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Isotope Compositions of Submarine Hana Ridge Lavas, Haleakala Volcano, Hawaii: Implications for Source Compositions, Melting Process and the Structure of the Hawaiian Plume

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We report Sr, Nd, and Pb isotope compositions for 17 bulk-rock samples from the submarine Hana Ridge, Haleakala volcano, Hawaii, collected by three dives by ROV Kaiko *during a joint Japan–US Hawaiian cruise in 2001. The Sr, Nd, and Pb isotope ratios for the submarine Hana Ridge lavas are similar to those of Kilauea lavas. This contrasts with the isotope ratios from the subaerial Honomanu lavas of the Haleakala shield, which are similar to Mauna Loa lavas or intermediate between the Kilauea and Mauna Loa fields. The observation that both the Kea and Loa components coexist in individual shields is inconsistent with the interpretation that the location of volcanoes within the Hawaiian chain controls the geographical distribution of the Loa and Kea trend geochemical characteristics. Isotopic and trace element ratios in Haleakala shield lavas suggest that a recycled oceanic crustal gabbroic component is present in the mantle source. The geochemical characteristics of the lavas combined with petrological modeling calculations using trace element inversion and pMELTS suggest that the melting depth progressively decreases in the mantle source during shield growth, and that the proportion of the recycled oceanic gabbroic component sampled by the melt is higher in the later stages of Hawaiian shields as the volcanoes migrate away from the central axis of the plume.*

KEY WORDS: *submarine Hana Ridge; isotope composition; melting depth; Hawaiian mantle plume*

INTRODUCTION

Hawaiian volcanoes track the largest, hottest and one of the longest-lived mantle plumes currently active on Earth (Sleep, 1990). Hawaiian volcanoes consist of large tholeiitic shields, which account for 95–98% of their mass (Clague & Dalrymple, 1987). It is likely that the shield lavas provide the most direct information about the composition of the mantle plume that has created the Hawaiian Ridge and Emperor seamounts over the last ~70 Myr (Frey *et al.*, 1994). Geochemical study of Hawaiian shield lavas is, therefore, very important in understanding the systematic compositional variation and evolution during Hawaiian volcano growth, the causes of geochemical differences between individual volcanoes, the temporal evolution of the Hawaiian plume, and the nature of various mantle reservoirs in the Earth's interior (Frey & Rhodes, 1993; Frey *et al.*, 1994;

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Kurz *et al.*, 1995; Hauri, 1996; Lassiter *et al.*, 1996; Lassiter & Hauri, 1998; Eisele *et al.*, 2003).

The Hawaiian–Emperor seamount chain forms a single continuous sequence of volcanoes that become progressively older to the NW (Jackson *et al.*, 1972). In detail, however, the loci of the individual main shield volcanoes of the Hawaiian Islands follow two parallel curved lines: the Loa (or southwestern trend) and the Kea (or northeastern trend) (Jackson *et al.*, 1972). Tatsumoto (1978) first pointed out that there is a distinction between the Kea and Loa trends of volcanoes on the island of Hawaii on a plot of $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$. The Loa trend volcanoes (Mauna Loa, Loihi, Hualalai, Kahoolawe, and Oahu) have lower $^{207}Pb/^{204}Pb$ for a given $^{206}Pb/^{204}Pb$ than the Kea trend volcanoes (Kilauea, Mauna Kea, Kohala, Haleakala, and Molokai). Other isotope differences also exist between Kea and Loa trend volcanoes. Loa trend tholeiites on average have higher $^{87}Sr/^{86}Sr$, and lower $^{206}Pb/^{204}Pb$ and ε_{Nd} than Kea trend tholeiites, although there is significant overlap between the two trends (Lassiter *et al.*, 1996). The apparent isotope distinction has led to the suggestion that the loci of Loa and Kea trend volcanoes are controlled by separate structural lineaments and they tap isotopically distinct plume sources (e.g. Staudigel *et al.*, 1984). This, in turn, has also led to the idea that the Hawaiian plume is concentrically zoned in both its chemical and isotopic composition (Hauri *et al.*, 1996; Kurz *et al.*, 1996; Lassiter *et al.*, 1996). Hauri (1996) proposed a schematic model of a zoned mantle plume beneath Hawaii and suggested that the passage of Loa trend volcanoes over the plume center causes them to have larger amounts of the Koolau component, whereas passage of Kea trend volcanoes over the periphery of the plume results in a large proportion of the upper-mantle Kea component. West & Leeman (1987), however, argued that the existence of these trends may be an artifact, caused by insufficient data for the other volcanoes, because the data for subaerial Haleakala lavas overlap both the Loa and Kea trends on Pb–Pb and Sr–Pb isotope plots. In fact, isotopic variability has also been documented for smaller time scales during the lifetime of the shield stage of individual volcanoes (West *et al.*, 1987; Kurz *et al.*, 1996; Jackson *et al.*, 1999; Pietruszka & Garcia, 1999; Abouchami *et al.*, 2000; Tanaka *et al.*, 2002; Eisele *et al.*, 2003; Mukhopadhyay *et al.*, 2003) and multiple components have been identified in a single shield, such as Haleakala (West & Leeman, 1987; this study), Mauna Kea (Eisele *et al.*, 2003) and Koolau (Jackson *et al.*, 1999; Tanaka *et al.*, 2002) volcanoes.

To document the geochemical evolution of a single Hawaiian shield and to evaluate the cause of geochemical diversity within the shield lavas, it is important to define and interpret temporal geochemical changes during growth of a single shield. Here, we have examined the Sr, Nd, and Pb isotopic compositions of a suite of rocks collected from the submarine Hana Ridge lavas of Haleakala volcano. Haleakala volcano on Maui Island is one of the largest volcanoes of the Hawaiian chain. It is one of the most useful volcanoes for the study of Hawaiian volcanism (or Hawaiian mantle plume process), because three of the four Hawaiian volcanic formation stages are well developed, namely: the shield-building, post-shield building, and rejuvenated stages. However, the shield-building Honomanu lavas are exposed only along the northern coast and in deep valleys on the northern and southern flanks of Maui. Most of the present shield is covered by postshield and rejuvenated-stage alkalic lavas and the Honomanu series represents only the final stage of the Haleakala shield, when the magma composition had already shifted from tholeiitic to transitional and alkalic basalts (Chen & Frey, 1985; Chen *et al.*, 1990, 1991).

Prior to joint Japan–US Hawaiian cruises in 2001–2002, little work had been carried out on the submarine Hana Ridge (Haleakala east rift zone). During these cruises, the deep submarine region (water depth 2500–5500 m) east of Haleakala volcano (the submarine Hana Ridge) was explored and sampled for the first time by submersible dives (ROV *Kaiko* and *Shinkai*). General dive localities are indicated in Fig. 1; detailed dive localities and sample points, and the petrography and major and trace element compositions of the submarine Hana Ridge lavas have been presented by Ren *et al.* (2004). In this paper, we compare the Sr–Nd–Pb isotope compositions of lavas from the submarine Hana Ridge and the subaerial Honomanu lavas to discuss the compositional evolution of Haleakala volcano and the causes of geochemical differences in the Hawaiian plume. In addition, we estimate the source mineralogy for the Hana Ridge lavas, and evaluate the melting process for the Hawaiian shield lavas.

DIVES AND SAMPLES

The Hana Ridge (Fig. 1), extending 140 km ESE from Maui Island, is the largest rift zone in Hawaii (Moore *et al.*, 1990). It is twice as long and nearly twice as wide as the Puna Ridge, the submarine east rift zone of Kilauea volcano. In comparison with other submarine rifts, Hana Ridge has a complex topography consisting of at least three partially overlapping rift segments and a large (22 km wide) arcuate structure at its eastern end (Smith *et al.*, 2002). A slope break that is thought to mark sea level during active shield development is now 1·5–2·5 km below sea level (Moore *et al.*, 1990). Moore & Fiske (1969) proposed that when this slope break subsided below sea level, this marked the end of shield volcanism. The age of this slope has been estimated at 0·85 Ma (Moore &

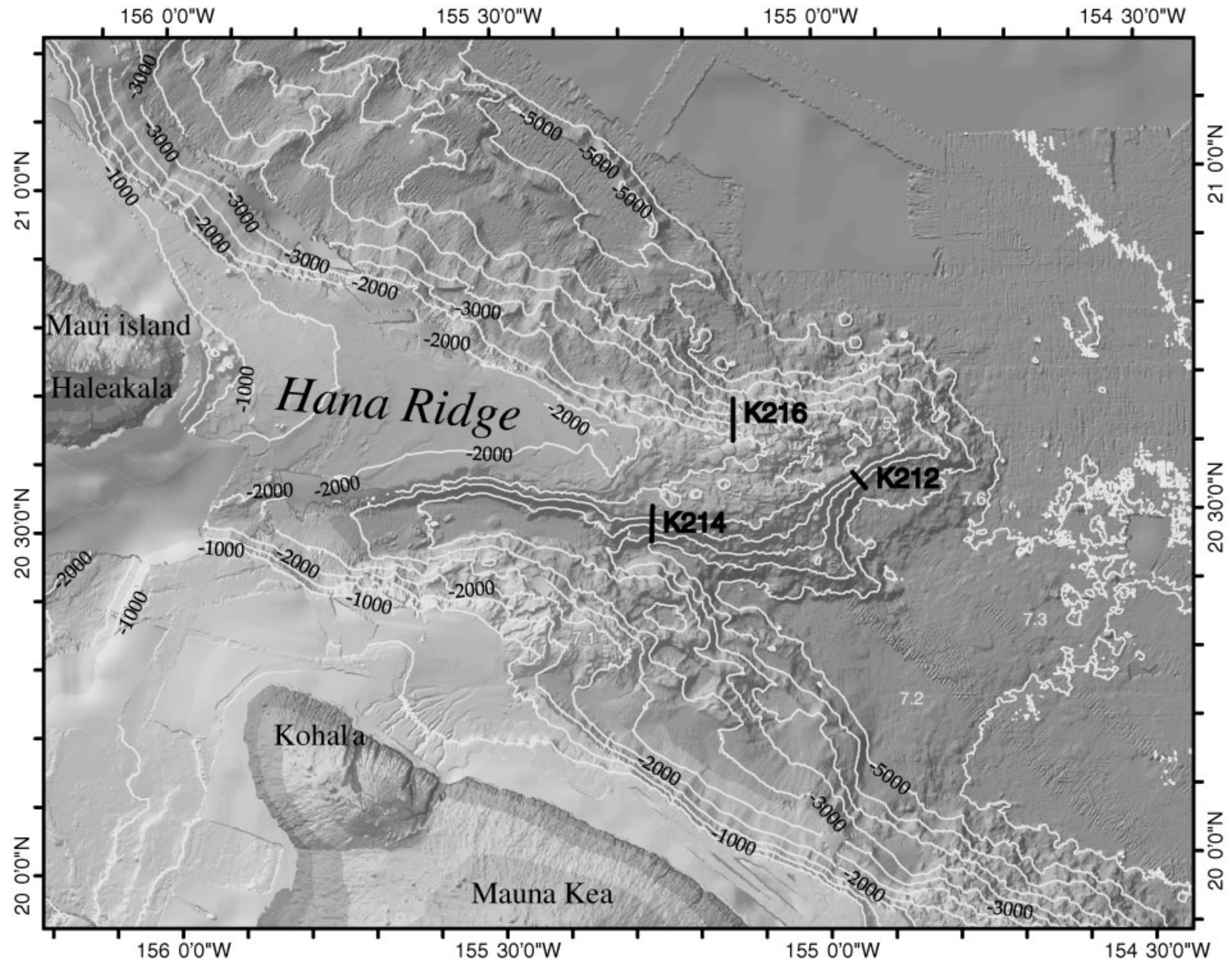

Fig. 1. Bathymetric map of the Hana Ridge showing locations of the Kaiko dives (K212, K214, and K216) in 2001. Contours in m below sea level.

Campbell, 1987), and a coral reef sampled 300 m above the slope break has been dated as 750 ± 13 ka (Moore *et al.*, 1990). Chen *et al.* (1991) studied a stratigraphic section of Haleakala volcano, a 250 m section in Honomanu Gulch, and their K–Ar ages show that the Honomanu basalt sequence contains intercalated tholeiitic and alkalic lavas ranging in age from ~1·1 to 0·97 Ma. These ages represent the end of the Haleakala shield stage; the submarine Hana Ridge lavas pre-date the Honomanu basalts, based on their relative stratigraphic position.

The samples discussed in this paper were collected from three dives: K212, K214, and K216 along the submarine Hana Ridge with the submersible *Kaiko* (Fig. 1). Dive 212 was carried out from the base (4855 m water depth) to the middle slope (3614 m water depth) of a portion of the inner wall of the arcuate, Y-shaped concavity at the eastern extremity of the Hana Ridge. Dive 214 was conducted on the southern rift of the Hana Ridge from 4439 m to 3127 m water depth. Dive 216 was from the middle slope to the top of the northern rift of Hana Ridge (from 3182 m to 2350 m water depth, Fig. 1). All sampled lavas from the submarine Hana Ridge are tholeiitic basalts or picrites. The lavas vary dramatically in mineralogy, ranging from weakly phyric (<2 vol. % phenocrysts) to highly olivine phyric (up to 30 vol. %). Olivine occurs as phenocrysts and micro-phenocrysts in all the samples. Clinopyroxenes are generally scattered throughout the rocks and occur as glomeroporphyritic aggregates with plagioclase in some lavas. Plagioclase is generally subhedral to euhedral, although rare, rounded or embayed plagioclase phenocrysts are present in some lavas. Both types occur as glomerocrysts with augite. Some olivine, clinopyroxene, and plagioclase phenocrysts contain melt inclusions. Ren *et al.* (2004) concluded that all the phenocryst minerals were crystallized from the host magma, based on the compositional relationship between minerals, melts inclusions, and host rocks.

ANALYTICAL TECHNIQUES

Powder preparation

The least altered rocks were chosen for Sr, Nd, Pb isotope analysis after thin-section examination. The samples were wrapped in plastic and broken into chips several millimeters in size using a hydraulic press; the chips were then carefully handpicked to avoid weathered parts. The chips were washed with 0·5N HCl for 20 min in an ultrasonic bath to remove surface contamination and were then rinsed with distilled milli-Q® water three times and dried at 60°C for 12 h. The dried chips were ground to a powder using an alumina ceramic swing mill. Seawater alteration is a potential concern because these rocks have been exposed to seawater for a long time. Acid-leaching has been used to remove the effects of post-eruptive seawater alteration or secondary contamination of fresh or little-altered samples and to obtain the original isotopic compositions of those samples (e.g. Verma, 1992; Abouchami *et al.*, 2000). The powders were leached using distilled 1·5N HCl at 100°C for 6 h, to remove secondary minerals and alteration products, prior to dissolution and analysis.

Isotope analyses

Analyses of Sr, Nd, and Pb isotopic compositions were carried at BGRL (Beppu Geothermal Research Laboratory) following the methods of Yoshikawa *et al.* (2001), Shibata *et al.* (2003), and Miyazaki *et al.* (2003). The samples were dissolved with HF–$HClO_4$, and Sr and Nd were isolated by cation-exchange chromatography. Pb was isolated by anion-exchange chromatography after dissolution in HF–HBr. All chemical procedures were carried out in the Class 100 clean room at BGRL. Total procedural blanks for Sr, Nd, and Pb were less than 10 pg, 10 pg, and 5 pg, respectively. Isotopic measurements were performed by static multi-collection mass spectrometry employing a Thermo-Finnigan Triton®, installed at BGRL by JAMSTEC, equipped with nine Faraday cup collectors. Normalizing factors used to correct for mass fractionation of Sr, Nd and Pb during the measurements are $^{86}Sr/^{88}Sr = 0{\cdot}1194$, $^{146}Nd/^{144}Nd = 0{\cdot}7219$ and 0·145% per atomic mass unit, respectively. Measured ratios of the standard materials were $^{87}Sr/^{86}Sr = 0{\cdot}710264 \pm 13$ (2σ) for NIST987 ($n = 93$), $^{143}Nd/^{144}Nd = 0{\cdot}511844 \pm 11$ (2σ) for La Jolla ($n = 10$), and $^{206}Pb/^{204}Pb = 16{\cdot}939 \pm 3$ (2σ), $^{207}Pb/^{204}Pb = 15{\cdot}495 \pm 4$ (2σ), $^{208}Pb/^{204}Pb = 36{\cdot}712 \pm 11$ (2σ) for NIST 981 ($n = 35$). The data are reported in Table 1.

We also analyzed the isotope composition of five unleached bulk-rock samples (K216-10, K214-9, K214-15A, K212-4B, and K212-13B) listed in Table 1, prior to acid leaching, to compare the data with those for the leached samples. The five unleached samples range in $^{87}Sr/^{88}Sr$ values from 0·70357 to 0·70373, and in $^{143}Nd/^{144}Nd$ values from 0·51293 to 0·51298. When leached (powder leached in 1·5N HCl at 100°C for 6 h) and unleached samples are compared, they show indistinguishable isotope ratios within analytical error (Fig. 2).

DISCUSSION

Isotopic evolution of the Haleakala volcano

Here, we compare the isotope compositions of lavas from the submarine Hana Ridge with those of the subaerial Honomanu lavas, to discuss the compositional evolution of the Haleakala shield volcano. When comparing these two phases of Haleakala shield-building, we must consider the following: (1) the subaerial Honomanu stage lavas have been dated and are believed to have erupted during the final stage of Haleakala shield formation (e.g. Chen *et al.*, 1991); (2) the geological relationship between the three sub-parallel submarine rift zones (Smith *et al.*, 2002) and the exact age of the Hana Ridge basalts is unknown. Therefore, the volcanic stage and stratigraphic order of the sampled Hana Ridge lavas remain uncertain.

A significant new result is that the $^{87}Sr/^{86}Sr$ compositions reported in this study from the Hana Ridge lavas (leached in 1·5N HCl; Table 1, Fig. 3) range from 0·70355 to 0·70371 and are lower than those of the subaerial Honomanu lavas (0·70364–0·70387; data from West & Leeman, 1987; Chen *et al.*, 1991; Figs 3 and 4). The $^{143}Nd/^{144}Nd$ ratios of the submarine Hana Ridge lavas fall in the range 0·51294 ($\varepsilon_{Nd} = 5{\cdot}93$) to 0·51299 ($\varepsilon_{Nd} = 6{\cdot}91$), and those of the Honomanu lavas are between 0·51291 ($\varepsilon_{Nd} = 5{\cdot}34$) and 0·51299 ($\varepsilon_{Nd} = 6{\cdot}91$) (Chen *et al.*, 1991; Figs 3 and 4). The $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ values of the Hana Ridge lavas are in the range 18·339–18·699, 15·463–15·499, and 37·946–38·293, respectively. In contrast, the subaerial Honomanu lavas have ratios of 18·245–18·336, 15·461–15·482, and 37·919–38·045, respectively (data from West & Leeman, 1987; Chen *et al.*, 1991). The $^{206}Pb/^{204}Pb$ values of the Hana Ridge lavas are higher than the ratios from the subaerial Honomanu lavas (Figs 3–5).

The range to higher $^{87}Sr/^{86}Sr$ in the subaerial samples could be interpreted as resulting from alteration; however, the subaerial samples would then be expected to have higher $^{206}Pb/^{204}Pb$ than the HCl-leached submarine samples, yet they have lower $^{206}Pb/^{204}Pb$ (Figs 3–5). There is no evidence that secondary contamination or alteration results in lower $^{206}Pb/^{204}Pb$ (e.g. Abouchami *et al.*, 2000). In other words, the lower $^{206}Pb/^{204}Pb$ ratios of the subaerial Honomanu lavas are probably not caused by secondary contamination or alteration. Furthermore, there are good correlations between isotope ratios and ratios of immobile incompatible trace elements (e.g. Zr/Nb; Fig. 6a–c).

Table 1: Sr, Nd and Pb isotopic composions of the submarine Hana Ridge lavas

Sample*	$^{87}Sr/^{86}Sr$	2σ	$^{143}Nd/^{144}Nd$	2σ	$^{206}Pb/^{204}Pb$	2σ	$^{207}Pb/^{204}Pb$	2σ	$^{208}Pb/^{204}Pb$	2σ
Dive K212										
K212-2A	0·70365	0·000012	0·51296	0·000012	18·5642	0·0017	15·4768	0·0014	38·1772	0·0034
K212-4B	0·70356	0·000010	0·51296	0·000008	18·5979	0·0020	15·4837	0·0020	38·2031	0·0040
K212-6B	0·70357	0·000008	0·51298	0·000008	18·5980	0·0014	15·4879	0·0014	38·2163	0·0036
K212-7A	0·70363	0·000012	0·51296	0·000008	18·5368	0·0056	15·4678	0·0044	38·1368	0·0100
K212-8	0·70356	0·000008	0·51297	0·000010	18·6582	0·0010	15·4890	0·0008	38·2314	0·0022
K212-9	0·70363	0·000012	0·51295	0·000010	18·5380	0·0014	15·4753	0·0011	38·1548	0·0026
K212-13B	0·70362	0·000008	0·51296	0·000010	18·5339	0·0020	15·4647	0·0020	38·1240	0·0020
Dive K214										
K214-3	0·70368	0·000008	0·51296	0·000011	18·6992	0·0030	15·4989	0·0026	38·2927	0·0062
K214-7	0·70359	0·000012	0·51297	0·000008	18·6292	0·0001	15·4856	0·0008	38·2265	0·0022
K214-8	0·70360	0·000008	0·51297	0·000010	18·5510	0·0034	15·4798	0·0026	38·1569	0·0070
K214-9	0·70358	0·000010	0·51299	0·000006	18·3819	0·0040	15·4787	0·0040	38·0140	0·0060
K214-10	0·70355	0·000008	0·51296	0·000014	18·6710	0·0020	15·4940	0·0017	38·2554	0·0044
K214-11	0·70368	0·000010	0·51297	0·000012	18·5375	0·0011	15·4733	0·0010	38·1543	0·0024
K214-15A	0·70359	0·000008	0·51298	0·000010	18·3389	0·0040	15·4627	0·0020	37·9460	0·0060
Dive K216										
K216-3	0·70355	0·000008	0·51296	0·000008						
K216-10	0·70371	0·000010	0·51294	0·000006	18·5079	0·0020	15·4777	0·0020	38·1581	0·0020
K216-11B	0·70355	0·000012	0·51297	0·000010	18·5027	0·0022	15·4738	0·0018	38·1034	0·0044

Isotopic compositions of the unleached powders

Sample	$^{87}Sr/^{86}Sr$	$^{143}Nd/^{144}Nd$
K212-4B	0·70357	0·51297
K212-13B	0·70365	0·51295
K214-9	0·7036	0·51298
K214-15A	0·70361	0·51297
K216-10	0·70373	0·51293

*All the powders of samples were leached using distilled 1·5N HCl at 100°C for 6 h.
Measured ratios for standard materials were $^{87}Sr/^{86}Sr = 0{\cdot}710264 \pm 13$ for NBS987 ($n = 93$, 2σ), $^{143}Nd/^{144}Nd = 0{\cdot}511844 \pm 11$ for La Jolla ($n = 10$, 2σ), and $^{206}Pb/^{204}Pb = 16{\cdot}939 \pm 3$, $^{207}Pb/^{204}Pb = 15{\cdot}495 \pm 4$, and $^{208}Pb/^{204}Pb = 36{\cdot}712 \pm 11$ for NIST 981 (2σ, $n = 35$).

Zr/Nb ratios from the Haleakala shield lavas also show good correlations with other highly incompatible trace element ratios (e.g. Ba/Nb; Fig. 6d). Previous studies have shown that some trace element ratios, such as Zr/Nb and Sr/Nb, correlate strongly with isotope ratios and, therefore, might reflect differences in the proportions of different source components in the Hawaiian plume (e.g. Frey & Rhodes, 1993; Chen *et al.*, 1996). Zr/Nb is particularly useful in this respect because it is less susceptible to changes associated with partial melting than other trace element ratios (Rhodes & Vollinger, 2004). In summary, the geochemical characteristics of the Haleakala shield lavas strongly suggest that the isotope ratios of the lavas from the subaerial Honomanu and the submarine Hana Ridge reflect the original magmatic compositions, rather than alteration and the effects of acid-leaching.

The Sr, Nd, and Pb isotopic ratios of the Hana Ridge lavas show no significant correlation with sample locality or depth below sea level (Fig. 3), and are similar to those of Kilauea lavas. In contrast, the Honomanu stage tholeiitic lavas plot in the Mauna Loa field or between the Kilauea and Mauna Loa fields in Figs 4 and 5. Similar conclusions can be reached from a study of trace element ratios such as Zr/Nb, Sr/Nb, and Ba/Nb in the Haleakala volcano. The major and trace element characteristics of lavas from the submarine Hana Ridge are similar to those of Kilauea lavas. In contrast, the trace

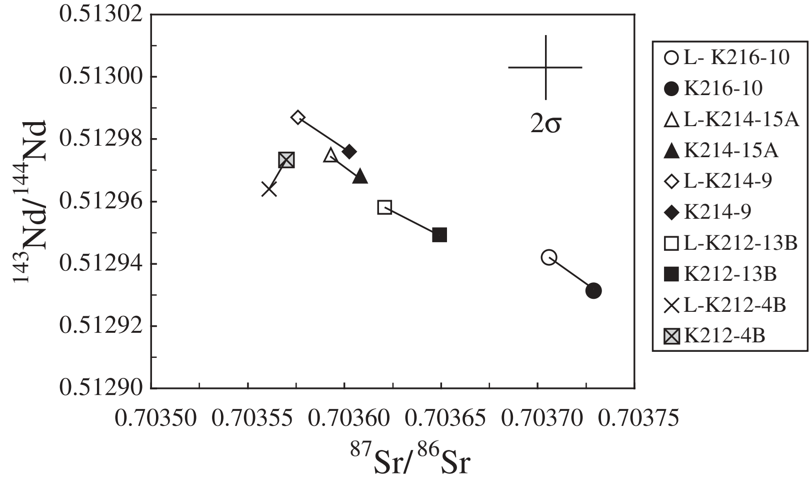

Fig. 2. Nd–Sr isotope compositions for leached and unleached bulk-rock samples. When leached and unleached samples are compared, they show indistinguishable isotope ratios within analytical errors. L- indicates bulk-rock powders leached in 1·5N HCl, at 100°C, for 6 h. The 2σ error bars are indicated.

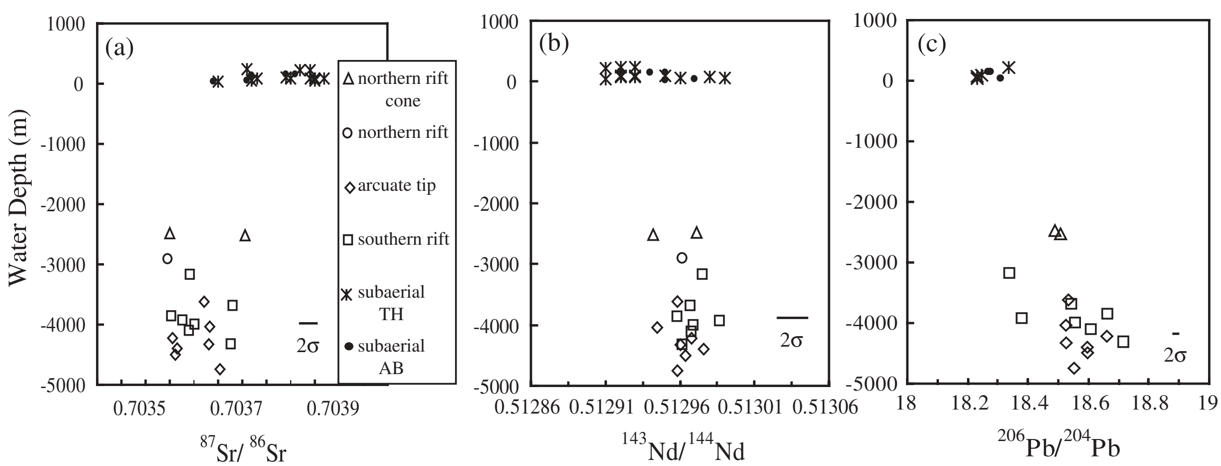

Fig. 3. $^{87}Sr/^{86}Sr$ (a), $^{143}Nd/^{144}Nd$ (b), and $^{206}Pb/^{204}Pb$ (c) variations of bulk rocks as a function of water depth. There is no correlation between isotopic ratios and water depth or sample localities. Data for subaerial Honomanu lavas from Chen *et al.* (1991). Here, northern rift core and northern rift are from Dive K216, arcuate tip from Dive K212, and southern rift from Dive K214 of the submarine Hana Ridge. Subaerial TH (tholeiitic lavas) and subaerial AB (alkalic lavas) are from the subaerial Honomanu stage of Haleakala shield. The 2σ error bars are given in a corner of each plot. (See text for further explanation.)

element characteristics (e.g. Zr/Nb, Sr/Nb) of the subaerial tholeiitic lavas from Honomanu overlap fields for tholeiitic lavas from Mauna Loa–Kilauea (Ren *et al.*, 2004). This suggests that Haleakala volcano originally erupted tholeiitic magmas whose source was geochemically similar to that of the Kilauea lavas. During the growth of the Haleakala volcano, the magma source shifted from a Kilauea-like to a Mauna Loa-like composition (Figs 4 and 5). Similar compositional variations during the late stages of shields have been reported for both Mauna Loa (Kurz *et al.*, 1995) and Koolau (e.g. Jackson *et al.*, 1999; Haskins & Garcia, 2000; Shinozaki *et al.*, 2002; Tanaka *et al.*, 2002).

In the Koolau volcano, the compositions of lavas change from what has been called 'Koolau' type (extreme Loa) on the upper part of the volcano to Mauna Loa (Loa) and Kilauea-like (Kea) with depth (e.g. Jackson *et al.*, 1999; Shinozaki *et al.*, 2002). Tanaka *et al.* (2002) studied the geochemistry of Nuuanu landslide deposits and suggested that the lavas from the main shield stage of Koolau encompass both Loa and Kea compositions; they are characterized by lower Ba/Nb, La/Nb, Pb/Nd, Sr/Nb, Zr/Nb and $^{87}Sr/^{86}Sr$ and by higher $^{143}Nd/^{144}Nd$ and $^{206}Pb/^{204}Pb$ than those of the Makapuu lavas (Koolau-type). They also proposed that the Koolau shield lavas were generated from at least three

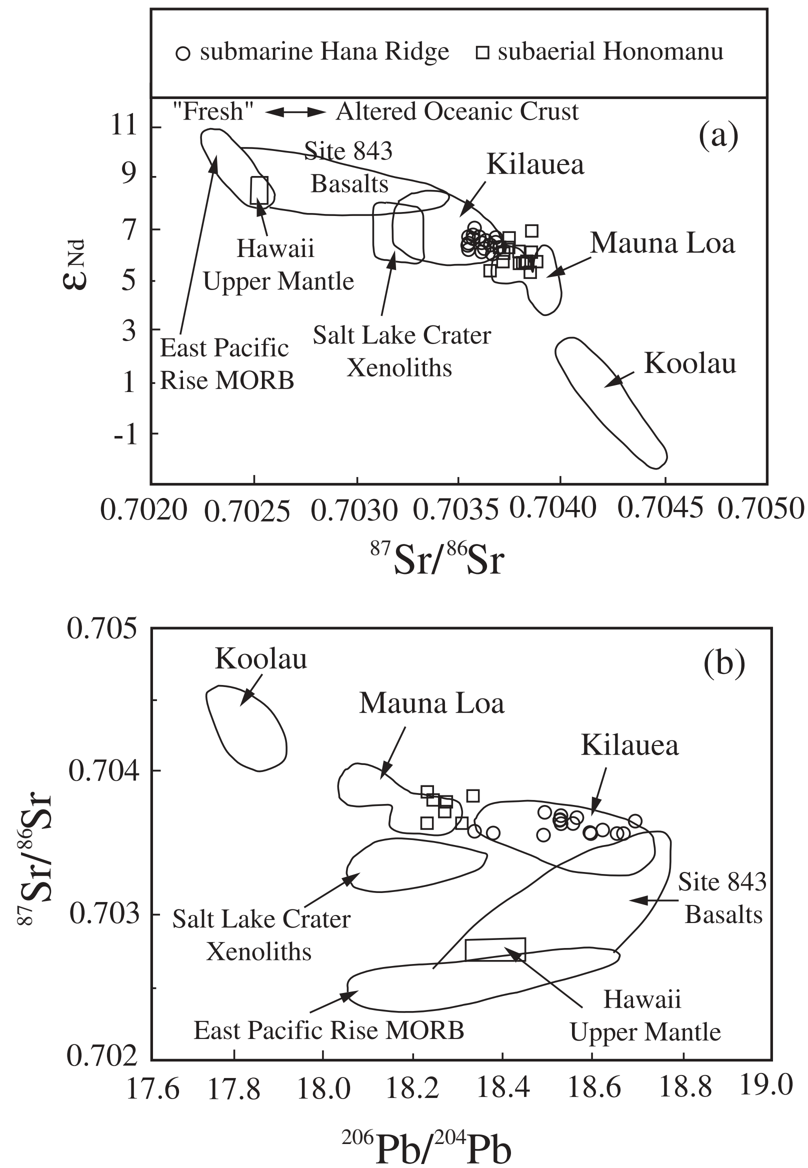

Fig. 4. (a) $^{87}Sr/^{86}Sr$ vs ε_{Nd} and (b) $^{206}Pb/^{204}Pb$ vs $^{87}Sr/^{86}Sr$ for submarine Hana Ridge and subaerial Honomanu lavas compared with Kilauea, Mauna Loa, and Koolau. Fields for Kilauea, Mauna Loa, and Koolau lavas from Lassiter *et al.* (1996) and Pietruszka & Garcia (1999). Data for subaerial Honomanu lavas from Chen *et al.* (1991). Fields for Salt Lake Crater xenoliths, East Pacific Rise MORB, Site 843 basalts, and Hawaii upper mantle after Pietruszka & Garcia (1999, fig. 6). (See text for further explanation.)

different mantle components, including an enriched Makapuu, a depleted Makapuu, and a Kea component. A change in composition of the shield lavas is also found in the Mauna Loa shield. The recent Mauna Loa lavas have higher $^{87}Sr/^{86}Sr$ and lower $^{143}Nd/^{144}Nd$ than the older lavas (Kurz *et al.*, 1995). Rhodes & Vollinger (2004) suggested that the source composition of Mauna Loa lavas is consistent with an increase in Kilauea (Kea) or Loihi (Loa) components with age, towards source compositions that are intermediate between those of modern Mauna Loa and Kilauea. In Mauna Kea volcano, Eisele *et al.* (2003) showed two types of lavas forming the Mauna Kea main shield. The low-SiO_2 lavas with high $^{3}He/^{4}He$ and high $^{208}Pb/^{204}Pb$ at a given $^{206}Pb/^{204}Pb$ are Loihi (Loa)-like whereas the dominant group is Kea-like. Taken together, these geochemical differences within individual shields provide evidence for a significant change in source composition, mixing of different proportions of components, and changes in melt production and depth of melt segregation during individual shield growth (see discussion below). These observations are inconsistent with the interpretation that the volcanic loci of the Hawaiian

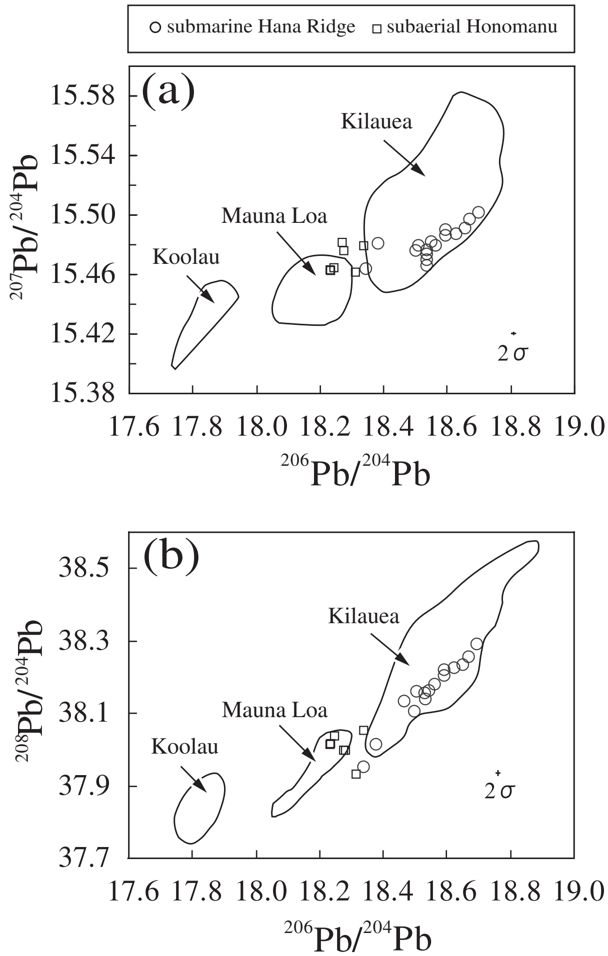

Fig. 5. (a) $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ and (b) $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ for submarine Hana Ridge and subaerial Honomanu lavas. Field for Kilauea lavas from literature sources available from the GEOROC database (http://georoc.mpch-mainz.gwde.de). Fields for Mauna Loa and Koolau from Mukhopadhyay *et al.* (2003). Pb isotopic data for subaerial Honomanu lavas from Chen *et al.* (1991). The 2σ error bars are given in a corner of each plot.

chain (Jackson *et al.*, 1972) control the geographical distribution of Loa and Kea trend geochemical characteristics (Tatsumoto, 1978), because both Kea and Loa components apparently coexist in the shields of some volcanoes. Overall there are geochemical differences between Kea- and Loa-trend volcanoes, but in detail these differences can exist within a single shield, and can vary with eruption age (e.g. Chen & Frey, 1985; Chen *et al.*, 1991; Tanaka *et al.*, 2002; Eisele *et al.* 2003; Rhodes & Vollinger, 2004; this study).

Origin of the Haleakala shield lavas

Origin of the depleted Kea component

Submarine Hana Ridge lavas are similar to Kilauea basalts, characterized by lower SiO_2, higher TiO_2 and CaO, and lower Zr/Nb and Sr/Nb at a given MgO in the Hawaiian shield lavas (Ren *et al.*, 2004). In addition, they have lower $^{87}Sr/^{86}Sr$, and higher $^{143}Nd/^{144}Nd$ and $^{206}Pb/^{204}Pb$ than many other Hawaiian shield lavas (Figs 4 and 5).

The Kilauea and submarine Hana Ridge lavas are part of the putative Kea component (e.g. Stille *et al.*, 1986; Frey & Rhodes, 1993; Roden *et al.*, 1994; Eiler *et al.*, 1996, 1998). The Kea component is characterized by the lowest $^{87}Sr/^{86}Sr$ and the highest $^{143}Nd/^{144}Nd$ and $^{206}Pb/^{204}Pb$ in Hawaiian shields (e.g. Stille *et al.*, 1986; Frey & Rhodes, 1993; Roden *et al.*, 1994). There are a number of different interpretations for the origin of the distinct isotopic compositions of the Kea component. These include: (1) assimilation of hydrothermally altered oceanic crust into plume-derived melts (Eiler *et al.*, 1996); (2) melting of upper mantle lithosphere or asthenosphere beneath Hawaii (e.g. Tatsumoto, 1978; Stille *et al.*, 1986; Hauri, 1996; Lassiter *et al.*, 1996); (3) melting of a long-term depleted component within a heterogeneous Hawaiian plume (West *et al.*, 1987; Chen *et al.*, 1991, 1996; Lassiter & Hauri, 1998; Pietruszka & Garcia, 1999; Abouchami *et al.*, 2000). Below, we evaluate various models for the origin of the submarine Hana Ridge lavas through examination of their Sr, Nd, and Pb isotope compositions, combined with previous geochemical studies on Kea-like lavas.

The isotopic signatures of submarine Hana Ridge lavas might be explained by assimilation of oceanic crust into a plume-derived magma. Cretaceous basalts collected from Ocean Drilling Program Site 843 serve as a reference for seawater-altered basaltic oceanic crust near Hawaii (King *et al.*, 1993) (Fig. 4). The Sr, Nd, and Pb isotopic ratios of altered lavas from Site 843 are close to those of Kilauea lavas. However, the relatively low and constant Rb/Nb and Ba/Nb and high Sm/Yb ratios in the submarine Hana Ridge lavas are inconsistent with the relatively high Rb/Nb, Ba/Nb and lower Sm/Yb ratios in seawater-altered oceanic crust (Fig. 7), suggesting that the lavas are unlikely to have resulted from assimilation of seawater-altered basalts by plume-derived magmas. Furthermore, Pietruszka & Garcia (1999) proposed that if the Kilauea isotope compositions result from assimilation of seawater-altered basalts, unreasonably large amounts of bulk assimilation would be required to produce the relatively high $^{206}Pb/^{204}Pb$ ratios of the Kea-like lavas.

The anomalously high $^{87}Sr/^{86}Sr$ in the submarine Hana Ridge lavas compared with fresh mid-ocean ridge basalt (MORB) samples cannot be generated simply by the melting of entrained MORB-source asthenosphere or lithosphere (Fig. 4). The submarine Hana Ridge lavas have higher $^{87}Sr/^{86}Sr$ than any of the MORB (East Pacific Rise) glasses analyzed (Fig. 4).

Mantle xenoliths from Salt Lake Crater on the Island of Oahu represent fragments of the mantle lithosphere

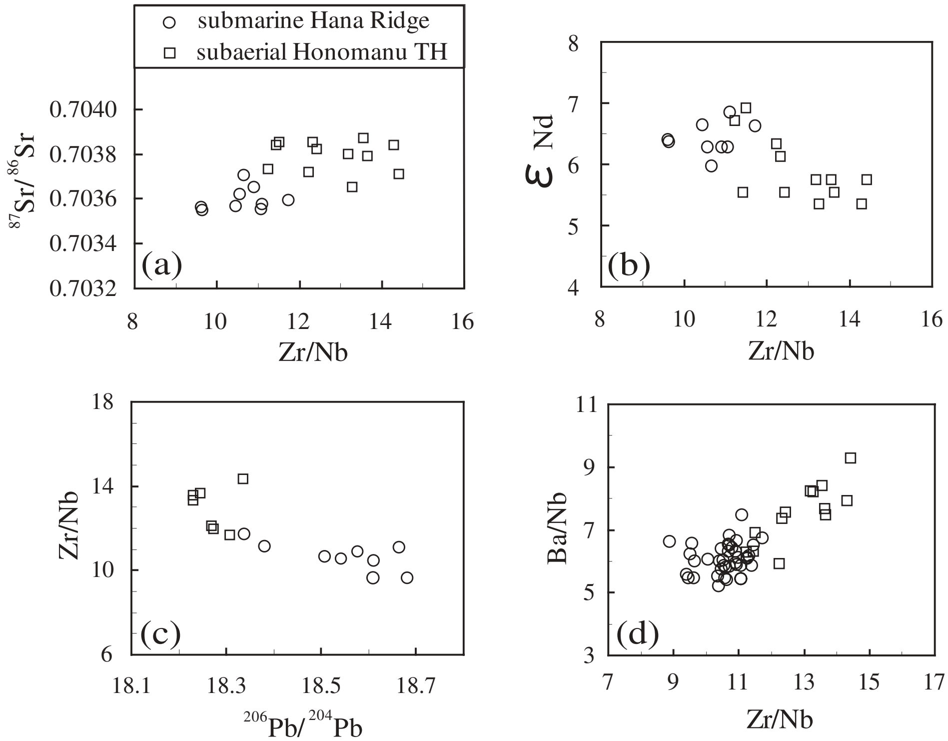

Fig. 6. (a) Zr/Nb vs $^{87}Sr/^{86}Sr$, (b) Zr/Nb vs ε_{Nd}, (c) Zr/Nb vs $^{206}Pb/^{204}Pb$, and (d) Zr/Nb vs Ba/Nb for submarine Hana Ridge and subaerial Honomanu lavas. Trace element data for submarine Hana Ridge lavas from Ren *et al.* (2004), and for subaerial Honomanu lavas from Chen *et al.* (1991). (See text for further explanation.) TH, tholeiitic lavas.

beneath Hawaii (Okano & Tatsumoto, 1996). Although these xenoliths have Sr and Nd and low ε_{Nd} isotope ratios that could account for the relatively high $^{87}Sr/^{86}Sr$ ratios of the submarine Hana Ridge lavas, their $^{206}Pb/^{204}Pb$ ratios are too low. The isotope compositions of the submarine Hana Ridge lavas are also different from the Hawaiian upper mantle composition inferred from the Site 843 basalts (Pietruszka & Garcia, 1999), which cannot explain the compositions of the submarine Hana Ridge lavas.

Based on the above discussion and the high $^{3}He/^{4}He$ ratios of the Kilauea lavas (Kurz, 1993), the chemical and isotopic signatures of the submarine Hana Ridge lavas are considered to have formed by melting of a long-term depleted component within the Hawaiian plume, rather than part of the oceanic crust or upper mantle below Hawaii. This conclusion is the same as that reached by Lassiter & Hauri (1998) for Mauna Kea and Pietruszka & Garcia (1999) for Kilauea.

Recycled oceanic gabbroic component present in the Hawaiian mantle plume source

At least three distinct mantle components, termed Loihi, Koolau, and Kea, are required to explain the isotopic variability in Hawaiian shield lavas (Staudigel *et al.*, 1984; Stille *et al.*, 1986; West *et al.*, 1987; Kurz *et al.*, 1995; Eiler *et al.*, 1996; Hauri, 1996). Although in general Hawaiian basalts require more than two components to account for their geochemical variations, to a first order, the isotopic variations in Hawaiian shield lavas appear dominated by a mixture of two components: a relatively enriched component (Koolau, extreme Loa) and a depleted component (Kea) (e.g. Lassiter & Hauri, 1998). The ε_{Hf}–$^{206}Pb/^{204}Pb$ correlation for the Hawaiian shield lavas is exceptionally good and strongly curved; the end-members are best represented by the Koolau and Kilauea basalts (see Blichert-Toft *et al.*, 2003, fig. 6). Here, it is necessary to address the origin of the enriched and depleted end-members in order to evaluate the isotopic variations of the Haleakala lavas in the context of other Hawaiian shield lavas. The enriched component (Koolau component) is characterized by tholeiitic shield lavas with high SiO_2 at a given MgO content, high $^{87}Sr/^{86}Sr$, and low $^{143}Nd/^{144}Nd$ and $^{206}Pb/^{204}Pb$ (e.g. Roden *et al.*, 1994; Eiler *et al.*, 1996; Hauri, 1996; Lassiter & Hauri, 1998) and has Sr, Nd, and Pb isotope compositions closest to those of primitive mantle [Bulk Silicate Earth (BSE), Fig. 8]. However, the abundance of highly incompatible elements is not indicative of a primitive mantle source (Frey *et al.*, 1994). Lassiter & Hauri (1998) also argued that the Koolau lavas were not derived from a

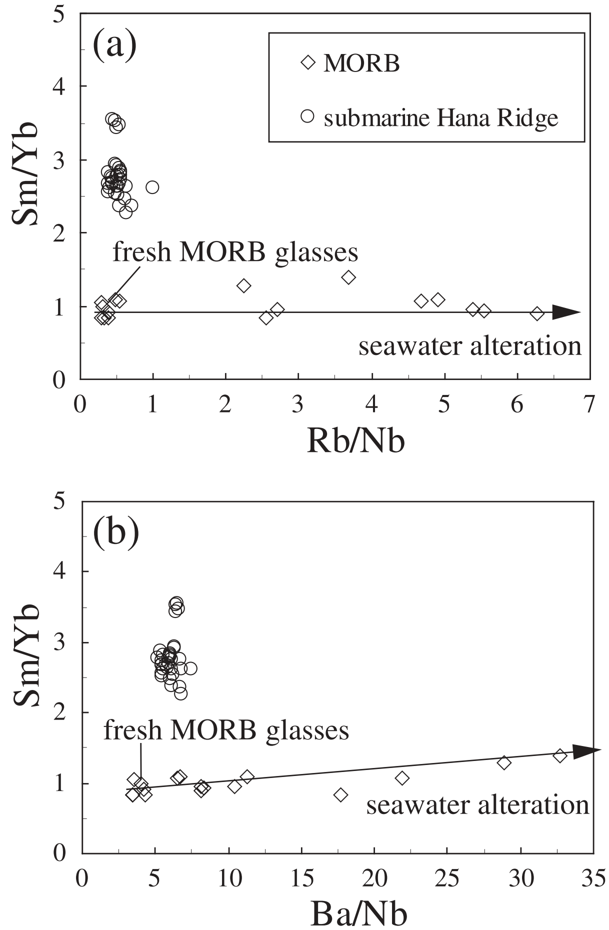

Fig. 7. (a) Sm/Yb vs Rb/Nb and (b) Sm/Yb vs Ba/Nb for submarine Hana Ridge lavas, altered MORB samples and fresh MORB glasses. Data for submarine Hana Ridge lavas from Ren *et al.* (2004), for altered MORB samples from Verma (1981) and for fresh MORB glasses from Hofmann *et al.* (1986), Jochum *et al.* (1993), and Jochum & Verma (1996).

primitive mantle source. Trace element ratios such as Rb/Sr, Nb/Th, Th/La and $^{187}Os/^{188}Os$ are also different from the primitive mantle values. The isotope composition of the Koolau component represents an enriched mantle source resembling EM1 (Hauri *et al.*, 1996; Lassiter & Hauri, 1998). Recycling of oceanic crust and sediments might explain the Koolau end-member (Hauri, 1996; Lassiter & Hauri, 1998; Blichert-Toft *et al.*, 1999).

Some researchers have argued that the depleted Kea component is derived from 'young' (<1·5 Ga) recycled oceanic crust (Eisele *et al.*, 2003), or derived from young HIMU (high-μ) mantle (Thirlwall, 1997). However, melting experiments (Kogiso *et al.*, 1998; Takahashi & Nakajima, 2002) have indicated that picritic primary magmas (e.g. 16–17 wt % MgO, for Haleakala, Chen, 1993; Wagner *et al.*, 1998; Ren *et al.*, 2004; and Kilauea shield, Clague *et al.*, 1995) cannot be derived from simple melting of recycled oceanic basalts. Furthermore, this model is also inconsistent with the higher $^{3}He/^{4}He$ values in the Kea lavas, because if the Kea-like source is recycled oceanic crust it should be degassed and would have a low $^{3}He/^{4}He$ value. The high $^{3}He/^{4}He$ values for Hawaiian lavas have been generally attributed to the presence of an 'undegassed' mantle reservoir, rich in primitive ^{3}He (Kurz *et al.*, 1996). Also, the identification of near-solar neon isotopic ratios in some glasses from Loihi and Kilauea (Honda *et al.*, 1993) suggests the presence of an 'undegassed' component with high $(Ne_{solar})/(U + Th)$.

Lassiter & Hauri (1998) have used combined O–Os–Pb isotopes to constrain the Kea and Koolau components. They postulated that the Kea end-member was derived from recycled, hydrothermally altered, ultramafic lower oceanic crust or lithospheric mantle. They found that the Kea lavas have unradiogenic Os isotopes and anomalously light oxygen isotopes, reflecting the presence of recycled, hydrothermally altered, ultramafic lower oceanic crust or lithospheric mantle, whereas the radiogenic Os isotopes and anomalously heavy oxygen isotopes of the Koolau lavas reflect melt generation from recycled oceanic crust plus pelagic sediment. However, this model is also insufficient to explain the observation that the trend in the Hawaiian data toward depleted Sr and Os isotope signatures (Kilauea and Loihi) is accompanied by a correlated increase in $^{3}He/^{4}He$ ratios (Kurz *et al.*, 1982, 1983), and that the $^{3}He/^{4}He$ ratios increase from Koolau to Mauna Loa to Kilauea (Hauri, 1996). Furthermore, the low $\delta^{18}O$ component is either a contaminant from the volcanic edifice or a partial melt of low $\delta^{18}O$, hydrothermally altered peridotites in the shallow Pacific lithosphere that increasingly contributed to Mauna Kea lavas near the end of the volcano's shield building stage (Wang *et al.*, 2003).

Another mantle component, which can be identified with the Hawaiian Kea-like component, has been identified by Hart *et al.* (1992), who proposed a mantle component for OIB termed the 'focal zone' (FOZO). In terms of three-dimensional Sr, Nd, Pb isotopic space, data from many individual islands and island groups show elongated arrays that converge towards FOZO (see Hart *et al.*, 1992). Hart *et al.* argued that the characteristics of the missing parent species for this focal zone are depleted Sr and Nd isotope ratios accompanied by high $^{206}Pb/^{204}Pb$; they also suggested that FOZO may be the high $^{3}He/^{4}He$ mantle reservoir. The existence of this mantle component has also been supported by Hauri *et al.* (1994). A similar mantle component termed the 'common mantle source' (C) was proposed by Hanan & Graham (1996). The linear arrays in Pb isotope space for mid-ocean ridge basalts also converge on a single end-member (Hanan & Graham, 1996).

The Sr, Nd, and Pb isotopic compositions of Hawaiian tholeiitic lavas define an elongated array that extends

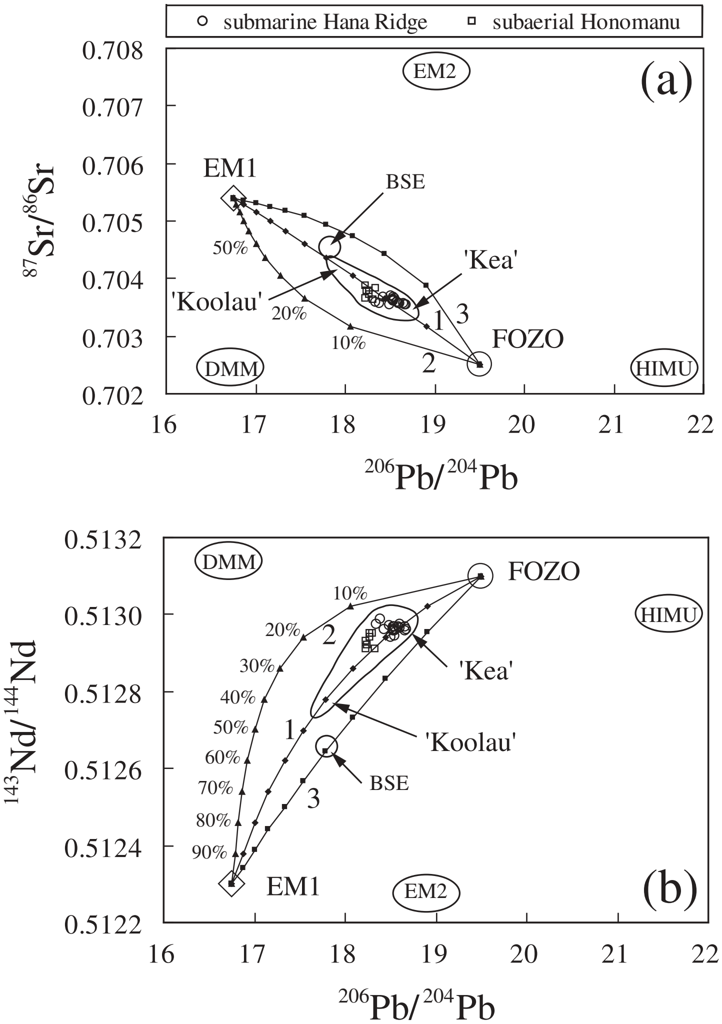

Fig. 8. (a) $^{87}Sr/^{86}Sr$ vs $^{206}Pb/^{204}Pb$ and (b) $^{143}Nd/^{144}Nd$ vs $^{206}Pb/^{204}Pb$ for Haleakala shield lavas together with the field for Hawaiian shield volcanoes tholeiitic lavas and the approximate locations of the mantle components DMM, HIMU, EM1, and EM2 of Zindler & Hart (1986) and the primitive mantle (BSE) estimated from the Sr–Nd isotope correlation and from the Nd composition of chondrites (Allègre *et al.*, 1979; O'Nions *et al.*, 1979). The FOZO mantle component (Hart *et al.*, 1992) is also plotted. The Hawaiian isotopic end-members Koolau and Kea are from Hauri (1996). Mixing lines assuming: ancient recycled ocean crust and pelagic sediment: Sr 80 ppm; $^{87}Sr/^{86}Sr = 0{\cdot}7054$; Nd 6 ppm; $^{143}Nd/^{144}Nd = 0{\cdot}5123$; Pb 0·5 ppm; $^{206}Pb/^{204}Pb = 16{\cdot}755$ (Weaver, 1991); and FOZO: $^{87}Sr/^{86}Sr = 0{\cdot}7025$; $^{143}Nd/^{144}Nd = 0{\cdot}5131$; $^{206}Pb/^{204}Pb = 19{\cdot}5$ (Hart *et al.*, 1992). Three different mixing trends are shown. The concentrations of Sr, Nd, and Pb for the FOZO component used are: Line 1: FOZO: Sr 30 ppm; Nd 6 ppm; Pb 0·2 ppm; Line 2: FOZO: Sr 30 ppm; Nd 6 ppm; Pb 0·05 ppm; Line 3: FOZO: Sr 10 ppm; Nd 3 ppm; Pb 0·2 ppm. Isotope data for subaerial Honomanu lavas from Chen *et al.* (1991).

between the FOZO and EM1 components (Fig. 8). Isotope compositions for Haleakala, together with other Hawaiian shield lavas, can be produced by mixing EM1 and FOZO mantle components. Using Sr, Nd, and Pb abundances in 1·5–2 Ga recycled ocean crust and pelagic sediment (Weaver, 1991), mixing of 60–85% of basaltic melt, derived from a mixture of 95% recycled oceanic basalt and 5% recycled ancient pelagic sediment, with 15–40 wt % of melt derived from FOZO (with Sr, Nd, and Pb abundances of approximately 30, 6 and 0·2 ppm, respectively), could generate isotope compositions similar to those of the Hawaiian shield lavas (Fig. 8). Hence, we suggest that the Haleakala shield lavas, as well as other Hawaiian shield tholeiitic lavas, are derived from mixed sources that are dominated by the EM1 and FOZO components.

The trace element characteristics of the Hawaiian shield lavas also suggest that recycled gabbroic oceanic crust is present in the source (e.g. Hofmann & Jochum, 1996; Sobolev *et al.*, 2000). The highly incompatible trace element ratios in the submarine Hana Ridge lavas (i.e. $La/Nb = 0{\cdot}89 \pm 0{\cdot}064$, $Ba/Nb = 6{\cdot}06 \pm 0{\cdot}49$, $Ba/Th = 100{\cdot}83 \pm 17{\cdot}43$, $Th/Nb = 0{\cdot}06 \pm 0{\cdot}01$, $Th/La = 0{\cdot}07 \pm 0{\cdot}012$, $Ba/La = 6{\cdot}84 \pm 0{\cdot}082$; 1σ) are not representative of EM1, EM2, or HIMU-type oceanic island basalts as defined by Zindler & Hart (1986), nor they are similar to any proposed primitive-mantle or MORB-source compositions (see Weaver, 1991, table 1). Hofmann & Jochum (1996) suggested that the Hawaiian source contains a significant amount of recycled gabbroic oceanic crust, based on the enrichment of Sr relative to light rare earth elements (LREE) and depletions of Th and U relative to Ba and La in tholeiites from Mauna Loa and Mauna Kea. In a plot of primitive mantle normalized $(Th/La)_n$ vs $(Th/Ba)_n$ (where n denotes primitive mantle; Fig. 9a), the Haleakala shield lavas are positive correlated and most of those ratios are less than unity. The presence of recycled gabbroic oceanic crust in the source is also indicated by a good correlation between $(Sr/Eu^*)_n$ and $(Eu/Eu^*)_n$ (where Eu* is the Eu concentration calculated by interpolating between neighbouring trivalent elements Sm and Gd). $(Eu/Eu^*)_n$ ratios are not correlated with Al_2O_3 (wt %) contents in the bulk rocks from the Haleakala shield, indicating that plagioclase has not fractionated during the eruption of the lavas and, thus, that the ratios probably reflect source characteristics (Fig. 9b). The $(Sr/Eu^*)_n$ and $(Eu/Eu^*)_n$ ratios show good correlation and most of those ratios are greater than unity (Fig. 9c), indicating that the Sr excess correlates with the positive Eu anomaly and, therefore, suggests the presence of recycled gabbroic oceanic crust in which the source composition is controlled by plagioclase fractionation (Gasperini *et al.*, 2000).

Estimation of source mineralogy and the depth of melting

It has been well argued, based on trace element characteristics, that the Hawaiian tholeiitic lavas are derived from a source containing residual garnet (e.g. Frey & Roden, 1987; Hofmann *et al.*, 1984; Frey & Rhodes, 1993; Norman & Garcia, 1999). The compositional characteristics of the submarine Hana Ridge lavas imply that both clinopyroxene and garnet are important residual phases during partial melting. This result is from calculations using the Hofmann & Feigenson (1983) trace element inversion model with the REE and Sr data as outlined below.

Highly incompatible trace element ratios (i.e. La/Nb = 0·89 ± 0·064, Ba/Nb = 6·06 ± 0·49, Ba/Th = 100·83 ± 17·43, Th/Nb = 0·06 ± 0·01, Th/La = 0·07 ± 0·012, Ba/La = 6·84 ± 0·082; 1σ) show little variation whereas ratios such as Zr/Nb, Sr/Nb, and Ba/Nb show limited variation and no correlation with MgO contents (Ren *et al.*, 2004). For this reason, we assume that the magma source for the Hana Ridge is relatively homogeneous in chemical composition. We assume that all the lavas are cogenetic and derived from one or more batches of source rock of uniform chemical composition.

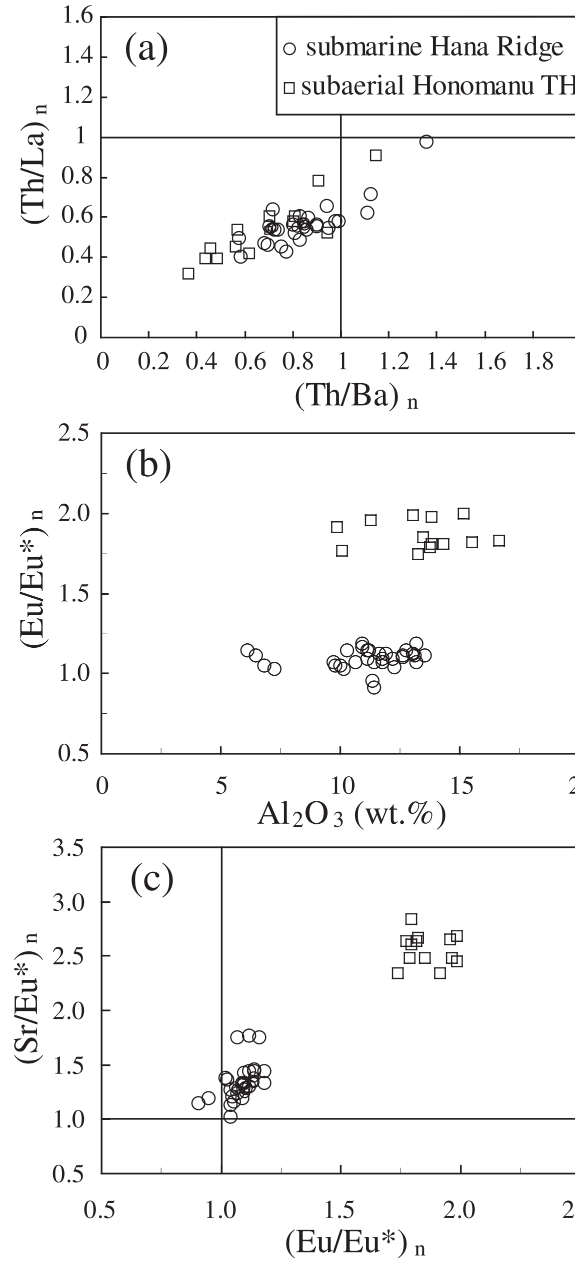

Fig. 9. (a) Primitive mantle normalized Th/La vs Th/Ba in tholeiitic lavas from the Haleakala shield. 'n' denotes primitive mantle and the ratios are normalized to the primitive mantle values of Sun & McDonough (1989). (b) $(Eu/Eu^*)_n$ vs Al_2O_3 (wt %) for tholeiitic lavas from Haleakala shield. Eu* is the Eu concentration calculated by interpolating between the neighboring trivalent elements Sm and Gd. (c) $(Sr/Eu^*)_n$ vs $(Eu/Eu^*)_n$ in lavas of the Haleakala shield. Trace element data for submarine Hana Ridge lavas from Ren *et al.* (2004); data for subaerial Honomanu tholeiitic lavas from Chen *et al.* (1991). TH, tholeiitic basalts.

We can never fully prove the assumption that any such suite of lavas is produced by batch melting. However, we can test the assumption using a simple inversion of the data, and compare the results with those of previous

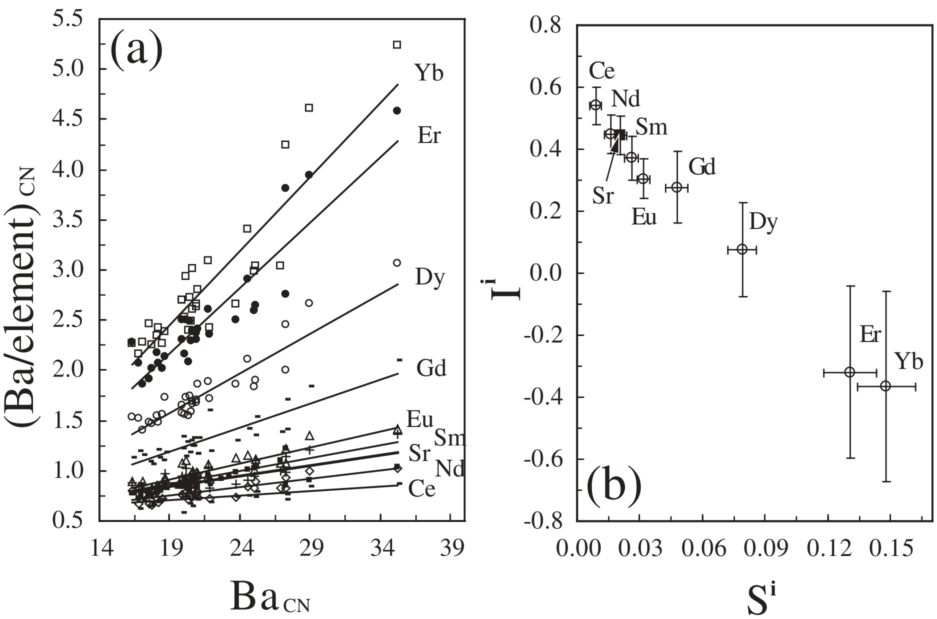

Fig. 10. (a) Ba/element ratios vs Ba concentration. All concentrations have been corrected for fractionation and normalized to chondritic abundances [Tera *et al.* (1970) for Sr and Ba; Nakamura (1974) for REE]. (b) Slope S^i and zero intercepts I^i of the regression lines shown in (a). The size of each cross corresponds to 1σ standard error in the regression parameters. Trace element data for submarine Hana Ridge lavas from Ren *et al.* (2004). (See text for further explanation.)

inversion models for Kilauea, Kohala and Mauna Kea trace element data, which employed similar techniques (e.g. Feigenson *et al.*, 1983, 1996, 2003; Hofmann *et al.*, 1984). This simple model produces different results from models based on fractional melting or continuous melting (e.g. McKenzie, 1985). However, modeling performed on phase 1 HSDP (Hawaiian Scientific Drilling Project) basalts (uppermost Mauna Kea lavas) (Feigenson *et al.*, 1996) showed that pure, end-member incremental melting models give unrealistic mantle source compositions, and require the complete absence of garnet in the Hawaiian source, even for the alkalic lavas. Better solutions are achieved by pooling fractional melts prior to extraction and eruption; those models closely approach the results calculated for batch melting processes (Feigenson *et al.*, 2003).

The primary magma composition (16·7 wt % MgO) is estimated and the major element composition of the lavas used to quantitatively assess the effects of fractional crystallization (Ren *et al.*, 2004). In the following discussion, the measured trace element concentrations of the lavas are corrected to MgO 16·7 wt % by adding (or subtracting) the appropriate amount of olivine. The corrected trace element data are plotted in Fig. 10a as chondrite-normalized concentration ratios vs normalized concentration, following the method of Hofmann & Feigenson (1983) and Hofmann *et al.* (1984). The intercepts and slopes (Fig. 10b) of the fitted straight lines (Fig. 10a) are used to calculate the garnet/clinopyroxene ratio of the source. This approach also follows the method of Hofmann & Feigenson (1983) and Hofmann *et al.* (1984).

The y-intercept of the regression line for each element (Fig. 10a) determines its abundance in the source relative to Ba, using equation (7′) of Hofmann & Feigenson (1983):

$$C_0^i/C_0^{\mathrm{H}} = (1 - P^i)/I^{\mathrm{i}}$$

where C_0 is the source concentration of element i (i denotes the elements of interest; H denotes the highly incompatible element, we use Ba instead of Rb because the analytical precision of the former is better than the latter), P is the weighted partition coefficient of the melting reaction, and I is the y-intercept value of the regression line.

The value of $I^{\mathrm{Yb}} = -0{\cdot}365 \pm 0{\cdot}306$ [$I^i = C_0^{\mathrm{H}}/C_0^{\mathrm{i}}(1-P^i)$], (see Hofmann & Feigenson, 1983) indicates $1 - P^{\mathrm{Yb}} < 1$ and $P^{\mathrm{Yb}} > 1$ ($P^{\mathrm{Yb}} = p_{\mathrm{olivine}}D_{\mathrm{olivine}} + p_{\mathrm{opx}}D_{\mathrm{opx}} + p_{\mathrm{cpx}}D_{\mathrm{cpx}} + p_{\mathrm{gnt}}D_{\mathrm{gnt}} + \ldots$, where D is the mineral/melt partition coefficient for element i). Because values of D^{Yb} for olivine, pyroxenes, and spinel are less than unity, and D^{Yb} for garnet is $\sim$7 (Johnson, 1998; Green *et al.*, 2000) (Table 2), the observation that $P^{\mathrm{Yb}} > 1$ requires garnet as a residual phase in the source. Although residual garnet is required, the lavas also show strong evidence for residual clinopyroxene in their source. The slope (S^i) and intercept (I^i) (Fig. 10b) [$S^i = D_0^i/C_0^i$; $I^i = C_0^{\mathrm{H}}/C_0^i(1 - P^i)$; where D_0^i is the bulk partition coefficient for element i in the source,

*Table 2: Partition coefficients**

Elements	Olivine, Ilmenite, Spinel	Orthopyroxene	Clinopyroxene	Garnet
Ba	0	0	0	0
Sr	0	0·0012	0·11	0·0023
Ce	0	0·0016	0·055	0·0029
Nd	0	0·0056	0·14	0·03
Sm	0	0·015	0·23	0·18
Eu	0	0·03	0·23	0·33
Gd	0	0·034	0·27	0·75
Dy	0	0·077	0·3	2·4
Er	0	0·12	0·24	4·4
Yb	0	0·22	0·22	6·5

*Data for orthopyroxene, clinopyroxene, and garnet from Green *et al*. (2000).

and S^i is the slope of the regression line from Fig. 10a; see Hofmann & Feigenson, 1983] for Sr are similar to those for Nd ($D^{Sr/Nd}$ for clinopyroxene is ~0·8; for garnet is ~0·08) and indicate that the D for Sr is moderately high in the bulk solid–melt and the presence of a residual phase with the partitioning properties of clinopyroxene is required (see Table 2).

The partition coefficient P^i, which appears in Hofmann & Feigenson's (1983) equations (3) $C^i = C_0^i/[D_0^i + F(1 - P^i)]$ and (7) $I^i = C_0^H/C_0^i(1 - P^i)$, is the sum of the mineral–melt partition coefficients for element i weighted in the proportions in which the minerals are consumed into the melt. We can directly determine P^i from the major-element composition of the primary melt, if the nature and composition of the solid phases consumed during the formation of this melt are known or assumed (Hofmann & Feigenson, 1983). Instead, we can constrain P^i by a method assuming that the source pattern for the REE is approximately smooth (Hofmann & Feigenson, 1983; Feigenson *et al*., 1996, 2003), and/or the pattern of P^i for REE must bear some resemblance to D_0^i because the minerals that enter the melt must have been initially present in the source (Feigenson *et al*., 2003). A large range of mineral combinations (here, the minerals are consumed into the melt) were used to calculate P^i until the patterns of both P^i and D_0^i/C_0^{Ba} for REE are smooth and are analogous. The best fit was obtained for ~32% garnet and ~16% clinopyroxene entering the melt (Fig. 11a and b). From this and the I and S values of Fig. 10b, and equations (7′) $C_0^H/C_0^H = (1 - P^i)/I^i$ and (10) $D_0^i/C_0^H = S^i(1 - P^i)/I^i$ of Hofmann & Feigenson (1983), we calculate C_0^i/C_0^{Ba} and D_0^i/C_0^{Ba} values. Finally, we plot the loci of the garnet and clinopyroxene fractions calculated from Hofmann & Feigenson (1983) ($X_{gnt}/C_0^H = -D^i_{cpx}X_{cpx}/D^i_{gnt}C_0^H + D^i_0/C_0^H D^i_{gnt}$) using D_0^i/C_0^{Ba} values

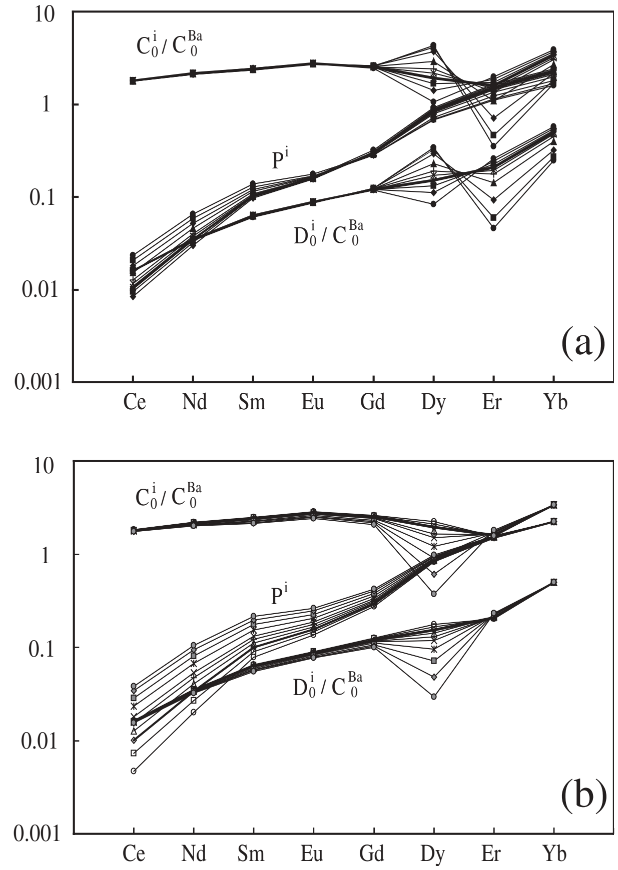

Fig. 11. (a) Calculated source REE concentration (C_0^i) and bulk partition coefficients (D_0^i), relative to C_0^{Ba} (source) for submarine Hana Ridge lavas. The spectrum of calculated source parameters is derived from variable input melt norms (P^i) including 0–40% garnet (only the spectrum derived from norms of 22–35% of garnet is shown). (b) Calculated source parameters as in (a). In this case, spectrum is derived from norms of 0–70% of clinopyroxene. The best fit (the bold lines, assuming that the source pattern for the REE is approximately smooth and a broad similarity between P^i and D_0^i/C_0^{Ba}) is obtained for ~32% garnet and ~16% clinopyroxene entering the melt. (See text for further explanation.)

and the mineral–melt partition coefficients from Table 2 (Fig. 12).

Our inversion shows that the submarine Hana Ridge source has a near flat REE pattern relative to chondrite, which is similar to the patterns obtained by inversion of Mauna Kea (Feigenson *et al*., 1996) and submarine Kilauea lavas compositions (Wagner *et al*., 1998). Simple equilibrium batch melting of a source with an approximately flat REE pattern can reproduce the observed variations in the submarine Hana Ridge lavas. Such a relatively flat REE source pattern is consistent with that calculated by inverse modeling of the Honomanu tholeiitic lavas (Chen & Frey, 1985).

The steadily increasing values for D_0^i/C_0^{Ba} reflect an important contribution from garnet in the source

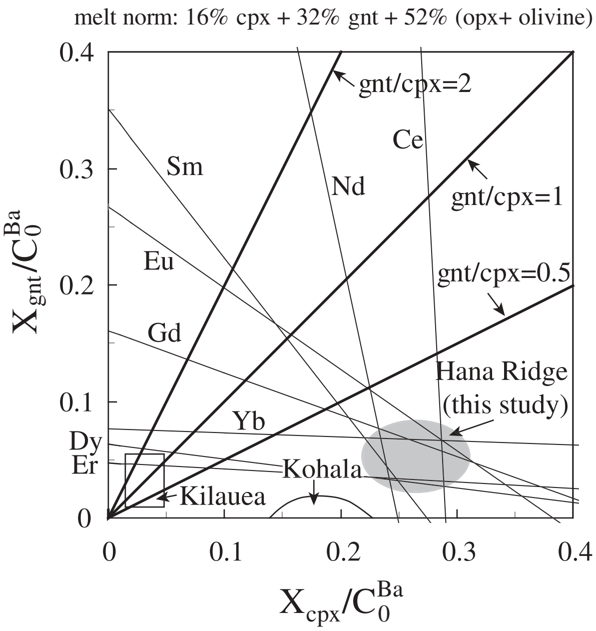

Fig. 12. Loci of calculated weight fractions of garnet and clinopyroxene, X_{gnt} and X_{cpx}, relative to the initial source concentration of Ba (C_0^{Ba}). These loci of each element are given by equation (14) of Hofmann & Feigenson (1983), for the melt norm 16% cpx, 32% gnt, 52% opx + olivine. The bulk partition coefficients of the source (D_0^i/C_0^{Ba}) are obtained from equation (10) of Hofmann & Feigenson (1983). We use D_0^i/C_0^{Ba} values and the mineral–melt partition coefficients from Table 2 to calculate weight fractions of garnet and clinopyroxene (X_{gnt}/C_0^{Ba} and X_{cpx}/C_0^{Ba}). Ideally, all lines should intersect at a point defining the source mineralogy. The calculated results show that the gnt/cpx ratio of the source for the submarine Hana Ridge lavas is <0·5, lower than the ratio for the Kilauea source (0·5–2) (Hofmann *et al.*, 1984), but higher than the ratio for Kohala (~0) (Feigenson *et al.*, 1983). Gnt, garnet; cpx, clinopyroxene; opx, orthopyroxene.

(Fig. 11). The calculated loci of the garnet and clinopyroxene fraction results show that the garnet/cpx ratio of the source for the submarine Hana Ridge lavas is <0·5, lower than the ratio for the Mauna Ulu lavas derived from the Kilauea source (0·5–2) (Hofmann *et al.*, 1984), but higher than the ratio during the transition from tholeiitic to alkalic basalts derived from the Kohala source (~0) (Feigenson *et al.*, 1983) (Fig. 12). Feigenson *et al.* (1983) suggested that the transition from the tholeiitic to the alkalic stage at Kohala volcano occurred in the presence of residual clinopyroxene; the presence of residual garnet is also possible but is not required by the data. This mineralogical variation between the sources of these Hawaiian volcanoes may be due to different depths of melt generation; the Haleakala and Kilauea source is within the stability field of garnet, whereas the source of the magmas produced during the transition from the tholeiitic to alkalic stage at Kohala may be shallower.

The proportions of garnet and clinopyroxene in the magma source may provide important evidence about melting depths. Melting experiments on peridotite show that, so far, none of the starting materials (e.g. Hirose & Kushiro, 1993; Kushiro, 1996; Walter, 1998) used can yield the primary magma composition of the submarine Hana Ridge (Ren *et al.*, 2004). The Hawaiian mantle plume source is believed to contain significant amounts of recycled, ancient oceanic crust (i.e. eclogite bodies, e.g. Hauri, 1996; Hoffman & Jochum, 1996; Lassiter & Hauri, 1998; this study). Experimental studies indicate that eclogite bodies will begin to melt at higher pressure than the ultramafic matrix in an ascending plume (Yasuda *et al.*, 1994; Yaxley & Green, 1998). The silica-rich melt from eclogite melting will react with the surrounding ultramafic peridotitic material to form pyroxenite (Yasuda *et al.*, 1994). Here, we use the pMELTS algorithm (Ghiorso *et al.*, 2002) to calculate the proportions of minerals (e.g. clinopyroxene and garnet) in the source for a range of possible compositions for the Hawaiian magma source: a peridotite (KR4003; Walter, 1998), mixed 90% peridotite (KLB1; Hirose & Kushiro, 1993) + 10% MORB (average; Patera & Hollaway, 1982), and mixed 80% peridotite (KLB1) + 20% MORB (average). If the source includes a significant amount of the basaltic component, then the proportions of clinopyroxene and garnet in the source would increase with increasing amounts of the basaltic component. The garnet proportions in the source also increase with increasing pressure (Fig. 13a and b). We found that, at temperatures from 1500 to 1600°C, the garnet/cpx ratio in the source increases from less than ~0·1, to 0·3–0·4, and finally to >0·42 at pressures of 3, 3·5, and 4 GPa, respectively (Fig. 13c). If this result is compared with the estimated garnet/cpx ratio in the magma sources (Fig. 12), it is suggested that the depth of the source for Kilauea, submarine Hana Ridge, and the transition from tholeiitic to alkalic basalts at Kohala changes from deeper to shallower (>4 GPa, 3–4 GPa, <3 GPa). This may also imply that the Kilauea lavas represent the early stage, and the transitional tholeiite to alkalic basalts from Kohala studied by Feigenson *et al.* (1983) may represent the final stage of the Kohala volcano; the difference could be attributed to the difference in the growth stage of the Hawaiian volcanoes. In other words, the difference in the depth of magma genesis might be due to the difference in the position of the melt zone with respect to the axis of the Hawaiian plume. The Kilauea lavas may have been produced at or close to the plume axis, whereas the transitional tholeiite to alkalic basalts from Kohala may have been formed at a significant distance from the plume axis. Because the center of the plume is at a higher temperature than its margins, lavas derived from the central position (e.g. Kilauea shield) would segregate at a higher mean pressure than lavas derived from off-centered positions (e.g. the transitional tholeiite to alkalic basalts from Kohala).

This interpretation is also supported by geochemical evidence from Haleakala shield lavas. The subaerial Honomanu tholeiitic lavas have lower ε_{Nd} and higher $^{87}Sr/^{86}Sr$ than the submarine Hana Ridge lavas. This implies that they are derived from a less depleted source than the submarine Hana Ridge lavas. However, ratios of relatively immobile trace elements, such as La/Yb, in the subaerial Honomanu tholeiitic lavas (4·1–5·94; average 5·3; data from Chen *et al.*, 1991) are lower than those in the submarine Hana Ridge lavas (4·12–9·91; average 6·4). Therefore, it is unlikely that the lower La/Yb in the subaerial Honomanu lavas results from lower La/Yb in the source relative to that of the submarine Hana Ridge lavas. The higher SiO_2 content (lower SiO_2 contents in some of the subaerial Honomanu samples are due to alteration or reflect the change to transitional and alkalic basalts; Chen *et al.*, 1991; Ren *et al.*, 2004) and lower La/Yb in the subaerial Honomanu lavas are consistent with generation at shallower depths through a higher degree of partial melting than the submarine Hana Ridge lavas. Lower La/Yb in the subaerial Honomanu lavas also indicates higher melt fractions, as La/Yb is highly sensitive to the degree of partial melting, particularly if there is residual garnet in the source, and will decrease with increasing melt fraction. Lassiter *et al.* (1996) also proposed a similar explanation, that the higher SiO_2, and lower La and La/Yb in the Mauna Loa lavas is consistent with magma generation at shallower depths through higher degrees of partial melting than for Mauna Kea or Kilauea. Melting experiments suggest that the SiO_2 content of the melt increases with decreasing pressure, whereas an increased degree of partial melting results in an increased SiO_2 content in the melt (Hirose & Kushiro, 1993; Kushiro, 1996; Kogiso *et al.*, 1998; Walter, 1998). In other words, the SiO_2 content of these associated tholeiites, transitional tholeiites and alkalic basalts magmas decreases with decreased degree of melting.

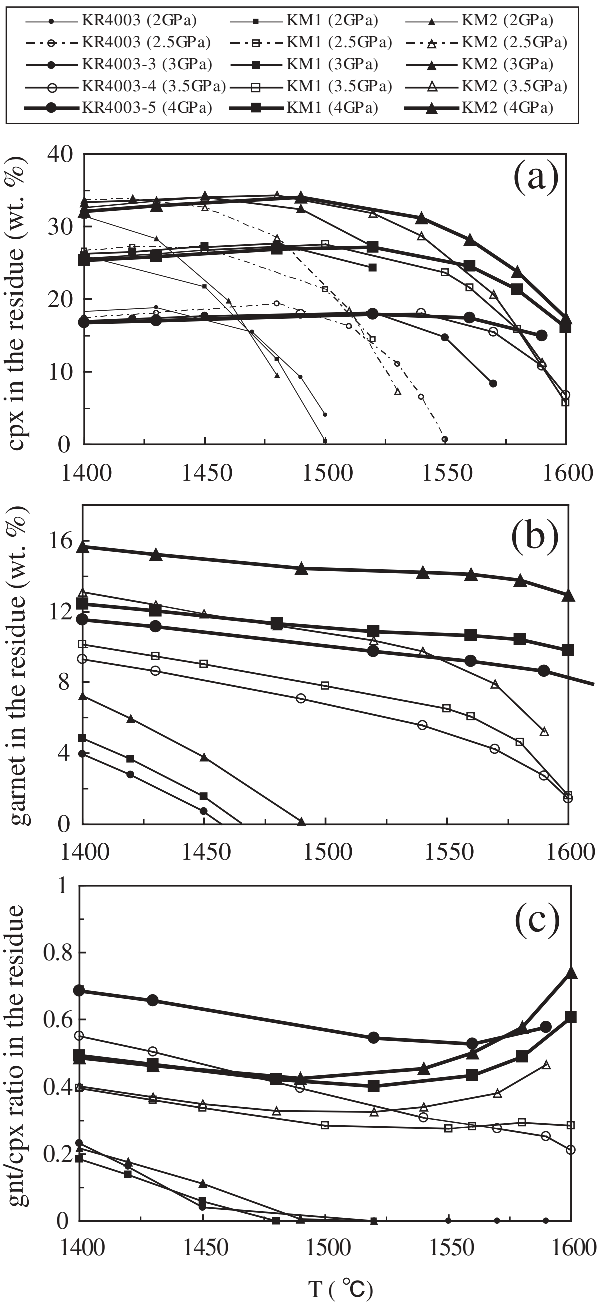

Fig. 13. (a) Mass proportions of clinopyroxene (cpx) in the residue of peridotite (KR4003), mixed 90% peridotite + 10% MORB (KM1), and mixed 80% peridotite + 20% MORB (KM2) vs temperature at pressures of 2, 2·5, 3, 3·5, and 4 GPa. Cpx proportion increases with increasing basaltic component in the source, but does not change significantly with increasing pressure. (b) Mass proportions of garnet in the residue of KR4003, KM1, and KM2 vs temperature at 3, 3·5, and 4 GPa. Garnet proportion increases with increasing basaltic component and with increasing pressure. (c) The garnet/clinopyroxene ratio in the residue of KR4003, KM1, and KM2 vs temperature at 3, 3·5, and 4 GPa. The gnt/cpx ratio in the source increases with increasing pressure. The composition of KR4003 (peridotite) is the same as that of the starting material for the high-pressure melting experiments of Walter (1998). KM1 and KM2 have compositions equivalent to mixtures of KLB-1 (peridotite) and average MORB in the proportion 0·9:0·1 and 0·8:0·2, respectively. Data for KLB-1 (peridotite) and average MORB from Hirose & Kushiro (1993) and Patera & Holloway (1982), respectively. Calculations were performed with pMELTS at an oxygen fugacity of QFM (quartz–fayalite–magnetite), at temperatures between 1400 and 1600°C. gnt, garnet; cpx, clinopyroxene.

Geochemical differences in the shield volcanoes and the structure of the Hawaiian mantle plume

Many workers have proposed that a concentrically zoned mantle plume can account for the geochemical characteristics of the Hawaiian lavas (e.g. Hauri *et al.*, 1996; Kurz *et al.*, 1996; Lassiter *et al.*, 1996; DePaolo *et al.*, 2001). These zoned plume models assume nearly constant

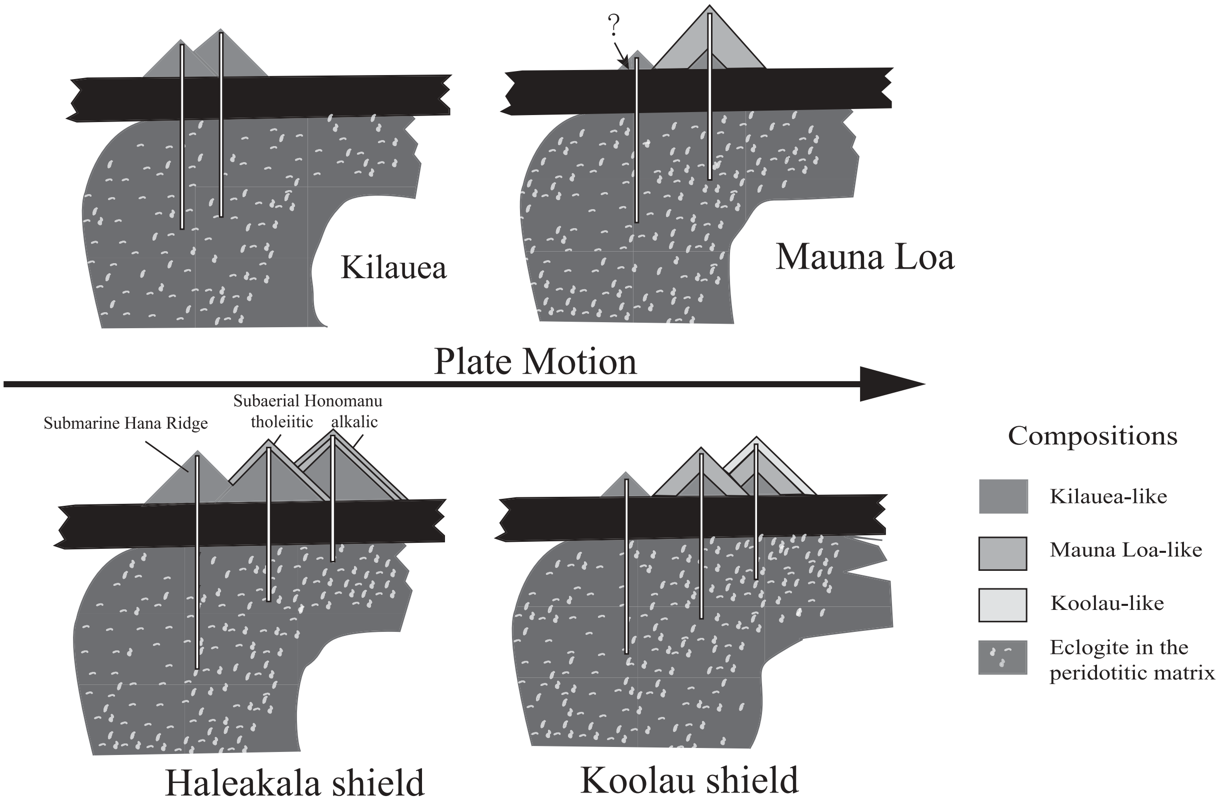

Fig. 14. A model for magma genesis in the Hawaiian plume. The geochemical differences between the various shield lavas reflect different mixing proportions of recycled gabbroic oceanic crust (eclogite) in the source. The melting depth decreases in the mantle plume during progressive growth of Hawaiian shield volcanoes as they migrate away from the central axis of the plume with plate motion, because the center of the plume is at a higher temperature than the margins. Lavas derived from the plume center segregate at a higher mean pressure than lavas derived from the margin. During later shield stages, the proportion of fertile pyroxenite consumed into the melt may be higher than that of the peridotite matrix, because melting in the periphery of the plume occurs at lower temperatures and therefore preferentially samples the lower melting point component (e.g. eclogite). (See text for further explanation.)

isotopic compositions during the shield stage of growth. However, several Hawaiian volcanoes show systematic compositional variation during the later stages of shield building (e.g. Koolau, Tanaka *et al.*, 2002; Mauna Loa, Kurz *et al.*, 1995; Haleakala, this study), as well as in the main stage of shield growth (e.g. Kilauea, Pietruszka & Garcia, 1999; Mauna Kea, Abouchami *et al.*, 2000; Eisele *et al.*, 2003). Although Mauna Kea and Mauna Loa lie almost equidistant from the proposed present-day center of the plume, the isotopic compositions of lavas from these two volcanoes do not overlap (Abouchami *et al.*, 2000; Eisele *et al.*, 2003). This implies that the plume structure is chemically more complicated than a simple concentrically zoned structure (e.g. Blichert-Toft *et al.*, 2003; Eisele *et al.*, 2003; Mukhopadhyay *et al.*, 2003).

Chemical heterogeneities with length scales of only a few kilometers can be preserved in the convecting mantle for long periods of time (Lassiter & Hauri, 1998). Eisele *et al.* (2003) suggested Pb isotope heterogeneities several tens of kilometers in size within the Hawaiian plume. Pietruszka & Garcia (1999) observed rapid changes in both chemical and isotope compositions in lavas erupted at Kilauea since 1790, and suggested that the length scale of source heterogeneity in the Hawaiian plume is small relative to the scale of the partial melting region. Because many of the chemical characteristics observed in the heterogeneous plume melts can be explained by melting of garnet pyroxenite–peridotite mixtures (see discussion above), we infer that subducted oceanic crust can retain much of its original geochemical signature throughout the convective cycle and remain essentially unmixed in the surrounding matrix (e.g. Hauri, 1996). This recycled ancient oceanic crust may form plumes or streaks that remain geochemically distinct (Morgan & Morgan, 1999; Davies, 2002). Material in the plume head may be highly deformed and stirred by a series of stretching and folding events that occurred during plume up-rise (Farnetani *et al.*, 2002).

Based on the above observations and discussions, we have constructed a model for magma genesis in the heterogeneous Hawaiian mantle plume that could explain the observed intershield geochemical variations (Fig. 14).

The entrained ancient oceanic crust (eclogite) may retain much of its original geochemical signature throughout the convective cycle and remain essentially unmixed with the surrounding matrix that was derived from the deep lower mantle. Hawaiian volcanoes sample heterogeneities in the plume during individual shield growth that may reflect mixing of variable proportions of the different plume components.

The plume rises from the lower mantle to the upper mantle and melts as a result of decompression. Because the center of the plume is at a higher temperature than the margins, lavas derived from the center segregate at a higher mean pressure than lavas derived from the margin. The Kilauea lavas may be produced at or close to the plume center, thus the melts formed in the deeper part of the plume melting regime (>130 km) and the proportion of material from the deep lower mantle may be higher than in other stages of shield growth. When the volcano moves away from the plume center, then the lavas corresponding to the Hana Ridge may be formed in a relatively shallower depth range (130–90 km). The Mauna Loa lavas were produced from a source that had a relatively higher proportion of the eclogite component than the Kilauea source and were generated at shallower depths through higher degrees of partial melting than lavas from Kilauea.

The mantle plume material at a position significantly away from the plume axis has a lower temperature than that at the plume center, and the proportion of the subducted oceanic crust (eclogite) component is higher than the proportion of the component of peridotitic matrix sampled by the melts. This is because at the plume center the higher temperatures lead to melting not only of the eclogite component, but also of the more refractory material (i.e. the peridotitic matrix); conversely, in the plume margin, lower temperatures favor melting of the more mafic component relative to the ultramafic peridotite. Therefore, melts formed away from the plume center may have isotopically 'enriched' characteristics, and have higher SiO_2 contents, such as in the last stage (Makapuu stage) of Koolau volcano or the Honomanu stage of Haleakala volcano. The transitional tholeiite to alkalic basalt magmas corresponding to the subaerial Honomanu stage of Haleakala volcano or the transitional tholeiite to alkalic basalts of Kohala may be produced by lower degrees of melting with low eruption rates at the cooler margins of the melt zone and in shallower parts of the plume.

CONCLUSIONS

The Sr, Nd, and Pb isotope compositions of submarine Hana Ridge lavas are similar to those of Kilauea; in contrast, most of the subaerial Honomanu lavas are in the Mauna Loa field and some are in the intermediate Mauna Loa–Kilauea field. Accordingly, the source of the Haleakala shield lavas appears to have changed during the evolution of the volcano. We propose that the source sampled in the mantle plume during the Haleakala shield stage changed slightly over time from the submarine stage to the subaerial stage. Similar compositional changes during the growth history have been reported from other Hawaiian volcanoes. More than one mantle source component (e.g. Kea, Loa and Koolau components) appears to play a dominant role within individual shields such as at Haleakala, Mauna Kea and Koolau. These observations contradict the widely accepted hypothesis that there are two major compositional and isotopic trends (the Kea trend and the Loa trend) among the Hawaiian shield volcanoes and that their geographical distributions are controlled by the loci of the volcanoes relative to the axis of the Hawaii plume.

The systematic variation of Pb, Sr, and Nd isotope ratios and trace elements ratios in lavas erupted at the Haleakala shield volcano requires a chemically heterogeneous source. The broad correlation between isotopic ratios and trace element ratios can be explained in the context of chemical heterogeneity and mixing if the submarine Hana Ridge lavas (with relatively low $^{87}Sr/^{86}Sr$) sampled a source with lower Ba/Nb and Zr/Nb, whereas the subaerial Honomanu tholeiitic lavas (with relatively higher $^{87}Sr/^{86}Sr$) sampled a source with higher Ba/Nb and Zr/Nb.

The compositional characteristics of the lavas imply that both clinopyroxene and garnet are important residual phases during partial melting. Inversion modeling indicates that the garnet/clinopyroxene ratio for the submarine Hana Ridge source (<0·5) is lower than the ratio for the Mauna Ulu lavas of Kilauea (0·5–2), but higher than the ratio for the transitional tholeiite to alkalic basalts of Kohala (~0). The major and trace element characteristics of the lavas might reflect variations in mean degree of melting and depth of melting during the different stages of growth of Hawaii shield volcanoes.

We propose that the geochemical differences among the Hawaiian shield volcanoes reflect different mixing proportions of recycled gabbroic oceanic crust in the source. The melting depth decreases in the mantle plume during the growth of Hawaiian shield volcanoes as they migrate away from the central axis of the plume. Some of the later-stage lavas of Hawaiian shields have isotopically 'enriched' characteristics, implying that the proportion of the subducted oceanic crust (eclogite) component contributing to the melt may be higher relative to the peridotitic matrix, because during the generation of the later-stage lavas their mantle source is located significantly away from the mantle plume axis where the temperature is lower than in the center of the plume.

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