	11.73	0.18	7.47	12.18	3.01	0.32	0.16	0.107	0.020	99.68
T318-R06	6	46.38	1.33	16.99	11.68	0.19	7.42	12.24	2.98	0.33	0.18	0.111	0.021	99.86
T318-R08	6	46.28	1.34	16.93	11.58	0.18	7.48	12.22	2.98	0.33	0.18	0.107	0.022	99.64
T318-R09	6	46.25	1.38	16.86	11.84	0.19	7.32	12.22	3.00	0.33	0.16	0.103	0.018	99.65
T318-R09 R	10	46.61	1.31	17.05	11.80	0.17	7.42	12.25	2.91	0.32	0.16	0.103	0.020	100.13
T318-R10	6	46.24	1.35	16.94	11.73	0.20	7.29	12.23	3.00	0.33	0.17	0.107	0.024	99.63
T318-R11	6	46.26	1.31	16.91	11.79	0.21	7.53	12.14	2.97	0.33	0.16	0.106	0.022	99.73
T318-R12	6	46.16	1.60	16.60	12.05	0.20	7.46	11.78	3.01	0.39	0.20	0.101	0.019	99.57
T318-R13	6	46.39	1.54	16.73	12.05	0.19	7.66	11.79	2.95	0.37	0.19	0.105	0.021	99.99
T318-R14	6	46.44	1.50	16.63	12.07	0.19	7.58	11.79	2.96	0.37	0.19	0.106	0.023	99.85
T318-R15	5	46.38	1.51	16.68	12.04	0.18	7.56	11.73	2.95	0.36	0.18	0.106	0.018	99.70
T318-R16	6	46.39	1.53	16.76	11.88	0.19	7.55	11.79	2.98	0.36	0.19	0.106	0.020	99.75
T318-R17	6	46.53	1.56	16.59	12.13	0.20	7.13	11.80	3.03	0.36	0.18	0.106	0.023	99.63
T322-R1	6	46.29	1.50	16.50	11.58	0.20	6.97	12.49	3.24	0.48	0.29	0.135	0.024	99.70
T322-R2	5	46.67	1.48	16.69	11.72	0.18	6.97	12.55	3.14	0.47	0.29	0.130	0.026	100.31
T322-R3	9	47.27	1.44	16.25	11.88	0.19	7.64	11.69	2.72	0.32	0.18	0.071	0.019	99.66
T322-R4	6	47.11	1.40	16.73	11.44	0.21	7.35	12.12	3.04	0.37	0.19	0.112	0.019	100.10
T322-R5	3	47.13	1.44	16.82	11.46	0.16	7.26	12.21	3.02	0.38	0.19	0.124	0.022	100.22
T322-R7	11	47.03	1.40	16.29	11.84	0.16	7.84	11.62	2.88	0.31	0.16	0.080	0.024	99.74
T322-R20	10	46.95	1.34	16.58	11.38	0.18	7.92	11.85	2.90	0.32	0.16	0.080	0.018	99.66
T322-R30	6	47.30	1.41	16.77	11.68	0.16	7.38	11.60	3.02	0.33	0.17	0.100	0.017	99.92
T322-R30 R	5	47.17	1.35	16.63	11.31	0.18	7.40	11.61	2.99	0.32	0.17	0.103	0.015	99.27
T322-R31	6	47.31	1.41	16.71	11.83	0.17	7.40	11.57	3.04	0.32	0.17	0.103	0.013	100.06
T322-R31 R	5	47.39	1.37	16.83	11.74	0.18	7.49	11.65	3.07	0.31	0.17	0.106	0.017	100.32
T322-R32	5	47.30	1.42	16.77	11.94	0.18	7.04	11.72	3.09	0.33	0.18	0.106	0.013	100.09
T322-R32 R	6	47.57	1.45	16.66	11.92	0.18	6.97	11.74	2.95	0.33	0.18	0.105	0.017	100.08
T322-R33	6	47.29	1.42	16.85	11.78	0.18	7.25	11.62	3.05	0.32	0.18	0.100	0.021	100.07
T322-R33 R	5	47.28	1.37	16.80	11.93	0.19	7.34	11.70	3.03	0.31	0.17	0.098	0.017	100.23
T323-R1	6	47.14	1.54	16.68	11.16	0.18	6.45	11.81	3.11	0.37	0.27	0.115	0.033	98.87
T323-R2	6	47.27	1.58	16.57	11.30	0.16	6.17	11.90	3.17	0.39	0.29	0.124	0.034	98.96
T323-R3	6	47.20	1.61	16.30	11.42	0.18	6.05	11.90	3.21	0.40	0.31	0.128	0.038	98.75
T323-R4	6	47.37	1.51	16.85	11.64	0.19	6.53	11.79	3.15	0.38	0.28	0.112	0.035	99.85
T323-R5	6	47.20	1.52	16.69	11.21	0.18	6.64	11.79	3.12	0.37	0.29	0.115	0.031	99.14
T323-R6	6	47.60	1.55	16.86	11.32	0.20	6.58	11.96	3.03	0.37	0.28	0.115	0.035	99.91
T323-R8	6	46.65	1.62	16.77	11.54	0.18	6.67	11.97	3.12	0.43	0.28	0.125	0.031	99.39
T323-R9	6	47.22	1.51	16.77	11.16	0.19	6.47	11.83	3.14	0.38	0.27	0.108	0.038	99.06
T323-R10	6	46.92	1.57	16.69	11.53	0.19	6.97	11.94	3.13	0.44	0.28	0.127	0.034	99.83
T323-R11	6	46.61	1.55	16.65	11.57	0.19	6.90	11.94	3.13	0.43	0.28	0.133	0.030	99.42
T323-R12	6	47.18	1.55	16.69	11.23	0.18	6.47	11.78	3.12	0.36	0.27	0.111	0.036	98.97
T323-R14	6	47.72	1.56	16.62	11.58	0.17	6.60	11.95	3.15	0.38	0.27	0.114	0.035	100.13
T323-R15	5	46.72	1.50	16.43	11.41	0.19	6.67	11.82	3.11	0.38	0.28	0.125	0.033	98.66
T323-R16	6	47.08	1.56	16.40	11.39	0.18	6.66	11.76	3.15	0.37	0.28	0.122	0.031	98.97
T323-R17	5	47.47	1.50	16.49	11.28	0.20	6.62	11.66	3.07	0.37	0.28	0.125	0.033	99.09

Table 2. (continued)

Sample	Number ^b	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S	Cl	Total
T323-R18	5	47.78	1.54	16.56	11.27	0.20	6.44	11.82	3.11	0.37	0.27	0.125	0.030	99.52
T323-R19	5	47.72	1.52	16.57	11.37	0.17	6.64	11.73	3.05	0.37	0.28	0.123	0.031	99.57
T323-R20	5	47.81	1.55	16.62	11.50	0.17	6.74	11.83	3.05	0.37	0.28	0.125	0.033	100.06
T323-R21	5	47.80	1.70	15.69	12.03	0.19	5.95	11.81	3.24	0.42	0.31	0.140	0.037	99.31

^aR indicates repeat analysis done during different microprobe session.

^bNumber indicates number of individual point analyses included in average.

infrared spectroscopy (Table 5). Glass chips were doubly polished to a thickness between about 50 and 200 μm . Transmission infrared spectra in the 4000–1200 cm^{-1} (2.5 to 8.3 μm) range were collected using an infrared microscope attachment to a Brüker IFS-66 FTIR spectrometer at the University of Miami according to the procedure of *Dixon and Clague* [2001]. Glass density was calculated for each sample using the Gladstone-Dale rule and the Church-Johnson equation as described by *Silver et al.* [1990]. We used a molar absorptivity of 330 ± 20 L/mole/cm for carbon dissolved as carbonate in alkali silicate glasses calculated according to *Dixon and Pan* [1995]. Precision is the about $\pm 2\%$ for total water and $\pm 10\%$ for molecular water and carbonate. The accuracy of the total water analyses is about $\pm 10\%$. The accuracy of the CO₂ and molecular water analyses are estimated to be about $\pm 20\%$.

[11] Twelve subaerial Kiekie Basalt samples and eight submarine Kiekie samples, all analyzed for major and trace elements, were analyzed for Sr, Nd, and Pb isotopic ratios (Table 6) at Carleton University, Ontario using techniques outlined by *Cousens* [1996]. Prior to dissolution, splits for Pb and Nd were acid washed in warm 1.5 N HCL for 12 hours, then rinsed three times with ultrapure H₂O. Splits for Sr were acid-washed in hot 6 N HCl for 4 days, then rinsed three times with ultrapure H₂O, followed by dissolution in HF/HNO₃. Two samples (T317-R18 and T323-R21) were run for Pb following an additional wash in hydroxylamine to eliminate traces of Mn oxides. All Pb mass spectrometer runs were corrected for fractionation using NIST SRM981. The ratios measured for SRM981 are $^{206}\text{Pb}/^{204}\text{Pb} = 16.890 \pm 0.020$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.429 \pm 0.026$, and $^{208}\text{Pb}/^{204}\text{Pb} = 36.498 \pm 0.048$ (2σ), based on multiple runs of standards and duplicates. The fractionation correction, based on the values of *Todt et al.* [1984], is $+0.13\%$ /amu. Sr isotopic ratios are normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.11940$ to correct for fractionation. Two Sr standards are run at Carleton, NIST SRM987 ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710251 \pm$

18) and the Eimer and Amend (E&A) SrCO₃ ($^{87}\text{Sr}/^{86}\text{Sr} = 0.708032 \pm 24$). Nd isotope ratios are normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.72190$ and 54 runs of the La Jolla standard average $^{143}\text{Nd}/^{144}\text{Nd} = 0.511876 \pm 18$.

4. Results

4.1. Major Elements

[12] Major element compositions (Tables 2–4) are plotted on an alkali-silica diagram in Figure 4. In general, rejuvenated-stage lavas are characterized by increasing alkalis with decreasing SiO₂ attributed to high concentration of incompatible elements at low extents of partial melting. The scatter in the data at low SiO₂ is caused by either loss of alkalis during subaerial weathering or a residual K₂O-bearing phase during melting. Kiekie lavas are only mildly alkalic with higher SiO₂ contents than most other rejuvenated-stage lavas. Also, the subaerial Kiekie lavas have distinctly lower alkali contents at a given silica content than the submarine lavas, most likely caused by weathering.

4.2. Trace Elements

[13] Trace element compositions are listed in Tables 3a, 3b, and 4. Figure 5 shows La plotted against MgO, a standard indicator of differentiation. Rejuvenated-stage lavas exhibit much greater compositional variability than shield lavas at a given MgO. Shield lavas with MgO > 6.5 wt% are characterized by steadily increasing concentrations of trace elements with decreasing MgO, interpreted to be the result of olivine fractionation. To remove the effects of olivine fractionation, olivine is typically added until the melt is in equilibrium with an assumed mantle olivine composition (e.g., Fo₉₀) or has reached an assumed primitive melt MgO. Olivine addition programs work well for tholeiitic compositions; however, uncertainties in the correction increase significantly as melt compositions become more alkalic. One important variable is oxygen fugacity (melt $\text{Fe}^{3+}/\text{Fe}^{2+}$);

Table 3a. Major and Trace Element Analyses of Submarine Kiekie Basalt

Sample	T317- R2	T317- R10	T317- R14	T317- R18	T318- R2	T318- R3	T318- R11	T318- R13	T318- R17	T318- R19	T322- R1	T322- R4	T322- R6	T322- R31	T322- R32	T323- R3	T323- R9	T323- R11	T323- R21
SiO ₂	47.69	46.46	47.17	45.46	46.23	46.33	46.25	46.08	45.81	43.12	47.04	46.95	46.99	47.04	46.75	47.42	47.6	47.08	48.13
TiO ₂	1.43	1.98	1.33	2.16	1.19	1.18	1.17	1.39	1.31	2.23	1.32	1.22	1.43	1.29	1.25	1.31	1.32	1.42	1.6
Al ₂ O ₃	15.75	15.95	15.05	15.91	15.35	15.03	15.31	15.24	15.13	12.22	16.1	15.08	17.28	15.56	14.95	14.75	15.08	15.24	16.31
FeO*	11.55	11.47	11.61	12.16	11.55	11.17	12.13	11.9	12.28	12.72	10.64	11.03	9.94	11.33	11.99	11.43	11.65	11.83	11.61
MnO	0.17	0.17	0.18	0.18	0.2	0.18	0.2	0.18	0.19	0.19	0.19	0.19	0.15	0.18	0.19	0.18	0.18	0.18	0.19
MgO	8.27	6.76	10.47	7.02	11.42	12.02	11.25	10.87	11.09	13.27	9.71	11.65	7.52	10.63	11.2	11.82	10.93	10.64	6.55
CaO	11.45	12.74	10.81	12.83	11.03	10.95	11.02	10.86	10.66	12.03	11.84	10.91	13.07	10.84	10.45	10.44	10.63	10.86	11.9
Na ₂ O	2.78	2.79	2.6	2.75	2.43	2.31	2.36	2.5	2.52	2.65	2.73	2.52	2.86	2.62	2.51	2.48	2.54	2.62	2.89
K ₂ O	0.44	0.8	0.34	0.77	0.32	0.44	0.38	0.43	0.38	1.02	0.54	0.38	0.42	0.34	0.34	0.59	0.47	0.53	0.62
P ₂ O ₅	0.31	0.32	0.26	0.38	0.16	0.16	0.15	0.18	0.17	0.46	0.27	0.18	0.3	0.17	0.17	0.25	0.25	0.27	0.3
Total	99.84	99.44	99.82	99.63	99.88	99.77	100.21	99.63	99.55	99.91	100.37	100.12	99.96	100	99.8	100.66	100.65	100.67	100.09
<i>XRF Trace Element Analyses</i>																			
Ni	172	95	224	77	285	334	293	272	269	327	171	255	92	270	281	317	287	261	64
Cr	373	231	459	199	359	389	352	351	350	531	275	473	164	366	372	521	492	431	147
V	259	306	224	305	250	235	238	241	235	337	252	233	277	237	226	232	238	257	281
Ga	16	18	17	17	17	17	18	15	18	17	16	15	21	16	16	14	16	17	19
Cu	87	85	84	61	100	98	103	92	97	79	90	84	97	99	91	82	86	90	102
Zn	88	86	87	86	79	83	78	82	80	92	79	81	78	84	78	86	88	86	88
<i>ICP-MS Trace Element Analyses</i>																			
La	12.38	17.96	10.81	22.26	7.60	8.15	7.49	9.16	8.16	22.28	12.68	7.99	16.15	7.69	7.53	10.17	10.52	11.69	13.00
Ce	25.07	35.54	22.33	43.65	15.59	16.45	15.30	18.99	16.99	44.85	25.06	16.46	31.42	16.26	15.85	21.21	21.68	24.19	27.07
Pr	3.37	4.65	3.03	5.64	2.11	2.19	2.07	2.57	2.33	5.70	3.23	2.22	3.96	2.25	2.20	2.87	2.96	3.27	3.67
Nd	14.98	20.06	13.43	24.13	9.52	9.74	9.32	11.48	10.50	23.96	13.75	9.85	16.90	10.17	9.90	12.69	13.13	14.43	16.18
Sm	3.70	4.79	3.39	5.50	2.62	2.66	2.54	2.97	2.78	5.42	3.37	2.69	3.99	2.78	2.69	3.21	3.33	3.54	4.10
Eu	1.28	1.60	1.19	1.86	0.96	0.94	0.92	1.07	1.01	1.73	1.16	0.96	1.36	1.00	0.97	1.13	1.17	1.22	1.41
Gd	3.91	4.91	3.69	5.33	2.96	3.00	2.91	3.25	3.11	4.95	3.48	3.06	4.08	3.13	3.04	3.45	3.54	3.68	4.34
Tb	0.60	0.73	0.57	0.77	0.50	0.49	0.48	0.52	0.50	0.70	0.54	0.49	0.63	0.50	0.49	0.54	0.56	0.58	0.69
Dy	3.44	4.23	3.36	4.41	3.01	3.01	2.96	3.13	3.06	3.70	3.18	2.96	3.72	3.08	2.98	3.19	3.32	3.42	3.99
Ho	0.68	0.81	0.66	0.81	0.63	0.61	0.61	0.64	0.62	0.67	0.64	0.59	0.74	0.62	0.60	0.63	0.66	0.67	0.80
Er	1.85	2.16	1.79	2.16	1.75	1.70	1.68	1.75	1.74	1.70	1.77	1.64	1.96	1.69	1.64	1.68	1.77	1.83	2.13
Tm	0.26	0.31	0.25	0.30	0.26	0.25	0.25	0.26	0.25	0.22	0.25	0.24	0.29	0.25	0.24	0.24	0.25	0.26	0.31
Yb	1.61	1.91	1.57	1.85	1.65	1.63	1.61	1.63	1.59	1.30	1.63	1.52	1.89	1.56	1.52	1.51	1.56	1.62	1.92
Lu	0.26	0.30	0.24	0.29	0.27	0.26	0.26	0.26	0.26	0.20	0.25	0.24	0.29	0.25	0.24	0.23	0.24	0.25	0.30
Ba	240	313	208	395	127	121	124	165	152	317	217	140	257	145	142	195	197	236	244
Th	0.80	1.35	0.68	1.79	0.57	0.61	0.55	0.60	0.52	1.71	0.95	0.58	1.22	0.49	0.47	0.59	0.59	0.70	0.74
Nb	10.46	19.84	9.79	24.51	8.85	8.74	8.70	8.85	8.14	28.39	14.35	10.01	16.50	7.79	7.59	8.62	8.83	10.63	10.95
Y	20.80	24.28	19.68	25.09	18.20	17.77	17.89	18.42	18.16	19.65	18.82	17.61	22.20	17.98	17.49	18.28	19.09	19.44	23.45
Hf	1.39	2.07	1.36	2.36	1.27	1.27	1.27	1.33	1.25	2.82	1.44	1.34	1.62	1.22	1.18	1.27	1.31	1.36	1.59
Ta	0.56	1.12	0.53	1.40	0.52	0.52	0.52	0.53	0.47	1.77	0.78	0.56	0.88	0.46	0.44	0.48	0.48	0.59	0.59
U	0.24	0.32	0.16	0.38	0.14	0.24	0.13	0.27	0.13	0.49	0.23	0.15	0.37	0.21	0.12	0.19	0.16	0.19	0.19

Table 3a. (continued)

Sample	T317- R2	T317- R10	T317- R14	T317- R18	T318- R2	T318- R3	T318- R11	T318- R13	T318- R17	T318- R19	T322- R1	T322- R4	T322- R6	T322- R31	T322- R32	T323- R3	T323- R9	T323- R11	T323- R21
Pb	0.77	1.14	0.66	1.62	0.54	0.58	0.55	0.62	0.55	1.68	0.78	0.54	0.98	0.51	0.48	0.58	0.59	0.66	0.74
Rb	8.35	17.10	5.40	16.90	5.95	7.60	9.70	6.80	6.10	21.00	9.50	6.00	8.60	5.20	5.30	6.80	6.80	9.90	6.70
Cs	0.23	0.56	0.08	0.45	0.09	0.19	0.61	0.12	0.11	0.24	0.17	0.09	0.09	0.10	0.07	0.17	0.26	0.42	0.09
Sr	539	566	473	709	270	275	276	346	319	589	416	299	518	302	299	381	397	403	448
Sc	31.8	37.4	30.6	35.1	32.8	29.0	31.0	29.9	28.9	29.4	29.7	30.3	33.8	29.3	27.9	26.4	27.4	29.3	33.2
Zr	53	81	51	96	46	44	45	46	44	110	57	51	65	43	42	46	47	50	58

strongly alkalic compositions tend to be more oxidized than tholeiitic ones [Dixon *et al.*, 1997]. For example, North Arch basalt with 7 wt% MgO at NNO-2 requires addition of 31% olivine, resulting in a primitive melt MgO content of 16.3 wt% to be in equilibrium with Fo₉₀. Under more oxidizing conditions (NNO + 1), the amount of olivine added is reduced to 16%, resulting in a primitive melt MgO content of 12.5 wt%. In the absence of Fe³⁺/Fe²⁺ measurements and given the uncertainties in conventional olivine addition programs, we corrected our data using a simple linear correction to MgO = 14 wt%. The solid line on Figure 5 shows this olivine correction, with slope defined by $-2.8\%/(1 \text{ wt\% MgO})$, consistent with the slope of shield basalts and the results of olivine-addition calculations. Many rejuvenated-stage lavas require little correction. For North Arch, Kiekie submarine and South Arch lavas, correction from 7 to 14 wt% results in a reduction of only $\sim 20\%$ in all trace elements.

[14] Figures 6–12 display correlations among the trace element data. Trace element variations discussed below will be shown as a function of Th, the most incompatible element in this setting. Figures 6a, 7a, 8a, 9a, 10a, 11a, and 12a (upper left-hand side) show the entire concentration range for all rejuvenated-stage lavas, while Figures 6b, 7b, 8b, 9b, 10b, 11b, and 12b (lower left-hand side) focuses on the Kiekie lavas (note scale change). Figures 6c–6d, 7c–7d, 8c–8d, 9c–9d, 10c–10d, 11c–11d, and 12c–12d (right-hand side) show the Mg14-corrected data for samples having MgO > 6.5 wt% along with model curves as described in section 5.

[15] Figures 6a and 6b show Ba plotted against Th for Hawaiian shield and rejuvenated-stage lavas. Both Ba and Th are highly incompatible; therefore a positive correlation is expected for samples related simply by magmatic processes, such as variable extents of melting of a homogeneous source region, variable enrichment or depletion of the source caused by addition or subtraction of melts, or extents of crystallization of a single parent magma. Such a correlation is observed for the tholeiitic shield lavas. Most rejuvenated-stage lavas have higher concentrations of both Ba and Th than the shield lavas. The nephelinites and melilitites from the subaerial Honolulu Volcanics have the highest Ba and Th, but a slightly lower Ba/Th ratio. Kiekie lavas have Th concentrations <2 ppm, lower than other rejuvenated-stage lavas (1 to 12 ppm), but have Ba concentrations significantly

Table 3b. ICP-MS Trace Element Analyses of Submarine Glasses

Sample	T318- R8	T318- R9	T323- R8	T323- R10	T323- R12	T323- R15	T323- R16
La	8.54	7.45	11.86	12.16	10.84	11.09	11.65
Ce	17.36	15.38	24.68	25.33	22.62	22.98	24.33
Pr	2.28	2.09	3.33	3.38	3.06	3.08	3.29
Nd	10.32	9.40	14.63	14.81	13.61	13.57	14.59
Sm	2.75	2.57	3.59	3.66	3.41	3.43	3.68
Eu	0.99	0.92	1.25	1.26	1.20	1.23	1.29
Gd	3.14	2.97	3.81	3.84	3.62	3.61	3.96
Tb	0.52	0.49	0.59	0.59	0.57	0.58	0.62
Dy	3.18	3.05	3.44	3.47	3.36	3.39	3.61
Ho	0.65	0.61	0.67	0.69	0.67	0.68	0.71
Er	1.80	1.74	1.84	1.85	1.77	1.79	1.89
Tm	0.27	0.26	0.26	0.27	0.26	0.26	0.27
Yb	1.73	1.67	1.66	1.68	1.64	1.63	1.68
Lu	0.27	0.26	0.26	0.26	0.25	0.25	0.26
Ba	135	127	237	244	206	206	218
Th	0.63	0.57	0.68	0.69	0.61	0.63	0.66
Nb	9.52	8.93	10.99	11.15	9.31	9.25	9.59
Y	19.33	18.40	20.33	20.64	20.12	19.97	20.52
Hf	1.34	1.29	1.43	1.43	1.36	1.37	1.41
Ta	0.50	0.48	0.56	0.56	0.47	0.47	0.49
U	0.17	0.15	0.18	0.18	0.16	0.16	0.16
Pb	0.63	0.62	0.72	0.73	0.64	0.69	0.70
Rb	7.0	6.9	7.2	7.4	5.9	5.9	5.9
Cs	0.09	0.09	0.09	0.09	0.06	0.06	0.08
Sr	297	266	420	427	416	417	428
Sc	32.9	33.6	30.5	30.9	29.5	30.5	26.5
Zr	49	46	53	53	50	49	51

in excess of the shield lavas (Figure 6b). Lavas collected furthest from the island (T323 lavas) have the greatest enrichments in Ba. Several other samples, including South Arch and three submarine Honolulu lavas (T273 lavas), are enriched in Ba similar to the Kiekie lavas. These lavas will be referred to as high-Ba lavas.

[16] High-Ba lavas are also enriched in Sr. Rejuvenated-stage lavas form a linear array extending to higher Sr and Th concentrations than shield lavas, but with a lower Sr/Th (Figure 7a). Kiekie and other high-Ba lavas have Sr and Th concentrations that overlap with the shield lavas, significantly enriched in Sr relative to an extrapolation through the trend formed by the other rejuvenated-stage lavas (Figure 7b). *Clague et al.* [2006] showed that similar Sr enrichments in the submarine Honolulu Series lavas can not be explained by seawater addition (<5% of Sr added by seawater).

[17] In contrast to Ba and Sr, high-field strength element concentrations in high-Ba samples show no enrichment relative to other rejuvenated-stage

lavas. Kiekie lavas have low Nb and Hf concentrations consistent with their low Th concentrations and the trend formed by the other rejuvenated-stage lavas (Figures 8a and 8b and Figures 9a and 9b). South Arch and three high-Ba Honolulu Volcanics lavas, however, have Nb and Hf concentrations slightly elevated above Kiekie lavas.

[18] La (Figure 10) and Lu (Figure 11) illustrate the range of behavior of the rare-earth elements (REE). Relative to the trends formed by representative rejuvenated-stage lavas, high-Ba lavas have higher concentrations of both light rare-earth (LREE) and heavy rare-earth (HREE) elements.

[19] Figure 12 shows Nb/La plotted against Ba/Th. It has long been recognized that Hawaiian lavas are characterized by higher Ba/Th than other oceanic island basalts (OIB) [e.g., *Hofmann and Jochum*, 1996; *Yang et al.*, 2003]. Hawaiian shield lavas cluster around a Ba/Th value of 132 ± 20 . In contrast, Easter Seamount Chain lavas [*Fontignie and Schilling*, 1991; *Kingsley*, 2002; *Kingsley et al.*, 2007] whose compositions are not shown but are representative of other Pacific plumes (e.g., Galapagos and Pukapuka), have significantly lower Ba/Th ranging from ~ 55 for the more depleted samples to ~ 70 for the more enriched samples. Most Hawaiian rejuvenated-stage lavas form a field with Ba/Th (153 ± 28) and Nb/La (1.43 ± 0.15), higher than the shield lavas. In contrast, Kiekie lavas form a distinct trend toward higher Ba/Th and lower Nb/La. This trend is consistent with the concentration data showing that Kiekie lavas are enriched in Ba and La, but not in Nb. High Ba/Th in the T323 submarine Kiekie lavas (up to 353) are the highest values ever measured in Hawaiian lavas. Though Kiekie lavas define the most extreme values, the signature is not limited to Kiekie. Honolulu Volcanics, Kaula nephelinites, and South Arch lavas all have higher Ba/Th and lower Nb/La than the representative Hawaiian rejuvenated-stage lavas.

4.3. Water, Carbon Dioxide, and Chlorine

[20] Dissolved water and carbon dioxide concentrations in quenched glassy rinds of the submarine lavas are listed in Table 5. Depth of vapor saturation and composition of the equilibrium vapor phase based on dissolved water and carbon dioxide concentrations are calculated according to *Dixon* [1997].

[21] Figure 13 shows the depth of vapor saturation plotted against the depth of sample collection. Most rejuvenated-stage lavas, including Kiekie

Table 4 (Sample). Wet Chemical Major Element and Trace Element Analyses of Subaerial Kiekie Basalt [The full Table 4 is available in the HTML version of this article at <http://www.g-cubed.org>]

Sample	69Nii-1	69Nii-3	69Nii-4	69Nii-5	69Nii-6	69Nii-7	69Nii-8	69Nii-9	70Nii-1	70Nii-4	70Nii-5	70Nii-6	70Nii-7	70Nii-8	70Nii-9	70Nii-10	70Nii-11	70Nii-12
SiO ₂	45.64	45.50	46.26	45.35	45.27	46.18	46.97	45.42	44.73	46.74	46.25	44.72	44.99	45.49	45.21	45.79	45.31	45.19
TiO ₂	1.16	1.07	1.10	1.35	1.15	1.18	1.38	1.12	1.38	1.48	1.44	1.17	1.25	1.36	1.32	1.49	1.28	1.28
Al ₂ O ₃	15.23	15.22	15.40	15.34	14.92	15.60	16.78	15.21	14.82	15.00	15.10	15.04	15.53	15.24	15.32	16.38	15.25	15.33
Fe ₂ O ₃	4.10	5.28	4.80	3.37	5.05	2.03	2.35	1.74	4.48	1.95	9.13	2.26	2.72	2.15	2.73	2.34	3.40	3.97
FeO	7.98	6.84	6.72	8.37	6.75	9.36	8.62	9.72	7.74	9.72	3.33	9.18	8.96	9.63	8.78	9.25	8.34	7.76
MnO	0.19	0.19	0.18	0.19	0.19	0.18	0.18	0.18	0.18	0.17	0.18	0.18	0.18	0.18	0.17	0.18	0.18	0.18
MgO	11.34	10.65	10.00	10.18	12.20	10.75	7.44	11.81	10.22	10.03	10.13	11.29	11.42	11.33	10.71	9.99	11.07	10.16
CaO	10.69	11.05	11.23	11.08	10.86	11.31	12.49	10.78	11.08	11.02	10.72	11.34	11.04	10.83	11.09	11.15	10.93	11.20
Na ₂ O	2.46	2.36	2.40	2.84	2.34	2.56	2.49	2.39	2.53	2.68	2.53	2.61	2.30	2.60	2.76	2.80	2.49	2.80
K ₂ O	0.29	0.22	0.21	0.37	0.31	0.28	0.31	0.25	0.29	0.29	0.28	0.34	0.31	0.33	0.39	0.39	0.34	0.39
P ₂ O ₅	0.19	0.12	0.13	0.30	0.18	0.17	0.19	0.18	0.18	0.20	0.21	0.25	0.26	0.25	0.27	0.27	0.24	0.29
H ₂ O ⁺	0.06	0.30	0.39	0.31	0.39	0.10	0.40	0.31	0.72	0.06	0.22	0.21	0.57	0.19	0.21	0.25	0.43	0.29
H ₂ O ⁻	0.21	0.53	0.47	0.35	0.28	0.13	0.23	0.30	0.91	0.26	0.28	0.37	0.38	0.22	0.39	0.36	0.39	0.48
CO ₂	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.11	0.04	0.00	0.00	0.35	0.19	0.02	0.01	0.10	0.08	0.00
S	0.06	0.14	0.17	0.13	0.02	0.03	0.03	0.12	0.11	0.08	0.02	0.18	0.03	0.03	0.12	0.05	0.04	0.20
Total	99.71	99.60	99.59	99.63	100.04	99.96	99.93	99.75	99.53	99.79	99.94	99.61	100.22	99.97	99.58	100.90	99.89	99.64

<i>XRF Trace Element Analyses</i>	
Ni	274
Cr	416
V	215
Ga	17
Cu	95
Zn	87
Co	63

<i>ICP-MS Trace Element Analyses</i>	
La	8.91
Ce	18.35
Pr	2.47
Nd	10.84
Sm	2.84
Eu	1.03
Gd	3.17
Tb	0.51
Dy	3.02
Ho	0.60
Er	1.64
Tm	0.24
Yb	1.55
Lu	0.25
Ba	147
Th	0.60

Ni	274	268	267	250	264	296	200	268	234
Cr	416	482	426	423	408	369	365	420	388
V	215	191	205	228	249	249	247	200	216
Ga	17	18	18	18	17	16	18	17	17
Cu	95	100	85	85	75	70	75	70	75
Zn	87	82	75	92	81	107	106	79	83
Co	63	60	60	55	60	59	55	60	59

La	8.91	8.04	9.19	13.22	16.84	10.74	9.19	17.69	21.51	10.74	8.34	10.72	9.53	8.99	15.67	16.52	14.21	16.61
Ce	18.35	15.22	14.68	22.15	32.87	21.51	17.69	21.51	21.51	21.51	17.30	19.58	20.21	19.58	30.70	32.73	28.21	32.48
Pr	2.47	2.16	2.16	3.02	4.19	2.88	2.44	2.88	2.88	2.88	2.32	2.77	2.84	2.70	3.90	4.25	3.69	4.19
Nd	10.84	9.92	9.94	13.26	17.60	12.90	11.03	12.90	12.90	12.90	10.26	12.57	13.10	12.44	16.59	17.83	15.62	17.67
Sm	2.84	2.69	2.77	3.22	3.99	3.47	2.91	3.47	3.47	3.47	2.71	3.34	3.57	3.41	3.76	4.24	3.61	4.06
Eu	1.03	0.98	1.03	1.14	1.36	1.27	1.08	1.27	1.27	1.27	1.00	1.19	1.29	1.23	1.30	1.44	1.23	1.36
Gd	3.17	3.19	3.33	3.64	3.98	3.95	3.30	3.95	3.95	3.95	3.00	3.70	3.99	3.75	3.75	4.17	3.63	3.90
Tb	0.51	0.51	0.53	0.59	0.59	0.52	0.52	0.52	0.52	0.52	0.47	0.58	0.62	0.59	0.56	0.63	0.54	0.58
Dy	3.02	3.11	3.24	3.45	3.29	3.69	3.13	3.69	3.69	3.69	2.87	3.49	3.74	3.51	3.27	3.63	3.20	3.37
Ho	0.60	0.65	0.65	0.67	0.67	0.74	0.63	0.74	0.74	0.74	0.57	0.70	0.73	0.68	0.63	0.70	0.63	0.66
Er	1.64	1.83	1.75	1.81	1.77	1.93	1.68	1.93	1.93	1.93	1.53	1.89	1.93	1.85	1.66	1.87	1.69	1.78
Tm	0.24	0.28	0.25	0.26	0.26	0.28	0.24	0.28	0.28	0.28	0.22	0.28	0.27	0.26	0.24	0.27	0.24	0.26
Yb	1.55	1.69	1.57	1.61	1.62	1.77	1.54	1.77	1.77	1.77	1.45	1.72	1.72	1.65	1.52	1.68	1.54	1.57
Lu	0.25	0.27	0.24	0.25	0.25	0.27	0.24	0.27	0.27	0.27	0.22	0.28	0.27	0.25	0.28	0.26	0.24	0.25
Ba	147	116	109	229	264	184	154	184	141	135	132	233	219	219	252	273	227	264
Th	0.60	0.47	0.45	0.69	1.13	0.77	0.65	0.77	0.59	0.62	0.58	0.91	0.95	0.94	1.14	1.12	0.93	1.12

Figure 4. Total alkalis versus silica diagram showing whole-rock and glass analyses for Kiekie lavas. Kiekie lavas are mildly alkalic compared to other Hawaiian rejuvenated-stage lavas. Representative rejuvenated-stage lavas (RSV) include submarine lavas from the Kauai-Oahu Channel and the North Arch and subaerial lavas from West Maui (Lahaina Basalt), East Molokai (Kalaupapa Basalt), and Kauai (Koloa Volcanics). Kiekie Submarine T323 samples are from the furthest dive location from the island of Niihau (Figure 3). See Table 1 for sources of data.

Basalts, lie within uncertainty ($\pm 25\%$) of the 1:1 line suggesting that melts were in equilibrium with a mixed $\text{CO}_2\text{-H}_2\text{O}$ vapor phase during eruption and little transport has occurred since eruption. This is important because only samples erupted deep on the seafloor are likely to have retained all or most of their original water contents. Kiekie sample T317R14 is slightly undersaturated and may have erupted at a shallower depth followed by transport by flow to their present collection depth. Two samples (Kiekie T317-R16A and North Arch 23D) are slightly oversaturated for their depth of eruption and may have had insufficient time to maintain vapor-saturation during eruption. (Table 6).

[22] Water and chlorine concentrations show a large amount of scatter at a given Th concentration (Figures 14 and 15, respectively). The most striking feature of Figure 14b is the large range of water concentrations at a constant Th for Kiekie T323 and South Arch lavas. Though both Kiekie T323 and South Arch lavas are enriched in Ba, Sr, and LREE, the enrichments in water and trace elements do not correlate in any simple way. The trend toward high water concentrations at nearly constant Th is extremely rare in MORB and OIB basalts. The only other published oceanic island basalt with similarly high water concentrations is in melt inclusions within olivine phenocrysts from Loihi,

interpreted to be due to assimilation of seawater [Kent *et al.*, 1999]. Typically, such large variations of water at relatively constant Th are observed in arc and back-arc environments and interpreted to be the result of subduction-related fluid fluxing [e.g., Sisson and Layne, 1993; Stolper and Newman, 1994; Danyushevsky *et al.*, 1993; Kamenetsky *et al.*, 1997; Newman *et al.*, 2000; Walker *et al.*, 2003].

[23] Some representative rejuvenated-stage lavas, specifically the strongly alkalic North Arch lavas, have water concentrations lower than expected. These low water concentrations have been previously modeled as water loss during degassing [Dixon *et al.*, 1997]. Degassing of water from submarine basalts is usually associated with some combination of shallow eruption depth, high vesicularity, or volatile-rich compositions due to low extents of melting or high extents of differentiation [e.g., Dixon *et al.*, 1997; Dixon and Clague, 2001; Simons *et al.*, 2002]. None of these factors apply to the Kiekie basalts.

[24] High-Ba lavas are characterized by high and highly variable $\text{H}_2\text{O/Ce}$. High water concentrations in the Kiekie T323 and South Arch samples result in anomalously high $\text{H}_2\text{O/Ce}$, up to 620, the highest value measured in OIB lavas. Representative sub-

Figure 5. MgO-variation diagram for La in shield and rejuvenated-stage lavas. Symbols are the same as in Figure 4 with the addition of high-MgO glasses from Kilauea's Puna Ridge [Clague *et al.*, 1991]. Solid line represents a linear approximation of variation produced by olivine-addition with a slope of -2.8% for every 1 wt% increase in MgO. Note that magnitude of trace element variation in rejuvenated-stage lavas is an order of magnitude greater than the variation produced by olivine fractionation.

Figure 6. Ba versus Th for Hawaiian shield and rejuvenated-stage lavas. (a) Uncorrected data for lavas with $\text{MgO} > 6.0$ wt%. (b) Close-up of low Th concentration data (note scale change) showing that Kiekie lavas are enriched in Ba at a given Th concentration relative to other rejuvenated-stage lavas. (c) Ba and Th corrected to $\text{MgO} = 14$ wt% (Ba_{14} , Th_{14}) using the linear correction from Figure 5. Because olivine addition correction was performed only on lavas with $\text{MgO} > 6.5\%$, some data on Figures 6a and 6b (in particular representative RSV with $1 < \text{Th} < 1.5$ ppm), do not appear on Figures 6c and 6d. Solid blue lines represent 1% to 20% batch melting of a metasomatized mantle source (Model 2, 98% depleted mantle +2% of a 0.5% incipient melt of the Hawaiian mantle). Batch melting calculations were performed using variable mantle mineralogy with 3% residual garnet (crosses), 6% residual garnet (open circles), and 3% residual garnet along with phlogopite and an oxide phase (open triangles). See Tables 7a, 7b, and 7c for details. Symbols on the batch melting curves represent 1% to 20% melting at increments of 1% melting. Orange solid line represents 1% to 20% batch melting of a more depleted source (Model 1, 99.2% depleted mantle + 0.8% of a 0.5% incipient melt of the Hawaiian mantle). Orange dashed lines represent 1% to 20% batch melting of Model 2 mantle to which 0.1% (open square with dot) and 0.2% (open square with cross) carbonatite melt has been added. (d) Close-up of Kiekie data. Because Ba and Th have similar bulk distribution coefficients, high Ba at low Th concentrations in Kiekie lavas can not be explained by simple melt metasomatism models. Other high-Ba lavas include South Arch and T273 Honolulu Volcanics. Addition of up to 0.2% carbonatite to Model 1 mantle source can explain preferential enrichment of Ba relative to Th.

marine rejuvenated-stage lavas have $\text{H}_2\text{O}/\text{Ce}$ consistent with those of Pacific MORB and other OIB (Easter Seamount Chain (210 ± 20) [Simons *et al.*, 2002], Kilauea 41D (196) [Dixon and Clague, 2001], and Loihi (173 ± 26) [Dixon and Clague, 2001]).

[25] High-Ba lavas, especially Kiekie T323 and South Arch, are also enriched in Cl (Figures 15a and 15b) relative to representative rejuvenated-stage lavas, although there is also considerable scatter in the representative rejuvenated-stage lavas (mainly North Arch lavas).

Figure 7. (a and b) Sr versus Th and (c and d) Sr_{14} versus Th_{14} , with format following Figure 6. Kiekie and other high-Ba lavas are also enriched in Sr. High Sr concentrations in Kiekie Basalts, South Arch, and Honolulu Volcanics T273 lavas can be explained by addition of 0.1 to 0.2% carbonatite to the more depleted Model 1 mantle composition.

[26] In summary, Kiekie Basalts have lower incompatible trace element concentrations than other rejuvenated-stage lavas. Relative to the trend extrapolated through other rejuvenated-stage lavas to low Th contents, however, Kiekie Basalts are enriched in Ba, Sr, LREE, H_2O , and Cl. No enrichments in Nb, Hf, and Ta are observed.

4.4. Radiogenic Isotopes

[27] In general, the Kiekie Basalts have radiogenic isotopic compositions similar to other rejuvenated-stage lavas in that their compositions are shifted away from Hawaiian shield lava compositions toward a depleted component (Figure 16). Kiekie lavas are shifted to higher $^{87}Sr/^{86}Sr$ and lower $^{206}Pb/^{204}Pb$ than rejuvenated-stage lavas erupted on other islands and marginal seafloor settings.

5. Modeling

5.1. Melt Metasomatism and Mantle Sources for Representative Rejuvenated-Stage Lavas

[28] Early modeling of formation of Hawaiian rejuvenated-stage lavas focused on metasomatism of OIB mantle by low degree partial melts from a MORB source [Chen and Frey, 1983, 1985;

Feigenson, 1984; Clague and Dalrymple, 1988; Chen *et al.*, 1990; Maaløe *et al.*, 1992]. Recent radiogenic isotopic studies [Bizimis *et al.*, 2005; Frey *et al.*, 2005; Salters *et al.*, 2006; Fekiacova *et al.*, 2007] show that the depleted component cannot be Pacific lithosphere (either young or aged), and instead is intrinsic to the Hawaiian plume. Other models have shown that trace element and radiogenic isotopic compositions of rejuvenated-stage lavas can be generated from depleted mantle recently metasomatized by incipient melts (<2%) from the Hawaiian plume [Roden *et al.*, 1984; Reiners and Nelson, 1998; Clague *et al.*, 1990; Dixon *et al.*, 1997; Frey *et al.*, 2000; Yang *et al.*, 2003]. In this metasomatized source, incompatible element abundances, as well as Sr and Nd isotopic ratios, are dominated by incipient melts.

[29] Our modeling builds on the work of Yang *et al.* [2003]. We use the depleted MORB source composition of Workman and Hart [2005]. Hawaiian mantle composition is estimated such that the compositional range of Hawaiian shield lavas is generated by 4–15% batch melting using accepted distribution coefficients and mantle modal mineralogy (Tables 7a, 7b, and 7c). Our Hawaiian mantle composition is consistent with estimates of Reiners and Nelson [1998] and Huang *et al.* [2005] for the subset of elements evaluated by those authors. We

Figure 8. (a and b) Nb versus Th and (c and d) Nb₁₄ versus Th₁₄, with format following Figure 6. Nb correlates positively with Th for most rejuvenated-stage lavas. The presence of garnet does not significantly change the bulk distribution coefficient of Nb; therefore melting curves of garnet (3%) and garnet (6%) lherzolite mineralogies are indistinguishable. The mantle source of the high-Th Honolulu Volcanics (lowest extent partial melts) most likely contains an additional accessory phase capable of retaining Nb. Kiekie Basalts contain Nb and Th concentrations lower than other rejuvenated-stage basalts, consistent with larger extents of melting of a more depleted source. Because carbonatites contain low concentrations of high-field strength elements, addition up to 0.2% carbonatite to the Model 1 mantle source has negligible effect on model melt compositions (Figures 8c and 8d) for the HFSE.

recognize that the Hawaiian mantle is lithologically and geochemically heterogeneous, but our estimated composition represents an average value that generates the overall compositional trends in Hawaiian shield tholeiites. We also recognize that batch melting is an overly simplistic mechanism, but believe that it is a valid approximation for aggregated fractional melting and is useful for determining bulk F and general trends (see discussion in the work of *Plank and Langmuir* [1992]).

[30] We generated a range of metasomatized mantle compositions by adding small amounts of incipient melts to the depleted MORB source (Tables 7a, 7b, and 7c). Though a larger compositional space was examined, we show only the results for the two most successful mantle compositions: Model 1 has 99.2% depleted mantle + 0.8% melt (0.5% melt of Hawaiian plume). Model 2 has 98% depleted mantle + 2% melt (0.5% melt of Hawaiian plume). These calculations are meant to illustrate a family of plausible models. As with any such model, there are uncertainties in bulk distribution coefficients, end-member mantle compositions, and extent of melting for both lavas and

incipient melts, leading to uncertainties in the final calculated product. Nevertheless, it is possible to construct a detailed model that is internally consistent, as well as consistent with a large body of published data, including experimental data on distribution coefficients and melting relations.

[31] Representative rejuvenated-stage lavas are best modeled by 0.8% to 9% batch melting of Model 2 mantle composition. Figures 6–12 and Figures 14–15 show the results of 1–20% batch melting of this metasomatized mantle composition (solid blue curves). Batch melting models are shown using a range of mantle mineralogies, which highlight the effects of variable garnet in the source (3% and 6%) and the presence of residual phlogopite and/or oxides such as ilmenite or titanite. See caption to Tables 7a, 7b, and 7c for details. Consistent with previous studies, the range in compositions of the representative rejuvenated-stage lavas can be modeled by variable degrees of partial melting of garnet-bearing lherzolite leaving residual apatite, phlogopite, and titanite at the smallest degrees of melting that produce nephelinites and nepheline melilitites [e.g., *Clague and*

Figure 9. (a and b) Hf versus Th and (c and d) Hf_{14} versus Th_{14} , with format following Figure 6. Because Hf is more compatible than Th, addition of incipient melt of Hawaii plume shifts mantle source composition to lower Hf/Th values. Representative rejuvenated-stage lavas are bounded by melts of Model 2 mantle of garnet lherzolite with 3% to 6% residual garnet. Low Hf concentrations in Kiekie Basalts require greater extents of melting (4 to 13%) of a more depleted source (Model 1). Addition of carbonatite results in negligible change in the Model 1 melting models for the HFSE.

Figure 10. (a and b) La versus Th and (c and d) La_{14} versus Th_{14} , with format following Figure 6. La correlates positively with Th for most rejuvenated-volcanics with a La/Th slightly lower than shield lavas. Kiekie Basalts, South Arch, and T273 Honolulu Volcanics lavas (Figure 10b) have higher La than expected for their low Th concentrations, consistent with addition of up to 0.2% carbonatite to Model 1 mantle source.

Figure 11. (a and b) Lu versus Th and (c and d) Lu_{14} versus Th_{14} , with format following Figure 6. Presence of residual garnet in the source greatly reduces Lu concentration in melts. Representative rejuvenated-stage lavas are consistent with melting of Model 2 mantle with up to $\sim 6\%$ garnet in the source. Most Kiekie Basalts require greater extents melting (7% to 13%) of a more depleted source (Model 1). A few Kiekie Basalts ($0.7 < Th_{14} < 1.5$), South Arch and T273 Honolulu Volcanics have Lu concentrations lower than melts of Model 1 mantle having garnet (3%) lherzolite mineralogy. These lavas are consistent with lower extents of melting (4 to 7%) of Model 1 mantle with up to 5% garnet. Addition of carbonatite does not significantly modify melting curves for HREE.

Frey, 1982; Yang *et al.*, 2003; Clague *et al.*, 2006]. Concentrations of all incompatible elements (including Ba, Sr, LREE, HFSE, and volatiles) in representative rejuvenated-stage lavas are consistent with the silicate melt metasomatism model.

[32] In general, radiogenic isotopic compositions are also consistent with the silicate melt metasomatism model.

Radiogenic isotopic compositions of Hawaiian shield lavas are heterogeneous and are typically modeled as mixtures of two main components: (1) a “KEA” source end-member with high $^{206}Pb/^{204}Pb$ and intermediate $^{87}Sr/^{86}Sr$ most clearly represented by some historic tholeiites from Kilauea [Stille *et al.*, 1986] and (2) a “KOO”

Figure 12. Nb/La versus Ba/Th showing (a) raw data and (b) superimposed model curves as described in Figure 6. Olivine-addition does not modify trace element ratios. Representative rejuvenated-stage lavas have significantly higher Nb/La and slightly higher Ba/Th consistent with melt metasomatism model. The fact that the representative rejuvenated-stage lavas have Ba/Th similar to shield lavas supports a Hawaiian plume origin for the incipient melt. High-Ba lavas (Kiekie Basalts, South Arch, T273 Honolulu Volcanics) form a trend orthogonal to that produced by variations in partial melting of mantle metasomatized incipient silicate melts. Negative correlation between Nb/La and Ba/Th can be produced by addition of small amounts (up to 0.2%) of carbonatite to Model 1 mantle.

Table 5. FTIR Analyses of Submarine Kiekie Basalt Glasses

Sample	H ₂ O (wt%)	sd	CO ₂ (ppm)	sd	Depth Collect (m)	Depth Equilibrium (m)	(X _{H₂O}) ^{vapor}
T317-R01	0.509	0.027	115	6	1691	1850	0.150
T317-R02	0.459	0.015	104	6	1692	1650	0.138
T317-R03	0.551	0.015	102	13	1692	1710	0.187
T317-R08	0.514	0.010	119	11	1700	1910	0.148
T317-R10	0.567	0.019	127	6	1657	1490	0.246
T317-R13	0.440	0.021	106	10	1691	1670	0.126
T317-R14	0.341	0.006	83	8	1662	1010	0.135
T317-R16	0.439	0.012	185	9	1659	2750	0.077
T317-R18	0.604	0.032	137	7	1673	1450	0.273
T318-R01	0.363	0.015	75	5	1046	880	0.176
T318-R02	0.382	0.013	73	5	1046	880	0.193
T318-R03	0.373	0.012	61	5	1037	780	0.207
T318-R04	0.392	0.009	83	5	1038	990	0.181
T318-R06	0.401	0.011	69	5	1040	880	0.211
T318-R08	0.382	0.022	106	6	1055	1210	0.142
T318-R09	0.382	0.007	76	10	1054	910	0.187
T318-R10	0.392	0.004	66	8	1054	820	0.218
T318-R11	0.392	0.009	72	7	1037	880	0.203
T318-R12	0.354	0.006	116	6	1015	1260	0.119
T318-R13	0.354	0.026	89	16	991	1040	0.142
T318-R14	0.325	0.008	113	9	973	1270	0.099
T318-R15	0.334	0.013	135	8	1034	1480	0.090
T318-R16	0.334	0.008	125	10	1050	1390	0.096
T318-R17	0.344	0.009	96	4	1103	1130	0.123
T322-R1	0.440	0.015	117	8	1391	1370	0.162
T322-R4	0.344	0.025	127	13	1384	1630	0.084
T322-R5	0.420	0.006	140	9	1385	1850	0.107
T322-R30	0.325	0.011	103	12	949	1390	0.087
T322-R31	0.325	0.004	86	4	947	1180	0.102
T322-R32	0.315	0.034	61	7	943	870	0.131
T322-R33	0.334	0.028	79	8	941	1100	0.115
T323-R1	1.24	0.09	148	5	3826	3400	0.490
T323-R2	1.33	0.07	140	5	3797	3600	0.531
T323-R3	1.32	0.06	143	8	3787	3580	0.527
T323-R4	1.13	0.04	150	6	3759	3220	0.422
T323-R5	1.16	0.06	143	2	3744	3140	0.459
T323-R7	1.31	0.05	164	7	3729	3860	0.481
T323-R8	1.05	0.06	201	6	3713	3310	0.364
T323-R9	1.22	0.03	173	6	3700	3670	0.438
T323-R10	0.76	0.04	264	16	3699	3550	0.170
T323-R11	0.87	0.02	294	8	3702	3870	0.211
T323-R12	1.25	0.03	195	10	3664	4000	0.425
T323-R15	1.12	0.06	188	12	3591	3370	0.407
T323-R16	1.20	0.03	142	2	3570	3190	0.487
T323-R17	1.09	0.02	146	3	3560	3110	0.402
T323-R18	1.08	0.06	170	3	3550	3580	0.341
T323-R19	1.15	0.01	141	4	3548	3310	0.419
T323-R20	1.30	0.29	174	6	3547	4220	0.426
T323-R21	1.31	0.04	179	3	3542	4320	0.424

source end-member with low ²⁰⁶Pb/²⁰⁴Pb and high ⁸⁷Sr/⁸⁶Sr most clearly represented by alkali-poor high-Zr/Nb basalts and basaltic andesites of Koolau Volcano, Oahu [Frey *et al.*, 1994; Roden *et al.*, 1994]. The Loihi source (LOI) is intermediate between KEA and KOO. Posterosional and rejuvenated-stage basalts require involvement of a depleted component [Tatsumoto, 1978; Stille *et*

al., 1986; Bizimis *et al.*, 2005; Frey *et al.*, 2005; Fekiacova *et al.*, 2007]. Figure 15 shows three separate curves for mixing between depleted mantle and metasomatic melts having various Hawaiian end-member isotopic compositions (KOO, KEA, and LOI). Isotopic compositions of most representative rejuvenated-stage lavas are consistent with our Models 1 and 2 mixing proportions.

Figure 13. Depth of vapor saturation plotted against depth of collection for submarine rejuvenated-stage glasses. Depths of vapor saturation calculated according to Dixon [1997]. Any sample lying on the 1:1 line would have vapor in equilibrium with the melt at the depth of collection (eruption). Dashed lines represent $\pm 25\%$ uncertainty. Most samples are within uncertainty of the 1:1 line, indicating that samples were erupted in the submarine environment close to their depth of collection.

5.2. Modeling Kiekie Compositions

[33] Partial melting of Model 2 mantle, however, cannot produce Kiekie compositions using reasonable extents of partial melting (Figures 6d, 7d, 8d, 9d, 10d, 11d, and 12d). Model 2 mantle would

have to melt 15% to 25% to reproduce the observed low Th and incompatible element concentrations in most Kiekie lavas, which is unlikely for these alkalic compositions. Similarly, melting of depleted mantle would require $\sim 1\%$ melting to generate the Th content of Kiekie lavas. This extent of melting is too low to produce such mildly alkalic lavas. A mantle composition more depleted (with less incipient melt added) than Model 2 is required. Melting of Model 1 (99.2% depleted mantle + 0.8% incipient melt) mantle provides an acceptable fit. The need for a lower proportion of incipient melt in the Kiekie source relative to that for the representative rejuvenated-stage lavas is well illustrated using the HREE (Figures 11c and 11d). Lu concentrations of the representative rejuvenated-stage lavas are bounded by melting of Model 2 (2% incipient melt) mantle with 3% to 6% garnet. Lu concentrations in most Kiekie lavas cannot be generated by melting of the Model 2 mantle regardless of the amount of garnet in the source. Nor can melting of depleted mantle reproduce the HREE concentrations. Model 1 mantle (0.8% incipient melt added) produces melts with appropriate HREE concentrations intermediate between melts of depleted and Model 2 mantle compositions. Mildly alkalic Kiekie Basalts are consistent with 7% to 13% batch melting of Model 1 mantle with about 3% residual garnet. Moderately alkalic South

Table 6. Kiekie Basalt Radiogenic Isotopic Data

Sample	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{87}\text{Sr}/^{86}\text{Sr}$	2s	$^{143}\text{Nd}/^{144}\text{Nd}$	2s
<i>Submarine</i>							
T317-R14	37.909	15.516	18.158	0.703449	10	0.513063	7
T317-R18	37.773	15.454	18.102	0.703474	18	0.513042	10
T318-R11	37.676	15.440	18.053	0.703444	13	0.513057	6
T318-R17	37.663	15.444	18.046	0.703501	13	0.513054	6
T322-R1	37.798	15.461	18.094	0.703458	15	0.513056	15
T322-R32	37.857	15.514	18.148	0.703523	20	0.513059	4
T323-R9	37.919	15.472	18.145	0.703466	18	0.513069	18
T323-R21	37.771	15.454	18.131	0.703464	17	0.513034	9
<i>Subaerial</i>							
OX-130	37.743	15.457	18.079	0.703340	13	0.513087	16
69Nii-3	37.727	15.443	18.109	0.703357	16	0.513067	9
69Nii-5	37.757	15.446	18.122	0.703299	35	0.512982	15
69Nii-9	37.673	15.441	18.078	0.703400	11	0.512957	12
70Nii-4	37.677	15.428	18.087	0.703354	20	0.513034	10
70Nii-8	37.731	15.432	18.102	0.703348	21	0.513054	22
70Nii-10	37.783	15.457	18.134	0.703338	33	0.513026	18
70Nii-11	37.755	15.445	18.122	0.703313	47	0.513065	16
70Nii-18	37.709	15.439	18.110	0.703382	7	0.513006	18
70Nii-21	37.736	15.442	18.142	0.703358	2	0.512957	22
70Nii-28	37.644	15.443	18.040	0.703373	6	0.513062	15
75Nii-13	37.634	15.453	18.109	0.703343	12	0.513046	11

Figure 14. (a and b) H₂O versus Th and (c and d) H₂O₁₄ versus Th₁₄, with format following Figure 6. Representative rejuvenated-stage lavas are consistent with partial melting of Model 2 mantle with 540 ppm H₂O. Submarine Kiekie Basalts (red filled circles) correlate positively with Th consistent with other undegassed representative rejuvenated-stage lavas. Kiekie T323 (red filled squares) and South Arch lavas form a vertical array with increasing water at relatively constant Th. No single model can explain both trends. Partial melting of Model 1 mantle with 255 ppm H₂O and up to 0.2% carbonatite with ~10 wt% H₂O can explain the H₂O concentrations of low-H₂O Kiekie Basalts. High H₂O concentrations in Kiekie T323 and South Arch samples require an additional hydrous component associated with carbonatite and/or assimilation of seawater-derived component.

Arch, three high-Ba lavas from the Honolulu Volcanics, and a few Kiekie Basalts (T322R1-B, T317R10-B, T317R18-B, and some subaerial lavas) plot below the Model 1 with 3% garnet curves. These lavas may be generated by 4 to 7% melting of garnet lherzolite with roughly 4% to 5% garnet in the source. Concentrations of high field strength elements (Nb and Hf, Figures 8 and 9, respectively) in Kiekie Basalts are also consistent with melt metasomatism models using the more depleted Model 1 mantle.

[34] Though the more depleted source successfully predicts HREE and HFSE element concentrations using reasonable extents of melting for the Kiekie lavas, it considerably underestimates concentrations of large ion lithophile elements (Ba, Sr, LREE) and volatiles (H₂O and Cl). This is most

dramatically illustrated on the plot of Nb/La versus Ba/Th (Figure 12). Both addition of a metasomatic melt and progressively lower extents of melting cause the melt compositions of rejuvenated-stage lavas to plot above and slightly to the right of the Hawaiian shield lavas. Kiekie Basalts form a trend orthogonal to that produced by magmatic processes. An additional component is therefore required to explain that trend.

[35] With respect to radiogenic isotopes (Figure 15), there are subtle, but nonunique, differences between the high-Ba and representative rejuvenated-stage lavas. The South Arch lavas have higher ²⁰⁶Pb/²⁰⁴Pb than representative rejuvenated-stage lavas consistent with a larger contribution from the KEA component within the plume, whereas Kiekie Basalts are shifted to higher ⁸⁷Sr/⁸⁶Sr and lower

Figure 15. (a and b) Cl versus Th and (c and d) Cl₁₄ versus Th₁₄, with format following Figure 6. Representative rejuvenated-stage lavas are consistent with partial melting of Model 2 mantle with 30 ppm Cl. As in Figure 14, Kiekie and South Arch lavas form two distinct trends. Kiekie (red filled circles) correlate positively with Th consistent with various degrees of melting of Model 1 mantle with 13 ppm Cl and addition of up to 0.2% carbonatite with 6000 ppm Cl. Kiekie T323 and South Arch lavas have higher concentrations of Cl, with the Kiekie T323 lavas forming a vertical trend similar to H₂O concentrations. Addition of 0.2% carbonatite with 6000 ppm Cl is insufficient to explain high Cl in these samples.

²⁰⁶Pb/²⁰⁴Pb consistent with a larger contribution from the KOO component.

5.3. Modeling of Carbonatite Metasomatism

[36] We propose that carbonatite melt is the likely source for the trace element characteristics of the Ba- and Sr-enriched Kiekie Basalts. While it has long been recognized that carbonatite metasomatism is a globally important process (see section 6.2 below), solid evidence for a carbonatite component in Hawaiian magmas has been lacking. Carbonatites are characterized by enrichments in Ba, Sr, and LREE, as well as depletions in high field strength elements. Carbonatite compositions are also notoriously heterogeneous. For our modeling, we use a carbonatite trace element composition based on the average composition of oceanic carbonatites from Cape Verde and the Canary Islands [Hoernle *et al.*, 2002]. In contrast to average continental carbonatites [Woolley and Kempe, 1989], oceanic carbonatites are not enriched in Pb, consistent with the negative Pb anomaly observed in the Kiekie lavas. The average oceanic carbonatite composition used here (Tables 7a, 7b, and 7c) was modified slightly to

provide an internally consistent result for all elements.

[37] Figures 6–12 show trends in lithophile trace elements produced by variable extents of melting of Model 1 mantle to which 0.1% and 0.2% carbonatite have been added (orange dashed lines). We assume closed-system metasomatism modeled by simple binary mixing but acknowledge that metasomatic fluids likely interact with mantle materials in a more complicated way. Concentrations of Ba, Sr, La, Nb, Hf, and Lu in Kiekie, South Arch, and the three high-Ba Honolulu Volcanics lavas are consistent with addition of up to 0.2% carbonatite (Figures 6c–6d, 7c–7d, 8c–8d, 9c–9d, 10c–10d, 11c–11d, and 12c–12d). Kiekie T323 lavas can be generated by 10% to 13% batch melting of Model 1 mantle with slightly less than 0.2% carbonatite added. The positive correlation between Ba and Th in Kiekie T323 lavas is consistent with trends produced by variations in partial melting. Most high-Ba lavas can be generated by 4 to 13% batch melting of Model 1 mantle with up to 0.1% carbonatite added. Because carbonatites are characterized by low concentrations of high field strength elements (Nb and Ta), addition of carbonatite does not modify the con-

Figure 16. Radiogenic isotopic compositions of shield and rejuvenated-stage lavas. End-member compositions from Dixon and Clague [2001, and references therein]. Shield lavas are dominated by mixtures of KEA and KOO components. All rejuvenated-stage lavas are shifted toward lower $^{87}\text{Sr}/^{86}\text{Sr}$ consistent with involvement of a depleted component. Melts that metasomatize depleted mantle surrounding the Hawaiian plume must have radiogenic isotopic heterogeneity similar to that of the shield lavas. Radiogenic isotopic compositions of rejuvenated-stage lavas are consistent with addition of 0.8% (Model 1) to 2% (Model 2) of incipient melt (0.5% melting) of the Hawaiian plume to average depleted mantle. The source of the South Arch lavas was metasomatized by melts with KEA-like isotopic signatures. The source of most representative rejuvenated-stage lavas was metasomatized by melts with intermediate LOI-type compositions. The source of high-Ba Kiekie lavas was metasomatized by melts with KOO-like affinity. A stronger KOO-like isotopic signature suggests involvement of carbonatite melt from recycled crustal components within the plume.

centrations of those elements. Addition of carbonatite provides a mechanism to produce enrichments in Ba and La, without enrichments in Nb, thus producing the distinct negative trend on the Nb/La versus Ba/Th plot (Figure 12).

[38] The volatiles require a more complicated scenario. The first complication is that initial volatile contents of carbonatites are highly uncertain. The freshest carbonatite ever sampled is a natrocarbonatite from Oldoinyo Lengai (BD 118 from Dawson *et al.* [1987] and Dawson [1989]), collected shortly after eruption in 1960. This sample underwent minimal modification due to alteration and contains 5.41 wt% H_2O . However, high vesicularity indicates that eruptive volatile loss occurred, making this value a minimum estimate. Experiments

show that carbonatitic melt is capable of dissolving significant quantities of water [Keppler, 2003]. At 1 kbar, the water solubility reaches nearly 10 wt%, two or three times that in most silicate melts. For our models, we arbitrarily assume a water content of 10 wt%. This is only a rough estimate, but serves as a starting point for our models. For Cl, natural concentrations are highly variable and we arbitrarily assume a concentration of 6000 ppm.

[39] Addition of carbonatite with 10 wt% H_2O adequately explains the water concentrations in the low- H_2O Kiekie lavas, but cannot explain the higher values in Niihau T323 and South Arch lavas (Figures 14c and 14d). No single carbonatite composition can explain the vertical array of H_2O and Cl data in those lavas. Either the metasomatizing carbonatite is heterogeneous with respect to volatiles or these lavas have interacted with seawater or seawater-derived brine. For South Arch lavas, addition of <0.1% carbonatite is sufficient to explain the Ba, Sr, and LREE concentrations. This carbonatite would have to have an associated hydrous component to produce the observed water enrichment. For Kiekie T323 lavas, addition of 0.2% carbonatite with about 20% to 40% H_2O could explain the water enrichment.

[40] Similar to the case for water, addition of carbonatite with a constant Cl content cannot explain all the data. Using 6000 ppm Cl adequately explains much of the data, but not the high-Cl Kiekie T323 and South Arch lavas (Figures 15c and 15d). Two possible mechanisms can explain highly variable water and Cl concentrations in the Hawaiian rejuvenated-stage lavas. Either (1) the metasomatic component is heterogeneous with respect to volatiles or (2) the high-Ba lavas also assimilated seawater or a seawater-derived brine during storage in the crust or eruption. The first mechanism implies a common origin (carbonatite magma with heterogeneous volatile contents), whereas the second mechanism requires a coincidental occurrence of two separate events (assimilation of brine limited to those samples metasomatized by carbonatite).

[41] Study of microinclusions in cloudy (inclusion-rich) diamonds provides insight into mantle fluid compositions [e.g., Navon *et al.*, 1988; Schrauder and Navon, 1994; Izraeli *et al.*, 2001; Klein-BenDavid *et al.*, 2004, 2007]. Bulk compositions of microinclusions are highly variable with three endmember compositions: (1) hydrous-silicic melt rich in water, Si, Al, and K; (2) carbonatitic melt rich in carbonate, Mg, Ca, Fe, K, and Na; and (3)

Table 7a. Mineral and Bulk Distribution Coefficients^a

	Olivine	Opx	Low-Ca Cpx	Garnet	Sulfide	Adj.	Hawaiian Mantle 1% gt	Hawaiian Mantle 3% gt
Rb	0.0003	0.0002	0.0004	0.0002	-		0.00032	0.00032
Ba	0.000005	0.000006	0.0004	0.00007	-	y-g	0.00014	0.00014
CO ₂						*	0.0002	0.0002
Th	0.00005	0.002	0.0057	0.009	-		0.0022	0.0024
Cl						*	0.004	0.0042
Nb	0.0005	0.004	0.010	0.015	-		0.0042	0.0045
Ta	0.0005	0.004	0.010	0.015	-		0.0042	0.0045
La	0.0005	0.004	0.015	0.007	-	y	0.0085	0.0085
H ₂ O	0.0005	0.004	0.02		-	y	0.0097	0.0097
Ce	0.0005	0.004	0.038	0.017	-	y	0.014	0.014
Pb	0.003	0.009	0.009	0.005	150		0.014	0.014
Sr	0.00004	0.0007	0.091	0.0007	-		0.031	0.031
Nd	0.00042	0.012	0.088	0.064	-		0.032	0.033
Sm	0.0011	0.02	0.151	0.23	-	y	0.047	0.052
Zr*					-	*	0.028	0.032
Hf	0.0022	0.03	0.14	0.40	-	y	0.041	0.048
Eu*					-	*	0.045	0.055
Gd	0.004	0.03	0.16	1.2	-	y	0.0614	0.085
Tb*					-	*	0.068	0.085
Dy	0.008	0.035	0.17	2.0	-		0.085	0.125
Y*					-	*	0.10	0.130
Ho*					-	*	0.102	0.140
Er	0.013	0.045	0.18	3.0	-		0.102	0.162
Tm*					-	*	0.115	0.175
Yb	0.03	0.08	0.25	4.0	-		0.148	0.228
Lu	0.02	0.12	0.2759	5.0	-		0.165	0.264

^a Bulk distribution coefficients for various mineral assemblages were calculated using the above mineral distribution coefficients from *Salters et al.* [2002], *Hart and Gaetani* [2006] for Pb, and *Aubaud et al.* [2004] for H₂O. Asterisks indicate interpolated bulk distribution coefficients. Mineral proportions for Hawaiian mantle based on melt reactions of *Salters et al.* [2002]. Hawaii Mantle 1% gt = garnet lherzolite composed of 57% olivine, 8% orthopyroxene, 34% low-Ca clinopyroxene, and 1% garnet. Hawaii Mantle 3% gt = garnet lherzolite composed of 55% olivine, 8% orthopyroxene, 34% low-Ca clinopyroxene, and 3% garnet. Pb distribution coefficients assume 0.015% sulfide in the source. Elements with a “y” have had their bulk distribution coefficients adjusted (Adj.) to provide a self-consistent model for generation of Hawaiian tholeiitic lavas.

saline fluids rich in Cl, K, and Na. All compositions are enriched in K and many other incompatible elements and are characterized by steep REE patterns similar to those in kimberlites and lamproites [*Schrauder et al.*, 1996; *Raga et al.*, 2003]. Water is always present in carbonatitic high-density fluids in diamonds [*Klein-BenDavid et al.*, 2007], with carbonate/(carbonate + water) molar ratios ranging from 0.5 to 0.7. Our estimated carbonatite composition (40 wt% CO₂ and 10 wt% H₂O) has a carbonate/(carbonate + water) molar ratio of 0.6, similar to carbonatitic fluids in diamonds. Chlorine in these carbonatitic inclusions ranges from 2 to 5 wt%. The saline fluid end-member is also water- and chlorine-rich, containing up to 20 wt% and 49 mol%, respectively [*Izraeli et al.*, 2001; *Klein-BenDavid et al.*, 2007].

[42] *Wyllie* [1989] showed that exsolution of a H₂O-CO₂ vapor phase with high concentrations of alkalis and other solutes is a normal consequence of crystallization of carbonated silicate

magmas or carbonatite magmas within the crust. These vapors or fluids are responsible for the common alteration around carbonatitic intrusions, called fenitization. More recent work [e.g., *Perchuk et al.*, 2002; *Klein-BenDavid et al.*, 2007] models the range of fluid compositions found in diamonds as the result of precipitation of alkali and divalent carbonates from the parental carbonatitic-fluid. The residual fluid composition is driven into an immiscibility gap and results in separation into saline and silicic high density fluids. These heterogeneous fluids continue to evolve separately as they migrate through, interact with, and fractionate within the mantle, potentially leading to a diverse range of mantle source volatile compositions. Thus, heterogeneous volatile contents in Kiekie Basalts affected by carbonatite metasomatism could easily result from heterogeneous fluids associated with carbonatite melts.

[43] Addition of a seawater-derived brine can also enrich lavas in H₂O and Cl without modifying

Table 7b. Bulk Distribution Coefficients for Refractory Mantle Composition^a

	Refractory Mantle 3% gt	RSV mantle 3% gt	RSV mantle 6% gt	RSV mantle 3% gt + phlog + ox
Rb	0.0003	0.003	0.003	0.062
Ba	0.00005	0.00006	0.00006	0.011
CO ₂		0.0002	0.0002	0.0002
Th	0.0011	0.0012	0.00145	0.00144
Cl		0.0028	0.0028	0.0028
Nb	0.0022	0.0028	0.0028	0.023
Ta	0.0022	0.0028	0.0028	0.033
La	0.0023	0.005	0.005	0.006
H ₂ O	0.0051	0.0057	0.0058	
Ce	0.0053	0.0061	0.0066	
Pb		0.028	0.028	
Sr	0.010	0.007	0.009	0.012
Nd	0.013	0.012	0.0165	
Sm	0.026	0.023	0.036	
Zr*		0.05	0.060	
Hf	0.031	0.04	0.052	0.08
Eu*		0.033	0.045	0.055
Gd	0.059	0.042	0.060	
Tb*		0.05	0.068	
Dy	0.087	0.07	0.085	
Y*		0.11	0.13	
Ho*		0.12	0.15	
Er	0.12	0.12	0.20	
Tm*		0.15	0.270	
Yb	0.18	0.18	0.300	
Lu	0.20	0.21	0.359	

^aRefractory mantle modal proportions: 80% olivine, 6% orthopyroxene, 11% low-Ca clinopyroxene, and 3% garnet. Bulk distribution coefficients for the RSV mantle were estimated to fit rejuvenated-stage lava trace element data and are similar to those for a refractory (pyroxene-poor) modal mineralogy. Bulk distribution coefficients for RSV mantle with accessory phlogopite and an oxide phase such as titanite were estimated to fit the basanitic and nephelinitic rejuvenated-stage lava compositions. Proportions of residual accessory phases were not estimated.

lithophile element concentrations. Assimilation of a seawater-derived brine usually occurs in systems with long-lived hydrothermal systems, as is found at fast spreading centers and Loihi Seamount [Michael and Schilling, 1989; Jambon *et al.*, 1995; Michael and Cornell, 1998; Kent *et al.*, 1999; Dixon and Clague, 2001]. Assimilation of a pure seawater contamination, possibly through interaction with serpentine, at slow-spreading centers or at small oceanic islands typically affects water, but not Cl [Simons *et al.*, 2002]. We do not find evidence for sustained hydrothermal systems associated with the submarine Kiekie vents. However, the submarine Kiekie Basalts erupted in flat-topped submarine cones [Clague and Reynolds, 2000], which may have provided more opportunity

for foundering of the lava lake crust and interaction of magma with altered materials. Though we cannot rule out contamination by seawater as the source of the high water and Cl concentrations in Kiekie T323 and South Arch lavas, we prefer a model in which carbonatite melt differentiates during flow through the mantle to produce heterogeneous fluid compositions as postulated for the origin of heterogeneous high-density fluids in diamonds [e.g., Perchuk *et al.*, 2002; Klein-BenDavid *et al.*, 2007].

5.4. Composition of Metasomatic Carbonatite Derived From Hawaiian Plume

[44] The primitive mantle-normalized trace element composition of the carbonatite required to produce the trace element composition of the high-Ba lavas is plotted on Figure 16a. In general, the composition of the carbonatite required by our modeling matches the overall primitive mantle normalized pattern of oceanic carbonatite with enrichments in Ba, Sr, LREE, and volatiles and relatively low concentrations of Nb, Ta, Pb, Zr, Hf, and HREE. All trace element concentrations lie within the minimum and maximum concentrations found in oceanic carbonatites from Cape Verde and Canary Islands [Hoernle *et al.*, 2002]. In order for addition of up to 0.2% carbonatite to explain the compositional variation in all high-Ba lavas, the model carbonatite must have higher Sr and Ba concentrations but lower Th, U, LREE, Zr, and Hf than the average oceanic carbonatite composition. Note that the enrichments of H₂O and Cl (10 wt% and 6000 ppm, respectively) relative to primitive mantle are similar to those observed for LREE.

5.5. Forward Model of Rejuvenated-Stage Magma Compositions

[45] Primitive mantle normalized trace element compositions of lavas predicted by the melt metasomatism and melt plus carbonatite metasomatism models are shown on Figure 17. Representative rejuvenated-stage lava Kauai-Oahu 4D can be generated by 7% melting of a Model 2 mantle (98% depleted mantle + 2% incipient melt) using garnet lherzolite mineralogy.

[46] Kiekie T323-R10 and -R03 represent the compositions of volatile- and Ba-rich lavas. Melting (10%) of Model 1 mantle (99.2% depleted mantle + 0.8% incipient melt) successfully predicts the Nb, Ta, Zr, Hf, Yb, and Lu concentrations but significantly underestimates the Ba, Sr, LREE, and volatile concentrations. Melting (10%) of Model 1

Table 7c. Mantle End-Member Trace Element Compositions^a

	DMM	HWM	0.5% Melt of HWM	Model 1	Model 2	Carbonatite	Model 1 + 0.1% Carb	Model 1 + 0.2% Carb
Rb	0.020	0.40	75.2	0.62	1.52	0.58	0.62	0.62
Ba	0.227	5	973	8.01	19.7	6000	14.0	20.0
CO ₂	50	500	96200	819	1970	400000	1220	1620
Th	0.004	0.04	5.43	0.047	0.112	3.35	0.051	0.054
Cl	1.3	13	1420	12.6	29.6	6000	18.6	24.6
Nb	0.0864	0.77	81.7	0.74	1.72	35	0.77	0.81
Ta	0.0056	0.05	5.31	0.048	0.11	0.050	0.048	0.048
La	0.134	0.79	58.7	0.60	1.31	250	0.85	1.10
H ₂ O	65	350	23800	255	540	100000	355	455
Ce	0.421	2.00	106	1.26	2.52	390	1.65	2.04
Pb	0.014	0.085	2.58	0.035	0.065	9.93	0.044	0.054
Sr	6.09	27	752	12.1	21.0	13000	25.1	38.0
Nd	0.483	1.7	44.7	0.84	1.37	270	1.11	1.38
Sm	0.21	0.57	10.0	0.29	0.41	50	0.34	0.39
Zr	3.5	12.5	339	6.19	10.2	3.41	6.18	6.18
Hf	0.127	0.37	7.03	0.18	0.27	0.05	0.18	0.18
Eu	0.086	0.19	3.18	0.11	0.15	6.43	0.12	0.12
Gd	0.324	0.69	7.72	0.38	0.47	23.0	0.41	0.43
Tb	0.064	0.11	1.23	0.073	0.087	2.6	0.076	0.078
Dy	0.471	0.75	5.80	0.51	0.58	14.6	0.53	0.54
Y	3.13	4.4	32.8	3.37	3.72	87.7	3.45	3.53
Ho	0.108	0.152	1.05	0.12	0.13	3.6	0.12	0.12
Er	0.329	0.43	2.59	0.35	0.37	9.2	0.36	0.37
Tm	0.045	0.059	0.33	0.047	0.051	0.90	0.048	0.049
Yb	0.348	0.44	1.90	0.36	0.38	4.0	0.36	0.37
Lu	0.056	0.070	0.26	0.058	0.060	0.50	0.058	0.059

^a All values in ppm by weight. Abbreviations: DMM is depleted MORB mantle from *Workman and Hart* [2005]. HWM is average Hawaiian plume mantle calculated in this study to fit Hawaiian shield lavas by 4–15% batch melting using bulk distribution coefficients for garnet lherzolite with 1 to 3% garnet. Incipient (0.5%) melt of Hawaiian plume mantle calculated using garnet (3%) lherzolite distribution coefficients. Model 1 is 99.2% depleted mantle +0.8% of 0.5% partial melt of Hawaiian plume. Model 2 is 98% depleted mantle +2% of 0.5% partial melt of Hawaiian plume. Carbonatite composition calculated to give compositions of high-Ba lavas by addition of 0.2% carbonatite to model 1 mantle. Resulting carbonatite composition is similar to average oceanic carbonatite [*Hoernle et al.*, 2002].

mantle to which 0.2% carbonatite has been added successfully predicts all trace element concentrations with the exception of H₂O and Cl. LREE concentrations in Kiekie T323-R10 suggest a larger carbonatite contribution than in Kiekie T323-R03; however, both H₂O and Cl in R10 are lower than in R03, implying decoupling of volatiles from other trace elements as discussed above.

6. Discussion

6.1. Source of Carbonate in Hawaiian Plume

[47] Recycling of crustal materials into the deep mantle by subduction is an important source of heterogeneity in the Earth's mantle. Recent studies have shown that water is efficiently dehydrated from the downgoing slab during subduction [*Dixon and Clague*, 2001; *Dixon et al.*, 2002; *Rüpke et al.*, 2006]. Carbonate, however, is widely thought to

mostly survive subduction-related dehydration and silicate melting [*Yaxley and Green*, 1994; *Molina and Poli*, 2000; *Kerrick and Connolly*, 2001; *Dasgupta et al.*, 2004; *Brenker et al.*, 2007]. Recent studies have shown that transport of CO₂ into the deep mantle through subduction and crustal recycling is likely [e.g., *Molina and Poli*, 2000; *Kerrick and Connolly*, 2001; *Dasgupta et al.*, 2004]. *Molina and Poli* [2000] present experimental results that show that amphibole coexists with calcite at ≤ 1.4 Gpa, with dolomite at $1.4 \leq P \leq 1.8$ Gpa, and with dolomite+magnesite at pressures higher than 1.8 Gpa. Significant decarbonation of subducted crust is feasible only at low pressures (in the forearc region) and at relatively high temperatures (e.g., young oceanic crust subducted at slow convergence rates) [*Molina and Poli*, 2000]. Once stable subduction conditions have been reached, CO₂ is fractionated into the solid phase and deep recycling of CO₂ is expected. *Kerrick and Connolly* [2001] present a subduction zone devolatilization

Figure 17. (a) Primitive mantle normalized trace element composition of oceanic carbonatites from Cape Verde and Canary Islands [Hoernle et al., 2002] and Hawaiian carbonatite composition. The Hawaiian carbonatite composition required to produce compositional variations observed in Kiekie lavas is similar to that of oceanic carbonatites. (b) Representative rejuvenated-stage lavas (e.g. Kauai-Oahu Channel 4D) can be generated by partial melting (7%) of Model 2 mantle using garnet (4.5%) lherzolite mineralogy. (c) Kiekie lavas cannot be generated by partial melting of silicate melt metasomatized mantle. Ten percent melting of mantle model 1 using garnet (3%) lherzolite mineralogy reproduces Th, HFSE, and HREE concentrations of Kiekie lavas but significantly underestimates Ba, Sr, LREE, H₂O, and Cl concentrations. Ten percent melting of Model 1 mantle, metasomatized by 0.2% carbonatite, predicts the concentrations of all nonvolatile trace elements. H₂O and Cl concentrations in Kiekie lavas require addition of a metasomatic component heterogenous with respect to volatiles.

model for pressures up to 6 Gpa (180 km) based on phase equilibria computed for an average oceanic metabasalt. They show that decarbonation is negligible along cold and intermediate geotherms and limited along high temperature geotherms. Thus, given that the Hawaiian plume is thought to contain recycled crustal components, it is reasonable to expect elevated carbonate contents in those components.

[48] Evidence for a recycled crustal component is strongest in lavas collected from the Koolau shield on Oahu. These lavas define an extreme endmember [e.g., Frey *et al.*, 1994; Roden *et al.*, 1994; Lassiter and Hauri, 1998; Blichert-Toft *et al.*, 1999; Jackson *et al.*, 1999; Huang and Frey, 2003, 2005] characterized by high $^{87}\text{Sr}/^{86}\text{Sr}$, $^{187}\text{Os}/^{188}\text{Os}$ and $\delta^{18}\text{O}$ and by low $^{143}\text{Nd}/^{144}\text{Nd}$, $^{176}\text{Hf}/^{177}\text{Hf}$, and $^{206}\text{Pb}/^{204}\text{Pb}$. In terms of major and trace elements, the Koolau lavas have relatively high SiO_2 content, $\text{SiO}_2/\text{total iron}$, $\text{Al}_2\text{O}_3/\text{CaO}$, La/Nb, Sr/Nb, and low total iron and CaO contents. These geochemical characteristics have been interpreted as evidence for recycled oceanic crust, including sediments, in the source of Koolau lavas. Huang and Frey [2005] argue that the distinctive geochemical characteristics of the Koolau lavas can be explained by mixing between high-temperature melts derived from garnet peridotite with <20% dacitic melt derived from garnet pyroxenite (recycled oceanic crust). Huang and Frey [2005] also suggest that the recycled crustal component contains carbonate, <3% of either ancient recycled phosphate-bearing carbonate or perhaps sediment with an abundant hydrothermal component. Thus, it is likely that the Koolau component within the Hawaiian plume contains the highest carbon concentrations that could be remobilized in the form of carbonatite melts, consistent with the KOO-like radiogenic isotopic compositions of the Kiekie lavas.

6.2. Evidence for Carbonatite Metasomatism in Oceanic Environments

[49] Metasomatism by either silicate and/or carbonatitic melts or H_2O - or CO_2 -rich fluids has been recognized in upper mantle rocks worldwide [e.g., Menzies and Hawkesworth, 1987; Dautria *et al.*, 1992; Ionov *et al.*, 1993; Rudnick *et al.*, 1993; Le Roex and Lanyon, 1998; Yaxley *et al.*, 1998; Yaxley and Brey, 2004; Tappe *et al.*, 2006, 2007]. The importance of CO_2 in the generation of strongly alkaline magmas is supported by both the common field association of alkaline and carbonatitic mag-

mas [e.g., Allgre *et al.*, 1971; Bell, 1998; Hoernle *et al.*, 2002; Schultz *et al.*, 2004; Tappe *et al.*, 2007] and results of experimental studies [e.g., Eggler and Mysen, 1976; Eggler, 1978; Hirose, 1997; Dasgupta *et al.*, 2005, 2006, 2007]. Though more commonly found in continental environments, carbonatite metasomatism in the oceanic mantle has been proposed by various researchers to explain (1) the presence of carbonate and/or microdiamonds in xenoliths [e.g., Kogarko *et al.*, 1995; Frezzotti *et al.*, 2002; Wirth and Rocholl, 2003]; (2) trace element compositions of secondary minerals within peridotite xenoliths [e.g., Hauri *et al.*, 1993; Salters and Zindler, 1995]; (3) the presence of incipient alkali silicate or carbonatitic glasses within peridotitic xenoliths [Hauri *et al.*, 1993; Schiano *et al.*, 1994; Schiano and Clocchiatti, 1994; Sen *et al.*, 1996; Wulff-Pedersen *et al.*, 1996; Neumann and Wulff-Pedersen, 1997; Vannucci *et al.*, 1998; Coltorti *et al.*, 1999; Wulff-Pedersen *et al.*, 1999; Keshav and Sen, 2003]; and (4) trace element trends in some posterosional lavas from Kauai [Maale *et al.*, 1992] and in three phlogopite nephelinites collected on the Hilina bench off of Kilauea [Sisson *et al.*, 2002]. In addition, carbonatite melts have been erupted in the Cape Verde Islands [Silva *et al.*, 1981] and in the Canary Islands [Hoernle *et al.*, 2002]. However, prior to this study, there has been no solid evidence that a carbonatite component has directly influenced eruptive products in Hawaii.

6.3. Experimental Basis for Generation of Carbonatites in Upwelling Mantle Plumes

[50] Our model of silicate melt and carbonatite metasomatism surrounding the Hawaiian plume is consistent with models of melting and metasomatism in upwelling carbonated oceanic mantle [e.g., Wyllie, 1988; Wyllie and Ryabchikov, 2000; Presnall and Gudfinnsson, 2005; Dasgupta *et al.*, 2005, 2006, 2007]. Wyllie [1988] first presented a melting model for the Hawaiian plume, which predicted formation of trace amounts of volatile-charged incipient melt at depths of 350 to 150 km as the plume crosses the solidus for peridotite-C-H-O. He predicted these incipient melts would be swamped by major melting at the center of the plume but might be detectable on the margins of the plume. This and subsequent models provided an important framework for the spatial and temporal variation in Hawaiian magmatism as a function of temperature variation but did not include lithologic heterogeneity, such as the presence of carbonated eclogite, within the plume.

Table 8. Volatile Contents in Modeled Mantle End-Members

	H ₂ O (ppm)	CO ₂ (ppm)
Depleted mantle	65	50
Hawaiian mantle	350	500
Model 1	255	820
Model 1 + 0.1% carbonatite	355	1220
Model 1 + 0.2% carbonatite	455	1620
Model 2	540	1970

[51] Experimental data at 1.5 to 5.5 GPa show that melting of carbonated peridotite and eclogite produces carbonatite melts [Falloo and Green, 1990; Yaxley and Green, 1994; Dalton and Presnall, 1998; Hammouda, 2003; Yaxley and Brey, 2004]. New melting experiments [Dasgupta et al., 2005, 2006, 2007] show that melting of carbonated eclogite and lherzolite at progressively higher temperatures produces carbonatite melt at roughly 300–400°C below their CO₂-free solidus, followed by formation of strongly silica-undersaturated silicate melt at 120 to 150°C below the CO₂-free solidus. Carbonate and silicate melts coexist over a wide range of temperatures during partial melting of carbonated eclogite and lherzolite at 3 GPa. Thus, recycled carbonates or carbonated eclogite/peridotite incorporated in upwelling mantle may produce carbonatite melt at depths of ~410 km in the plume center and at ~300 km along the plume margin [Dasgupta et al., 2004, 2006, 2007]. Small volume, highly mobile carbonatite melts released from carbonated eclogite/peridotite at these depths could be an effective metasomatic agent for surrounding peridotite and would be expected to migrate greater distances from the hot plume core than incipient silicate melts because of their greater mobility [Minarik and Watson, 1995]. Production of carbonatite at these depths favors metasomatism of depleted mantle thermally entrained by the plume, rather than shallow lithosphere, consistent with recent Pb-isotopic studies [Bizimis et al., 2005; Frey et al., 2005; Fekiacova et al., 2007].

[52] Dasgupta et al. [2006] propose that melting of a heterogeneous carbonated mantle involves repeated melting of heterogeneities, metasomatism of surrounding, more refractory peridotite, followed by partial melting of the metasomatized region, with correspondingly large effects on highly incompatible trace elements. This model provides a good explanation for compositional variations observed in Hawaiian rejuvenated-stage lavas. Carbonated

eclogite within the Hawaiian plume is the first to melt during plume ascent. Carbonatitic melt metasomatizes the plume itself and depleted asthenosphere thermally entrained on the margins of the Hawaiian plume. At lower pressures, silica-undersaturated silicate melts are also produced from carbonated eclogite/lherzolite and contribute to the metasomatic signature. At the plume center, the metasomatic component is drowned out by the high-extent melting of the lherzolitic plume material that produces tholeiitic shield lavas. The metasomatic component is best preserved at the margins of the plume, where low extents of melting of the metasomatized depleted mantle surrounding the plume are sampled during flexural uplift.

[53] Similar multistage metasomatic models have been used to explain the occurrence of carbonatites and alkalic magmas other locations, including Aillik Bay, Labrador [Tappe et al., 2006, 2007], the In Teria district in the Sahara Basin [Dautria et al., 1992], the Himalayan collision zone in western Sichuan, SW China [Hou et al., 2006], and northwestern Namibia [Le Roex and Lanyon, 1998], indicating that this is a significant process world-wide.

6.4. Implications for Melt Generation Models

[54] An alternate model proposed for generation of rejuvenated-stage lavas involves progressive depletion of heterogeneous mantle during multistage melting [Bianco et al., 2005]. In their model, “primary” melting to produce shield lavas depletes the mantle in more enriched and fusible pyroxenite and hydrous peridotitic components. This depleted mantle is laterally advected beneath the flexural arch, where it undergoes a second stage of decompression melting. Though we agree with their overall physical model for generating rejuvenated-stage lavas, their geochemical model cannot explain the Kiekie Basalt compositions. First, progressive melting of a heterogeneous mantle cannot produce the observed enrichments in Ba, Sr, LREE, and volatiles relative to Th and HFSE. Second, their model predicts significantly lower extents of partial melting beneath the flexural arch compared to that within the plume center. Though this is true for some rejuvenated-stage lavas, Kiekie Basalts (4–13% melting) are produced by extents of melting comparable that of many shield lavas (4–15%). The easiest way to increase extents of melting at a given temperature is to increase the mantle volatile

content. The volatile contents of our various mantle compositions are shown in Table 8.

[55] The water content in our Hawaiian plume mantle (350 ppm) is within error of the value (450 ± 190 ppm) determined by *Wallace* [1998] based on undegassed Kilauea lavas. Our metasomatized sources have water contents slightly less than to greater than the Hawaiian plume end-member. The water content for Model 2 mantle source (540 ppm) for the representative rejuvenated-stage lavas is identical to the value (525 ± 75 ppm) previously determined for the source of the North Arch volcanics [*Dixon et al.*, 1997]. Our estimated mantle CO₂ concentrations (0.08 to 0.2 wt%) are consistent with the results of *Dasgupta et al.* [2007], who state “the characteristic enrichments in CaO and depletions in SiO₂ of nephelinites and melilitites may be matched by small-degree (1–5%) partial melts of peridotite with 0.1 to 0.25% wt% bulk CO₂.” Thus for a given amount of decompression, our metasomatized mantle compositions will begin melting at lower temperatures and produce more melt than volatile-free depleted mantle compositions predicted by progressive depletion models. In fact, metasomatic enrichment in volatiles may be required to produce melt during lithospheric flexure decompression.

6.5. Plume “Degassing”: Decoupling of Volatile and Lithophile Tracers

[56] Several studies have documented decoupling of noble gas and radiogenic isotopic tracers within and surrounding the Hawaiian plume. First, the highest ³He/⁴He ratios in Hawaiian lavas are observed at Loihi [e.g., *Rison and Craig*, 1983; *Kurz et al.*, 1983, 1987; *Honda et al.*, 1993; *Valbracht et al.*, 1996; *Kaneoka et al.*, 2002], spatially offset from the maximum in radiogenic isotopic tracers defined by the Mauna Kea (KEA) and Koolau (KOO) end-members. Second, lavas from the South Arch, 200 km upstream from the plume center, have elevated ³He/⁴He, in contrast to the MORB-like values found in other rejuvenated-stage lavas [*Dixon and Clague*, 2001; *Hanyu et al.*, 2005]. *Valbracht et al.* [1996] first proposed that plume “degassing” was responsible for the decoupling of noble gas and radiogenic isotopic tracers within the Hawaiian plume. They proposed that incipient CO₂-dominated melts form at relatively shallow depths near the base of the lithosphere, possibly when the plume begins to flex by drag of the overriding lithosphere. They argued that noble gases preferentially partition into these gas-dominated melts, which then permeate and

metasomatize the lithosphere. The residual plume mantle will be strongly depleted in noble gases but not in lithophile tracers. *Schilling et al.* [1999] propose a similar mechanism (defluidization) to explain the longer wavelength of the ³He/⁴He gradient relative to that of Sr-Nd-Pb isotopic ratios along the Kolbeinsey Ridge north of the Iceland plume. Formation of a CO₂-vapor phase at these depths (>100 km), however, is unlikely. *Dixon* [1997] showed that exsolution of a CO₂-rich fluid phase for a range of alkalic to tholeiitic basalts does not begin until much shallower depths (~20–50 km), well within the lithosphere.

[57] *Dixon and Clague* [2001] proposed that while metasomatism occurs everywhere surrounding the Hawaiian plume, a distinctive hydrous melt derived from the plume is required in advance of the plume, in order to explain the distinct KEA-like radiogenic isotopic compositions along with elevated ³He/⁴He and water contents in South Arch lavas compared to other rejuvenated-stage lavas. *Hanyu et al.* [2005] builds on this model, suggesting a temporal variation of incipient melt compositions. They proposed the earliest formed incipient melts of the Hawaiian plume will be volatile-rich and will metasomatize the asthenosphere-lithosphere boundary upstream of the plume. Incipient melts produced downstream from the plume will be volatile-poor. *Hanyu et al.* [2005] suggest that the South Arch taps the volatile-rich metasomatized zone characterized by high water and ³He/⁴He, while other rejuvenated and submarine alkalic lavas are derived from the volatile-poor metasomatized zone characterized by low water and MORB-like ³He/⁴He. Kiekie Basalts do not support *Hanyu et al.*’s model because they are volatile-rich but yet have MORB-like ³He/⁴He [*Hanyu et al.*, 2005].

[58] By adding lithologic heterogeneity to this model, we can reconcile this seeming inconsistency. Melting of carbonated eclogite (KOO component) may produce volatile-rich carbonatite compositions with low ³He/⁴He, whereas melting of carbonated peridotite (KEA component) may produce carbonatites with higher ³He/⁴He. Thus, heterogeneity in the composition of metasomatizing melts may reflect both the lithology of the plume component being melted and the location of melting (early versus late). In contrast to *Valbracht et al.* [1996] and *Hanyu et al.* [2005], we suggest that incipient melting of the Hawaiian plume begins as deep as 400 km, where melting of carbonated eclogite/lherzolite within the plume produces

both carbonatite and silicate incipient melts. Deep metasomatism will allow the metasomatic signature to be transported away from the plume by both diffusion (percolation) and plume-driven advection.

6.6. Implications for Seismic Low Velocity Zone

[59] It has been proposed that low seismic velocities near the top of the mantle transition zone (~410 km depth) [Revenaugh and Sipkin, 1994; Vinnik and Farra, 2002; Song et al., 2004] represent the effects of high water content [e.g., Berco-*vici and Karato*, 2003]. Laboratory experiments that produce hydrous phases stable at these pressures [e.g., Kohlstedt et al., 1996; Smyth et al., 1997] are frequently cited to support this hypothesis. However, a wet transition zone is inconsistent with geochemical data and models suggesting efficient dehydration of subducted lithosphere resulting in a net flux of water out of the mantle into the exosphere [Dixon and Clague, 2001; Dixon et al., 2002; Rüpke et al., 2006]. Carbonatite melts, not hydrous melts or minerals, may account for these slow seismic velocities [Dasgupta et al., 2004; Presnall and Gudfinnsson, 2005].

7. Conclusions

[60] 1. Trace element concentrations of most rejuvenated-stage lavas can be generated by small degrees (1% to 9%) of melting of depleted peridotite recently metasomatized by a few percent of an enriched incipient melt (~0.5% melting) from the Hawaiian plume.

[61] 2. Kiekie lavas from Niihau differ from other rejuvenated-stage lavas in that they show overall depletion in incompatible elements combined with variable degrees of Ba, Sr, LREE, H₂O, and Cl enrichment.

[62] 3. Compositions of Kiekie Basalts are best explained by partial melting of a depleted peridotite source recently metasomatized by up to 0.2% carbonatite, in addition to small amounts of incipient silicate melt of the Hawaiian plume.

[63] 4. The carbonatite metasomatic component is similar in composition to oceanic carbonatites from Cape Verde and the Canary Islands.

[64] 5. We prefer a model whereby heterogeneous fluids, similar to those observed as microinclusions in diamonds, are produced as the carbonatite infiltrates and interacts with the surrounding peridotite

producing elevated H₂O and Cl contents. We cannot rule out assimilation of seawater or a seawater-derived brine to explain the extreme enrichment in H₂O and Cl in Kiekie and South Arch lavas.

[65] 6. Our model is consistent with predictions based on carbonated eclogite and peridotite melting experiments in which multistage metasomatism of the surrounding asthenosphere by carbonatite and silica-undersaturated silicate melts is a natural consequence of melting of heterogeneous lithologies within the Hawaiian plume.

[66] 7. The metasomatic component is best preserved at the margins of the plume, where low extents of melting of the metasomatized depleted mantle surrounding the plume are sampled during flexural uplift.

[67] 8. Partitioning of He into incipient carbonatite and silicate melts formed during plume ascent starting as deep as ~400 km provides a mechanism to decouple He from lithophile tracers of plume end-members.

[68] 9. Formation of incipient melts at depths of 100 to 400 km caused by carbon-related reduction in solidus temperatures of eclogitic and peridotitic materials should be considered as an alternate to wet transition zone models.

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