Horizontal and vertical zoning of heterogeneities in the Hawaiian mantle plume from the geochemistry of consecutive postshield volcano pairs: Kohala-Mahukona and Mauna Kea–Hualalai

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Sr-Nd-Pb-Hf isotopic compositions of postshield lavas from two pairs of Hawaiian volcanoes, Mauna Kea and Kohala (Kea trend) and Hualalai and Mahukona (Loa trend), allow for identification of small-scale (tens of kilometers) heterogeneities in the Hawaiian mantle plume and provide constraints on their distribution. The postshield lavas range from transitional/alkalic basalt to trachyte and are enriched in incompatible trace elements (e.g., La_N/Yb_N = 6.0–16.2). These lavas are characterized by a limited range of Sr-Nd-Hf isotopic compositions (\(^{87}\text{Sr}/^{86}\text{Sr} = 0.70343–0.70365, {^{143}\text{Nd}}/{^{144}\text{Nd}} = 0.51292–0.51301, \text{and} {^{176}\text{Hf}}/{^{177}\text{Hf}} = 0.28311–0.28314\)) and have distinct Pb isotopic compositions (\(^{206}\text{Pb}/^{204}\text{Pb} = 17.89–18.44, {^{207}\text{Pb}}/{^{204}\text{Pb}} = 15.44–15.49, \text{and} {^{208}\text{Pb}}/{^{204}\text{Pb}} = 37.68–38.01\)) that correspond to their respective Kea or Loa side of the Pb-Pb isotopic boundary. Mauna Kea lavas show a systematic shift to less radiogenic Pb isotopic compositions from the shield to postshield stage and they trend to low \(^{87}\text{Sr}/^{86}\text{Sr} toward, but not as extreme as, compositions characteristic of rejuvenated stage lavas. Hualalai postshield lavas lie distinctly above the Hf-Nd Hawaiian array and have much lower Pb isotopic ratios than shield lavas, including some of the least radiogenic values (e.g., \(^{206}\text{Pb}/^{204}\text{Pb} = 17.89–18.01\)) of recent Hawaiian volcanoes. In contrast, comparison of Kohala with the adjacent Mahukona volcano shows that these older postshield lavas become more radiogenic in Pb during the late stages of volcanism. The isotopic systematics of the postshield lavas cannot be explained by mixing between Hawaiian plume end-members (e.g., Kea, Koolau, and Loihi) or by assimilation of Pacific lithosphere and are consistent with the presence of ancient recycled lower oceanic crust (±sediments) in their source. More than one depleted component is sampled by the postshield lavas and these components are long-lived features of the Hawaiian plume that are present in both the Kea and Loa source regions. The depleted components in the postshield lavas, particularly as sampled at Hualalai, are different from the much more homogeneous component present in rejuvenated lavas. The geochemistry of the postshield lavas provides evidence for a bilateral symmetry to the plume where the compositional boundary between the Kea and Loa sources is complex and vertical components of heterogeneity are significant.
1. Introduction

[2] The ~6000 km long Hawaiian-Emperor Seamount Chain represents the surface expression of the Hawaiian mantle plume and is the classic example of intraplate volcanism [DePaolo and Weis, 2007]. The Hawaiian plume is long-lived and one of the hottest plumes with the largest buoyancy flux [Sleep, 1990], and it is inferred to have a deep mantle origin [e.g., Courtillot et al., 2003; Montelli et al., 2006]. Volcanoes at the young end (<5 Ma) of the Hawaiian chain define two parallel geographic trends, termed Loa and Kea [Dana, 1849; Jackson et al., 1972], and systematic geochemical variations are observed between lavas erupted from the two trends and during different growth stages (preshield, shield, postshield, rejuvenated) of the volcanoes [e.g., DePaolo et al., 2001; Blichert-Toft et al., 2003; Eisele et al., 2003; Abouchami et al., 2005; Bryce et al., 2005; Marske et al., 2007]. These variations are generally explained by inferring that the Hawaiian plume is either concentrically zoned [e.g., Hauri, 1996; Kurz et al., 1996; Lassiter et al., 1996] or bilaterally zoned [Abouchami et al., 2005] in cross section. However, vertical heterogeneities within the upwelling plume are also likely to be an important factor in creating the observed geochemical variability [Blichert-Toft et al., 2003; Marske et al., 2007]. In this study, we use the geochemistry of postshield lavas, which are derived from low degrees of partial melting and thus are potentially capable of sampling small-scale heterogeneities in the melting region, from Mauna Kea, Hualalai, and Kohala volcanoes on the island of Hawaii to assess the structure of the Hawaiian plume source.

[3] Individual Hawaiian volcanoes evolve through four different growth stages [Clague and Dalrymple, 1987]: (1) a small volume (~3%) alkalic preshield stage, (2) the main tholeiitic shield stage during which the majority (95%–98%) of the volcano is built, (3) a small volume (~1%) alkalic postshield stage, and (4) following 0.5–2.5 Myr of quiescence, a volumetrically minor (<1%) strongly alkalic rejuvenated stage. The compositional range of Hawaiian shield stage lavas is typically accounted for by mixing of at least three isotopically distinct end-members, referred to as Loihi, Kea, and Koolau [e.g., Staudigel et al., 1984; Stille et al., 1986; West et al., 1987; Eiler et al., 1996; Hauri, 1996; Tanaka et al., 2008]. The depleted isotopic signatures of postshield and rejuvenated stage lavas require contributions from an additional component that may be intrinsic to the plume [e.g., Frey et al., 2005] or derived at least in part from external sources, including entrained upper mantle and the underlying Pacific lithosphere [e.g., Chen and Frey, 1985; Gaffney et al., 2004]. However, recent studies of rejuvenated stage lavas [e.g., Fekiacova et al., 2007; M. O. Garcia et al., Petrology, geochemistry and geochronology of Kauai’s lavas over 4.5 Ma: Implications for the origin of rejuvenated volcanism and the evolution of the Hawaiian plume, submitted to Journal of Petrology, 2009] argue against lithosphere involvement and support a heterogeneous plume model, where distinct isotopic signatures are derived by melting of vertically stretched lithologies intimately associated with the upwelling plume. The distribution of heterogeneities in the Hawaiian plume, and in particular the depleted component involved in the postshield and rejuvenated stages, remains a controversial unresolved aspect of Hawaiian volcanism.

[4] The advantage to studying postshield lavas, which occur on many Hawaiian volcanoes (including Haleakala, West Maui, East and West Molokai, Waianae, Kauai), is that they are derived from...
significantly lower degrees of partial melting (i.e., a few percent [Clague and Dalrymple, 1988]) compared to the shield stage lavas and can thus provide finer resolution of compositional variations in the plume source. The lower magma supply during the postshield stage (<0.005 km$^3$/yr; one tenth to one hundredth of the rate during the shield stage) prevents a single long-lived conduit from being maintained, and each eruption is likely to be associated with a separate vent and path through the lithosphere [e.g., Frey et al., 1990; Wolfe et al., 1997; Hieronymus and Bercovici, 2001]. Assuming that melt can be extracted from small regions (length scale < 10 km) within the melting zone without substantial subsequent chemical modification [Marske et al., 2007], the geochemistry of postshield lavas permits identification of small-scale heterogeneities within the plume that might not be resolvable in the main tholeiitic shield-building stage. Furthermore, because these lavas erupt after the volcano has migrated to the periphery of the plume, studies of postshield lavas have implications for the distribution of these heterogeneities in the plume.

[5] High-precision trace element concentrations and Sr, Nd, Pb and Hf isotopic compositions of 32 postshield lavas from Mauna Kea, Hualalai, and Kohala volcanoes are used to identify systematic temporal trends as they evolve from the shield to postshield stage. We evaluate if the distinct isotopic compositions of the postshield lavas can be explained by mixing between the shield end-members or by contributions from the underlying Pacific lithosphere, shallow asthenosphere, or components within the plume. The identification of similar depleted isotopic signatures in late shield, postshield, and rejuvenated stage lavas from other Hawaiian volcanoes demonstrates the widespread occurrence of such depleted components in Hawaiian lavas. Integration of these results with new high-precision isotopic data from Mahukona volcano allows the geochemistry of two consecutive Loa-Kea volcano pairs to be compared, and thus provides both spatial and temporal constraints on the geochemical structure of the Hawaiian plume.

2. Samples

[6] Thirty-two subaerial postshield lavas were collected from Kohala, Mauna Kea, and Hualalai volcanoes on the northern part of the island of Hawaii (Figure 1). The samples were taken from lava flows that could be traced back to a specific vent from gulches and road cuts on the flanks of these volcanoes (Table S1 in the auxiliary material). The collected samples are fresh; olivine phenocrysts are unaltered and there is only rare minor alteration of the groundmass. The bottom left inset in Figure 1 shows the age distribution of the postshield lavas and their relative timing compared to shield basalts [Aciego et al., 2009].

[7] At Kohala, the oldest and most extensively eroded volcano on the island of Hawaii, seven samples were collected, including three late shield lavas (Polulu Volcanics) that range in age from 450 ± 40 ka to 375 ± 22 ka. The four samples belonging to Kohala’s postshield stage (Hawaii Volcanics) are significantly younger, with ages ranging from 190 ± 20 ka [Aciego et al., 2009] to 137 ± 5 ka [McDougall, 1969]. For Mauna Kea, where postshield volcanism is divided into an earlier basaltic substage (Hamakua Volcanics) and a later hawaiitic substage (Laupahoehoe Volcanics) [Wolfe et al., 1997], 12 samples were collected (six from each substage). The basaltic samples range in age from 239 ± 84 ka to 123 ± 5 ka, and the hawaiitic samples are as young as 19 ± 4 ka [Aciego et al., 2009]. Thirteen samples were selected from Hualalai, which is almost completely covered by a thin veneer of postshield lavas (Hualalai Volcanics). Most of these samples range in age from 13 ka to 2.3 ka [Wolfe and Morris, 1996], except for one sample from the young Waha Pele flow (0.71 ka) on the southwestern flank of the volcano, and one from the Puu Waawaa pumice cone (Waawaa Trachyte Member) on the northern slope, dated at 113.5 ± 3.2 ka [Cousens et al., 2003].

[8] This study is complemented by a selection of tholeiitic to transitional/weakly alkalic basalts from Mahukona, a submerged Hawaiian shield volcano found off the northwest coast of the island of Hawaii (Figure 1) that has also experienced postshield volcanism [Clague and Calvert, 2009]. The location and age of Mahukona enables comparison with the adjacent Kohala volcano and the younger Hualalai volcano, thus allowing the geochemical systematics of two sequential Loa-Kea volcano pairs to be evaluated. Due to the importance of fully characterizing this volcano, which has recently been dated by the Ar-Ar method and confirmed to have reached the postshield stage [Clague and Calvert, 2009], the trace element and isotope geochemistry, along with new gravity and magnetics...
data, will be presented elsewhere (M. O. Garcia et al., manuscript in preparation, 2009).

3. Methods

[9] The 32 postshield lavas were analyzed for major and trace element abundances (Table 1) and for Sr, Nd, Hf, and Pb isotopic compositions (Table 2) following the methods of Weis et al. [2006, 2007]. Analytical procedures, as well as evaluation of the accuracy and precision of these analyses, are described in sections 1 and 2 of Text S1, respectively. Whole rocks were coarsely crushed in a hydraulic piston crusher between tungsten carbide (WC) plates and ground to a fine powder in a WC mill for major element analyses and an agate planetary mill for trace element and isotope analyses. The potential effect of WC contamination on trace elements and Pb and Hf isotopes is discussed in section 3 of Text S1.

[10] The major element oxides and some trace elements were determined by XRF using a Philips PW2400 spectrometer at the Center for Isotope Geochemistry (CIG), University of California, Berkeley.
### Table 1 (Sample). Major and Trace Element Abundances of Hawaiian Postshield Lavas

The full Table 1 is available in the HTML version of this article.

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<th>K₂O</th>
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**Major elements (wt %)**
- SiO₂
- TiO₂
- Al₂O₃
- Fe₂O₃
- MnO
- MgO
- CaO
- Na₂O
- K₂O
- P₂O₅

**Trace elements (ppm)**
- Sr
- Ba
- Rb
- Sr
- Sr
- Sr
- Sr
- Sr
- Sr

**Notes:**

- Major element abundances were determined by XRF, trace element abundances were determined by either XRF or HR-ICP-MS (denoted as ICP). XRF compositions are the mean of duplicate analyses, Fe₂O₃ = total Fe, Mg # = (Mg/Mg + Fe²⁺), and A.I. (alkalinity index) = (Na₂O + K₂O) / 0.37 * SiO₂ + 14.43.
- HR-ICP-MS abundances are the mean of duplicate or replicate analyses.
- ICP-MS abundances are the mean of duplicate or replicate analyses.

Values of the USGS reference materials AGV-1, BHVO-1, and BCR-2 used for calibration show good agreement with recommended values (Table S2).

Complete trace element characterization by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) was carried out at the Pacific Centre for Isotopic and Geochemical Research (PCIGR), University of British Columbia, on a Thermo Finnigan Element2 (see Figure S1 for a comparison of XRF and HR-ICP-MS values). For
**Table 2.** Hf, Sr, Nd, and Pb Isotopic Compositions of Hawaiian Postshield Lavas

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<th>Volcanic Series</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
<th>$^{143}\text{Nd}/^{144}\text{Nd}$</th>
<th>$^{176}\text{Hf}/^{177}\text{Hf}$</th>
<th>$^{208}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{207}\text{Pb}/^{204}\text{Pb}$</th>
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most elements, values of the USGS reference materials AGV-2 and BCR-2 are within 2σ error of literature and recommended values (Tables S3 and S4). Procedural duplicates and replicate measurements show excellent agreement, with relative standard deviations (RSD) less than 5% for most elements. Procedural blank values for the rare earth elements (REE) and most other elements are in the ppt range, and are considered negligible in comparison to the sample concentrations, which are in the ppm range. Column blanks for Sr, Nd, Hf and Pb isotope chemistry are also negligible (Sr: 0.63 ng; Nd: 0.67 ng; Hf: 0.01 ng; Pb: 0.16 ng).

[11] Sr and Nd isotopic compositions were determined at the CIG, University of California, Berkeley, with a VG Sector 54 multicollector thermal ionization mass spectrometer. Hf and Pb isotopic compositions were determined at the PCIGR, University of British Columbia, on a Nu Plasma (Nu Instruments) MC-ICP-MS. The average $^{87}$Sr/$^{86}$Sr of the SRM 987 Sr standard was 0.710281 ± 0.000015 (2σ; n = 140) during the course of the postshield analyses. For Nd, which was run as an oxide, mean values of $^{143}$Nd/$^{144}$Nd were 0.510977 ± 0.000006 (2σ; n = 86) for the Berkeley Ames standard and 0.511876 ± 0.000005 (2σ; n = 10) for BCR-1 (equivalent to a value of 0.512629 for an Ames value of 0.510939) that is equivalent to a La Jolla value of 0.511858. The JMC 475 Hf standard gave a mean $^{176}$Hf/$^{177}$Hf of 0.282157 ± 0.000015 (2σ; n = 175). The NBS 981 Pb standard gave average values (n = 226) of $^{206}$Pb/$^{204}$Pb = 16.9413 ± 0.0030 (2σd), $^{207}$Pb/$^{204}$Pb = 15.4981 ± 0.0024 (2σd), and $^{208}$Pb/$^{204}$Pb = 36.7187 ± 0.0076 (2σd) during the course of the postshield analyses, which are within the 2σ error of the accepted triple spike values. External reproducibility is better than ~50 ppm for Hf and ~150 ppm for Pb isotopic compositions (Tables S5 and S6). All values reported in Table 1 have been normalized to $^{87}$Sr/$^{86}$Sr = 0.710248 for SRM 987, to $^{143}$Nd/$^{144}$Nd = 0.510939 for the Berkeley Ames standard (equivalent to a La Jolla value of 0.511858 [Weis et al., 2006]), to $^{176}$Hf/$^{177}$Hf = 0.282160 for JMC 475, and to the triple spike values of Galer and Abouchami [1998] for SRM 981.

4. Results

4.1. Major and Trace Elements

[12] The postshield lavas range widely in composition from basalt to trachyte (Figure 2), are mostly alkalic, and have highly variable MgO contents
At Kohala and Mauna Kea, late shield and early postshield lavas are characterized by transitional/alkalic basalts, whereas late postshield lavas include hawaiites, mugearites, and benmoreites. In contrast, at Hualalai there is a large compositional gap between the alkalic basalts and trachytes of the postshield stage. For the transitional/alkalic basalts (>5 wt % MgO), Ni is strongly correlated with MgO, which is consistent with the combined effects of olivine fractionation and olivine accumulation. For the alkalic lavas (<5 wt % MgO), Fe$_2$O$_3$, TiO$_2$, CaO, and Sc abundances decrease strongly with decreasing MgO, indicating fractionation of Fe-Ti oxides and clinopyroxene. The anomalously higher P$_2$O$_5$ contents (1.6–2.2 wt %) of three alkalic lavas from Kohala are likely related to accumulated apatite, whereas the low values in the benmoreite and trachyte reflect apatite fractionation. For most samples (31 of 32), K$_2$O/P$_2$O$_5$ > 1, which indicates that they have not undergone significant posteruptive alteration [e.g., Feigenson et al., 1983; Chen and Frey, 1985; Frey et al., 1994].

Abundances of incompatible trace elements are generally well correlated with Nb concentration (15–70 ppm), although some subtle differences exist (Figure 3). The Ba and Rb abundances of basalts from Hualalai define a separate, steeper trend than the other postshield lavas. The trachyte from Hualalai (140 ppm Nb) has anomalous trace element contents, including extremely low Sr (37 ppm) and Ba (281 ppm) concentrations that are indicative of extensive feldspar (+apatite) fractionation. The alkalic lavas from Kohala are shifted to slightly higher La concentrations and have elevated Sr concentrations (~1800 ppm Sr) that are consistent with accumulated apatite.

Postshield lavas have steep REE patterns (La$_N$/Yb$_N$ = 6.0–16.2) (Figure 4). The alkalic lavas from Kohala have the highest REE abundances (e.g., La = 215–340 times chondrites), and the transitional/alkalic basalts from Mauna Kea and Hualalai have the lowest (e.g., La = 50–95 times chondrites). Nearly all of the postshield lavas show a prominent Pb trough, as well as enrichment in the high field strength elements, but with a distinctive convex-down shape defined by lower U, Th, and especially Cs (Figure 4). The trachyte from Hualalai is distinctive, showing enrichment in the light and heavy REE relative to the middle REE, a positive Rb anomaly and negative Ba, Sr, and Eu anomalies, which reflect the effects of extensive feldspar (+apatite) fractionation. The trachyte also has elevated Zr and Hf abundances signaling the presence of accumulated zircon. As expected, the postshield lavas become progressively more enriched in incompatible trace elements with time, relative to late shield transitional/alkalic basalts or typical shield tholeiites.

4.2. Sr-Nd-Hf-Pb Isotopic Compositions

The majority of the postshield lavas are characterized by a relatively limited range of Sr, Nd, and Hf isotopic compositions ($^{87}$Sr/$^{86}$Sr = 0.70345–0.70365; 143Nd/144Nd = 0.51292–0.51302; 176Hf/177Hf = 0.28311–0.28314) (Table 2). In contrast, their Pb isotopic compositions range to a greater extent (e.g., 206Pb/204Pb = 17.90–18.45) and show a clear separation between the Kea trend (Mauna Kea and Kohala) and Loa trend (Hualalai and Mahukona) volcanoes. The transitional/alkalic basalts and alkalic lavas, which are distinguished by major and trace element chemistry, also exhibit differences in Sr and Pb isotopic compositions. As commonly observed for trachytes on oceanic islands [e.g., Weis et al., 1998], the trachyte from Hualalai has higher Sr and slightly lower Nd and Hf isotopic compositions than the other postshield lavas, but does not have a distinctive Pb isotopic composition. The youngest sample in this study (710 years; Waha Pele, Hualalai) has the highest Hf and lowest Pb isotopic ratios of the postshield lavas.
The postshield lavas lie toward the more depleted (i.e., low $^{87}\text{Sr}/^{86}\text{Sr}$, high $^{143}\text{Nd}/^{144}\text{Nd}$, high $^{176}\text{Hf}/^{177}\text{Hf}$) end of the Hawaiian array in Nd-Sr and Hf-Nd diagrams (Figure 5). Postshield lavas from Mauna Kea, Kohala and Mahukona have Sr, Nd, and Hf isotopic compositions that overlap with shield stage lavas from Mauna Kea, Kilauea, and West Maui. In contrast, postshield lavas from Hualalai are shifted to slightly lower $^{87}\text{Sr}/^{86}\text{Sr}$ and higher $^{176}\text{Hf}/^{177}\text{Hf}$ compared to other Loa trend volcanoes (e.g., Mauna Loa), having values more similar to Kea trend volcanoes and plotting distinctly above the $\varepsilon\text{Hf}-\varepsilon\text{Nd}$ Hawaiian array. Furthermore, these lavas do not overlap with any other Hawaiian volcano in Hf-Pb and Sr-Pb diagrams (Figure 6). Shield and late shield lavas from Kohala have the least radiogenic Pb isotopic compositions of any Kea trend volcano, whereas the postshield lavas have higher $^{206}\text{Pb}/^{204}\text{Pb}$ values that are more characteristically Kea-like, overlapping with lavas from Mauna Kea, Kilauea, and West Maui. Postshield lavas from Mauna Kea extend to less radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ than most lavas from Kea trend volcanoes, similar to the trend observed in late shield lavas from West Maui [Gaffney et al., 2004].

In Pb-Pb isotope diagrams (Figure 7), the postshield lavas plot in fields that are distinct from their respective shield stage lavas. Postshield
lavas from Hualalai are significantly less radiogenic in Pb than the shield tholeiites and have some of the least radiogenic Pb isotopic compositions \((^{208}\text{Pb}/^{204}\text{Pb} = 37.67; \quad ^{206}\text{Pb}/^{204}\text{Pb} = 17.89)\) observed in recent (<5 Ma) Hawaiian lavas. Similarly, lavas from Mauna Kea show a systematic shift from their most radiogenic Pb isotope ratios during the shield stage to less radiogenic values during the early basaltic postshield substage to the lowest values yet observed at Mauna Kea \((^{208}\text{Pb}/^{204}\text{Pb} = 37.93; \quad ^{206}\text{Pb}/^{204}\text{Pb} = 18.34)\) during the late hawaiitic postshield substage. In contrast, at Kohala, the postshield lavas have distinctly more radiogenic Pb isotopic compositions than the late shield lavas and shield tholeiites.

5. Discussion

5.1. Isotope Systematics and Mixing Relationships in Postshield Lavas

\[ \text{[18]} \] Pb isotopes are one of the most powerful isotopic tracers and have a demonstrated ability in identifying heterogeneities and source components associated with the Hawaiian plume \citep[e.g.,][]{Eisele2003, Abouchami2005, Fekiacova2009}.
2007; Marske et al., 2007]. For example, Loa trend volcanoes have higher $^{208}\text{Pb} / ^{204}\text{Pb}$ for a given $^{206}\text{Pb} / ^{204}\text{Pb}$ than Kea trend volcanoes [Tatsumoto, 1978; Abouchami et al., 2005] (Figure 7a). At Mauna Kea, Kohala, and Hualalai, shield and postshield lavas from the same volcano form linear correlations in Pb-Pb isotope diagrams (Figures 7b and 7c). Importantly, the postshield lavas from Mauna Kea lie along and extend the “Kea-lo8” array of HSDP-2, which is defined by the youngest lavas from the uppermost part of the section [Eisele et al., 2003]. Given that in Hawaii such linear arrays are better interpreted as binary mixing lines (rather than isochrons) [e.g., Abouchami et al., 2000], this indicates that shield and postshield lavas may be derived from common source components mixed in variable proportions. Therefore, with respect to Pb, compared to during the shield stage, a contribution from a more radiogenic end-member is required during the postshield stage at Kohala and Mahukona volcanoes, whereas a less radiogenic end-member dominates the postshield stage at Mauna Kea and Hualalai. However, the Pb-Pb arrays of Mauna Kea and Hualalai are subparallel (Figure 7c), each remaining on its respective side of the Loa-Kea Pb isotopic division, which suggests that two separate unradiogenic (lower $^{208}\text{Pb} / ^{204}\text{Pb}$ and $^{206}\text{Pb} / ^{204}\text{Pb}$) end-members are required. Such temporal Pb iso-
Isotope variations are accompanied by systematic changes in Sr, Nd, and Hf isotopic compositions and trace element chemistry that have been documented from the shield to postshield to rejuvenated stages at many Hawaiian volcanoes, including Haleakala [Chen and Frey, 1985], East and West Molokai [Xu et al., 2005, 2007] and Kauai (Garcia et al., submitted manuscript, 2009).

[19] At least three isotopically distinct components, referred to as Loihi, Koolau, and Kea, are required to explain the compositional variability in Hawaiian shield stage lavas [e.g., Staudigel et al., 1984; Stille et al., 1986; West et al., 1987; Eiler et al., 1996; Hauri, 1996]. However, principal component analysis of Sr, Nd, Pb, He, and O isotopic ratios in Hawaiian shield lavas indicates that almost 90% of the variation can be explained by mixing between the Koolau and Kea end-members [Eiler et al., 1996]. The Koolau end-member has the highest $^{87}\text{Sr}/^{86}\text{Sr}$ and lowest $^{144}\text{Nd}/^{144}\text{Nd}$, $^{176}\text{Hf}/^{177}\text{Hf}$ and Pb isotopic ratios, and is best expressed in lavas from Koolau and other Loa trend volcanoes; although a recent paper by Tanaka et al. [2008] on Hf isotopes from Koolau volcano documents the need for a depleted and an enriched Makapuu component (DMK and EMK) to account for the vertical spread in $^{208}\text{Pb}/^{204}\text{Pb}$ in Koolau lavas (Figure 7a). The Koolau source is thought to contain recycled oceanic crust and pelagic sediments [e.g., Lassiter and Hauri, 1998; Blichert-Toft et al., 1999]. In contrast, the Kea end-member is characterized by the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ and highest $^{144}\text{Nd}/^{144}\text{Nd}$, $^{176}\text{Hf}/^{177}\text{Hf}$ and Pb isotope ratios, and it is best expressed in lavas from Kea trend volcanoes including Mauna Kea and Kilauea. The origin of the Kea component is still debated, and has been variously interpreted to be assimilated Pacific Ocean lithosphere, entrained asthenosphere (MORB source mantle), or recycled oceanic crust [e.g., Eiler et al., 1996; Lassiter et al., 1996; Lassiter and Hauri, 1998].

[20] In Hf-Pb and Sr-Pb isotope diagrams (Figure 6), Hawaiian shield lavas form strongly concave hyperbolic mixing trends between the Kea and Koolau end-members, which are inferred to have very different Hf/Pb and Sr/Pb abundance ratios [Blichert-Toft et al., 1999; Huang et al., 2005]. Both late shield and postshield lavas from Kohala and Mahukona lie within the mixing trend for Hawaiian shield lavas. In contrast, postshield lavas from Hualalai and Mahukona are displaced to significantly lower $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ and higher $^{176}\text{Hf}/^{177}\text{Hf}$ and do not lie within the shield mixing trend. Postshield lavas from Mauna Kea deviate slightly from the Sr-Pb hyperbola, trending oblique to the shield array toward less radiogenic Sr and Pb isotopic compositions (Figure 6b). The isotopic compositions of postshield lavas from Hualalai and Mauna Kea therefore cannot be explained by binary mixing between the Koolau and Kea end-members. The unradiogenic Pb isotopic compositions at Hualalai and the positive Sr-Pb correlation defined by Mauna Kea, which define two different mixing trends, preclude their generation from these.

Figure 5. (a) $^{144}\text{Nd}/^{144}\text{Nd}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ and (b) $\varepsilon_{\text{Hf}}$ versus $\varepsilon_{\text{Nd}}$ for the postshield lavas from Mauna Kea, Kohala, Hualalai, and Mahukona compared to selected Hawaiian shield stage lavas. Loa trend volcanoes are represented by circles, and Kea trend volcanoes are represented by triangles; the 2σ error bars are smaller than the symbol sizes. Inset diagrams show the isotopic covariation of the studied postshield lavas (using the same color coding as in the legends of Figures 1–4) and Mahukona (tholeiitic basalts are dark blue, and transitional/weakly alkalic basalts are light blue) only, with representative 2σ error bars indicated. For context, the depleted Makapuu (DMK), enriched Makapuu (EMK), and Kea end-members from Tanaka et al. [2002] and the Loihi end-member from Tanaka et al. [2008] are shown (open symbols). Also shown in Figure 5a is a field for Hawaiian rejuvenated stage lavas (Haleakala [late postshield/rejuvenated?], West Maui, East Molokai, Oahu, Kauai, North Arch) and East Pacific Rise mid-ocean ridge basalts (EPR MORB). The Hawaiian and OIB arrays in Figure 5b are from Blichert-Toft et al. [1999]. Data sources are as follows: Loihi, Blichert-Toft et al. [1999] and Abouchami et al. [2005]; Mauna Loa, Blichert-Toft et al. [2003] and D. Weis (unpublished data, 2001); Hualalai, Yamasaki et al. [2009]; Kahoolawe, Blichert-Toft et al. [1999], Abouchami et al. [2005], and Huang et al. [2005]; Lanai, Abouchami et al. [2005] and Gaffney et al. [2005]; Koolau, Blichert-Toft et al. [1999] and Abouchami et al. [2005]; Kilauea, Blichert-Toft et al. [1999] and Abouchami et al. [2005]; Mahukona, Huang et al. [2009]; Mauna Kea, Blichert-Toft et al. [2003], Eisele et al. [2003], and Bryce et al. [2005]; Kohala, Feigenson et al. [1983], Abouchami et al. [2005], M. O. Garcia (unpublished data, 2001), and D. Weis (unpublished data, 2001); Hualalai, West and Leeman [1987], Chen et al. [1990, 1991], and Blichert-Toft et al. [1999]; West Maui, Gaffney et al. [2004]; East Molokai, Xu et al. [2005]; Oahu, Reiners and Nelson [1998]; Kauai, Reiners and Nelson [1998] and Lassiter et al. [2000]; North Arch, Frey et al. [2000]; EPR MORB, Niu et al. [1999], Regelous et al. [1999], and Castillo et al. [2000]. All literature data have been normalized to the same standard values, i.e., La Jolla $^{143}\text{Nd}/^{144}\text{Nd} = 0.511858$, NBS 987 = 0.710248, and JMC 475 $^{176}\text{Hf}/^{177}\text{Hf} = 0.282160$ [Weis et al., 2006].
two end-members. In addition, the Nd and Hf isotopic compositions of the Hualalai postshield lavas plot above the ocean island basalt (OIB) and Hawaiian arrays (Figure 5b), indicating a source with higher $^{176}$Hf/$^{177}$Hf for a given $^{143}$Nd/$^{144}$Nd. The observed isotope systematics require a contribution from at least one additional component with relatively unradiogenic $^{87}$Sr/$^{86}$Sr and $^{206}$Pb/$^{204}$Pb (and more radiogenic $^{176}$Hf/$^{177}$Hf) that is not expressed in Hawaiian shield stage lavas and that is not depleted mantle as sampled by Pacific MORB.

Figure 6. (a) $\varepsilon_{\text{Hf}}$ versus $^{206}$Pb/$^{204}$Pb and (b) $^{87}$Sr/$^{86}$Sr versus $^{206}$Pb/$^{204}$Pb for the postshield lavas from Mauna Kea, Kohala, Hualalai, and Mahukona compared to Hawaiian shield and rejuvenated stage lavas. The inset diagram in Figure 6a shows the isotopic covariation of the studied postshield lavas and Mahukona only. The Kea and Koolau end-members defined by Blichert-Toft et al. [1999] (filled symbols) and the DMK, EMK, and Kea end-members from Tanaka et al. [2002] (open symbols) are shown for context. In Figure 6b the field for EPR MORB and isotopic compositions of the Pacific middle-lower crust (gabbroic xenoliths, Hualalai [Lassiter and Hauri, 1998]) and Pacific upper crust (fresh to altered basalts, ODP Site 843 [King et al., 1993]) are shown for comparison. For the Pacific crust, unleached and measured isotopic ratios were used. The blue line in Figure 6b represents a mixing line between the 2 Ga lower and upper oceanic crust end-members from Gaffney et al. [2004]. Symbols, data sources, and standard normalization values are the same as in Figure 5, plus Galer and Abouchami [1998] for SRM 981.
5.2. Role of Oceanic Lithosphere: Ambient Pacific Crust or Recycled Plume Component?

Although many ocean island basalts are characterized by enriched geochemical signatures, some also contain trace element abundances and isotope ratios with compositional similarities to MORB (i.e., La/SmN < 1; high $^{143}$Nd/$^{144}$Nd and $^{176}$Hf/$^{177}$Hf, and low $^{87}$Sr/$^{86}$Sr compared to primitive mantle). These depleted signatures have been observed in a number of hot spot settings, including Iceland.

Figure 7. $^{208}$Pb/$^{204}$Pb versus $^{206}$Pb/$^{204}$Pb for the postshield lavas from Mauna Kea, Kohala, Hualalai, and Mahukona compared to Hawaiian shield and rejuvenated stage lavas. (a) The thick gray line represents the Pb isotopic division for Loa and Kea trend volcanoes as defined by Abouchami et al. [2005]. The Hawaiian end-members (open symbols) are from Tanaka et al. [2002, 2008]. (b and c) The isotopic compositions of shield and postshield lavas from two consecutive pairs of volcanoes (Mahukona-Kohala and Hualalai-Mauna Kea) as well as EPR MORB. For Mauna Kea, the field represents all shield stage lavas; however, for clarity, only lavas assigned to the “Kea-lo8” array of HSDP-2 [Eisele et al., 2003] are shown. The thin colored lines are regression lines through shield and postshield lavas from the same volcano. The thick black arrows show the temporal geochemical trend from the shield to postshield stage and point toward a hypothetical end-member. Symbols and data sources are the same as in Figure 5.
Kerguelen, Galapagos, and Hawaii [e.g., Blichert-Toft and White, 2001; Doucet et al., 2002; Fitton et al., 2003; Mukhopadhyay et al., 2003; Frey et al., 2005]. The origin of these signatures is the subject of continued discussion, but is commonly attributed to assimilation of the underlying oceanic crust or entrained shallow asthenosphere (MORB source mantle) [e.g., Chen and Frey, 1985; Gaffney et al., 2004]. In Hawaii, however, lavas with depleted isotope ratios are associated with enriched rather than depleted trace element abundances. In particular, the combination of low $^{87}$Sr/$^{86}$Sr and high $^{143}$Nd/$^{144}$Nd with high Rb/Sr and low Sm/Nd is a paradox that has been known for some time [e.g., Chen and Frey, 1983], but that remains largely unresolved. To explain the enrichment in trace elements, assimilation models must invoke a source recently enriched (metasomatized) in incompatible trace elements [e.g., Yang et al., 2003; Shafer et al., 2005] or very small degree melts (0.1%–1%) of a depleted source [e.g., Chen and Frey, 1985]. In contrast, other studies attempt to overcome the paradox by arguing that the depleted isotopic signatures are derived from within the plume itself or from entrained deep mantle material [e.g., Frey et al., 2005; Fekiacova et al., 2007]. Studies of pyroxenite and peridotite mantle xenoliths sampled in rejuvenated lavas on the island of Oahu [Bizimis et al., 2005, 2007] conclude that the depleted material is ancient oceanic lithosphere (and sediments) that have been subducted, recycled, and become part of the upwelling plume. In addition, the shallow slope, relative to the OIB array, in a Hf-Nd isotope diagram for shield basalts from Koolau is related to the presence of a high-$^{176}$Hf/$^{177}$Hf component (also present in the Salt Lake Crater peridotite xenoliths) representing ancient depleted lithosphere in the Koolau enriched end-member and not simple addition of a sediment component in the source of these basalts [Salters et al., 2006].

[22] To determine the origin of the observed isotope systematics in the postshield lavas, we investigate possible contributions from both ambient and recycled oceanic lithosphere. Basalts from ODP Site 843, located 320 km west of the island of Hawaii, are representative of the ambient ~110 Ma Pacific upper oceanic crust [King et al., 1993]. Gabbroic xenoliths from the 1800–1801 Kaupuhoheue flow on Hualalai are inferred to represent the Pacific middle-lower oceanic crust [Lassiter and Hauri, 1998]. Taking into account that the postshield lavas share a source with their respective shield stage lavas, the depleted end-members required for post-shield Hualalai and Mauna Kea must have relatively unradiogenic $^{87}$Sr/$^{86}$Sr and $^{206}$Pb/$^{204}$Pb. Fresh Pacific upper crust, Pacific middle-lower crust, and EPR MORB have the low $^{87}$Sr/$^{86}$Sr required of an end-member (Figure 6b). However, the $^{206}$Pb/$^{204}$Pb of these sources, especially the Pacific upper crust, is too radiogenic to be a plausible depleted end-member for the Hualalai postshield lavas. Involvement of upper mantle material can also be excluded based on the binary Hf-Pb mixing trend of Hawaiian lavas [e.g., Blichert-Toft et al., 1999]. Furthermore, none of the linear Pb-Pb isotope trend lines from the studied postshield lavas intersect the EPR MORB field (Figure 7c), which provides compelling evidence against assimilation of MORB-related lithosphere or asthenosphere.

[23] The depleted component sampled by the postshield lavas must therefore be closely related to the Hawaiian plume, either as material within the plume core, or as mantle material that is thermally accreted to the sides of the plume during ascent. Suitable candidates for this depleted source material include ancient recycled oceanic lithosphere and associated oceanic sediments. Preferential removal of the mobile elements U and Rb during subduction dehydration may lead to low U/Pb and Rb/Sr and the development of unradiogenic $^{206}$Pb/$^{204}$Pb and $^{87}$Sr/$^{86}$Sr [McCulloch and Gamble, 1991; Weaver, 1991]. Forward modeling of the composition of 2 Ga oceanic lithosphere shows that gabbroic lower oceanic crust evolves to unradiogenic $^{206}$Pb/$^{204}$Pb and $^{87}$Sr/$^{86}$Sr over time [Gaffney et al., 2004], and could thus account for the Sr and Pb isotopic compositions of the postshield lavas (Figure 6b). Similarly, pelagic sediments develop unradiogenic $^{206}$Pb/$^{204}$Pb because of long-term evolution with low U/Pb. The presence of pelagic sediments, with high Lu/Hf [e.g., Patchett et al., 1984; Blichert-Toft et al., 1999; Vervoort et al., 1999; Chauvel et al., 2008], could also explain the Hf-Nd isotope systematics of the Hualalai postshield lavas (Figure 5b). These observations are consistent with the recycling model and provide evidence for ancient lower oceanic crust (and possibly sediments) in the mantle source of the postshield lavas from Hawaii.

5.3. Identification of Depleted Signatures at Several Hawaiian Volcanoes

[24] The extent to which depleted components are sampled by Hawaiian lavas varies considerably between different volcanoes and is mainly restricted
to lavas erupted after the volcano has migrated away from the plume center following the main shield-building stage. The low degrees of partial melting from which such postshield lavas are derived correspond to small volumes within the melting region and may allow for these isotopic signatures to be more readily identified. The trend to low $^{87}\text{Sr}/^{86}\text{Sr}$ and low $^{206}\text{Pb}/^{204}\text{Pb}$ observed in postshield lavas from Mauna Kea has also been found for late shield and postshield lavas from Haleakala [Chen et al., 1991], West Maui [Gaffney et al., 2004], and East Molokai [Xu et al., 2005]. The presence of this isotopic signature at these four consecutive Kea trend volcanoes indicates that this depleted component is a persistent feature of the Kea source [Xu et al., 2005]. The isotopic compositions of postshield lavas from Hualalai represent the first example of a low $^{87}\text{Sr}/^{86}\text{Sr}$, low $^{206}\text{Pb}/^{204}\text{Pb}$ signature at a Loa trend volcano. This demonstrates that depleted components, albeit with slightly different geochemical characteristics, are also present in the Loa source and are therefore more widely distributed within the plume than previously thought.

A depleted component has also been sampled by rejuvenated stage lavas from East Molokai, Oahu, Kauai, and the North Arch Volcanic Field, which have the highest $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ and lowest $^{87}\text{Sr}/^{86}\text{Sr}$ of all Hawaiian lavas [e.g., Frey et al., 2000; Lassiter et al., 2000; Bizimis et al., 2005; Xu et al., 2005; Bizimis et al., 2007; Fekiacova et al., 2007; Garcia et al., submitted manuscript, 2009]. It is therefore important to determine whether or not the postshield lavas share a source with these rejuvenated lavas. However, in contrast to postshield lavas, rejuvenated stage lavas are characterized by a more limited range of Pb isotope ratios and plot almost exclusively on the Kea side of the Pb isotopic boundary [e.g., Fekiacova et al., 2007] (Figure 7a). Late shield lavas from West Maui were interpreted to have a distinct source from Hawaiian rejuvenated lavas [Gaffney et al., 2004], whereas at East Molokai, late shield/postshield and rejuvenated lavas were found to contain variable amounts of the same depleted component [Xu et al., 2005]. Postshield lavas from Mauna Kea trend toward the field for rejuvenated lavas, which suggests that the two types of lavas may share a common depleted end-member component. Given that rejuvenated lavas erupt considerably later (~0.25–2 Myr) than postshield lavas and at a distance significantly further from the plume center, this depleted component is inferred to be a relatively long lived feature of the plume. In contrast, postshield lavas from Hualalai are Loa-like and have Pb isotopic compositions that are too unradiogenic to share a source with these rejuvenated lavas (Figure 7a). These observations, combined with the elevated Hf isotopic compositions of the postshield Hualalai lavas (Figure 5b), indicate sampling of source material at Hualalai that is not expressed at any other Hawaiian volcano and provides additional evidence that more than one depleted component is present within the plume.

A depleted component is required to explain some of the isotopic variability observed in shield lavas from Kauai, and may also be present to a lesser degree and in varying proportions at other Hawaiian volcanoes [Mukhopadhyay et al., 2003]. Despite proximity of the plume to a spreading ridge axis at the time of formation, the depleted component that contributed to lavas from the 76–81 Ma Detroit Seamount at the northern end of the Emperor seamount chain is thought to be intrinsic to the Hawaiian plume [Frey et al., 2005]. Thus, sampling of depleted components is not solely restricted to the late stages (late shield/postshield and rejuvenated) of volcanism or to the recent (<5 Ma) volcanoes of the Hawaiian chain. Instead, these depleted components represent a fundamental part of the Hawaiian plume that may only be sampled under specific melting conditions or in certain geodynamic settings. For example, melting of distinct plume components could be facilitated under thin lithosphere [Regelous et al., 2003] or, alternatively, in a secondary melting zone [Ribe and Christensen, 1999] or by flexural arch decompression [Bianco et al., 2005], as has been proposed to explain Hawaiian rejuvenated volcanism.

5.4. Horizontal Zoning in the Hawaiian Plume: Constraints From the Shield to Postshield Transition

The geochemical differences between lavas erupted along the Loa and Kea spatial trends are typically explained by two different models for the geochemical structure of the plume beneath Hawaii (Figure 8). The concentrically zoned model [e.g., Hauri, 1996; Kurz et al., 1996; Lassiter et al., 1996] proposes a plume core with enriched (Loa-type) compositions and an outer margin with more depleted (Kea-type) compositions. In contrast, the Pb isotope systematics of Hawaiian lavas suggest that the plume is bilaterally zoned [Abouchami et al., 2005] into southwest and northeast halves
that correspond to Loa and Kea source regions, respectively.

[28] The geochemistry of the shield to postshield transition provides the opportunity to discriminate between the concentrically and bilaterally zoned plume models (Figure 8). During the time period corresponding to shield and postshield volcanism, individual volcanoes traverse the plume conduit from a more central to peripheral location due to the motion of the Pacific lithosphere. In a concentrically zoned plume, where Loa trend volcanoes are inferred to sample the plume center and Kea trend volcanoes sample the plume edge, both Loa and Kea trend shield volcanoes are predicted to be Kea-like during the postshield stage. In contrast, in a bilaterally zoned plume, Loa and Kea trend volcanoes will retain their initial Loa- and Kea-like geochemical characteristics, respectively.

[29] Postshield lavas from the Kea trend volcanoes, Mauna Kea and Kohala, are Kea-like, and postshield lavas from the Loa trend Hualalai are Loa-like with respect to their Pb isotopic compositions (Figure 7a). Transitional to weakly alkaline basalts from Mahukona, a submerged Hawaiian shield volcano located ~50 km west of Kohala on the Loa spatial trend, likely belong to the early postshield stage of this volcano and are also Loa-like [Clague and Calvert, 2009; Huang et al., 2009; Garcia et al., manuscript in preparation, 2009]. The persistence of the Kea and Loa Pb signatures from the shield to postshield stage at these four Hawaiian volcanoes is inconsistent with a concentric

Figure 8. Schematic comparison of the two main models for the spatial distribution of Loa and Kea source compositions in the Hawaiian plume: (a) concentric and (b) bilateral zonation. The map of the plume melting region (colored areas) beneath the island of Hawaii is after DePaolo et al. [2001], based on the melt supply models of DePaolo and Stolper [1996] and Ribe and Christensen [1999]. The outer field represents the lateral extent of the primary melting zone; the darker inner circle corresponds to a melt supply rate of >0.05 cm/yr. In the concentric model (Figure 8a), Loa source material (blue) is in the core of the plume, and Kea source material (red) is restricted to the plume margin [e.g., Hauri, 1996; Kurz et al., 1996; Lassiter et al., 1996], whereas in the bilateral model (Figure 8b), Loa and Kea source material is divided into southwest and northeast sides of the plume, respectively [Abouchami et al., 2005]. The shaded boundary between the two sources reflects the presence of a possible “mixed” zone. Superimposed on the map are the outline of the island of Hawaii and the current summits of Mahukona, Kohala, Hualalai, and Mauna Kea (white circles). Also shown are the summit locations of these volcanoes at the time of eruption of the postshield lavas (sample/vent locations are omitted for clarity), assuming a Pacific plate velocity of 9 cm/yr. The color of the paleosummits corresponds to the isotopic signature of the lavas (blue indicates Loa-like lavas, and red indicates Kea-like lavas) and show that the postshield lavas are consistent with a bilaterally zoned plume (Figure 8b).
zonation and strongly supports some bilateral plume zonation (Figure 8). However, these observations could also be explained by a concentrically zoned plume that has been distorted in the downstream direction by the movement of the overriding Pacific lithosphere, where the postshield lavas sample the stretched plume tail material [DePaolo et al., 2001; Bryce et al., 2005].

[30] Information from the southwest side of the hot spot track is required to differentiate between these two models; regardless of the stage in which the lavas were erupted, Loa-like isotopic compositions to the southwest would support the bilateral model, whereas Kea-like compositions would support the distorted concentric model. Tholeiitic basalts from Penguin Bank, which lies west of the main Hawaiian Ridge, have Loa-like Sr, Nd, and Hf isotopic compositions and Pb isotopic compositions that lie along the Loa-Kea Pb isotopic division [Xu et al., 2007]. The dominantly Loa-like isotopic compositions of lavas from Penguin Bank are consistent with a bilateral plume zonation.

[31] The oblique trend defined by Kohala lavas that crosses the Pb isotopic division (Figures 7a and 7b) reflects sampling of Loa source material by a Kea trend volcano and indicates that the boundary between Loa and Kea sources in most zoned plume models (whether they be bilateral or concentric) is oversimplified. The presence of both Loa and Kea geochemical characteristics within a single Hawaiian volcano has been documented at Mauna Kea [Eisele et al., 2003], Haleakala [Ren et al., 2006], Kilauea [Marske et al., 2007], West Molokai [Xu et al., 2007] and Mahuakona [Huang et al., 2009; Garcia et al., manuscript in preparation, 2009]. These observations may be explained by the presence of a "mixed" zone within the plume conduit that contains both Loa and Kea source material, or if the boundary between the two sources fluctuates horizontally with time.

5.5. Vertical Heterogeneity in the Hawaiian Plume: Constraints From Consecutive Volcano Pairs

[32] The previous discussion has assumed a time-invariant geochemical cross section of the plume conduit. However, the geochemical variability observed in Hawaiian lavas may also be related to vertical heterogeneities within the upwelling plume. Due to the high upwelling velocities (>1 m/yr) predicted for the Hawaiian plume, the vertical component of heterogeneity cannot be ignored [Blichert-Toft et al., 2003; Marske et al., 2007]. In addition to investigating the compositional evolution of a single volcano, which is thought to record a horizontal geochemical gradient across the plume conduit, we compare the shield to postshield transition at two consecutive pairs of Hawaiian volcanoes: Mahuakona-Kohala and Hualalai-Mauna Kea.

[33] Lavas from the older Mahuakona and Kohala volcanoes initially have similar isotopic compositions and become more radiogenic in Pb with time (Figure 7b). In contrast, lavas from the younger Hualalai and Mauna Kea volcanoes become less radiogenic in Pb from the shield to the postshield stage (Figure 7c). Mahuakona and Kohala were thus sampling a more enriched (high $^{208}$Pb/$^{204}$Pb and $^{206}$Pb/$^{204}$Pb) source that was present in the melting region of the plume during postshield volcanism. As these older volcanoes migrated farther away from the plume axis, the mantle continued to rise and was replaced by relatively depleted (low $^{208}$Pb/$^{204}$Pb and $^{206}$Pb/$^{204}$Pb) source material that was subsequently sampled by Hualalai and Mauna Kea during their respective postshield stages. The sampling of isotopically similar source material at another pair of neighboring volcanoes, Mauna Loa and Kilauea, is thought to have been caused by the passage of a small-scale heterogeneity (either a single body or the plume matrix itself) through their melting regions [Marske et al., 2007]. Although for Mahuakona-Kohala and Hualalai-Mauna Kea, the Pb-Pb arrays do not converge to a common composition, the observed Pb isotope systematics provide compelling evidence that, in addition to large-scale horizontal zoning, there is a significant component of vertical heterogeneity within the upwelling Hawaiian plume.

6. Conclusions

[34] High-precision trace element concentrations and Sr, Nd, Pb, and Hf isotopic compositions of Hawaiian postshield lavas from Mauna Kea, Kohala, and Hualalai show that the shield to postshield transition was accompanied by systematic changes in the types and proportions of discrete components sampled by each volcano. The unradiogenic Pb isotopic compositions at Hualalai and positive Sr-Pb isotope correlation at Mauna Kea preclude generation of these postshield lavas from mixing between the Kea and Koolau endmembers. These lavas require contributions from two different additional source components with relatively unradiogenic $^{87}$Sr/$^{86}$Sr and $^{206}$Pb/$^{204}$Pb, as well as more radiogenic $^{176}$Hf/$^{177}$Hf, that are not
expressed in Hawaiian shield lavas. These depleted isotopic signatures cannot be explained by assimilation of the underlying Pacific oceanic crust or shallow entrained asthenosphere.

[35] The Sr, Nd, Pb, and Hf isotopic compositions of the postshield lavas reflect sampling of an intrinsic plume component and are consistent with the presence of ancient lower oceanic crust (+sediments) in their source. Postshield lavas from Mauna Kea trend to low $^{87}$Sr/$^{86}$Sr and $^{206}$Pb/$^{204}$Pb, toward compositions characteristic of Hawaiian rejuvenated stage lavas. This trend is observed at four consecutive Kea trend volcanoes and indicates that this depleted component is characteristic of the Kea source and is a long-lived feature of the Hawaiian plume. A different low-$^{87}$Sr/$^{86}$Sr, low-$^{206}$Pb/$^{204}$Pb component is sampled by postshield lavas from Hualalai, which indicates that several depleted components may be present in the Hawaiian plume and that they are widely distributed in both the Kea and Loa sources. The postshield lavas retain their characteristic Loa- and Kea-like Pb isotope signatures and are consistent with a bilateral or distorted concentric model of plume zonation. The Pb-Pb array for Kohala crosses the Loa-Kea Pb isotopic division and indicates that the boundary between Loa and Kea source material within the plume may fluctuate with time or that a mixed zone is present. The contrasting Pb isotope systematics of the consecutive pairs of volcanoes, in which Mahukona and Kohala become more radiogenic and Hualalai and Mauna Kea become less radiogenic with time, imply that the vertical component of heterogeneity is significant and also contributes to the observed geochemical variation observed in Hawaiian lavas.

Acknowledgments

[36] We thank the staff of the Pacific Centre for Isotopic and Geochemical Research (PCIGR) at UBC, including J. Barling, B. Kieffer, B. Mueller, and W. Pretorius, for their assistance with MC-ICP-MS, TIMS, and HR-ICP-MS analyses. C. Maerschalk and R. Friedman are also thanked for analytical advice and support in the lab. The manuscript benefited from discussion with A. Greene and M. O. Garcia and from the reviews of M. Bizimis, G. Ito, and Editor V. Salters. D. Hanano was supported by an NSERC (Canada) Postgraduate Scholarship (CGS-M). Funding for this research was provided by NSERC Discovery Grants to D. Weis and J. S. Scoates.

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