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OXYGEN ISOTOPE CONSTRAINTS ON THE STRUCTURE AND EVOLUTION OF THE HAWAIIAN PLUME

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ABSTRACT. The oxygen isotope stratigraphy of Ko‘olau volcano, Hawaii, is constructed by analyzing olivine phenocrysts from the KSDP drill core and submarine land-slide deposits. Along with those of subaerial (Makapu‘u) Ko‘olau olivines (Eiler and others, 1996a), they span the full range of the $\delta^{18}\text{O}_{\text{VSMOW}}$ variation previously observed in “Loa-trend” Hawaiian volcanoes (Lō‘ihi, Mauna Loa, Hualalai, and Ko‘olau), vary systematically with the stratigraphic position, and correlate with other geochemical properties of their host lavas (Tanaka and others, 2002; Haskins and Garcia, 2004; Huang and Frey, 2005; Salters and others, 2006; Fekiacova and others, 2007). These observations can be explained if the “Loa-trend” volcanoes (including Ko‘olau) are constructed of magmas made by mixing peridotite melt with variable proportions of eclogite melt derived from a mafic constituent of the Hawaiian plume having a composition resembling recent mid-ocean-ridge basalts. We present a model of this magma mixing process that simultaneously explains the correlations among oxygen isotopes, major elements, trace elements and radiogenic isotopes. Although a number of models of this kind, differing in several parameters, describe the data equally well, all statistically acceptable models require an “enriched” component with a MORB-like HREE pattern and enriched oxygen isotope composition ($\delta^{18}\text{O}_{\text{VSMOW}} = 7.8\text{--}9.7\text{‰}$), consistent with this component being an upper crustal (layer 1 or 2) basalt or gabbro with a low-temperature alteration history, possibly containing a small amount of sediment. Abundances of some minor elements—Ni and Ti—are not well described by this model; we show that these shortcomings are derived from the compositional assumption and operational difficulties, that is, TiO_2 content is too high in our assumed eclogite end-member, and the inversion of NiO content in the melt by the olivine addition calculation is imprecise due to the sensitivity of $D_{\text{NiO}}^{\text{olivine/melt}}$ to the melt composition and to crystallization process. Previous studies have advocated that Hawaiian lavas were derived from partial melts of an olivine-free pyroxenite formed by reaction of eclogite-derived melt with peridotite (for example, Sobolev and others, 2005). Our study shows that the peridotite-derived and eclogite-derived melt-mixing model can explain the geochemistry of Hawaiian lavas as well, including high-Ni Ko‘olau olivines. We find that an olivine-free mantle source for Hawaiian lavas is unnecessary, although melt-rock interaction could be important in modifying melt composition. Inverting for mixing proportions and degree of melting, we estimate that the amount of recycled crust in the Hawaiian plume is <24 weight percent. Comparison of the late shield-stage “Loa-trend” (particularly Ko‘olau lavas) and “Kea-trend” (particularly Mauna Kea lavas) suggests that the geochemical diversity of Hawaiian lavas is produced by a thermally and chemically-zoned plume.

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INTRODUCTION

Tholeiitic basalts from shield-stage Ko'olau volcano, O'ahu, are characterized by distinctive radiogenic isotope, trace element and major element compositions that are generally believed to reflect the presence of recycled crustal materials (for example, Eiler and others, 1996a; Hauri, 1996; Lassiter and Hauri, 1998; Blichert-Toft and others, 1999; Mukhopadhyay and others, 2003; Haskins and Garcia, 2004; Abouchami and others, 2005; Huang and Frey, 2005; Ren and others, 2005; Sobolev and others, 2005; Fekiacova and others, 2007). However, a variety of mutually inconsistent hypotheses have been put forward to describe the abundance, origin and melting properties of these materials in the Hawaiian plume. At one extreme, it has been argued that variations in melting depths of a lithologically homogeneous (though perhaps geochemically heterogeneous) peridotite mantle source are sufficient to yield observed differences in Na/Ti, Lu/Hf, and Sm/Yb between Hawaii and the East Pacific Rise (EPR), implying that high-pressure mafic rocks (garnet pyroxenite and/or eclogite) need not be present in the Hawaiian plume (Putirka, 1999). At the other extreme, it has been suggested that melt derived from recycled oceanic crust and/or sediments contributes up to ~20 percent (dacitic melt, Hauri, 1996) or 81 percent (pyroxenite melt, Sobolev and others, 2005) of Makapu'u stage Ko'olau lavas. Moreover, even among those studies concurring that the Hawaiian plume contains non-peridotitic constituents, there is diversity of opinion about their origin and makeup—either basaltic (Lassiter and Hauri, 1998; Sobolev and others, 2000) or marine sediment (Blichert-Toft and others, 1999). Moreover, although it is well-known that the majority of these crustal materials would turn into eclogite (containing garnet and clinopyroxene) during subduction, it is open to debate if partial melts of the recycled eclogite can be transported to shallow depth and mix with peridotite melt or will instead react with olivines in the mantle to form hybrid pyroxenite that melts later (for example, Eiler and others, 1996a; Hauri, 1996; Hirschmann and Stolper, 1996; Lassiter and Hauri, 1998; Yaxley and Green, 1998; Lassiter and others, 2000; Takahashi and Nakajima, 2002; Kogiso and others, 2004; Sobolev and others, 2005; Wang and Gaetani, 2008). Finally, and most problematically, few previous studies have reached quantitative, and therefore testable, conclusions about the amounts of recycled materials in the mantle sources of Hawaiian lavas (for example, Eiler and others, 1996a; Hauri, 1996; Sobolev and others, 2005). Resolving this question is essential to understanding the thermal, mineralogical and chemical structure of the Hawaiian plume.

It is challenging to precisely estimate the mixing proportions of components in the sources of magmas using trace and minor elements and their isotopes because of the confounding effects of element partitioning at various conditions of partial melting and/or fractional crystallization. Oxygen isotopes are helpful with such problems because oxygen is similar in concentration among all common silicate rocks and because oxygen isotopes are only weakly (and generally predictably) fractionated by partial melting and crystallization. Therefore, oxygen isotope ratios are a relatively straightforward measure of mixing proportions of isotopically-distinct source components and/or contaminants. Moreover, oxygen isotope compositions of the upper mantle span a narrow range (ca. $5.5 \pm 0.5\%$ for whole rocks, Kyser, 1986; Taylor and Sheppard, 1986; Harmon and Hoefs, 1995). In contrast, crustal rocks that have interacted with the hydrosphere exhibit large variations in $\delta^{18}\text{O}_{\text{VSMOW}}$ values (ca. $0 \sim 42\%$). In particular, pelagic sediments in the modern oceanic crust have average $\delta^{18}\text{O}_{\text{VSMOW}}$ values of 30 ± 8 permil; pillow basalts and sheeted dikes that have undergone low temperature hydrothermal alteration have average $\delta^{18}\text{O}_{\text{VSMOW}}$ values of 7.8 ± 2.0 permil; and sheeted dikes and layered/massive gabbros that have

experienced high-temperature hydrothermal alteration have average $\delta^{18}\text{O}_{\text{VSMOW}}$ values of 4.5 ± 2.0 permil (all $\pm 2\sigma$ deviations listed here are relative to mean values without being weighted by mass, Gregory and Taylor, 1981; Muehlenbachs, 1986; Taylor and Sheppard, 1986; Alt, 1993; Staudigel and others, 1995; Eiler, 2001). Studies of diamond-bearing eclogites, mineral inclusions in diamonds and melt inclusions in mantle minerals demonstrate that much of this range in oxygen isotope composition of crustal materials survives subduction and persists as isotopic heterogeneities in the mantle (for example, Taylor and Sheppard, 1986; Yui and others, 1995; Zheng and others, 1998; Eiler, 2001; Schulze and others, 2003).

Alternatively, recent studies advocate utilizing a relatively small number of minor elements in mantle olivines (for example, Ni and Mn) to estimate the amounts of recycled materials in the mantle (Sobolev and others, 2007; Sobolev and others, 2008). This approach is vulnerable to potentially large systematic errors due to the following two limitations. First, Ni partitioning between melt and olivine is strongly dependent on the melt composition, therefore, high-Ni olivines could be produced either by mixing eclogite-derived and peridotite-derived melt or by interaction of eclogite-derived melt with host peridotites at shallow levels (for example, Wang and Gaetani, 2008). Second, although other minor elements (for example, Mn) may have reliably near-constant partition coefficients that offer an accurate measure of the amount of each component in melt/rock mixtures, the mixing proportion in the melt mixture will only correspond to that in the host rock if the melting is modal. With a lithologically heterogeneous source in the Hawaiian plume as proposed by several studies (for example, Eiler and others, 1996a; Hauri, 1996; Salters and others, 2006; Sobolev and others, 2007), the degree of melting for each component varies according to the thermal structure of the Hawaiian plume (for example, Yaxley and Green, 1998; Takahashi and Nakajima, 2002; Pertermann and Hirschmann, 2003b; Pertermann and Hirschmann, 2003a; Ren and others, 2005). Likewise the proportion of recycled materials in the mantle cannot be directly taken from the mixing proportion in the melt. The latter limitation also applies to estimations using oxygen isotopes. It is thus imperative to develop internally-consistent multi-element and multi-isotope systematics to evaluate the amount and evolution of recycled crustal materials in the mantle.

Olivine phenocrysts from surface-exposed "Loa-trend" Hawaiian volcanoes have been previously shown to have $\delta^{18}\text{O}_{\text{VSMOW}}$ values equal to or higher than typical values of olivines from mantle peridotites ($5.2 \pm 0.2\text{‰}$); the high-end of this range is found from Makapu'u stage Ko'olau lavas (up to 6.0‰ in $\delta^{18}\text{O}_{\text{VSMOW}}$, Eiler and others, 1996a). In this study, we examine two suites of Ko'olau shield building lavas: 1) those sampled from the core recovered by the Ko'olau Scientific Drilling Project (KSDP, fig. 1A, after Haskins and Garcia, 2004), and 2) samples recovered from submarine landslides off the north shores of Ko'olau and Molokai (fig. 1B, after Clague and others, 2002). We present oxygen isotope compositions of olivine phenocrysts from these lavas. Combined with previous studies from this and other Hawaiian volcanoes (Eiler and others, 1996a; Eiler and others, 1996b; Wang and others, 2003), these oxygen isotope data are used to test a geochemical model that attempts to simultaneously explain major element, trace element, radiogenic isotope and O isotope compositions of "Loa-trend" Hawaiian shield-building lavas. This model defines an enriched end-member contributing to the sources of these lavas as recycled crust sharing many properties with modern Mid-Ocean-Ridge basalts (MORBs) and has implications for the thermal and chemical structure of the Hawaiian plume.

SAMPLES AND ANALYTICAL METHOD

Oxygen isotope ratios were analyzed in olivines and plagioclases/glasses from 22 tholeiites in the KSDP core (fig. 1A) between 305.3 and 529.5 meters below sea level (mbsl), and from 15 samples collected by the KAIKO and SHINKAI 6500 (two

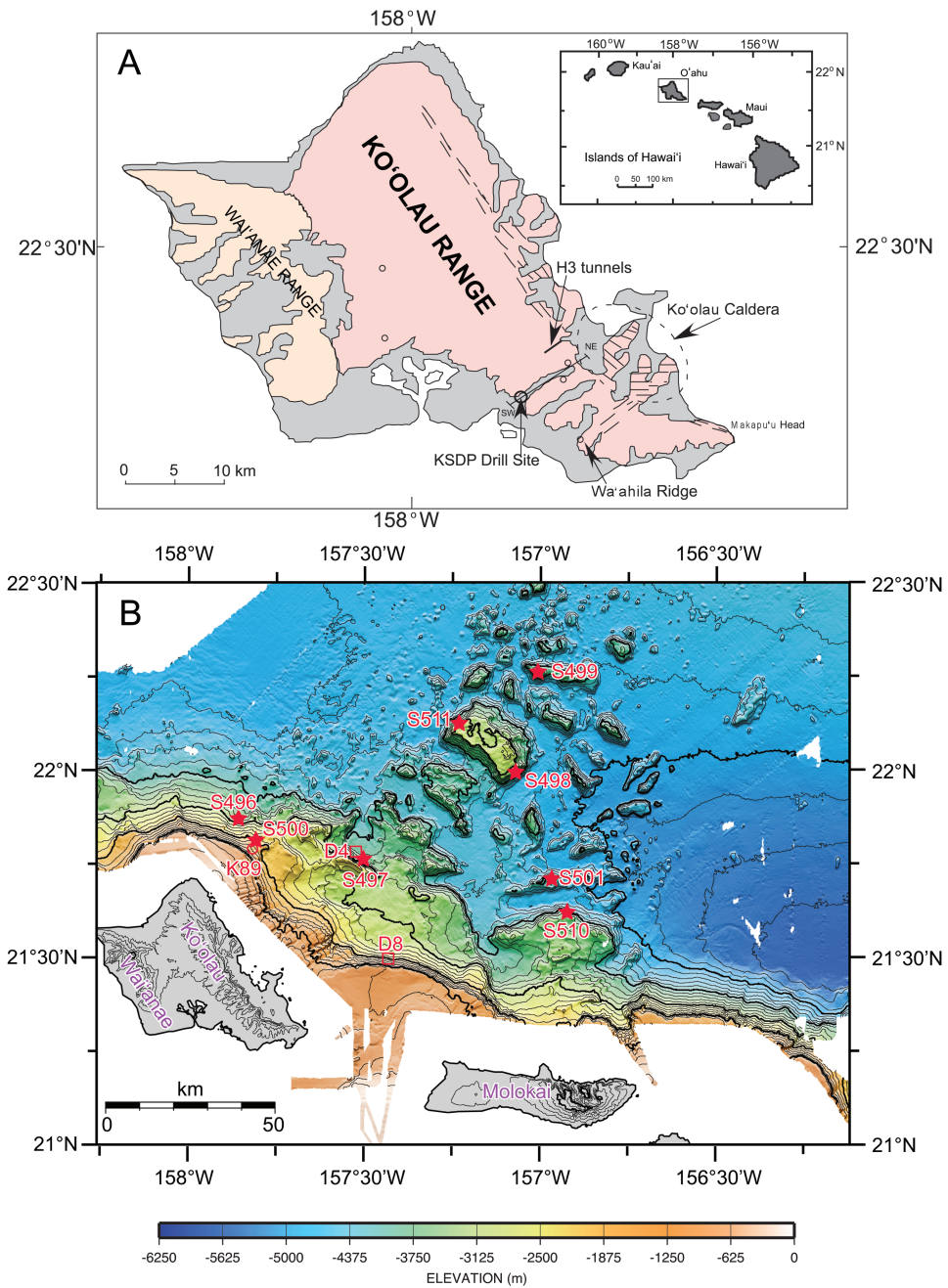


Fig. 1. Geological map of sampling locations: (A) O'ahu island and Ko'olau range, after Haskins and Garcia (2004); (B) submarine land slide blocks, after Clague and others (2002).

submarine vessels from the Japan Marine Science and Technology Center) during joint Japan-U.S. cruises in 1998 and 1999 (fig. 1B). The KSDP core penetrates subaerial shield-building Ko'olau lavas stratigraphically below the Makapu'u stage subae-

TABLE 1

Oxygen isotope composition of olivines and selected plagioclases/glasses from KSDP core and landslide deposits of Ko'olau and Molokai volcanoes

Unit	Depth(masl*)	$\delta^{18}\text{O}_{\text{olivine}}$	1σ	$\delta^{18}\text{O}_{\text{plagioclase}}$	1σ	Sample	$\delta^{18}\text{O}_{\text{olivine}}$	1σ	$\delta^{18}\text{O}_{\text{glass}}$	1σ
<u>KSDP drill core</u>						<u>Landslide sample</u>				
1	-305.3	5.51	0.01			<u>O'ahu North-a</u>				
2	-308.2	5.55	0.09	5.99	0.01	K89-02	6.01	0.05		
3	-308.8	5.44	0.07	6.16	0.06	K89-04	5.89	0.04		
4	-311.6	5.46	0.10			K89-05	5.87	0.07		
5	-314.4	5.46	0.05			K89-06	5.82	0.03		
6	-317.3	5.61	0.01			S500-1	5.91	0.08		
7	-324.8	5.51	0.05			S500-2B	5.80	0.06		
8	-327.7	5.52	0.01			S500-5B	5.91	0.01		
10	-334.4	5.54	0.07			S500-6	5.77	0.04		
15	-343.4	5.52	0.07			<u>O'ahu North-b</u>				
20	-358.9	5.52	0.03			S496-3	5.10	0.01		
29	-381.3	5.35	0.04			S496-6C			6.46	0.04
31	-387.7	5.54	0.10			S496-6E	5.17	0.06		
32	-388.3	5.29	0.05			<u>Nu'uaniu-1</u>				
36	-394.4	5.37	0.14			S497-2A	5.31	0.05		
47	-418.5	5.30	0.07			S497-2B	5.27	0.12		
50	-427.7	5.43	0.07			S497-2	5.19	0.10		
52	-438.9	5.33	0.02			S497-6	5.24	0.02		
53	-439.2	5.60	0.08			S497-7	5.26	0.09		
64	-493.5	5.39	0.08			S497-9	5.25	0.03		
65	-495.9	5.35	0.10			D4-7	5.41	0.06		
67	-510.9	5.41	0.02			<u>Nu'uaniu-2</u>				
						S498-4	5.10	0.03		
						<u>Nu'uaniu-3</u>				
						S499-6A	5.21	0.04		
						<u>Wailau-1</u>				
						S501-7	5.13	0.01		
						<u>Wailau-2</u>				
						S510-6A	5.16	0.10		
						S510-6B	5.21	0.12		
						<u>Molokai</u>				
						S501-2	5.04	0.06		
						D8-1	4.83	0.02		

* Meters above sea level.

rially exposed at Makapu'u head, and samples some of the same stratigraphic intervals exposed by a highway (H3) tunnel (fig. 1A, and see Jackson and others, 1999; Haskins and Garcia, 2004 for detailed sample locations and descriptions). Only samples from the cored section of the KSDP drill hole were measured for oxygen isotope compositions (materials from above 305.3 mbsl were sampled as cuttings from rotary drilling). Ko'olau submarine landslide samples are from several submarine landslide blocks (for example, O'ahu, Nu'uaniu, and Wailau series in fig. 1B and table 1, see also Clague and others, 2002; Garcia, 2002; Tanaka and others, 2002). Blocks "O'ahu North-a" and "O'ahu North-b" are closest to the Ko'olau volcano, and blocks "Nu'uaniu-1," "Nu'uaniu-2" and "Nu'uaniu-3" are further away. Geological observations and geochemical evidence suggest the relative distances of these blocks from Ko'olau volcano roughly correlate with the original stratigraphic positions in the volcanic edifice; that

is, blocks farther away from the volcano correspond to older lava flows (Clague and others, 2002; Garcia, 2002; Tanaka and others, 2002; Coombs and others, 2004). Most samples from these blocks are subaerially erupted lavas, except those from block “Nu‘uanu-3” and parts of “Nu‘uanu-2,” which are suggested to represent shallow submarine lavas (Shinozaki and others, 2002; Tanaka and others, 2002). Blocks “Wailau-1” and “Wailau-2” are believed to have slumped off Molokai volcano. They were analyzed for comparison with our samples from Ko‘olau volcano, but are not interpreted as members of the Ko‘olau suite.

All samples were coarsely crushed in a steel percussion mortar. The resulting powders were then sieved, ultrasonically cleaned first in distilled water or 1N HCl and then in ethanol and finally dried. Olivine separates were handpicked from these cleaned, sieved powders (200–400 μm portions) under a binocular microscope. Mineral fragments containing visible inclusions and alteration products were discarded during handpicking. All data are for $\geq 200 \mu\text{m}$ olivine separates. All mineral separates were analyzed by CO_2 laser fluorination system at the California Institute of Technology using methods previously described by Eiler and others (Eiler and others, 2000), based on methods developed by Sharp (1990) and Valley and others (1995). A total of 35 UWG-2 (garnet) and 36 SCO3 (olivine) standards were analyzed interspersed with analyses of samples. Results for these standards are as follows: UWG-2 = 5.85 ± 0.08 permil, SCO3 = 5.40 ± 0.07 permil. (All standard deviations refer to long-term reproducibility of raw measurements and are 1σ). These values compare with the accepted values of UWG-2 = 5.80 permil and SCO3 = 5.35 permil (Valley and others, 1995; Eiler and others, 2000). All oxygen isotope measurements of unknowns were corrected by the differences between measured and accepted values for standards on that day. An average of 0.05 permil was corrected for each unknown sample. All samples were analyzed in duplicate. Duplicates measured on different days were within 0.10 permil of each other after correction. Sample averages and standard deviations for replicate measurements of each sample are reported in table 1.

RESULTS

Temporal Oxygen Isotope Variation in the KSDP Core

Figure 2D depicts the stratigraphic profile of oxygen isotope compositions of olivines from the KSDP core and Makapu‘u stage lavas. Olivines collected between 381 and 511 mbsl in the KSDP core have $\delta^{18}\text{O}_{\text{VSMOW}}$ values ($5.39 \pm 0.1\text{‰}$) slightly higher than those in typical upper mantle peridotites ($5.2 \pm 0.2\text{‰}$; Matthey and others, 1994; Eiler, 2001) and Mauna Loa lavas ($5.17 \pm 0.11\text{‰}$, Eiler and others, 1996a; Eiler and others, 1996b; Eiler, 2001; Wang and others, 2003), whereas olivines collected between 304 and 359 mbsl are even higher in $\delta^{18}\text{O}_{\text{VSMOW}}$ ($5.56 \pm 0.05\text{‰}$). This later value is similar to olivines from plagioclase-spinel peridotite xenoliths collected on O‘ahu ($5.51 \pm 0.05\text{‰}$, Ducea and others, 2002) and approaches exceptionally high numbers previously reported for subaerial Makapu‘u stage lavas ($5.89 \pm 0.12\text{‰}$, Eiler and others, 1996a).

Figures 2A through 2C compare stratigraphic variations of $\delta^{18}\text{O}_{\text{VSMOW}}$ values of olivines to variations in $\text{CaO}/\text{Al}_2\text{O}_3$ and Sr/Nb ratios and ϵ_{Nd} values of whole-rock samples of the same and related lavas (as representative major incompatible element, trace element and radiogenic isotope ratios). In general, stratigraphic variations in oxygen isotope compositions of olivines track changes in other geochemical indices. For example, Makapu‘u stage lavas average 0.67 ± 0.02 in $\text{CaO}/\text{Al}_2\text{O}_3$, 45 ± 4 in Sr/Nb and 1.8 ± 1 in ϵ_{Nd} , whereas lavas from the base of the KSDP core (> 500 mbsl) average 0.74 ± 0.06 in $\text{CaO}/\text{Al}_2\text{O}_3$, 31 ± 5 in Sr/Nb and 5.7 ± 0.6 in ϵ_{Nd} (oxygen isotope compositions from this study and Eiler and others, 1996a; other data are from Frey and others, 1994; Roden and others, 1994; Lassiter and Hauri, 1998; Haskins and Garcia,

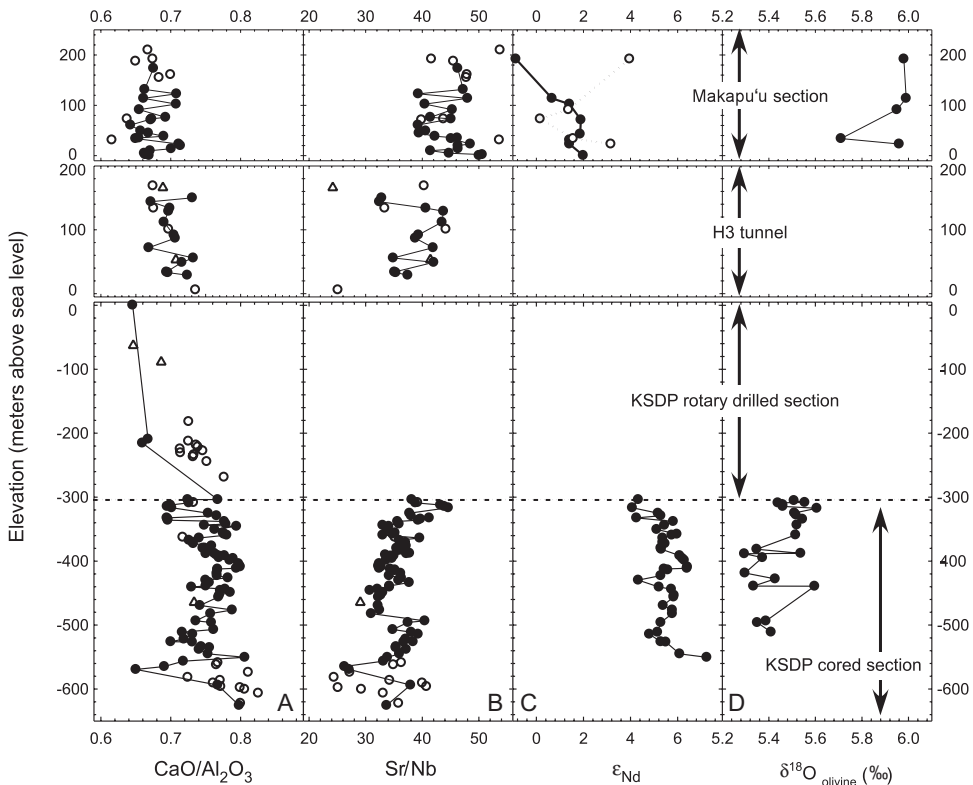


Fig. 2. Stratigraphic profile of geochemical indices from Makapu'u head, H3 tunnel and KSDP drill core; (A) $\text{CaO}/\text{Al}_2\text{O}_3$ (Frey and others, 1994; Haskins and Garcia, 2004); (B) Sr/Nb (Frey and others, 1994; Haskins and Garcia, 2004; Huang and Frey, 2005); (C) ϵ_{Nd} (Roden and others, 1994; Lassiter and Hauri, 1998; Salters and others, 2006) and (D) $\delta^{18}\text{O}_{\text{VSMOW}}$ values of olivines (this study and Eiler and others, 1996a). Note $\text{CaO}/\text{Al}_2\text{O}_3$, Sr/Nb and ϵ_{Nd} are for whole rock samples, open symbols here represent weathered samples.

2004; Huang and Frey, 2005; Salters and others, 2006). There are also second-order variations in these geochemical indices, superimposed on the gradual changes in average values. These oscillations are not generally coherent from one geochemical index to another, and could reflect uncorrelated variations in primary lava composition, differences in sampling density from one index to another, and/or variable effects of post-eruptive alteration.

Stratigraphic Oxygen Isotope Variations in Land-slide Samples

Figure 3 summarizes the oxygen isotope compositions of olivines alongside $\text{CaO}/\text{Al}_2\text{O}_3$, Sr/Nb and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, and ϵ_{Nd} values of lavas from landslide samples, and compares them with KSDP and subaerial Makapu'u samples. The landslide lavas from Ko'olau volcano are arranged in approximate stratigraphic order, from the oldest at the bottom to the youngest at the top, based on estimates of block positions prior to their slumps off the volcanic edifice. The majority of these samples show monotonic compositional gradients from "Nu'uauu-3" to "O'ahu north-a," defining a trend of increasing $\delta^{18}\text{O}_{\text{VSMOW}}$ and Sr/Nb , and decreasing $\text{CaO}/\text{Al}_2\text{O}_3$, ϵ_{Nd} and $^{206}\text{Pb}/^{204}\text{Pb}$ as one approaches O'ahu island (going up section). This reconstructed geochemical stratigraphy generally resembles the one shown in the KSDP and

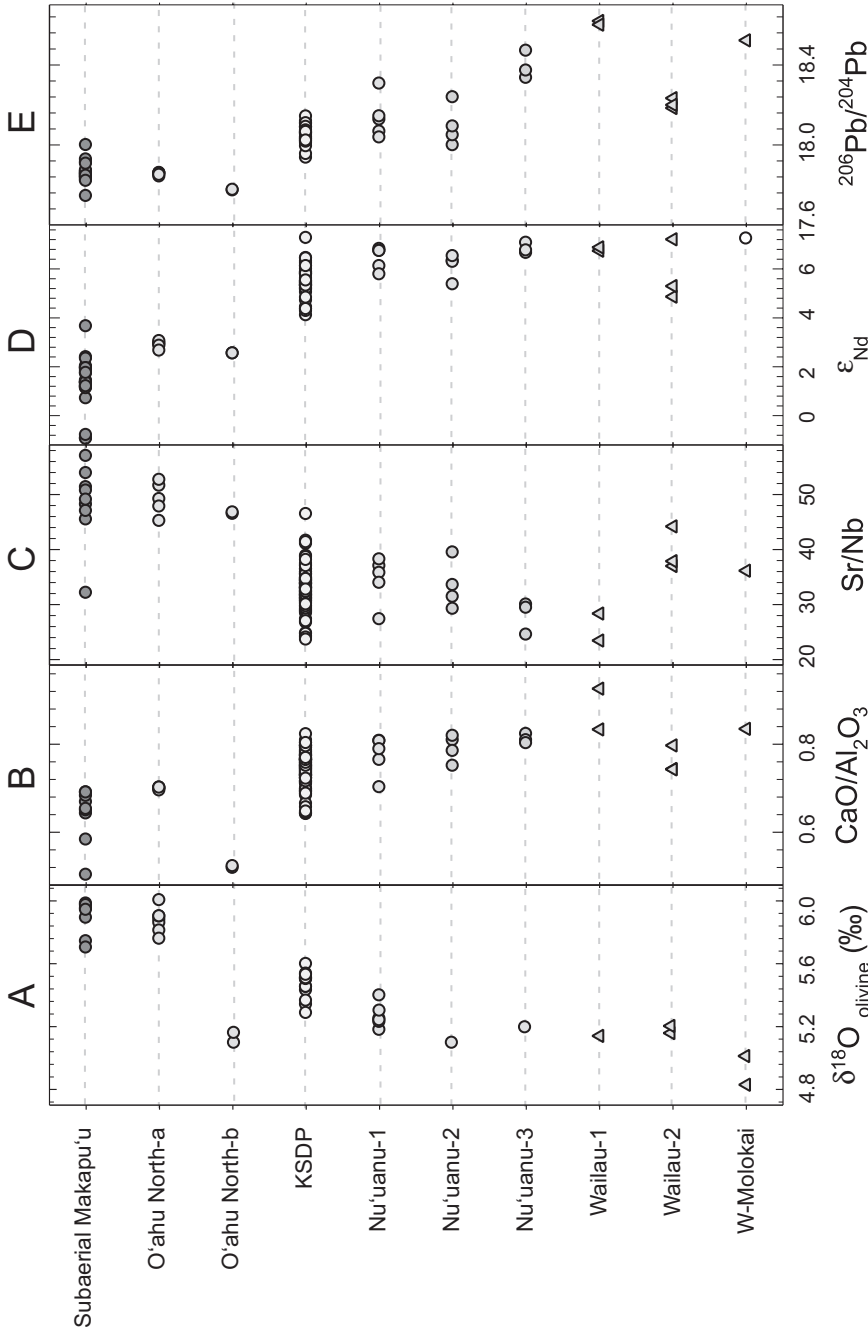


Fig. 3. Comparison among geochemical indices from KSDP, Makapu'u head and landslides: (A) Oxygen isotope compositions of olivines; (B) $\text{CaO}/\text{Al}_2\text{O}_3$; (C) Sr/Nb ; (D) ϵ_{Nd} and (E) $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. Oxygen isotope compositions of the landslide samples are from this study, others are from Tanaka and others (2002). $\text{CaO}/\text{Al}_2\text{O}_3$, Sr/Nb and ϵ_{Nd} for KSDP and Makapu'u samples are taken from same references as in figure 2 caption. $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of lavas in KSDP and Makapu'u samples are from Roden and others (1994), Lassiter and Hauri (1998), and Tektatova and others (2007). Note $\text{CaO}/\text{Al}_2\text{O}_3$, Sr/Nb , $^{206}\text{Pb}/^{204}\text{Pb}$ and ϵ_{Nd} are for whole rock samples.

Makapu‘u stage lavas: that is, lavas from “O‘ahu North-a” are similar in composition to Makapu‘u stage lavas, whereas lavas from “Nu‘uanu-1” and “Nu‘uanu-2” are similar to the lower section of KSDP lavas.

However, olivines in “O‘ahu North-b” show oxygen isotope disequilibrium with their host-lavas. Whole rock samples S496-3, S496-6C and S496-6E from “O‘ahu North-b” are similar in Sr/Nb and CaO/Al₂O₃ ratios and Sr-Nd-Pb isotope compositions to those from “O‘ahu North-a” and Makapu‘u stage lavas (fig. 3). Oxygen isotope compositions of the glass from olivine-aphyric S496-6C have $\delta^{18}\text{O}_{\text{VSMOW}} = 6.46 \pm 0.04$ permil, implying that equilibrium olivines would have $\delta^{18}\text{O}_{\text{VSMOW}} = \sim 5.96$ permil ($\sim 0.5\%$ fractionation factor between melt and olivine, Eiler, 2001), similar to olivines from “O‘ahu North-a.” In contrast, olivines in S496-3 and S496-6E have $\delta^{18}\text{O}_{\text{VSMOW}} = 5.14 \pm 0.05$ permil, in oxygen isotope disequilibrium with glasses in S496-6C from the same block. We thus suggest olivines, particularly of S496-3 and S496-6E, in “O‘ahu North-b” are olivine xenocrysts that were erupted with lavas similar to those in “O‘ahu North-a” block but crystallized from magma parental to earlier lava flows in the volcanic edifice (hence resembling olivines from the stratigraphically lower “Nu‘uanu-2” or “Nu‘uanu-3”). This conclusion is also supported by the wider variation in major element compositions (FeO, MgO and SiO₂) of whole rocks and glasses in “O‘ahu North-b” compared with in “O‘ahu North-a” (Clague and others, 2002) and the petrological observation (for example, 9.2% olivine phenocrysts and 10.3% olivine xenocrysts were reported in sample S496-3, Garcia, 2002). These xenocrystic samples are excluded from the following discussion.

Correlation Between $\delta^{18}\text{O}_{\text{olivine}}$ Value and Other Geochemical Indices

Figure 4 compares $\delta^{18}\text{O}_{\text{VSMOW}}$ values of olivines to other geochemical indices measured in the same KSDP and land-slide lavas. When these data are combined with previous analyses of surface-exposed Ko‘olau lavas from Makapu‘u head (Eiler and others, 1996a), we find that Ko‘olau olivine phenocrysts span a large range in $\delta^{18}\text{O}_{\text{VSMOW}}$ values—5.2~6.0 permil—comparable to olivines from the full range of all Loa-trend Hawaiian lavas and $\sim 2/3$ of the known range defined by olivines from almost all fresh, unaltered basalts world-wide. Moreover, the entire sample suite shows correlations of $\delta^{18}\text{O}_{\text{VSMOW}}$ with CaO/Al₂O₃, Sr/Nb, ϵ_{Nd} and $^{206}\text{Pb}/^{204}\text{Pb}$ (among other geochemical indices). These trends define a compositional continuum from a high- $\delta^{18}\text{O}_{\text{VSMOW}}$, enriched (in crust-forming elements) end member to a more normal- $\delta^{18}\text{O}_{\text{VSMOW}}$ (similar to average mantle), relatively depleted mantle composition (roughly resembling the average composition of Mauna Loa shield building lavas). A sample from West Molokai (table 1) is shown to represent the most depleted end member of Loa trend lavas, plotting on the extension of the Ko‘olau correlations in all indices shown. Because partial melting cannot produce the observed radiogenic and oxygen isotope range (even if it could be responsible for some variations in major and trace element ratios), these geochemical variations and correlations cannot be explained by variations in degrees of partial melting of a uniform source. Thus, Ko‘olau shield-building lavas sample at least two geochemically distinct reservoirs as has been previously concluded based on radiogenic isotope, trace element and major element data (for example, Bennett and others, 1996; Eiler and others, 1996a; Hauri, 1996; Tanaka and others, 2002; Huang and Frey, 2005; Salters and others, 2006; Fekiacova and others, 2007).

The enriched end member of this data array differs significantly in radiogenic isotope composition (Sr-Nd-Pb-Hf) from local oceanic crust (for example, ODP 843 and North Arc, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7026\text{--}0.7031$, $\epsilon_{\text{Nd}} = 8.1\text{--}11.0$, $^{206}\text{Pb}/^{204}\text{Pb} = 18.1\text{--}19.1$, Ito and others, 1987; King and others, 1993; Lassiter and others, 1996; Blichert-Toft and others, 1999; Yang and others, 1999) or depleted mantle (based on studies of mantle xenoliths: $^{87}\text{Sr}/^{86}\text{Sr} = 0.7027\text{--}0.7035$, $\epsilon_{\text{Nd}} = 7.1\text{--}10.8$, $^{206}\text{Pb}/^{204}\text{Pb} = 18.0\text{--}18.4$, and EPR

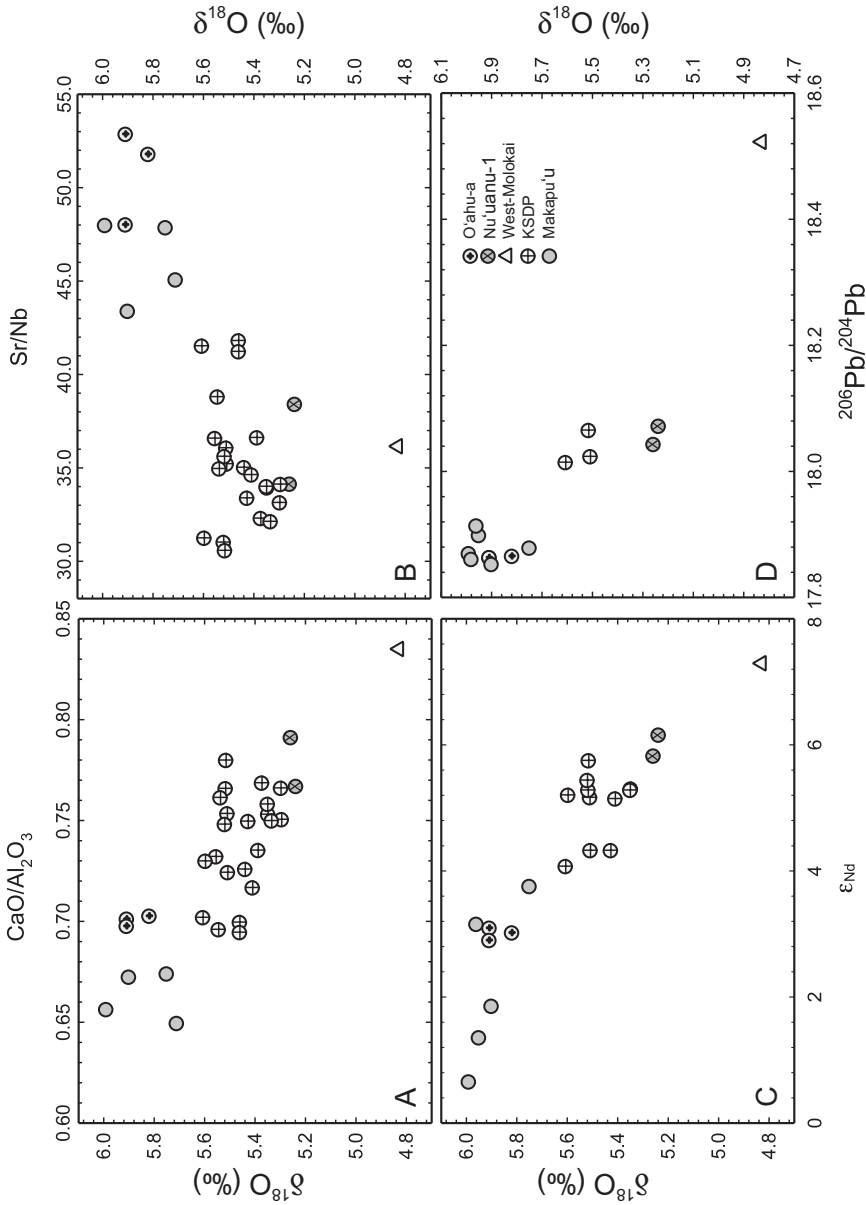


Fig. 4. Correlation between $\delta^{18}\text{O}_{\text{VSMOW}}$ values of olivines and geochemical indices of their host lavas from Ko'olau and Molokai volcanoes; (A) $\delta^{18}\text{O}_{\text{VSMOW}}-\text{CaO}/\text{Al}_2\text{O}_3$; (B) $\delta^{18}\text{O}_{\text{VSMOW}}-\text{Sr}/\text{Nb}$; (C) $\delta^{18}\text{O}_{\text{VSMOW}}-\epsilon_{\text{Nd}}$; (D) $\delta^{18}\text{O}_{\text{VSMOW}}-^{206}\text{Pb}/^{204}\text{Pb}$. Oxygen isotope composition is for olivine phenocrysts, $\text{CaO}/\text{Al}_2\text{O}_3$, Sr/Nb , $^{206}\text{Pb}/^{204}\text{Pb}$ and ϵ_{Nd} are for their host lavas. Data references for Ko'olau samples are the same as in the captions of figures 2 and 3. Data for Molokai samples come from this study for $\delta^{18}\text{O}_{\text{olivine}}$ and from Tanaka and others (2002) for major elements and radiogenic isotope compositions.

MORBs: $^{87}\text{Sr}/^{86}\text{Sr} = 0.7024\text{--}0.7030$, $\epsilon_{\text{Nd}} = 8.1\text{--}11.0$, $^{206}\text{Pb}/^{204}\text{Pb} = 18.1\text{--}18.9$; Bohron and Clague, 1988; Chen and others, 1992; Ducea and others, 2002; Weinstein and others, 2004) and differs in trace-element ratios and $\delta^{18}\text{O}_{\text{VSMOW}}$ values from the estimated compositions of primitive mantle (for example, Hofmann, 1988; Sun and McDonough, 1989; Eiler, 2001), suggesting that it reflects the presence of recycled crustal materials in the mantle sources of Ko'olau lavas (Eiler and others, 1996a; Hauri, 1996; Lassiter and Hauri, 1998; Sobolev and others, 2000). The inferred crustal materials might be composed of any combination of eclogitized basaltic oceanic crust or gabbro cumulates (Eiler and others, 1996a; Hauri, 1996; Lassiter and Hauri, 1998; Sobolev and others, 2000), pyroxenite (for example, Hirschmann and Stolper, 1996), and/or pelagic sediments (Blichert-Toft and others, 1999). The mixing trend defined by these data indicates that Makapu'u stage lavas contain the largest proportion of melts derived from the enriched, recycled crustal materials among all Hawaiian lavas.

Quantitative understanding of these mixing relationships (that is, an interpretation that specifies the amounts of end members in the source and their relative contributions to lavas) would constrain the origins and melting properties of enriched, presumably recycled materials, and more broadly, help us understand the composition, structure and dynamics of the Hawaiian plume. In the following sections, we present a quantitative geochemical model constructed using the major element compositions of Hawaiian lavas. In this model, we hypothesize that the parent magmas of Ko'olau lavas are mixtures of partial melts of peridotite and eclogite/pyroxenite, and fit a forward model of melting of such sources to simultaneously explain the concentrations of all major elements in Ko'olau lavas (and we extend the model to fit "Loa trend" lavas in general). We then compare the fitted amounts of each of these components to the trace-element, radiogenic-isotope and oxygen-isotope compositions of Ko'olau lavas, showing that they correlate with the relative amounts of these two end members (which were defined purely based on major element data alone). Finally, we use those correlations to constrain the trace-element and isotopic compositions of the end members. These fitted model parameters are then examined for their significances regarding the origins and melting behaviors of components in the Hawaiian plume.

A MAJOR ELEMENT MODEL OF KO'OLAU LAVAS

Major Element Variations of Hawaiian Lavas

Hawaiian lavas have considerable compositional diversity as shown in figure 5, which illustrates major-element compositions of ~6700 Hawaiian lavas including shield, pre-shield and post-shield lavas. From them a number of first-order fractional crystallization trends for most shield-building Hawaiian lavas can be generalized. First, primary melts of most Hawaiian shield lavas have MgO contents of about 18~20 percent (or Mg#=0.76), in equilibrium with Fo₉₁₋₉₂ olivines (similar to the most magnesian olivines found in Hawaiian lavas, for example, Norman and Garcia, 1999). Second, when undergoing crystallization-differentiation between 18~20 weight percent and ~7 weight percent MgO, melts are saturated only in olivine and a small amount of spinel (~1 wt.% of the fractionating solid assemblage) resulting in a clear olivine-control line evident in figure 5. Third, when undergoing crystallization-differentiation between ~7 and ~6 weight percent MgO, melts are saturated in both olivine and plagioclase, reflected in figure 5E by a subtle break in slope of the trend for Al₂O₃ (a small kink with slight drop in Al₂O₃). Fourth, clinopyroxene is saturated shortly after plagioclase between 5 and 6 weight percent MgO, as shown by the sharp reversal of the CaO-MgO trend in figure 5D. Finally, Fe-Ti oxide starts to precipitate when MgO falls below ~5 weight percent as shown in figures 5B and 5C. Lavas that substantially deviate from these general trends are explicable by unusually low degrees

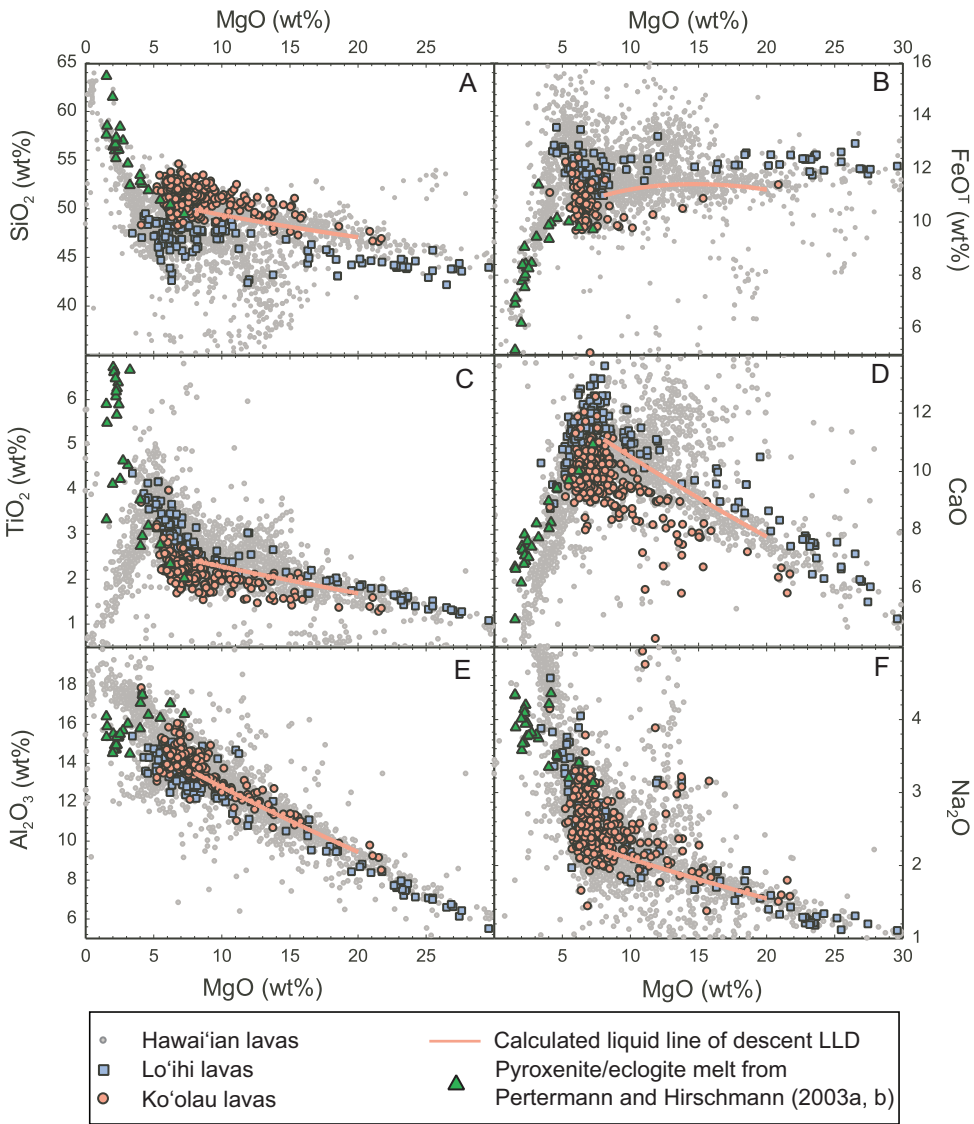


Fig. 5. Major element variations of about 6700 Hawaiian lavas as a function of MgO. Data are from GEOROC database (<http://georoc.mpch-mainz.gwdg.de/georoc/>). Lō'ihi and Ko'olau lavas are square and dots, respectively. The liquid line of descent is inferred from a Lō'ihi glass by adding olivines. Compositions of eclogite/pyroxenite melt from recent melting experiments (Pertermann and Hirschmann, 2003a; Pertermann and Hirschmann, 2003b) are also plotted for comparison (triangles).

and/or high pressures of melting (for example, some low-SiO₂, alkali-rich Lō'ihi lavas) and accumulation of excess olivines (for example, picrites with MgO > 18~20 wt.%). The similar relationships have also been noted in other Hawaiian lavas (for example, Mauna Kea lavas, Rhodes and Vollinger, 2004).

In order to retrieve primary melt composition, we need to correct for these variable effects of fractional crystallization (for example, Hauri, 1996). Figure 5 shows a representative model of the liquid line of descent (LLD), or, for relatively magnesian lavas, the “olivine-control line,” that we use to interpret and correct for the effects of

crystallization-differentiation evident in the measured whole-rock compositions of Lō'ihī lavas and other Hawaiian lavas that contain the least contributions from the enriched component. This model LLD is calculated by incrementally adding to Lō'ihī glass KK29-10 (~8% MgO, Byers and others, 1985; Dixon and Clague, 2001) olivines in Fe-Mg exchange equilibrium with the glass in 0.1 percent steps (K_D is from Herzberg and Zhang, 1996; Herzberg and others, 2007, around 0.29~0.34 as a function of MgO wt.%). We chose this Lō'ihī glass to calculate the LLD because 1) it lies near the normal- $\delta^{18}\text{O}_{\text{VSMOW}}$, depleted end of geochemical trends in figure 4, and thus, is a plausible "eclogite-melt-free" end member (or, at least, contains the minimum abundance of the eclogite-melt end member) and 2) it is magnesian enough to have undergone only olivine fractionation (we ignored spinel precipitation here). While we could have chosen other Lō'ihī glasses to represent our depleted end-member, it appears to make little difference; trial calculations using other possible samples showed that all tholeiitic Lō'ihī glasses with MgO > 7.0 weight percent (olivine-control segment of the LLD ends at 7.0 wt.% MgO) lead to similar final results. This LLD appears to be at the boundary between Lō'ihī and Ko'olau lavas in figure 5, rather than passing through the majority of Lō'ihī lavas, because a large number of the Lō'ihī lavas are either alkali or transitional lavas. The similar stable and radiogenic isotope compositions of the alkali, transitional and tholeiitic Lō'ihī lavas (for example, Garcia and others, 1993; Eiler and others, 1996a) suggest that alkali lavas could be derived from lower degree partial melting of mantle peridotite than tholeiites, and therefore are not on the LLD defined by tholeiitic glass. If a LLD is chosen to pass through the center of all Lō'ihī lavas, the mixing proportion calculated from major elements will be overestimated due to the lower degree of melting of the primitive component and will not be consistent with isotope mixing relationships. Our chosen LLD can reduce this effect.

Lavas from Hawaiian volcanoes other than Lō'ihī depart from this LLD, and thus apparently are not on the same fractional-crystallization path. Neither can they be explained by olivine accumulation (which results in a vector that passes through the composition space broadly similar in slope to that resulting from olivine crystallization and points to the composition of Fo_{89-91} olivines). For example, Makapu'u-stage Ko'olau lavas are systematically higher in SiO_2 and lower in FeO^{T} (total Fe) at a given MgO than the LLD defined by Lō'ihī glasses (fig. 5). This difference becomes even more pronounced at MgO = 5~7 weight percent where Ko'olau lavas continue to increase in SiO_2 and decrease in FeO^{T} with decreasing MgO, whereas Lō'ihī lavas exhibit the opposite trends (presumably because Lō'ihī lavas are plagioclase saturated below 7 weight percent MgO whereas Ko'olau lavas are not).

Figure 5 also plots the compositions of partial melts of eclogite having major element compositions resembling average oceanic crust in melting experiments conducted at 2 to 3 GPa (Pertermann and Hirschmann, 2003b). Most of these experimental melts coexist with garnet and clinopyroxene except a couple of them only with clinopyroxene after garnet being exhausted during high temperature melting (1375°C at 2 GPa and 1500°C at 3 GPa). The experimental melts of the mafic materials lie along extensions of the trends in major element compositions defined by Hawaiian lavas for all elements other than TiO_2 (which is systematically higher in the experimental melts than in Hawaiian lavas; the reason for this exception is discussed in *The Titanium Puzzle* section). More importantly, they plot at such a position that mixing them into a liquid anywhere along the Lō'ihī fractionation trend could yield a liquid that would fractionate along the Ko'olau trend (again, except for TiO_2). Therefore, they could represent a mixing end-member for all "Loa trend" Hawaiian lavas at least with respect to major elements other than Ti. Moreover, oxygen and radiogenic isotope compositions of Makapu'u stage Ko'olau lavas indicate the enriched

component in Ko‘olau lavas could derive from the upper part of the oceanic crust (White and Hofmann, 1982; Zindler and Hart, 1986; Hart and others, 1992; Eiler and others, 1996a; Hauri, 1996; Blichert-Toft and others, 1999; Sobolev and others, 2005). Thus, we define melts from Pertermann and Hirschmann (2003b) as our enriched component.

Model Construction

Our model assumes that compositions of all “Loa trend” lavas, especially those from the Ko‘olau volcano, are mixtures of melts from peridotite and eclogite. Given this assumption, one can formulate a variety of mixing scenarios that could produce the major element compositions of Ko‘olau lavas by varying the degree of melting in the eclogite component and/or extent of fractional crystallization in both melt end-members, and by allowing the interaction between the eclogite melt and mantle peridotite (for example, Sobolev and others, 2005). We focus on the following two limiting cases, where: 1) peridotite melts that are on the LLD of Lō‘ihi glasses mix with a specific partial melt of eclogite having MORB-like major element compositions (Case I); this eclogite partial melt is chosen from a pool of experimental eclogite melts (an actual melt in Pertermann and Hirschmann, 2003b) so as to minimize the overall fitting residual for all Ko‘olau lavas simultaneously; and 2) peridotite melts that are on the LLD of Lō‘ihi glasses mix with magmas generated by variable degree melting of eclogite having MORB-like major element compositions (interpolated melt composition based on experimental eclogite melts, Case II); that is, the eclogite melt mixing end-member varies from sample to sample. We focus on these two cases because they are plausible, moderate representatives of a wide range of similar models (and, models that call for melt-rock interaction can derive from these two cases). In this model, no attempt is made to vary the degree of melting of the peridotite component, because three more variables (temperature, pressure and degree of melting) would have to be fitted for the Lō‘ihi end-member and a major element composition of the peridotite source rock would need to be assumed. Instead, we use major element compositions of Lō‘ihi glasses that, after fractional crystallization correction, can represent the partial melt of the peridotite source. This simplification has little effect on our estimation of the mixing proportions of eclogite and peridotite partial melt, but significant effect on evaluation of the amount of recycled materials in the Hawaiian plume (see *Estimation of the Amount of Recycled Materials in Hawaiian Mantle Plume* section).

Eclogite melts are highly siliceous (or olivine under-saturated) and reactive to mantle peridotite (for example, Yaxley and Green, 1998; Takahashi and Nakajima, 2002; Morgan and Liang, 2003). The following three scenarios could occur after the production of eclogite melt: 1) a small amount of eclogite melt will freeze completely due to reaction with mantle peridotite, perhaps modifying the peridotite sufficiently to form olivine-free pyroxenite, which may melt later; 2) eclogite melt may assimilate or react with mantle peridotites until they are in thermodynamic equilibrium with each other, having a modified composition but without consuming the melt; 3) eclogite melt may pass through channels whose wall rocks are in thermodynamic equilibrium with the eclogite melt, armoring that melt from further reaction, and then mix with peridotite melts at shallow depth. Our models assume direct mixing of peridotite-derived and eclogite-derived partial melts, and therefore implicitly assume a physical scenario similar to this third scenario. For scenarios 1 and 2, the chemistry of the eclogite melt will evolve during its transit through the mantle. However, these complications will not significantly alter our estimation of mixing relationships in major element and oxygen isotope spaces, because our calculation is essentially based on mass-balance. To illustrate this point, consider a simple case of the eclogite melt from melting experiment A200K (Pertermann and Hirschmann, 2003b) reacting with peridotite at shallow levels

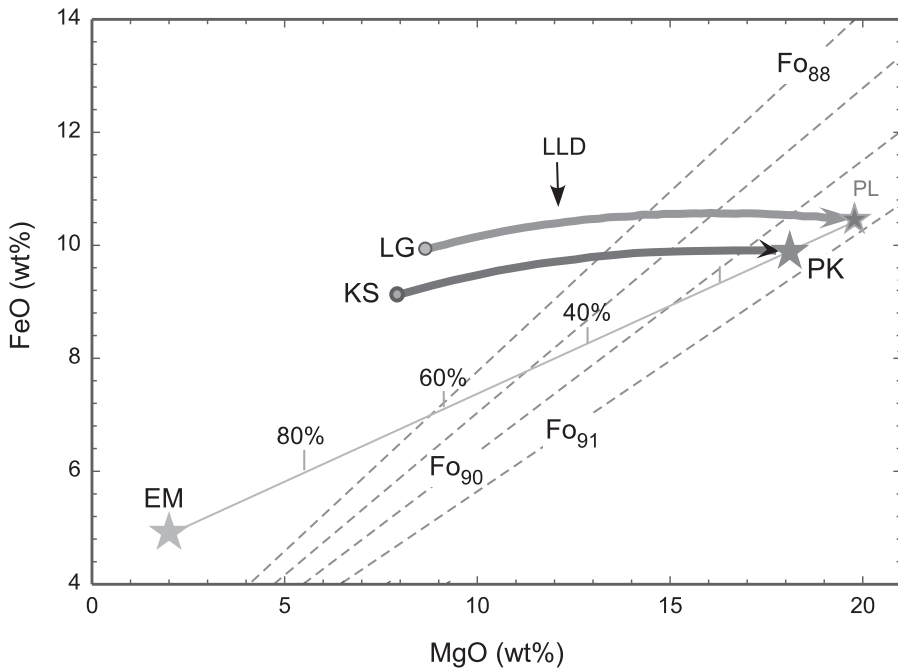


Fig. 6. Schematic description of model implementation procedures in FeO-MgO space. LG: Lō'ihī glass; PL: primary magma of Lō'ihī lava; KS: a Ko'olau lava sample; PK: parent melt of a Ko'olau sample; EM: eclogite melt; LLD: liquid line of descent (olivine precipitation controlled segment). The solid line with tick marks represents the mixing line. The dashed line represents melts with Fe/Mg in thermodynamic equilibrium with olivines having the same Fo# (K_d is about 0.30).

(low pressure). The liquid will assimilate about 18 weight percent olivines before reaching $Mg\# = 0.76$, in equilibrium with Fo_{91} olivines (Wang and Gaetani, 2008). Therefore, the mixing proportion of the modified eclogite melt would be increased by a factor of 1.18, calculated using major element inversions, but the proportion of the original eclogite and the incompatible trace element concentration of the original eclogite calculated using our model remain the same.

As depicted in figure 6, several constraints need to be satisfied for the compositions of mixing end-members and mixtures: 1) primary magma of Lō'ihī lavas (PL in fig. 6) has to be on the liquid line of descent inverted from Lō'ihī glass (LG) KK29-10 (Byers and others, 1985; Dixon and Clague, 2001). This line is close to most tholeiitic Lō'ihī glasses and lavas and defines a boundary between Lō'ihī and Ko'olau lavas (fig. 5); 2) the parental melt of a given Ko'olau sample (PK in fig. 6) has to be on the olivine control line defined by this Ko'olau sample (KS); 3) the eclogite melt composition is from a parameterization of the melting experiment data (EM, Pertermann and Hirschmann, 2003a, 2003b) as a function of pressure and degree of melting using the bicubic spline method (Press and others, 2002) to interpolate data between experiments; and 4) point PK marks the intersection of olivine control line (defined by a given Ko'olau sample) with the mixing line between model primitive Lō'ihī-like melt and eclogite melt, and is our model estimate for the composition of the parent melt from which a Ko'olau lava differentiated.

To find the location of PK, we establish an optimizing algorithm to minimize the overall distance in major element composition space between the parental melt of a Ko'olau sample and the mixing line by iteratively varying the eclogite/

pyroxenite melt composition given these constraints. Although it is clear that a wide range of compositions and proportions of eclogite melt could explain equally well the composition of Ko‘olau lavas in the FeO-MgO space (fig. 6), the end member compositions, mixing proportions and extent of fractional crystallization can be constrained when we perform this geometric analysis simultaneously in all major-element dimensions (SiO₂-MgO-FeO^T-CaO-Al₂O₃-TiO₂-Na₂O; other than TiO₂ which we note is systematically too high in all experimental melts we considered, and will be discussed in the *The Titanium Puzzle* section of this paper). We only perform this optimizing procedure on Ko‘olau lavas with ≥ 6.5 weight percent MgO to restrict ourselves to compositions of lavas that are on the olivine control line. If a Ko‘olau whole rock has $Mg\# > 0.706$ (melts in equilibrium with Fo_{88.5} olivine—the majority of olivine phenocrysts in Ko‘olau lavas based on Norman and Garcia, 1999; Norman and others, 2002), this sample is assumed to be a mixture of melt and Fo_{88.5} olivines, and a melt based on unmixing enough Fo_{88.5} olivine to get $Mg\# = 0.706$ in the liquid is calculated and then used in the optimization procedure (the correlations between calculated mixing proportions with geochemical indices are shown in fig. 7).

Once the major-element compositions and mixing proportions of the depleted and enriched end members are determined for each sample, we then calculate the concentrations and, when appropriate, isotopic compositions of other elements in the enriched end member by assuming that the depleted end member is the primary melt of Lō‘ihi glass (trace element and isotopic compositions are adopted from Garcia and others, 1993), and solving for the composition of the enriched component by mass balance. Mixing lines are then forward-calculated in major element, trace element, and isotope spaces and compared independently with trends defined by data for samples (mixing lines are shown in fig. 8).

Finally, based on melting conditions, inverted mixing proportions, and the trace element partition coefficients determined in the same set of MORB-like eclogite experiments (Pertermann and others, 2004), trace element and isotope compositions of this eclogite component can be calculated for both models; these are presented in figure 9 and tables 2 and 3.

Model Result

The calculation described above was carried out for 196 samples from Makapu‘u lavas, KSDP drill core, and submarine landslide blocks from Ko‘olau volcano for the two cases mentioned above (Case I and Case II). Results are shown in figures 7 through 10. A detailed calculating example is also presented in table 2 for Ko‘olau sample KOO-8 (Frey and others, 1994) in Case I. In both cases, 23 out of 196 lavas that are strongly altered by post-eruptive weathering ($K_2O/P_2O_5 < 1.0$ or > 3.0) will not normally converge to an acceptable minimum in the optimization procedure, and are therefore not shown in figures 7 through 10.

In Case I, the major element composition of the single eclogite melt is searched through experimentally-determined eclogite melt composition space. The optimization solution suggests: 1) most lavas require Lō‘ihi primary melt to have $Mg\# = 0.77$ (this was originally set as a limit for Lō‘ihi primary melt in order to co-exist with Fo_{91.5} olivine); six out of 173 samples require $Mg\# = 0.702\sim 0.77$, indicating their peridotite melt end members are fractionated melt. Variation in $Mg\#$ by 0.03 around $Mg\# = 0.77$ will change the mixing ratio by 1.2 percent. (2) Eclogite melt from the melting experiment A200K (Pertermann and Hirschmann, 2003b) is the best candidate among the available melting experiments for the enriched component. This melt is produced from starting material G2k at 30 kbar, 1275°C after melting 14.3 percent of a MORB-like eclogite with clinopyroxene, garnet, quartz and rutile as coexisting phases. Our preferred model eclogite melt is

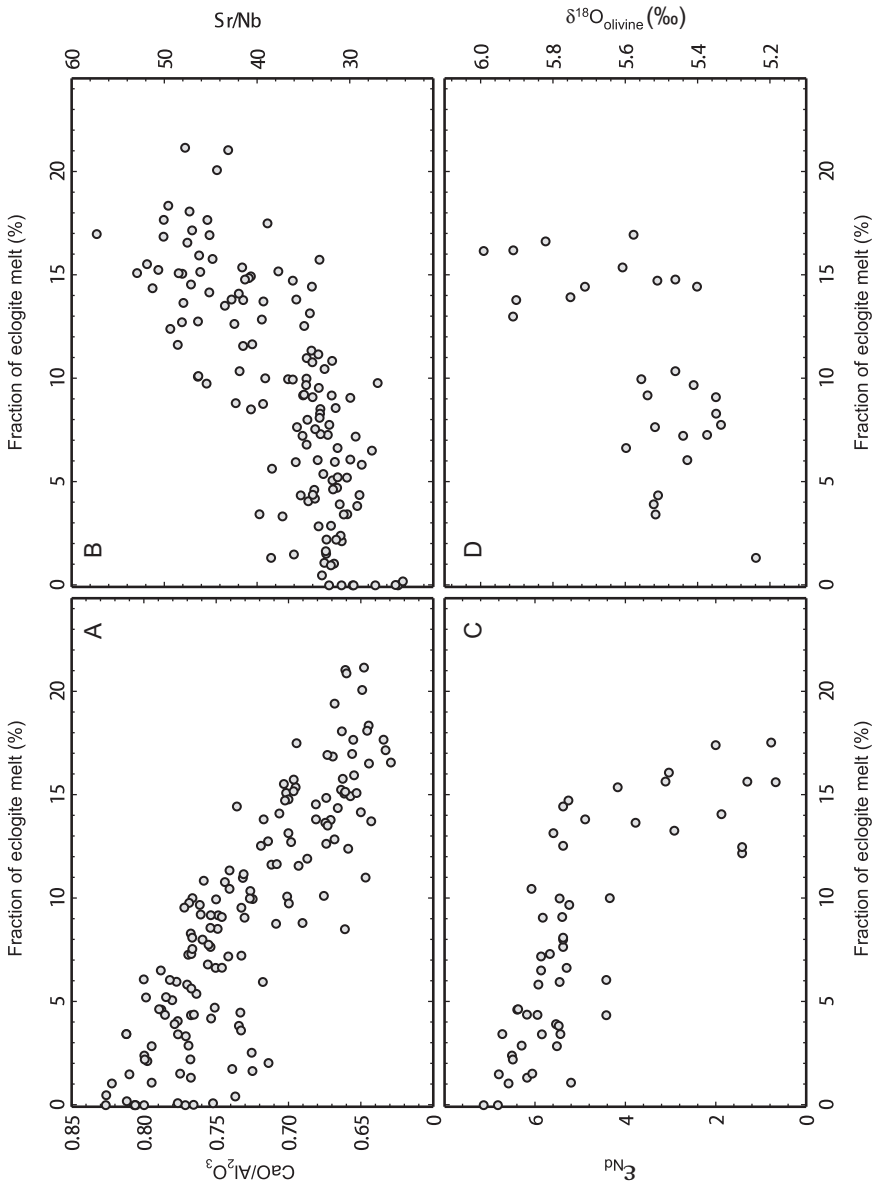


Fig. 7. The calculated proportion of eclogite melt (Case I fitting) for Ko'olau samples varies with four geochemical indices: (A) $\text{CaO}/\text{Al}_2\text{O}_3$; (B) Sr/Nb ; (C) ϵ_{Nd}^t ; (D) $\delta^{18}\text{O}_{\text{VSMOW}}$ values of olivines. $\text{CaO}/\text{Al}_2\text{O}_3$, Sr/Nb , and ϵ_{Nd}^t are for whole rock samples. Original data are from the same references in the captions of figures 2 and 3.

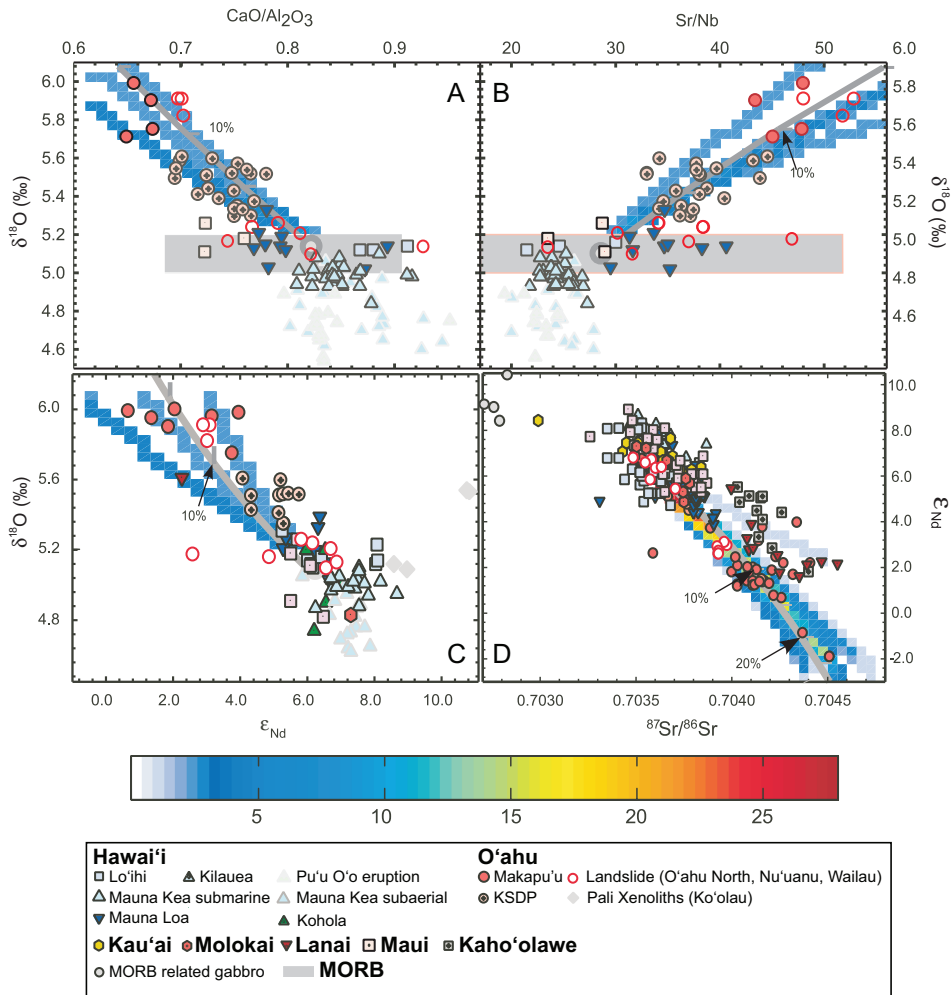


Fig. 8. Correlation between oxygen isotope compositions of olivines and different geochemical indices of their host lavas. (A) $\text{CaO}/\text{Al}_2\text{O}_3$ vs. $\delta^{18}\text{O}_{\text{olivine}}$; (B) Sr/Nb vs. $\delta^{18}\text{O}_{\text{olivine}}$; (C) ϵ_{Nd} vs. $\delta^{18}\text{O}_{\text{olivine}}$; and (D) ϵ_{Nd} vs. $^{87}\text{Sr}/^{86}\text{Sr}$. Only tholeiites are shown here. Faded symbols are from Pu'u O'o eruption of Kilauea volcano and subaerial Mauna Kea volcano (Eiler and others, 1996a; Eiler and others, 1996b; Garcia and others, 1998; Huang and Frey, 2003; Wang and others, 2003; Rhodes and Vollinger, 2004; Bryce and others, 2005). They represent progressive rift zone contamination, therefore deviate from the main mixing trend. Dark gray lines with a tick mark at every 5% percent are binary mixing lines between primary melt of Lo'ihii and inverted average parent melt of Ko'olau lavas. Mosaic color blocks are statistical presentation of the frequencies at which mixing lines occur within a region for Case II with various degree of melting. Both models adequately describe the compositional variations of Ko'olau lavas in all of the major-element, trace-element and radiogenic-isotope dimensions considered. Gray diamonds are Pali xenolith data from Ko'olau volcano. They were suggested to reflect the metasomatism of lithospheric mantle by enriched eclogitic melts (Ducea and others, 2002). MORB zones are defined after previous work (Hofmann, 1988; Note the gray zone represent 1σ variation).

similar to the dacitic melt component proposed by Hauri (1996) in SiO_2 , Al_2O_3 , FeO , Na_2O and K_2O , but significantly different in MgO and CaO . In Case II, the degree of melting of the eclogite is considered as an additional variable during the minimization. The residuals for this model are expectedly much smaller than for Case I. The optimization solution suggests that: 1) Lo'ihii primary melt has $\text{Mg}^\# =$

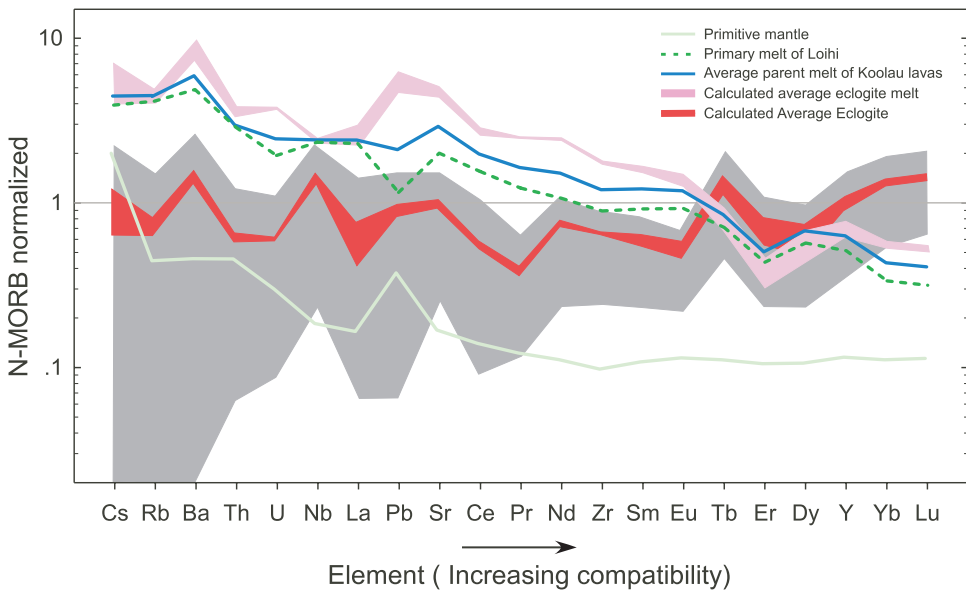


Fig. 9. N-MORB normalized average trace element concentrations of the calculated eclogite source rock (for both Case-I and II), compared with primitive mantle (Hofmann, 1988), primary melt from Lō'ihi and average parental melt of Ko'olau lavas (for Case-I). Both models have the similar patterns in the composition of the inverted eclogite, but inversion results for Case-I have a limited variation in large ion lithophile elements. Calculated eclogite source rock has N-MORB like HREE pattern, but different from melt inclusions from Mauna Loa (Sobolev and others, 2000). The primitive melts of Lō'ihi lavas in general can be interpreted as <10% melting of primitive mantle. The gray area surrounding the inverted average trace element concentrations of eclogite source rock combines $\pm 1 \sigma$ range of case-I and case-II, which is calculated by propagating the uncertainties of the trace element compositions and mixing proportions. Note that only calculated positive concentrations are averaged and plotted here. Some inverted concentrations of highly incompatible elements Cs, Rb and Ba have negative numbers probably because the estimation of mixing proportion has large errors and these elements are very sensitive to estimation of degree of melting and mixing proportion (see DISCUSSION section for details). The calculated average eclogite sources appear to have anomalous pattern (for example, positive Tb and negative Pr anomaly relative to the neighboring trace elements). These elements also have bigger relative errors comparing with neighboring trace elements. These errors are derived from concentration measurements (their concentrations are typically lower than other trace elements), and error propagation, and therefore, are not discussed in the paper.

0.59 ~ 0.77, and the parent melt of Ko'olau lava has $Mg^\# = 0.56 \sim 0.77$; 2) the degree of melting of the eclogite varies from 0 ~ 0.60 over a pressure range of 15 ~ 35 kbar (fig. 10); and 3) the mixing ratio varies from 0 ~ 0.77, with an average value of 0.27 (fig. 10).

Model Consistency and Sensitivity

Figure 7 shows a) Ca_2O_3/Al_2O_3 ; b) Sr/Nb; c) ϵ_{Nd} ; and d) $\delta^{18}O_{VSMOW}$ for all Ko'olau volcanoes (except strongly altered samples) as a function of calculated mixing ratios of eclogite/pyroxenite melt component required for fitting the major element composition (Calculation result for Case II is also similar to those shown in fig. 7). Figure 7A is essentially a consistency test of our model for Case I, as it compares a major element index with one of the fitted parameters that was calculated based on major element data. Other panels in figure 7 compare our model fits based on major elements with independent trace-element and isotope variables. All plots show that as the mixing ratio of eclogite melt component increases, major element, trace element, and isotope ratios of the Ko'olau lavas systematically trend towards an enriched end member and away

TABLE 2A
Binary mixing calculation results for major elements of a Ko'olau lava (KOO-8)

Oxides	Lō'ihī ^a (wt.%)	Ko'olau ^b (wt.%)	Eclogite Melt ^c (wt.%)	Ko'olau ^d (wt.%)
SiO ₂	47.14	49.10	63.64	49.11
TiO ₂	1.70	1.56	3.33	1.90
Al ₂ O ₃	9.54	10.22	15.35	10.23
FeO ^T	11.25	10.93	5.18	10.52
MnO	0.11	0.12	0.06	0.11
MgO	19.67	17.55	1.53	17.50
CaO	7.84	7.27	4.93	7.49
Na ₂ O	1.56	2.24	4.34	1.89
K ₂ O	0.25	0.35	1.63	0.41
Mg#	0.770	0.755	0.345	0.758
Optimized mixing proportion of eclogite melt			11.93	

^a The calculated primary melt of Lō'ihī lavas from sample KK29-10 by olivine addition (Byers and others, 1985; Dixon and Clague, 2001), trace element and isotopic compositions are inferred from other Lō'ihī glasses (García and others, 1993).

^b The calculated parent melt of Ko'olau lava KOO-8 by olivine addition, major element, trace element and isotope compositions are from Frey and others (1994), Roden and others (1994), Lassiter and Hauri (1998), Blichert-Toft and others (1999), and Huang and Frey (2005).

^c The eclogite melt from a melting experiment at 30 kbar, 1275°C after melting 14.2% of a MORB-like eclogite with clinopyroxene, garnet, quartz and rutile as coexisting phases (Pettermann and Hirschmann, 2003b).

^d The calculated parent melt of Ko'olau lava KOO-8 by mixing Lō'ihī primary magma and eclogite melt with optimized eclogite proportion; note this calculated KOO-8 on the mixing line is very close to the result in *b*.

from the compositions of Lō'ihī lavas. In this case, they show that Ko'olau lavas from Makapu'u section, KSDP, and submarine landslides contain between 0 ~ 25 percent of the eclogite melt component, whereas in case II, this range is between 0 ~ 50 percent (fig. 10). These calculations indicate that the eclogite component has variable contributions to Ko'olau Lavas.

From this example, we can also estimate that the uncertainty in the mixing proportion for any given sample is approximately $\sim \pm 3$ percent (1σ), simply based on this being half of the range in mixing proportion for a given value of one of the geochemical indices that correlate with the amount of eclogite melt (although the scatter is higher for fig. 7D). We suspect these uncertainties are caused by the geochemical variation in Lō'ihī primary melts and the eclogite component, and the precision in measuring these geochemical quantities. In general, our inversion method results in large uncertainties in the composition of the enriched component contributing to relatively depleted lavas, but acceptably small uncertainties in more enriched lavas. Therefore, only mixing proportions larger than 5 percent are considered in the further discussion of properties of the eclogitic end member. We propagate these errors to the final inverted eclogite melt composition (typically $\sim 30\%$, much higher for highly incompatible elements). In the next section, we will first evaluate and test our models using geochemical observations and discuss the properties of the enriched end member.

DISCUSSION

Evaluating the Mixing Model with Geochemical Data

Our mixing model has the potential to explain most of the geochemical variations seen in shield-building lavas from "Loa-trend" volcanoes, including Lō'ihī, Mauna Loa,

TABLE 2B

Calculation result for trace elements of the parent melt of a Ko'olau lava (KOO-8)

	Lō'ihī ^a (ppm)	Ko'olau ^b (ppm)	EclogiteMelt ^c (ppm)	D _{Total} ^e	Eclogite ^f	NMORB ^g	N-MORB Normalized
ICP-MS analyses ^h							
La	9.32	8.89	6.41	0.021	1.03	3.895	0.26
Ce	19.73	22.79	46.04	0.044	8.32	12.001	0.69
Nd	12.61	15.59	38.25	0.164	10.85	11.179	0.97
Sm	3.61	3.97	6.69	0.233	2.29	3.752	0.61
Ba	73.70	83.15	154.87	0.006	22.94	1.335	1.65
Eu	1.27	1.32	1.68	0.241	0.59	0.885	0.44
Dy	3.70	3.35	0.65	1.027	0.66	3.9	0.10
Er	1.82	1.63	0.25	1.795	0.43	0.589	0.10
Yb	1.32	1.28	0.93	2.553	2.16	13.87	0.55
Lu	0.19	0.18	0.07	2.903	0.19	3.507	0.33
Y	17.93	18.93	26.53	1.38	35.17	35.82	0.98
Hf	2.21	2.69	6.34	0.302	2.55	2.974	0.86
Rb	6.00	5.32	0.19	0.004	0.03	1.262	0.02
Cs	0.06	0.06	0.06	0.004 ⁱ	0.01	0.01408	0.62
ICP-ES analyses ^j							
K	2689.72	2900.50	4508.10	0.024	737.38	883.7	0.83
Sr	236.63	356.35	1265.19	0.054	239.47	113.2	2.12
Ba	78.11	83.15	121.37	0.006	17.98	13.87	1.30
Zr	95.30	114.33	258.77	0.233	88.68	104.24	0.85
La	8.10	8.98	15.70	0.021	2.53	3.895	0.65
Nd	12.02	15.59	42.67	0.164	12.10	11.179	1.08
Sm	3.14	3.97	10.26	0.233	3.52	3.752	0.94
Eu	1.09	1.32	3.05	0.241	1.06	1.335	0.80
Dy	2.94	3.35	6.44	1.027	6.59	6.304	1.05
Yb	1.20	1.28	1.87	2.553	4.36	3.9	1.12
Lu	0.17	0.18	0.27	2.903	0.70	0.589	1.19
Th	0.55	0.50	0.11	0.0034	0.02	0.1871	0.09
Y	15.27	18.93	46.71	1.38	61.92	35.82	1.73
Pb*	0.40 ^k	0.95	5.12	0.001 ^l	0.74	0.489	1.50

^{a, b, c} are the same as in table 2B.^e Unless otherwise noted, partition coefficients are experimentally determined for A200K (G2k, Pertermann and Hirschmann, 2003b).^f Inverted trace element concentrations of the eclogite.^g Trace element concentrations of N-MORB is from Hofmann (1988).^h Trace element concentrations are averages of Lō'ihī glasses and KOO-8 lavas measured by ICP-MS (García and others, 1993; Huang and Frey, 2005).ⁱ Cs partition coefficient is estimated to be the same as Rb.^j Trace element concentration using averages of Lō'ihī glasses by ICP-ES (Frey and others, 1994).^k Pb concentration is estimated using $Pb = 0.0866 \times La - 0.30$, based on linear regression ($R^2 = 0.9$) over samples measured for both La and Pb of Ko'olau lavas from GEOROC database (<http://georoc.mpchmainz.gwdg.de/georoc/>).^l An estimated value.Note in ⁱ and ^l trace element composition of Cs and Pb in the melt is controlled mostly by the degree of melting (>10%) and their concentration in the source rock due to their significantly low partition coefficients.

TABLE 2C
 Calculation result for isotope mixing end-members for a Ko'olau lava
 (KOO-8)

Isotope ratio	Lō'ihī ^m	Ko'olau ^o	Eclogite Melt ^p
$\delta^{18}\text{O}_{\text{VSMOW}}^m$ (‰)	5.65	6.30	11.1
$^{87}\text{Sr}/^{86}\text{Sr}$	0.70361	0.70408	0.70475
$^{143}\text{Nd}/^{144}\text{Nd}$	0.51296	0.51271	0.51209
$^{206}\text{Pb}/^{204}\text{Pb}$	18.252	17.879	17.659
$^{207}\text{Pb}/^{204}\text{Pb}$	15.433	15.447	15.455
$^{208}\text{Pb}/^{204}\text{Pb}$	38.001	37.826	37.723
$^{176}\text{Hf}/^{177}\text{Hf}$	0.28311	0.28294	0.28249

^m Whole rock $\delta^{18}\text{O}_{\text{VSMOW}}$ value, assuming fractionation factor between melt and olivine is 0.5‰ (Eiler and others, 2000; Eiler, 2001).

^o The average value of all samples from published Lō'ihī glasses and a Ko'olau lava, KOO-8 (Frey and others, 1994; Roden and others, 1994; Eiler and others, 1996a; Lassiter and Hauri, 1998; Blichert-Toft and others, 1999).

^p The calculated isotopic composition of the eclogite melt end-member in the mixing model.

east O'ahu (Makapu'u, Landslides, KSDP, and Pali xenoliths), Kauai, Lanai, and Kaho'olawe (for example, figs. 7 and 8), using mixing end-members listed in tables 2 and 3. Figure 8 illustrates the characteristic mixing curves in $\text{CaO}/\text{Al}_2\text{O}_3$ vs. $\delta^{18}\text{O}_{\text{olivine}}$, Sr/Nb vs. $\delta^{18}\text{O}_{\text{olivine}}$, ϵ_{Nd} vs. $\delta^{18}\text{O}_{\text{olivine}}$, and ϵ_{Nd} vs. $^{87}\text{Sr}/^{86}\text{Sr}$ spaces, compared with compiled geochemical data from other Hawaiian lavas (Roden and others, 1984; Frey and others, 1994; Roden and others, 1994; Eiler and others, 1996a; Eiler and others, 1996b; Lassiter and others, 1996; Garcia and others, 1998; Lassiter and Hauri, 1998; Blichert-Toft and others, 1999; Dixon and Clague, 2001; Garcia, 2002; Huang and Frey, 2003; Wang and others, 2003; Haskins and Garcia, 2004; Huang and Frey, 2005; Salters and others, 2006; Fekiacova and others, 2007). The binary mixing lines in figure 8 (dark gray) are constructed from Case I. They pass through compositions of most "Loa trend" Hawaiian lavas, and particularly the three suites of Ko'olau lavas (Makapu'u, Landslides, and KSDP). More importantly, the mixing proportions are consistent among all geochemical indices. That is, a model description of one set of chemical

TABLE 3

The calculated radiogenic isotope composition of the eclogite end member using different models compared with enriched-mantle and the calculated depleted mantle model age based on Nd isotopes

	Case I	Case II	EM-I ^q
$^{87}\text{Sr}/^{86}\text{Sr}$	0.70507(32)	0.70458(23)	0.704 ~ 0.706
$^{143}\text{Nd}/^{144}\text{Nd}$	0.51222(13)	0.51246(9)	< 0.5123
$^{206}\text{Pb}/^{204}\text{Pb}$	17.30(25)	17.55(16)	16.8 ~ 17.8
$^{176}\text{Hf}/^{177}\text{Hf}$	0.28258(5)	0.28275(3)	
$\delta^{18}\text{O}_{\text{VSMOW}}$ (whole rock)	9.7(1.5)	7.8(1.0)	
DMM-Model Age (Ga) of melt mixed	1.3(0.2)	1.2(0.2)	
DMM-Model Age (Ga) of source rock	1.7(0.4)	0.46(0.07)	

Note: Units in parentheses represent one standard deviations of the least units, thus 9.7(1.5) should be read as 9.7 ± 1.5 .

^q The isotopic composition of the enriched mantle is from Zindler and Hart (1986).

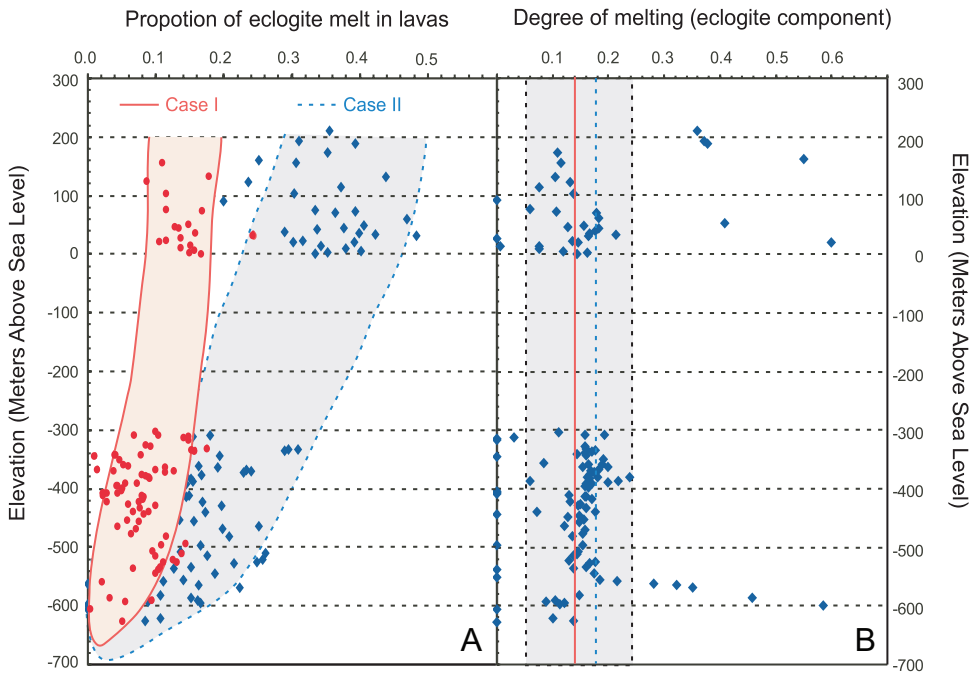


Fig. 10. The stratigraphic profile of the inverted mixing proportions of eclogite/pyroxenite component in (A), and the extent of melting of this component in (B). Vertical axis represents the stratigraphic position in the KSDP core, and Makapu'u stage Ko'olau lavas in meters above sea level. The inversion for the submarine landslide samples are not shown here because their stratigraphic positions are not well-defined.

indices in one 2-dimensional plot is generally consistent with the position of that sample in some other 2-dimensional plot. This internal consistency of the model across composition space is the primary strength of our approach to this problem.

The mosaic color grids in figure 8 are a statistical presentation of the frequencies at which mixing lines occur within a region for Case II (allowing for a range of degrees of melting of the enriched component). The color spectrum from white to red represents the number of forward-modeled mixing curves that pass through each given block (0 to 30 curves, the block width is 0.05‰ for $\delta^{18}\text{O}_{\text{olivine}}$, 50 ppm for $^{87}\text{Sr}/^{86}\text{Sr}$, 0.04 for ϵ_{Nd} , 2.0 for Sr/Nb, 0.02 for CaO/Al₂O₃). As shown in figure 8, blocks seeing most mixing curves follow closely the mixing curve in Case I, and the composition of most “Loa-trend” Hawaiian lavas. That is, when we permit the degree of melting of the eclogite source to vary freely from sample to sample, the mean result closely resembles that obtained by simply adopting a single, average degree of melting. Because melt composition does not necessarily vary linearly with degree of melting, this was not a necessary or circular result. These calculations show that both models adequately describe the compositional variations of most Ko'olau lavas in major-element, trace-element and radiogenic-isotope dimensions. Therefore, these models provide a self-consistent description of the production properties and mixing proportions of eclogite melt and peridotite melts contributing to Hawaiian lavas.

A large number of calculated concentrations of several elements, including TiO₂, Ta, Nb, Rb and Cs, and some minor elements in olivines (for example, Cr, Ni) are negative numbers for the eclogite melt component (that is, concentrations of these elements in parent melt of Ko'olau lavas are significantly lower than those of primitive

melt of Lō‘ihi lavas). These unreasonable values are not shown in figure 9. We suggest that these anomalies could derive from the following sources: 1) highly incompatible elements such as Cs, Rb, and Ba are sensitive to measurement errors and modeling uncertainties (for example, wide variations in the calculated eclogite component in fig. 9), the variations of these elements are also large even in modern MORBs compared with other trace elements (for example, Hofmann, 1988); 2) errors or oversimplifications in our description of fractional crystallization corrections, mixing, melting, and/or the effects of melt-rock interaction; or 3) the limitation inherited from defining experimental eclogite melt as our enriched end-member, that is, TiO_2 in the starting material of these experiments is much higher than what has been estimated for MORB (1.97 vs. 1.268 wt.%). Some of these issues will be elaborated in sections titled *Understanding the Ni Problem* (Ni) and *The Titanium Puzzle* (TiO_2).

Properties of the Enriched Component

Figure 9 shows the trace element compositions of the primitive mantle, the calculated primary melt of our representative Lō‘ihi lava, the calculated average parent melt of Ko‘olau lavas, and the calculated average enriched component (the eclogite melt component), all normalized relative to N-MORB and plotted in the order of increasing compatibility (primitive mantle and N-MORB from Hofmann, 1988, similar results will be obtained if using Workman and others, 2004). Several features can be noticed in this figure. First, the heavy REEs of current N-MORB (more compatible than Sr) indicate it can be produced by ~ 10 percent batch melting of the primitive mantle (much less if it melts in fractions), consistent with Workman and Hart (2005) who estimate current NMORB is produced by ~ 6 percent melting of DMM that was depleted by 2 to 3 percent over geological time. Second, the typical primitive melt of Lō‘ihi lavas (inverted using KK29-10, Byers and others, 1985; Dixon and Clague, 2001) is more depleted in heavy rare earth element pattern (HREE, for example, Y, Yb, and Lu), but more enriched in light rare earth element pattern (LREE) than NMORB, consistent with a garnet signature (for example, as also observed by Dixon and Clague, 2001). This observation suggests that primitive melt of Lō‘ihi lavas has garnet in its residue and/or interacted with garnet in the sub-oceanic mantle during its ascent. Third, Pb concentration in the primitive melt of Lō‘ihi lavas is similar to that of NMORB, producing a negative Pb anomaly (relative to La and Sr) larger than that of NMORB. This negative Pb anomaly cannot be produced by melting a mixture of primitive mantle and depleted mantle rocks or primitive mantle and recycled oceanic crust. Instead, it requires a Pb-compatible phase in the melting source (for example, sulphide, Hart and Gaetani, 2006) and/or interaction with such a phase during its ascent (for example, sulphide or plagioclase). The calculated average parental melt of Ko‘olau lavas has a higher concentration of Pb and a smaller Pb anomaly, presumably due to the high Pb content of eclogite melt. Finally, the two cases (Case I and II) produce similar average trace element patterns for the eclogite melts and source rocks (outlined by pink and red envelopes, respectively), and our model suggests this calculated eclogite component has average trace element abundances (particularly heavy REE) similar to mid-ocean-ridge basalts (NMORBs), implying the protolith of this source is recycled NMORB-like basalts and consistent with our *a priori* assumption for the major element composition.

The gray zone surrounding the inverted average eclogite source rock composition in figure 9 combines the $\pm 1\sigma$ range of both cases, each of which is calculated by propagating the uncertainties of the trace element compositions and mixing proportions. The HREEs of the calculated eclogite span a narrow range. In contrast, highly incompatible elements except Cs, Rb and Ba (for example, Th, U, La, Pb, and Ce) have large variations from close to NMORB to extremely low values. The range of variations for these elements are larger than the uncertainties introduced from our inversion

calculation procedures, and could be derived from the following possible sources: 1) some of this recycled MORB-like basalt (the source rock of the our enriched component) might have undergone partial melting or fluid-mobilization prior to the melting event in the Hawaiian plume (for example, during its ancient subduction), and/or 2) the eclogite source rock is heterogeneous, that is, the protolith is composed of various constituents of the oceanic crust (including cumulates, which are generally poor in the most incompatible elements).

Table 3 lists the isotopic compositions of the enriched component and its partial melts. In both models, our inverted isotopic composition of this eclogite source rock agrees well with the previous definition of the EM-I reservoir (for example, Stille and others, 1983; Hart and Zindler, 1989) in Sr, Nd and Pb isotope composition space (in tables 2 and 3), implying the source materials for EM-I reservoir could be partial melts from recycled crust (though the obverse is not universally true, since EM-I type OIBs lack the oxygen isotope anomaly characteristic of Ko'olau lavas, Eiler and others, 1995). Case I and Case II predict that oxygen isotope compositions of this enriched component are 9.7 ± 1.5 permil and 7.8 ± 1.0 permil, respectively, consistent with an origin as upper oceanic crust with a low-temperature alteration history, possibly with a minor component of pelagic sediments.

Estimation of the Amount of Recycled Materials in Hawaiian Mantle Plume

Our models can be used to estimate the degree of melting of the eclogitic component and amount of the melt contributing to Hawaiian lavas. Figure 10 shows the melt mixing proportion (fig. 10A) and degree of melting (fig. 10B) of the enriched component calculated from KSDP and Makapu'u lavas as a function of stratigraphic position. The mixing ratios progressively increase as the shield-building stage of Ko'olau volcano approaches its end (0 to 15% in Case I and 0 to 40% in Case II). The degree of melting is fixed (ca. 14.3%) in Case I, but varies within 0 to 25 percent with occasional excursion to 60 percent in Case II. Even in Case II, the degree of eclogite/pyroxenite melting varies little throughout most of the studied section except at a few excursions. Therefore, these calculation results imply that the mixing ratios of the eclogite partial melts and the geochemistry of Ko'olau lavas are mostly determined by the degree of peridotite melting, the variation in the amount of eclogite in the mantle plume, or both of these (but not the degree of eclogite melting).

Our calculations can provide constraints on the amount of recycled materials in Hawaiian mantle plume. By integrating over the lower section of Ko'olau lavas (between 300-650 mbsl), we can estimate the average melting degree of the eclogite is around 14.3 percent for Case I and 16 percent for Case II, and the mixing ratios average ~ 7.5 percent for Case I and ~ 15 percent for Case II. Assuming 10 percent peridotite melting based on the calculated trace element concentration of primitive melt of Lō'ihi lavas (primitive Lō'ihi lavas should have $\leq 10\%$ peridotite melting that results in N-MORBs in fig. 9), we find that a mantle plume composed only of fertile mantle and eclogite blocks contains 5 to 9 weight percent recycled crust. When the upper section is integrated, that is, from the top of the Makapu'u section to the end of H3 tunnel section (0-200 m), the mixing ratios average about 15 percent for Case I and 35 percent for Case II and the degree of melting of the eclogitic source is about 14.3 percent for Case I and about 17 percent for Case II. In this case, the following two estimations can be conducted: 1) the fraction of recycled crust in the plume source could be constant at 5 to 9 weight percent but the degree of melting of the peridotite fraction decreases to ~ 4 percent; and 2) the degree of melting of the peridotite remains at ~ 10 percent but the fraction of recycled crust in the plume source increases to 10 to 24 weight percent. The formal estimation is consistent with several studies that suggest a specific thermal structure of Hawaiian plume underneath Ko'olau volcano, that is, the plume center moves away from Ko'olau volcano, peridotite melting is

reduced relative to eclogite melting as mantle temperature decreases (for example, Haskins and Garcia, 2004; Huang and Frey, 2005; Ren and others, 2005; Fekiacova and others, 2007; Tanaka and others, 2008), because experimental petrology demonstrates that eclogite/pyroxenite or metasomatized peridotite typically have lower solidus temperature than mantle peridotite at a given pressure (for example, Takahashi and Nakajima, 2002; Pertermann and Hirschmann, 2003a). The latter estimation approaches but is still lower than the estimate of >26 percent recycled crust by Sobolev and others (Sobolev and others, 2005) based on compatible minor elements (for example, Ni, Mn and Cr) in olivines. Our model is not able to distinguish between these two possibilities (constant vs. variable degree of melting of the peridotite component over the later shield-building stage of Ko'olau volcano), because reducing peridotite melting from 10 percent to 4 percent will not significantly alter the major element composition, and variation of incompatible elements is around a factor of two (fig. 10). But our calculations indicate that any estimation of the amount of eclogite in the mantle should not just be based on extreme compositions, but rather consider the spatial distribution of samples that contain eclogite melt component and appropriate thermal structure. Because the estimation of 10 to 24 weight percent is based on the largest amount of peridotite melting (10%) and this component also contributes largest to Makapu'u stage Ko'olau lavas according to the isotope mixing relationship, our estimate (10-24 wt. %) offers an upper limit on the amount of recycled crustal materials in the Hawaiian plume. Therefore, our modeling exercise reveals that the amount of eclogite component in the mantle could be overestimated using compatible minor elements (for example, Ni) in olivines (Sobolev and others, 2005; Sobolev and others, 2007; Sobolev and others, 2008) because the concentrations of these elements in the crystallized olivines are sensitive to the chemistry of the melting mixtures, but they are less sensitive to the low degree of peridotite partial melting.

We can also estimate that the total volume of eclogite that passed through the melting column beneath Ko'olau volcano during its Makapu'u stage is about 250 to 540 km³ using the estimated volume of 1,100 to 2,300 km³ for the Makapu'u stage Ko'olau lavas (Takahashi and Nakajima, 2002; Haskins and Garcia, 2004). It corresponds to a sphere 8 to 10 km in diameter if it is one block (though we have no reason to suggest it is). Recent theoretical study suggests that spherical blobs of recycled material are highly unlikely due to dynamic stretching in the plume flow (Farnetani and Hofmann, 2009). This indicates the cross section of the filaments should be smaller than 8 to 10 km by some geometric factor, even if in the form of a single block, and likely smaller still if multiple filaments are present. Single eclogite lenses larger than a few kilometers across can survive diffusive re-equilibration of trace element and isotope ratios with enclosing peridotite over billion-year timescales in the absence of intergranular melts (for example, Zindler and Hart, 1986). But meter size blocks cannot escape recent homogenization after melt has been produced, except for the most compatible elements (for example, Kogiso and others, 2004). Current geophysical tools (seismic tomography, receiver function and reflection method) could at best detect heterogeneous domains larger than a few tens of kilometers across in the shallow upper mantle (for example, Dunn and Forsyth, 2003). These eclogite blocks are therefore not readily detectable, even if there is only one block, using current technology.

Understanding the Ni Problem

Our inverse model failed to correctly predict the concentration of some minor elements (for example, Ni and Cr) in the primitive melt of Lō'ihī lavas and the eclogite melt (giving negative concentrations) because the partition coefficients of these elements are strongly sensitive to variations in melt composition. Wang and Gaetani (2008) show that NiO contents of olivines from Kilauea lavas are significantly higher

than predicted using simple fractional crystallization model after 10 percent olivine precipitation, suggesting olivine accumulation plays a key role in partitioning Ni between the melt and olivines at a later stage of the fractionation process. Therefore, our model, which assumes simple fractional crystallization, will overestimate Ni content in the melt—more for the primitive melt of Lō‘ihi lavas than for the parent melt of Ko‘olau lavas (in other words, more olivine addition is needed to bring Lō‘ihi lavas into equilibrium with $F_{0.1}$ than to bring Ko‘olau lavas into equilibrium with $F_{0.88.5}$). Thus, the low Ni content in eclogite melt (a few tens of ppm, compared with hundreds of ppm in lavas, Sobolev and others, 2005) is smaller than modeling uncertainty caused by this effect, and thus difficult to calculate. Additionally, our calculated Ni content of primitive melt of Lō‘ihi lavas is significantly higher than the parent melt of Ko‘olau lavas, which is not predicted in olivine-free mantle source model (Sobolev and others, 2005).

However, our melt-mixing model can explain high-Ni olivines from Ko‘olau lavas. Anomalously high Ni content in olivines from Ko‘olau lavas were first observed by Garcia (2002), later used to support the olivine-free source model (Sobolev and others, 2005), and served as a basis for estimating a large amount of recycled crust in the Hawaiian plume (26% for Mauna Loa lavas and much higher in Koolau lavas, for example, Sobolev and others, 2005; Sobolev and others, 2007). Using the calculated primitive melt of Lō‘ihi lavas and one eclogite melt (table 2), Wang and Gaetani (2008) show high-Ni olivines naturally precipitate from the melt mixtures, and Ni content in olivines increases with increasing proportion of eclogite melt component in the melt mixture, due to strong dependence of the olivine/melt partition coefficient for Ni on melt chemistry (the Ni partition coefficient could increase by a factor of two after mixing between peridotite and eclogite partial melts or the eclogite melt-peridotite interaction, for example, Wang and Gaetani, 2008). A similar effect should be present for other minor compatible elements such as Cr and Co and ignoring this effect will lead to an overestimate of the fraction of petrological and chemical heterogeneities in the Hawaiian mantle plume.

The Titanium Puzzle

As mentioned in the section titled *Model Construction* (also shown in fig. 5) our model also failed to correctly predict the TiO_2 content of the eclogite melt, because all melts from known eclogite/pyroxenite melting experiments (using starting material with composition similar to MORBs) have TiO_2 contents too high to be a mixing end-member for lavas from Ko‘olau volcano. More interestingly, TiO_2 contents of Ko‘olau lavas are systematically lower than those of Lō‘ihi lavas (fig. 5C), and TiO_2 contents of the Makapu‘u stage Ko‘olau lavas are systematically lower than those of lavas from lower sections of KSDP drill core (or Mauna Loa lavas) at a given MgO content (for example, Haskins and Garcia, 2004). This presents a puzzle, as isotopic and most major element evidence suggests that Makapu‘u stage Ko‘olau lavas contain the highest proportion of eclogite/pyroxenite melt, TiO_2 content (which is very high in experimental melts of this kind) seems to suggest that Makapu‘u stage lavas have the lowest proportion of eclogite melt.

High TiO_2 content, as well as elevated Ta and Nb abundances, has been observed in OIBs globally by several recent studies. For example, Prytulak and Elliott (2007) pointed out that peridotitic mantle generally cannot produce titanium-rich OIBs, calling upon ~10 percent recycled mafic crust that could melt deeper during ascent. Jackson and others (2008) reveal that extremely high Ti, Ta and Nb correlate with $^3He/^4He$ and $^{187}Os/^{188}Os$ in OIBs from a few ocean islands, proposing these OIBs were derived from a mixture of 20 to 25 percent ancient refractory eclogite (~3 Ga) and high $^3He/^4He$ primitive peridotites. Our observation from the three suites of Ko‘olau lavas argue that the high-Ti content of Lō‘ihi lavas could derive from deep

melting of primitive mantle, rather than the addition of MORB-like eclogite into the plume source.

To illustrate this, we first calculate the bulk partition coefficients for TiO_2 from peridotite and eclogite melting experiments as examples (Baker and Stolper, 1994; Walter, 1998; Pertermann and Hirschmann, 2003b). Because TiO_2 contents of pyroxene and garnet in these melting experiments are low (close to the detection limit of the electron microprobe) and the presence of minor phases could also contribute measurably to the partition coefficient (for example, rutile in eclogite), we here only consider the bulk partition coefficients calculated by TiO_2 in the melt, TiO_2 in the starting material and the degree of melting. As shown in figure 11 and table 4, this treatment has the advantage of reducing data-scattering at each experimental condition.

Since the TiO_2 partition coefficient between peridotite and melt is less than 0.077 (table 4), TiO_2 contents of partial melt from peridotite melting are mostly controlled by TiO_2 of the source rock and the extent of melting when melt fraction is >10 percent (fig. 11A). For example, using average bulk partition coefficient (0.068) determined at 1.0 GPa for spinel peridotite melting experiments (bulk $\text{TiO}_2 = 0.11\%$, Baker and Stolper, 1994) and $\text{TiO}_2 = 0.16$ weight percent, TiO_2 of the batch melt in the garnet peridotite experiments conducted at 3 to 7 GPa (Walter, 1998) can be predicted at higher degrees of melting ($>10\%$ fig. 11). The temperature and pressure effects on the bulk partition coefficient are secondary (only important for low degree of melting, for example, $<10\%$): partition coefficient of TiO_2 decreases slightly with increasing temperature, and even more subtly with decreasing pressure (fig. 11B). Composition also affects the bulk partition coefficient, that is, bulk partition coefficient for eclogite melt is higher than peridotite-melt by a factor of 4 to 10 due to the presence of rutile as a residue phase at melt fraction less than 10 percent and slightly higher partition coefficient of TiO_2 for clinopyroxene in the eclogite melting experiments (Pertermann and Hirschmann, 2003b).

These calculated bulk partition coefficients provide a constraint on the source of TiO_2 in Lō'ihī and Ko'olau lavas. For example, our model in the section titled A MAJOR ELEMENT MODEL OF KO'OLAU LAVAS estimated the primitive melt of Lō'ihī lavas contains ~ 1.7 percent TiO_2 (table 2). Our calculations show that TiO_2 of 0.22 ± 0.03 percent is needed for a garnet lherzolite to produce primitive melt of Lō'ihī lavas after 10 percent melting (table 4). This composition is consistent with $\text{TiO}_2 = 0.217$ percent in the primitive mantle (PM) estimated by Sun and McDonough (1989), slightly higher than 0.181 (PM estimate of Hofmann, 1988) and consistent with similar inferences of near-primitive source concentrations for moderately incompatible elements with bulk partition coefficients from ~ 0.04 to 0.08 (for example, Sr, Ce, Pr, Nd, and Zr, section titled *Properties of the Enriched Component*). High $^3\text{He}/^4\text{He}$ ratios and enriched trace element patterns of high- TiO_2 OIBs suggest they are derived from a primitive mantle source compared with DMM (the source of MORBs). Melting these rocks will facilitate producing high- TiO_2 basalts. Although the non-chondritic Sr-Nd isotopes of high $^3\text{He}/^4\text{He}$ basalts indicate they experienced small degree of partial melting, this melting could have occurred earlier whereas the ~ 10 percent inferred from trace elements is the apparent time-integrated extent of batch melting of an originally primitive source. It is also possible that the source of Lō'ihī lavas could contain mafic part of oceanic crust or old refractory eclogite (Prytulak and Elliott, 2007; Jackson and others, 2008), but source rocks of Lō'ihī lavas are unlikely to contain more than ~ 8 percent of mafic part of oceanic crust (assuming it has $\text{TiO}_2 = 1.268\%$, and the source of Lō'ihī lavas is as depleted as DMM that has $\text{TiO}_2 = 0.11\%$), significantly less if they were metasomatized by melts originated from deep melting of eclogite ($<3\%$ if eclogite melted by 10%). Moreover, melting at higher temperature

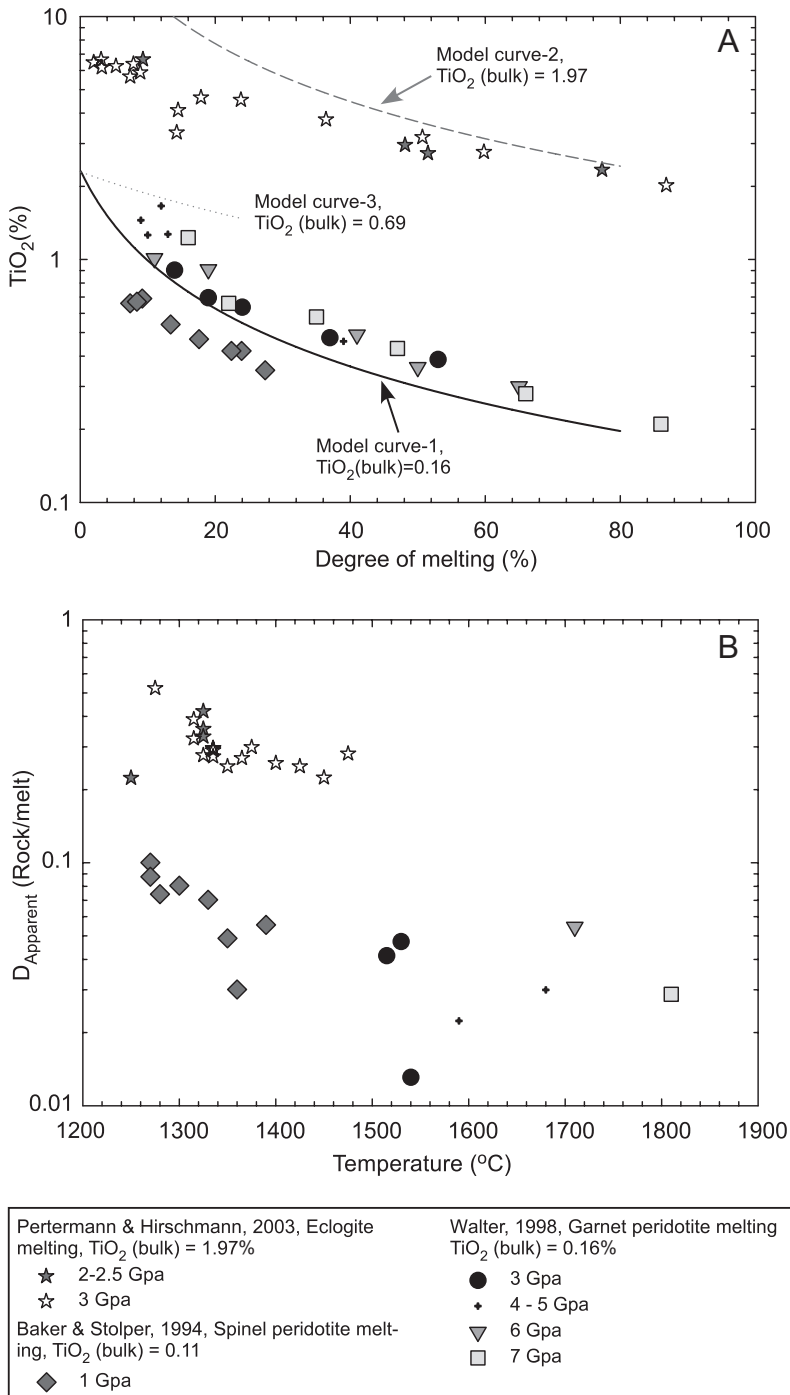


Fig. 11. TiO₂ partitioning between melt and rock in peridotite/eclogite melting experiments (Baker and Stolper, 1994; Walter, 1998; Pertermann and Hirschmann, 2003b): (A) TiO₂ contents of glasses varied as a function of the extent of melting; Model curves are calculated using 1) D_{TiO₂} = 0.068 (Baker and Stolper, 1994); TiO₂ (bulk) = 0.16% in model curve 1; 2) D_{TiO₂} = 0.068, TiO₂ (bulk) = 1.97% in model curve 2; and 3) D_{TiO₂} = 0.30 (Pertermann and Hirschmann, 2003b), TiO₂ (bulk) = 0.69% in model curve 3; (B) Bulk TiO₂ partition coefficients varied as a function of temperature.

TABLE 4
Calculated TiO₂ content of source rock for peridotite and eclogite melting

D _{TiO₂}	P (Gpa)	T (°C)	Lithology	TiO ₂ (bulk, ppm)	Ref
0.077(17)	1.0	1270-1350	spinel peridotite	0.29(3) ^r	Baker and
0.043(18)	1.0	1360-1390	spinel peridotite	0.24(3) ^r	Stolper(1994)
0.034(18)	3.0	1515-1540	Garnet peridotite	0.22(3) ^r	Walter(1998)
0.026(5)	4-5	1590-1680	Garnet peridotite	0.21(1) ^r	
0.33(8)	2.0	1250-1325	Eclogite	0.36(3) ^s	Pertermann and
0.30(7)	3.0	1315-1500	Eclogite	0.34(2) ^s	Hirschmann (2003b)

Units in parentheses as in table 3.

^r The calculated bulk TiO₂ content of peridotite that will produce TiO₂ = 1.7 wt.% melt after 10% batch melting.

^s The calculated bulk TiO₂ content of eclogite that will produce TiO₂ = 0.84 wt.% melt after 15% batch melting with/without rutile present.

will reduce the required TiO₂ content in the source of Lō'ihī lavas due to the slight decrease in bulk partition coefficient (table 4 and fig. 11). Petrological evidence shows that the primitive melt of Lō'ihī and Mauna Kea lavas is systematically higher in liquidus temperature than N-MORBs (by more than 200°C, for example, Courtier and others, 2007; Herzberg and others, 2007; Herzberg and Gazel, 2009). Therefore, the high melting temperature in the mantle plume can also contribute to producing high-TiO₂ OIBs. In fact, most non-arc type Archaen greenstone basalts contain higher concentration of HFSEs than current N-MORB (for example, Stone and others, 1995; Condie, 2005; Sharkov and Bogina, 2009), probably due to both a higher mantle temperature and less differentiated mantle.

Given typical bulk partition coefficients from eclogite melting experiments (Pertermann and Hirschmann, 2003b), our calculation shows that the eclogite melt mixing end-member contains $\sim 0.84 \pm 0.55$ weight percent TiO₂ and the eclogite source rock has $\sim 0.39 \pm 0.3$ weight percent TiO₂ (including the presence and absence of rutiles, for example, tables 2 and 4). These values are lower than the estimate of GLOSS (TiO₂ = $0.62 \pm 0.04\%$, Plank and Langmuir, 1998), the MORBs (TiO₂ = 1.268%, Sun and McDonough, 1989), and the starting rock composition in the eclogite melting experiments (TiO₂ = 1.97%, Pertermann and Hirschmann, 2003b). Therefore, the reason of our failure in modeling TiO₂ content in Ko'olau lavas is because we automatically assumed TiO₂ = 1.97 percent when we adopted melt composition in MORB-like eclogite melting experiments (Pertermann and Hirschmann, 2003b). The extremely low-Ti signature of the eclogite source rock could be obtained through the following ways: 1) it could originate from strongly-depleted mantle that has been metasomatized by fluid (for example, similar to modern boninite, after partially exhausting HFSE but enriching LREEs); 2) it could be a mixture of oceanic crust, sediments and carbonate rocks that dilute the concentration of HFSEs; 3) it could melt at low degree at depth in the mantle plume where major Ti-bearing phase (rutile) is exhausted and decoupled from other major elements (for example, Gaetani and others, 2008); these initial melt from eclogite could have contributed to other Hawaiian lavas (but with an insignificant amount, refer to the discussion of previous paragraphs). All of these possibilities can produce rocks having our calculated oxygen isotope composition and MORB-like HREEs, more work is required to tell them apart.

Thermal and Chemical Structure of Hawaiian Plume

It has been debated over the last decade whether the chemical diversity of Hawaiian lavas is derived from zoned chemical heterogeneity in the mantle plume (for

example, DePaolo and Stolper, 1996; Hauri, 1996) or the zoned thermal profile evolved over the life-time of an individual Hawaiian volcano (for example, Abouchami and others, 2005; Ren and others, 2005). The temporal evolution of Ko‘olau volcano can help to put constraints on this debate.

As discussed in the *Estimation of the Amount of Recycled Materials in Hawaiian Mantle Plume* section, the correlated temporal geochemical variations in lavas from Ko‘olau volcano suggest the presence of an enriched component most likely to be N-MORB-like eclogite originating from the recycled crust, although it is arguable whether the anomalous chemical signature in Makapu‘u stage Ko‘olau lavas is derived from bigger average size of eclogite/pyroxenite blocks or a cooler thermal structure in the peripheral part of the plume. In contrast, the subaerial Mauna Kea lavas from HSDP (the end of shield-building stage of Mauna Kea volcano) show similar Sr-Nd-Hf isotope compositions as submarine shield-building Mauna Kea lavas (for example, fig. 10 and also Blichert-Toft and Albarede, 2009). The difference in the temporal geochemical evolution at the end of shield-building stage of Mauna Kea and Ko‘olau volcano clearly suggests the existence of chemical heterogeneity between the source of Ko‘olau and Mauna Kea lavas (possibly “Loa-trend” and “Kea-trend” of Hawaiian volcanoes) that cannot be explained solely by thermal structure of Hawaiian plume. That is, the thermal structure of the mantle plume beneath Hawaiian volcanoes must act to magnify or mitigate the expression of compositional differences between geochemical end-members having different melting points. Therefore, we suggest the geochemical diversity of Hawaiian lavas is produced by a compositionally zoned plume that is sampled in systematically variable ways by zonation in thermal structure.

As shown in figure 8, lavas from a few “Kea trend” volcanoes—such as Kilauea, Mauna Kea (subaerial/submarine), Kohala, Maui and Molokai—lie on the extension of our calculated mixing lines for “Loa trend” Hawaiian lavas, and overlap with them around our modeled Lō‘ihi end-members (particularly for lavas from submarine shield-stage lavas, for example, fig. 8D). However, “Kea trend” Hawaiian lavas are unlikely to be simple mixture of the depleted mantle and an enriched component, since submarine shield-stage “Kea trend” lavas also have high $^3\text{He}/^4\text{He}$ ratios (up to $\sim 20 R_A$, for example, Kurz and others, 1983; Valbrachta and others, 1996; Kaneoka and others, 2002; Kurz and others, 2004). Therefore, they can only represent a mixture of our modeled “Lō‘ihi end-member” and a depleted component (most likely the depleted mantle). Clearly, then, at least three components are required to describe all Hawaiian lavas: an enriched component, a depleted component and a high $^3\text{He}/^4\text{He}$ component (for example, Eiler and others, 1996a; Hauri, 1996). This requirement for three or more end members in the sources of shield-building Hawaiian lavas has long been recognized, but is generally neglected in most recent treatments of this problem (for example, Fekiacova and others, 2007; Tanaka and others, 2008). One could argue that our understanding of Hawaiian volcanism has in some sense regressed over the last decade, at least in this respect. The overlaps in chemistry between “Kea trend” and “Loa trend” volcanoes indicate these three components all could contribute to the melts with compositions around our “Lō‘ihi end-member,” but that the depleted component dominates in “Kea trend” volcanoes and the enriched component in “Loa trend” volcanoes (while the third component dominates nowhere).

The isotopic composition of our modeled “Lō‘ihi end-member” is within the range of the FOZO (“focus zone”) component defined in Sr-Nd-Pb space as the converging zone of the highest $^3\text{He}/^4\text{He}$ values (Hart and others, 1992; Hofmann, 1997), in part because Lō‘ihi lavas figured prominently in the initial definition of “FOZO.” Our modeled “Lō‘ihi end-member” has Sr-Nd-Pb-Hf isotope compositions more depleted than primitive mantle but more enriched than N-MORB. Thus, the Lō‘ihi end-member could be a simple partially-depleted mantle. Such a component

could arise in many ways. In a whole mantle convection model this might be a sample of average Archaean upper mantle that has been stored in the lower mantle while continued continent extraction generated the more depleted DMM component. In a layered mantle model such a component could be restricted to a depth that experienced low-degree melting in a hot early Earth but was brought below the solidus by overall mantle cooling and remained solid ever since until being entrained by mantle plume. It could also be a mixture of primitive mantle and depleted mantle. If the Lō'ihī end-member contains recycled crust, only a very small amount is allowed and, furthermore, this recycled crust must be almost completely homogenized into mantle peridotite since the contrast in lithology will magnify this component close to the end of the shield-building stage of a Hawaiian volcano. Although the distinctly low $\delta^{18}\text{O}_{\text{VSMOW}}$ values of subaerial Mauna Kea lavas and the Pu'u O'o eruption of Kilauea might imply a significant incorporation of ancient lower-oceanic crust, it has been shown that this signature is absent in submarine lavas that span a similar range in major element and radiogenic isotope ratios, suggesting contamination by progressive rift zone processes and/or current lower oceanic crust (for example, Eiler and others, 1996a; Eiler and others, 1996b; Garcia and others, 1998; Wang and others, 2003; Wang and Eiler, 2008). The wide range of Sr-Nd-Pb-Hf-Os isotope compositions of highest $^3\text{He}/^4\text{He}$ samples found in various OIBs (Jackson and others, 2008) suggest the mixing proportion of each of these components (primitive mantle, depleted mantle and/or recycled materials) could vary from place to place. We suspect that the physical properties of the mantle plume could determine the amount of primitive and depleted mantle entrained and therefore, the chemical composition of the local FOZO, and melt mixing and melt-rock interaction modulated by individual thermal structure in the mantle plume also play important roles during the interaction of these components.

Finally, the melt from our modeled "Lō'ihī end-member" can also influence the current sub-oceanic mantle. The progressive variations in radiogenic isotope compositions (for example, Sr-Nd) from ODP 843, Hualalai xenoliths, submarine lavas from North Arch, SLC xenoliths (Salt Lake crater, O'ahu) and Honolulu volcanics (O'ahu) define a mixing trend from DMM to our modeled "Lō'ihī end-member" (King and others, 1993; Lassiter and Hauri, 1998; Frey and others, 2000; Lassiter and others, 2000, fig. 4C in Fekiacova and others, 2007), whereas they have little difference in oxygen isotope compositions (except some xenolith samples, fig. 10). Two possible scenarios can occur during this interaction: 1) melt generated from the plume source might metasomatize the sub-oceanic mantle which will melt later to produce post-erosional lavas; or 2) partial melt from the plume source might mix with partial melt from upper mantle. In the latter case, those xenoliths are actually cumulates. We prefer the first scenario to explain the petrogenesis of lavas in the Honolulu volcanic series, because isotopically un-equilibrated peridotites were discovered in SLC (for example, Ducea and others, 2002). Spinel peridotites among the Pali and SLC xenoliths have low $^{87}\text{Sr}/^{86}\text{Sr}$, high $^{143}\text{Nd}/^{144}\text{Nd}$ and normal $^{18}\text{O}/^{16}\text{O}$ ratios overlapping with those of MORB-related gabbroic crustal xenoliths from Hualalai lavas (Lassiter and Hauri, 1998) and ODP-843 Pacific crust (King and others, 1993), whereas plagioclase-spinel peridotites in Pali xenoliths have high $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{18}\text{O}/^{16}\text{O}$ ratios that are interpreted as melting residues of mantle lithosphere underlying the Ko'olau volcano, metasomatized by plume-related Ko'olau lavas (Ducea and others, 2002). Nevertheless, significantly higher concentration of He is needed in the sub-oceanic mantle than in the plume source to explain the $^3\text{He}/^4\text{He}$ ratios ($<8.2 R_A$, Frey and others, 2000; Kaneoka and others, 2002) in Honolulu series and North Arc submarine lavas, because more than 50 percent of our modeled "Lō'ihī end-member" is required in these lavas based on the Sr-Nd isotope systematics.

SUMMARY

Across all three sample suites that were the focus of this study (KSDP drill core, Makapu'u subaerial lavas and Ko'olau submarine land-slides), $\delta^{18}\text{O}_{\text{VSMOW}}$ values of olivines correlate with trace element and radiogenic isotope compositions of host lavas, defining a compositional continuum from a high- $\delta^{18}\text{O}_{\text{VSMOW}}$, enriched end member, toward a more normal- $\delta^{18}\text{O}_{\text{VSMOW}}$, "Mauna Loa-like" composition. We interpret this trend as reflecting mixing between partial melts of high- $\delta^{18}\text{O}_{\text{VSMOW}}$ components and normal- $\delta^{18}\text{O}_{\text{VSMOW}}$ components of the Hawaiian plume, and have constructed a model to simultaneously explain the oxygen isotope, major element, trace element and radiogenic isotope variations defined by this trend.

Our modeling exercise suggests the petrogenesis of Ko'olau lavas can be understood by assuming they are mixtures of peridotite melt and melt of a recycled MORB-like eclogite. Most notably, we developed a model by fitting the major element chemistry of Ko'olau and other Hawaiian lavas, and then show that this major element model independently correlates with and provides an explanation for trace element and isotopic data. Although a variety of models can be easily imagined (for example, varying mixing ratio, degree of melting, DMM-model age of the source rock, LREE concentration of eclogite/pyroxenite), successful models of this kind share several similar characteristics: MORB-like HREE patterns and enriched oxygen isotope composition (7.8-9.7‰) in the eclogite-melt end member (consistent with the premise of the major-element model). This implies that this enriched component is an upper crustal (layer 1 or 2) basalt or gabbro with a low-temperature alteration history, possibly containing a small amount of sediment. The inability of our simple model to invert the composition of certain elements (for example, Ni and Ti) suggests that composition of the enriched end-member, melting temperature, melt mixing and melt-rock interaction have played significant roles in modifying the geochemistry of selected elements in Hawaiian lavas.

Based on our calculated mixing proportions and degrees of melting of the peridotite and eclogite components, we estimate the amount of recycled crust in the Hawaiian plume varies from 5 to 9 weight percent to 10 to 24 weight percent, depending on the degree melting of peridotite (which is not constrained in the model). Nevertheless, the maximum volume of a single eclogite/pyroxenite block contributing to Makapu'u stage Ko'olau lavas is $250 \sim 540 \text{ km}^3$, corresponding to maximum linear dimension of $\sim 10 \text{ km}$, but likely smaller in the horizontal direction if it is stretched or comprises more than one block.

Comparison of the late shield-stage "Loa trend" (particularly Ko'olau lavas) and "Kea trend" (particularly Mauna Kea lavas) suggests that the geochemical diversity of Hawaiian lavas reflects a compositionally zoned plume that samples its enriched and depleted end members variably due to its lateral temperature gradients.

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