The geochemical components that distinguish Loa- and Kea-trend Hawaiian shield lavas

Frederick A. Frey a,⇑, Shichun Huang b, Guangping Xu c, Klaus P. Jochum d

a Massachusetts Institute of Technology, Cambridge, MA 02139, United States
b University of Nevada Las Vegas, Las Vegas, NV 89154, United States
c Schlumberger – Doll Research, Cambridge, MA 02139, United States
d Climate Geochemistry Department, Max Planck Institute for Chemistry, D-55020 Mainz, Germany

Received 20 July 2015; accepted in revised form 5 April 2016; available online 30 April 2016

Abstract

Recent (<5 Ma) Hawaiian volcanoes define two sub-parallel spatial trends, Loa and Kea. Despite the short distance (~30 km) between adjacent volcanoes on these trends, most of the Loa-trend shield lavas are geochemically distinct from most of the Kea-trend shield lavas. These geochemical differences arise from small amounts of the LOA component in the source of Loa-trend shield lavas. This component is most prominent in the uppermost shield lavas of Koolau, Lanai and Kahoolawe volcanoes. Correlations between abundance ratios of incompatible elements and isotopic ratios of Sr, Nd, Hf and Pb in Hawaiian shield lavas indicate that the LOA component consists of three geochemically distinct materials formed by diverse processes. A gabbroic adcumulate (i.e. no trapped melt) with abundant cumulus plagioclase is responsible for the high Sr/Nd, La/Th and La/Nb in Loa-trend shield lavas relative to Kea-trend shield lavas. Also it has relatively low 206Pb/204Pb and high 208Pb/204Pb at a given 206Pb/204Pb, consistent with the low U/Pb and Th/Pb that are characteristic of plagioclase; these distinctive Pb isotope ratios require a long-time interval, ~3 Ga, to develop. This material is most abundant in the uppermost shield lavas of Koolau volcano. Possible origins of adcumulate gabbros with abundant cumulus plagioclase are the lower oceanic and continental crust. A second material in the LOA component is distinctive because it is offset from the linear trend of 176Hf/177Hf versus 143Nd/144Nd, known as the terrestrial array, to high 176Hf/177Hf at low 143Nd/144Nd. This offset requires an ancient material with high Lu/Hf. A third material in the LOA component is characterized by relatively high 87Sr/86Sr, but the Rb/Sr of this material is too low to explain the high 87Sr/86Sr in 4.5 Ga. A relatively recent (<1 Ga) event must have lowered the Rb/Sr. This material is most abundant in the shield lavas of Kahoolawe volcano.

© 2016 Elsevier Ltd. All rights reserved.

Keywords: Mantle plume; Hawaiian volcanism; Mantle heterogeneity

1. INTRODUCTION

From 1838 to 1842 a US Navy operation, the US Exploring Expedition, was charged with mapping and charting little-known regions of the Pacific and Southern Oceans. From September 1840 to April 1841 the expedition was in Hawaii. The young geologist, J. D. Dana, one of nine on board scientists, made many significant observations of Hawaiian volcanoes, including recognition of a systematic age progression to the northwest, now described as a hotspot track, and a spatial arrangement of volcanoes that are now known as the Loa- and Kea-trends (Dana, 1849; Appleman and Dana, 1987). In order to understand
the volcanism that occurs along a hotspot track it is necessary to understand (1) the physical processes that created discrete islands forming sub-parallel trends (Hieronymus and Bercovici, 1999), and (2) the processes that determine the geochemical characteristics of magmas erupted along the hotspot track. In this research we use geochemical differences between Loa- and Kea-trend shield lavas to understand the processes that created geochemical differences between volcanoes forming Loa-trend shields from Mauna Loa to Koolau and Kea-trend shields from Kilauea to East Molokai (Fig. 1).

The archetype Loa and Kea volcanoes, Mauna Loa and Kilauea, are in the subaerial shield stage of rapid growth and samples of unaltered lava flows are easily collected; consequently there are abundant compositional data for Mauna Loa and Kilauea shield lavas. Powers (1955) found that at a given MgO content, the abundance of SiO₂ is ~2% lower in Kilauea lavas than in Mauna Loa lavas. He inferred that these differences reflect distinct magma batches whose compositions reflect different sources for each volcano. Wright (1971) also compared the composition of shield lavas erupted at Mauna Loa and Kilauea volcanoes. He found that lavas from both volcanoes have the same range of K₂O/P₂O₅ and concluded that uniformity of shield lavas erupted at Mauna Loa to Koolau and Kea-trend shields from Kilauea to East Molokai (Fig. 1).

Wright (1971) also compared the compositional data for lavas from East Molokai-West Molokai-Penguin Bank volcanoes that define a transect perpendicular to the strike of the Loa and Kea trends (Fig. 1) and even to Kauai further to the northwest (e.g., Weis et al., 2011). They showed that for each pair at a given MgO content data for incompatible trace elements in Hawaiian shield lavas. These data show that at a given MgO content there are differences in abundance of SiO₂, CaO, K₂O and TiO₂. The development of new analytical techniques, such as instrumental neutron activation analysis (INAA), isotope dilution (ID) using mass spectrometers and most recently inductively coupled plasma mass spectrometry (ICP-MS), has led to acquisition of precise and accurate concentration data for incompatible trace elements in Hawaiian shield lavas. These data show that at a given MgO content, Kilauea lavas have higher abundances of incompatible elements than Mauna Loa lavas, and different incompatible element ratios, such as Th/La, Zr/Nb, Sr/Nb and K/Nb, than Mauna Loa lavas (Fig. 3; Pietruszka et al., 2013). Frey and Rhodes (1993) also showed that the incompatible element ratios, such as Sr/Nb and Zr/Nb, are correlated with ⁸⁷Sr/⁸⁶Sr and ¹⁴₃Nd/¹⁴⁴Nd. In each Loa- and Kea-trend pair, the Loa-trend lavas have higher ⁸⁷Sr/⁸⁶Sr and lower ¹⁴₃Nd/¹⁴⁴Nd than the shield lavas in the adjacent Kea-trend volcano. However, there are poor correlations between the parent/daughter ratio, Rb/Sr, and ⁸⁷Sr/⁸⁶Sr were caused by differences in process rather than differences in source compositions.

Do different sources or different processes cause the geochemical differences between Loa- and Kea-trend shield lavas? Tatsumoto (1978) answered this question when he found that lavas from each volcano on the Island of Hawaii have distinctive Pb isotope ratios. In particular, he emphasized that lavas erupted at Kea-trend volcanoes have higher ²⁰⁶Pb/²⁰⁴Pb than lavas erupted at Loa-trend volcanoes, a result that provides strong evidence for geochemically distinct sources for Loa- and Kea-trend volcanoes. The usefulness of Pb isotopic ratios to distinguish Loa- and Kea-trend volcanoes was strengthened by Abouchami et al. (2005) who found that ²⁰⁶Pb*/²⁰⁴Pb* is a better discriminant between Loa- and Kea-trend lavas than ²⁰⁶Pb/²⁰⁴Pb. ²⁰⁸Pb*/²⁰⁶Pb* = (²⁰⁸Pb/²⁰⁶Pb – 29.475)/(²⁰⁶Pb/²⁰⁴Pb – 9.307) is a measurement of the radiogenic ingrowth of ²⁰⁸Pb and ²⁰⁶Pb since earth formation.

Abouchami et al. (2005) used Pb isotope data for Loa- and Kea-trend volcanoes to infer an asymmetrically zoned plume (Fig. 2). The zonation in this model differs from the previous concentrically zoned models (Hauri et al., 1996; Kurz et al., 1996; Lasister et al., 1996). However, Pb isotope data for lavas from East Molokai-West Molokai-Penguin Bank volcanoes that define a transect perpendicular to the strike of the Loa and Kea trends (Fig. 1) shows that it is not possible to use Pb isotope ratios to distinguish between Loa- and Kea-trend lavas in these older shields (Xu et al., 2014). For example, the West Molokai shield on the Loa-trend (Fig. 1) includes lavas with both Loa- and Kea-type geochemical characteristics (Xu et al., 2007). Additional complexity in using ²⁰⁶Pb*/²⁰⁴Pb* as a discriminant between Loa- and Kea-trend lavas is that the Kea-trend volcanoes, Kilauea, Mauna Kea and Haleakala have some basalts with ²⁰⁶Pb/²⁰⁴Pb* ratios like Loa-trend lavas (Eisele et al., 2003; Marske et al., 2007, 2008, respectively).

The geochemical characteristics of shield lavas at two pairs of adjacent volcanoes, Koolau and Waianae volcanoes on Oahu and Mauna Loa and Kilauea volcanoes on Hawaii (Fig. 1) were compared by Frey and Rhodes (1993). They showed that for each pair at a given MgO content there are differences in abundance of SiO₂, CaO, K₂O and TiO₂. The development of new analytical techniques, such as instrumental neutron activation analysis (INAA), isotope dilution (ID) using mass spectrometers and most recently inductively coupled plasma mass spectrometry (ICP-MS), has led to acquisition of precise and accurate concentration data for incompatible trace elements in Hawaiian shield lavas. These data show that at a given MgO content, Kilauea lavas have higher abundances of incompatible elements than Mauna Loa lavas, and different incompatible element ratios, such as Th/La, Zr/Nb, Sr/Nb and K/Nb, than Mauna Loa lavas (Fig. 3; Pietruszka et al., 2013). Frey and Rhodes (1993) also showed that the incompatible element ratios, such as Sr/Nb and Zr/Nb, are correlated with ⁸⁷Sr/⁸⁶Sr and ¹⁴₃Nd/¹⁴⁴Nd. In each Loa- and Kea-trend pair, the Loa-trend lavas have higher ⁸⁷Sr/⁸⁶Sr and lower ¹⁴₃Nd/¹⁴⁴Nd than the shield lavas in the adjacent Kea-trend volcano. However, there are poor correlations between the parent/daughter ratio, Rb/Sr, and ⁸⁷Sr/⁸⁶Sr.
and between Sm/Nd and $^{143}$Nd/$^{144}$Nd (e.g., Roden et al., 1994).

Frey and Rhodes (1993) discussed constraints on the structure of the Hawaiian plume arising from the differences between adjacent volcanoes in major and trace element abundances and in Sr and Nd isotope ratios. They proposed alternative physical characteristics of the Hawaiian plume that could lead to the geochemical differences between the Loa- and Kea-trend volcanoes. For example, tilting of an ascending plume caused by interaction with the overlying oceanic lithosphere, varying proportions of geochemical heterogeneities distributed within the plume or a plume consisting of separate diapirs for each volcano. Also the source of Hawaiian shield lavas may have varying proportions of peridotite and pyroxenite. Hauri (1996) concluded that the composition of lavas forming Loa-trend shields contain a SiO$_2$-rich melt (dacite) derived from a pyroxenite in the source of Loa-trend shield lavas. In Hawaiian shield lavas isotope ratios of Sr, Nd and Pb are correlated with abundance of SiO$_2$, TiO$_2$ and CaO, after adjustment to a common MgO content. Jackson et al. (2012) evaluated in more detail the correlations between major element compositions and radiogenic isotopic ratios in Hawaiian shield lavas. They suggested that lavas with relatively low SiO$_2$ and radiogenic Pb isotope ratios (Kea geochemical characteristics) are derived from a source of mixed pyroxenite/eclogite and peridotite whereas the lavas with relatively high SiO$_2$ and unradiogenic Pb isotope ratios (Loa geochemical characteristics) are derived from pyroxenite/eclogite. The pros and cons for derivation of Loa-trend shield lavas from a pyroxenite source are discussed by Hauri (1996), Herzberg (2006), Sobolev et al. (2005), Jackson et al. (2012), Rhodes et al. (2012), Herzberg et al. (2014) and Huang and Humayun (2016).

Jackson et al. (2012) also proposed that the variable SiO$_2$ content of Kea- and Loa-trend shield lavas reflects the extent of slab dehydration during subduction; in particular the high SiO$_2$ content of the LOA component reflects the absence of dehydration. Variable extents of dehydration of a subducted oceanic lithosphere are a variable that has been used to explain intershield differences in abundances of fluid mobile elements such as Ba and Sr.

2. DATA

Large data sets of accurate abundances of highly incompatible elements in basaltic rocks have only recently become available as ICP-MS emerged as the analytical method of choice. This paper uses abundance data for the incompatible elements Ba, Th, Nb, La, Sr, Nd, Zr, Sm, Eu, Dy and Lu in Hawaiian shield lavas, Kilauea (82 samples), Mauna Loa (36 samples), Lanai (40 samples), Kahoolawe (29 samples) and Koolau (34 Makapuu-stage samples and 90 samples recovered by the Koolau Scientific Drilling Project (KSDP)). Isotopic ratios of Sr, Nd, Hf and Pb for a subset of these samples were also used. These data are compiled in Appendix A. Our approach is to utilize isotopic ratios and ratios of incompatible element abundances to understand igneous processes. It is necessary to be aware of element mobility during post-eruption alteration (Appendix B: Clague et al., 2016 and Huang et al., 2016), contamination during sample preparation (Appendix B) and inter-laboratory differences (Appendix C).
3. DISCUSSION

3.1. Overview

Our goals are: (1) to establish the geochemical differences between the shield lavas erupted on the Kea- and Loa-trend; (2) to evaluate the geochemical heterogeneity of the LOA component and its variable abundance in the source of lavas forming different shields; and (3) to present hypotheses for the origin and processes that created the LOA component.

We use abundance ratios of incompatible elements to evaluate the mass balance equation:

\[
\text{Mauna Loa shield lava} = \text{Kilauea shield lava} + \text{LOA component.}
\]

This mass balance equation is used to determine the abundance ratios of incompatible elements and radiogenic isotope ratios of the LOA component that must be added to a Kilauea basalt to make a Mauna Loa basalt. This equation is used because relative to Kea-trend lavas, Loa-trend lavas have unusual geochemical characteristics (e.g., Frey and Rhodes, 1993; Pietruszka et al., 2013). Kilauea shield lavas are assumed to be derived from a peridotite source. The shield lava compositions used are Mauna Loa and Kilauea samples in Fig. 3 (Appendix D).

The first step is to determine the differences in incompatible element abundance ratios between Loa- and Kea-trend shield lavas. Such differences have previously been recognized (e.g., Frey et al., 1994; Hemond et al., 1994; Hofmann and Jochum, 1996; Huang and Frey, 2003, 2005; Pietruszka et al., 2013). However the recent increase in high quality abundance data for highly incompatible elements such as Th, Nb and La, combined with long drill cores into the shields of Koolau and Mauna Kea volcanoes led us to look for trends that were not previously recognized.

3.2. Abundance ratios of selected elements

We first identify the abundance ratios that distinguish Loa- and Kea-trend lavas. A plot of incompatible element abundances in lavas from Loa- and Kea-trend volcanoes normalized to primitive mantle (PM) shows important features (Fig. 5). For example, \((\text{Ba}/\text{Th})_{PM} > 1\) for both Loa- and Kea-trend lavas whereas \((\text{Ba}/\text{Th})_{PM} < 1\) for MORB; \((\text{Nb}/\text{La})_{PM} < 1\) in both MORB and Loa-trend shield lavas but \(> 1\) in Kea-trend lavas; \((\text{Th}/\text{La})_{PM} < 1\) in MORB and both Loa- and Kea-trend lavas; \((\text{Sr}/\text{Nd})_{PM} < 1\) for MORB but both Loa- and Kea-trend lavas have \((\text{Sr}/\text{Nd})_{PM} > 1\) with Loa-trend shield lavas having the highest values; \((\text{Zr}/\text{Nd})_{PM} < 1\) in MORB but \(< 1\) in Loa- and Kea-trend lavas with Loa lavas having higher Zr/Nb than Kea lavas. Also MORB have \((\text{Dy}/\text{Lu})_{PM} < 1\) whereas \((\text{Dy}/\text{Lu})_{PM} > 1\) in both Loa- and Kea-trend shield lavas (subscript PM indicates the ratio normalized to the Primitive Mantle ratio and MORB is Mid-Ocean Ridge Basalt).

3.2.1. Sr and Nd

During igneous processes that do not involve feldspar, Sr and Nd are similar in incompatibility; that is, the ratio of solid/melt partition coefficients, \(D_{\text{Sr}}/D_{\text{Nd}}\), is close to 1. Because \(D_{\text{Sr}}\text{Liquid}/\text{Melt} > 1\) and \(D_{\text{Nd}}\text{Solid}/\text{Melt} < 1\) (e.g., Drake and Weill, 1975; Bindeman and Davis, 2000; Bédard, 2006), the simplest process for explaining Sr enrichment, i.e., \((\text{Sr}/\text{Nd})_{PM} > 1\), is formation of an adcumulate rock rich in cumulus plagioclase. It is necessary that the cumulate rock be an adcumulate, that is without trapped melt, because such melt would overwhelm the geochemical signature of plagioclase. If this adcumulate is metamorphosed to pyroxene/eclogite in a closed system and then partially melted to \(> 50\%\), the melt will inherit the high Sr/Nd of the source rock (Appendix E).

A large variation in MgO content, \(~5\% - 25\%\) (Fig. 4b), is typical of Hawaiian shield lavas and is caused by olivine removal or addition. However, olivine does not affect the Sr/Nd ratio because olivine/melt partition coefficients for Sr and Nd are very low (Bédard, 2005). Combined geochemical and petrographic studies of the liquid line of descent for Hawaiian tholeiitic basalt find that plagioclase saturation is not reached until the MgO content of the melt has decreased to about 7% MgO (e.g., Wright, 1971). Fractionation of plagioclase from melts with \(< 7%\) MgO lowers
Fig. 4. Panels a–e: Sr/Nd versus Sr/Nb, MgO, \(^{143}\text{Nd}/^{144}\text{Nd}\), \(^{206}\text{Pb}/^{204}\text{Pb}\) and Ba/Th in Loa and Kea shield lavas. Primitive mantle (PM) element ratios are indicated by arrows. Because Sr in shield lavas can be mobile during alteration, only samples with K\(_2\)O/P\(_2\)O\(_5\) in the interval from 1.3 to 2.2 are plotted in Figs. 4, 7–9 and 12 (see Appendix B; Huang and Frey, 2003; Xu et al., 2007; Huang et al., 2016). Shield basalt samples from Kahoolawe are not plotted because this filter eliminates most of the samples. In this and subsequent figures the geochemical differences between Mauna Loa lavas and the two Kea shields (Kilauea and Mauna Kea) in our figures are modest. Lavas from the Koolau, Lanai and presumably Kahoolawe shields define the extreme geochemical characteristics of Loa-trend lavas. Koolau lavas are divided into the youngest shield lavas that are exposed at Makapuu Point and older samples recovered in a 679 m drill core obtained by the Koolau Scientific Drilling Project (KSDP). Panel a: Sr/Nb and Sr/Nd are highly correlated, and range by factors of 3.3 and 2.4, respectively. The superimposed black and red squares indicate mean MORB (Gale et al., 2013) and old Pacific MORB (Fekiacova et al., 2007). Panel b: Sr/Nd vs. MgO showing that at >8% MgO, Sr/Nd does not vary systematically with MgO content. In contrast, two Mauna Loa samples with low, <7% MgO content, have the lowest Sr/Nd and Sr/Nb because they have fractionated plagioclase which lowers Sr content. The near vertical trend for Lanai samples with 6–7% MgO is also likely to be a result of plagioclase fractionation. Panels c and d: Sr/Nd vs \(^{143}\text{Nd}/^{144}\text{Nd}\) and \(^{206}\text{Pb}/^{204}\text{Pb}\) showing that, except for the two Mauna Loa samples with low MgO contents, in each panel the fields for individual shields define an inverse trend. Panel e: Sr/Nd vs Ba/Th. This trend is surprisingly poor suggesting that different processes controlled these ratios. However the two Mauna Loa lavas with low MgO have low Sr/Nd and Ba/Th, probably reflecting plagioclase fractionation. The gray field showing no correlation is for tholeiitic basalt from the Galapagos archipelago (Saal et al., 2007). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
the Sr/Nd ratio significantly. In Fig. 4b examples of plagioclase fractionation are the near vertical trend of Lanai lavas and the two Mauna Loa lavas with Sr/Nd <10. Scatter in the Sr/Nd vs MgO trend for a specific shield trend can reflect mixing of low-MgO magmas that are plagioclase saturated with high-MgO olivine-saturated magmas (Fig. 12 of Rhodes and Vollinger, 2004).

Although Sr enrichment can occur as result of processes occurring in the crust, the correlations of Sr/Nd with 143Nd/144Nd and 206Pb/204Pb (Fig. 4c, d) indicate that relative enrichment of Sr in Loa-trend shield lavas is a source characteristic. Fig. 4a–d is an example of the trends defined by the intershield differences between Loa- and Kea-trend shield lavas. In this paper our focus is on understanding the processes that created geochemical differences between shields. In all figures that plot ratios of incompatible elements and isotopic ratios, the fields for lavas from the two Kea-trend volcanoes Kilauea and Mauna Kea overlap. The Loa-trend lavas from the Makapu'u stage of Koolau and Lanai volcanoes are the most extreme; lavas cored by the Koolau Scientific Drilling Project (KSDP) are older than the Makapu'u stage lavas and together with Mauna Loa lavas they fill the gap between the Kea-trend lavas and Loa extreme lavas (Fig. 4). Lavas from Loa-trend Kahoolawale volcano are not included in plots involving incompatible element abundances because most Kahoolawale lavas are highly altered; however isotopic ratios of Kahoolawale lavas are in Figs. 12 and 13 because the effects of alteration were minimized by acid leaching prior to analysis.

The largest Sr enrichments, (Sr/Nd)PM = 3.1, have been found in a small number of melt inclusions in olivine phenocrysts of Mauna Loa lavas by Sobolev et al. (2000) who proposed that Sr enrichment in melt inclusions in olivine phenocrysts of some Mauna Loa shield lavas could be explained by a source composed of gabbros that contain cumulus plagioclase with Sr/Nd of ~200 that was subducted and incorporated into the Mauna Loa mantle source. Plagioclase and clinopyroxene have very different mineral/melt partition coefficients that can be used to identify a petrogenetic role for these two minerals (Fig. 5a). Gabbroic rocks with cumulus plagioclase and clinopyroxene are common in the lower oceanic crust (e.g., Meyer et al., 1989; Elthon et al., 1992; Hart et al., 1999; Natland and Dick, 2001; Coogan et al., 2001). Analyses of coexisting cumulus plagioclase and clinopyroxene in these gabbros from the oceanic crust reflect their mineral/melt partition coefficients; that is relative to clinopyroxene, plagioclase is enriched in Ba, La, Pb, Sr and Eu and depleted in Nb and Zr (Fig. 5a, b). Also the abundances of incompatible elements in coexisting cumulus plagioclase and clinopyroxene in gabbroic cumulates from the lower oceanic crust are consistent with forming in equilibrium with a MORB melt (Fig. 5c, d).

Increasing pressure as the oceanic plate subducts converts the gabbroic cumulate to eclogite. If this metamorphism occurs in a closed system, the eclogite retains the Sr enrichment resulting from cumulus plagioclase. If this eclogite is then incorporated into the mantle source of Loa-trend basalt, the basalt will have a high Sr content inherited from the cumulus plagioclase that is no longer present in the eclogite. Sobolev et al. (2000) described this Sr enrichment as resulting from “Ghost Plagioclase”.

An alternative hypothesis for the relative enrichment of Sr in ocean island basalt is assimilation of plagioclase in the gabbroic lower crust of islands (Danyushevsky et al., 2003; Saal et al., 2007; Peterson et al., 2014). Sobolev et al. (2000) evaluated this alternative for the melt inclusions in olivine phenocrysts of Mauna Loa lava. They argued that the major element contents of the melt inclusions were not saturated with plagioclase, a necessity for the shallow-level assimilation model. In a study of basalt erupted in the Galapagos Islands, Saal et al. (2007) found that basalt in the eastern part of the archipelago have the trace element signature of plagioclase, e.g., high Sr/Nd. They concluded that direct assimilation of plagioclase-rich lower crust is unlikely because this process requires “an unreasonably large proportion of digested plagioclase-rich gabbro” (see Supplementary material Fig. 3 of Saal et al. (2007)); they favored a more complex crustal process that involves diffusive control during reaction of percolating basaltic magma with plagioclase-rich cumulates in the lower crust underlying the volcano.

A strong argument against the Sr enrichment in the LOA component arising from interaction of hotspot derived magmas with the lithosphere beneath Hawaiian volcanoes is that the Sr/Nd is inversely correlated with 143Nd/144Nd (Fig. 4c); that is, the high Sr/Nd of the LOA component has relatively low 143Nd/144Nd. This result is inconsistent with the high 143Nd/144Nd typical of MORB related lithosphere (Fig. 4c).

Lead isotope ratios provide a way to assess the timing of the process that created the geochemical characteristics of Ghost Plagioclase (Peterson et al., 2014). In plagioclase Pb is a moderately incompatible but U and Th are highly incompatible (Fig. 5a; Leeman, 1979; Bindeman et al., 1998; Bindeman and Davis, 2000; Norman et al., 2005; Bédard, 2006; Bédard, 2007). Clinopyroxene also has DpB > DU and DTh (Fig. 5a; Pertermann et al., 2004). Since the major phases of a plagioclase- and clinopyroxene-rich cumulate have low U/Pb, little ingrowth of 206Pb and 207Pb will occur. If ascending basaltic magma interacts with cumulates in the lower oceanic crust of islands, this lower crust will be too young to have developed retarded 206Pb/204Pb and 207Pb/204Pb. In contrast, a long time is required for recycling of eclogite derived from a plagioclase-rich cumulate in the lower oceanic crust into the mantle where it was incorporated into a mantle plume, such as the Hawaiian hotspot. If the gabbro to eclogite transition occurred within a closed system, the eclogite will have retarded 206Pb/204Pb and 207Pb/204Pb ratios reflecting the low U/Pb of the gabbroic cumulate. Melting of this eclogite in a hotspot environment could explain the low 206Pb/204Pb (Fig. 5a), and 207Pb/204Pb ratios of the LOA Component (Fig. 8c of Xu et al., 2014).

What age of the recycled gabbro is consistent with the measured Pb isotope ratios of the LOA component? To answer this question the first step is to take the Pb isotopic compositions of average modern MORB and calculate the temporal trend of Pb isotope ratios in the MORB mantle source backwards in time in 0.5 Ga increments (Fig. 6b).
Fig. 5. Panel a – Clinopyroxene/melt partition coefficients define a positive slope with small anomalies (such as for Pb). Plagioclase/melt partition coefficients are very distinctive in having a negative slope, indicated by red solid and dashed line, from light REE (La, Ce and Nd) to heavy REE (Er to Lu), strong peaks for Ba, Sr and Eu, a moderate peak at Pb and valleys at Th, Nb, Zr and Hf (data from Appendix G).

Panel b: Plagioclase/Clinopyroxene abundance ratios of incompatible elements in gabbroic cumulates recovered by drilling on the Atlantis Massif on the Mid-Atlantic Ridge (Drouin et al., 2009). Note that relative to clinopyroxene, plagioclase has peaks in Ba, Pb, Sr and Eu and valleys for Nb and Zr. Panels c and d: Primitive mantle-normalized abundances of incompatible elements in clinopyroxene and plagioclase from gabbroic adcumulates recovered by ODP drilling on the Atlantis Massif (Drouin et al., 2009). In both panels the abundance patterns in cumulus clinopyroxene and plagioclase are similar to clinopyroxene and plagioclase in equilibrium with MORB (the thick black lines) using the partition coefficients in Appendix G.

Panel e: Garnet/melt and clinopyroxene/melt partition coefficients (experimental sample A343 of Pertermann et al., 2004). Both minerals show the expected positive slope indicating that their mineral/melt partition coefficients decrease as the elements become more incompatible. Important differences between these minerals are that garnet has a much steeper slope from Dy to Lu and pronounced minimums at Sr and Th. The high $D_{Zr}/D_{Nb}$ (~10) in both minerals indicates that Zr/Nb is affected by variable extents of melting garnet peridotite. Nevertheless Zr/Nb in oceanic island basalt, including Hawaiian lavas, is usually correlated with $^{143}Nd/^{144}Nd$; consequently, Zr/Nb differences in the sources of Hawaiian shield lavas are not completely masked by the effects of processes. There is very good agreement between different experimental studies of clinopyroxene and garnet; e.g., for garnet see Figs. 2 and 5 in Pertermann et al. (2004). For clinopyroxene/melt partition coefficients note the similarity of experimental results of Pertermann et al. (2004) with clinopyroxene phenocryst/melt ratios in a Kilauea basalt (Norman et al., 2005). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
using the average U/Pb and Th/U ratios of MORB (Gale et al., 2013). Then we choose the average of eight least altered gabbros from a 500 meter gabbroic section of drill core from Ocean Drilling Project Hole 735B near the Southwest Indian Ridge (Table 2 of Hart et al., 1999). This average has the geochemical characteristics of cumulate plagioclase, such as high Sr/Nd (Fig. 9 of Hart et al., 1999). However, plagioclase has very low partition coefficients for Th and U, much lower than clinopyroxene (Table 3 of Blundy and Wood, 2003). Therefore clinopyroxene with its high U/Pb, Th/Pb and Th/U will control the evolution of lead isotopic ratios. Evidence that cumulus clinopyroxene in the gabbros at Hole 735B controlled the evolution of Pb isotope ratios is that the Th/U in unaltered gabbro is 3.75 (Table 2 of Hart et al., 1999) results in a ratio of (cumulus cpx in gabbro = 3.75)/(MORB average 3.09) equal to 1.21. This value is within the experimentally determined range of 0.8–1.3 for (Th/U)_{cpx}/(Th/U)_{melt} (Fig. 1 of Blundy and Wood, 2003).

We assume that this gabbro formed at various times in the past in increments of 0.5 Ga from 0.5 to 3.5 Ga. Using the average Th/U and U/Pb of the gabbros, we calculated the evolution of the 206Pb/204Pb and 208Pb*/206Pb* to present day. These are the blue and black lines in Fig. 6c. The intersection of these lines with the red regression line defined by Pb ratios for Loa- and Kea-trend shield lavas shows that to create the Pb isotopic characteristics of the LOA component the average age of unaltered gabbro is slightly greater than 3 Ga. For altered gabbro with lower Th/U of 1.78, reflecting a higher U content caused by low temperature alteration, the calculated formation age is slightly greater than 3.5 Ga.

It is a surprising result that both the altered gabbro and unaltered gabbro yield similar model Pb ages for the LOA component.

Fig. 6. (a) 206Pb/204Pb versus 208Pb*/206Pb* for Hawaiian shield lavas. Data are from the compilation of Huang et al. (2011a), with additional data for Mauna Loa and Lanai (Appendix A). The change from Kea- to Loa-trend shields is a decrease 206Pb/204Pb and increase in 208Pb*/206Pb*. Estimates of upper continental crust (UCC) and lower continental crust (LCC) are from Zartman and Haines (1988). Clearly UCC is not suitable for the LOA component. In contrast, LCC has the low 206Pb/204Pb and high 208Pb*/206Pb* that are characteristics of the LOA component. (208Pb*/206Pb* = (208Pb/204Pb – 29.475)/(206Pb/204Pb) –9.307) is a measure of the radiogenic ingrowth of 208Pb and 206Pb since earth formation). (b) 206Pb/204Pb versus 208Pb*/206Pb* for MORB mantle source from present day to 3.5 Ga. We start with the average modern MORB values of 206Pb/204Pb = 18.412, 207Pb/204Pb = 15.515, 208Pb/204Pb = 38.100, U/Pb = 0.179, and Th/Pb = 0.551 (Gale et al., 2013). Assuming that melting at mid-ocean ridge does not fractionate U/Pb or Th/Pb, we calculate the Pb isotopic compositions of MORB source backwards in time in steps of 0.5 Ga. (c) A plagioclase-rich adcumulate gabbro formed from ancient MORB will have U/Pb and Th/Pb ratios determined by its cumulus phases and their proportions. The Pb isotopic evolution of this gabbro will deviate from that of MORB source. We calculated forward in time the present-day Pb isotopic signature of the gabbro using the unaltered and altered gabbro compositions from Tables 2 and 7 of Hart et al. (1999). The labeled ages are the ages of the gabbro formation, and unless specified, the incremental step is 0.5 Ga. The LOA component is at the intersection of the regressed Hawaiian data (red line) with ancient, 3–3.5 Ga, gabbros indicated by the curved trends (black and blue). The model ages of ancient gabbros are not very sensitive to the U/Pb and Th/Pb ratios of the gabbros. This is because 206Pb/204Pb decreases and 208Pb*/206Pb* increases with the age of MORB mantle source, and ancient MORB mantle source has lower 206Pb/204Pb and higher 208Pb*/206Pb*. As long as the gabbros have sufficiently low (U, Th)/Pb ratios, they preserve their ancient Pb isotopic signatures, i.e., low 206Pb/204Pb and high 208Pb*/206Pb*, which are not sensitive to the Th/U ratios of the gabbros. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
component, despite their very different Th/U ratios (1.78 vs. 3.75, respectively). The explanation is that radiogenic ingrowth of $^{208}\text{Pb}$ is slower than that of $^{206}\text{Pb}$ in the MORB source reservoir; consequently, its $^{206}\text{Pb}/^{204}\text{Pb}$ increases and $^{208}\text{Pb}*/^{206}\text{Pb}*$ decreases with time (Fig. 6b). That is, ancient Pb is characterized by low $^{206}\text{Pb}/^{204}\text{Pb}$ and high $^{208}\text{Pb}*/^{206}\text{Pb}*$; this Pb isotopic signature is characteristic of the LOA component. Panel b shows that Zr/Nb is highest in Loa shields lavas and that Zr/Nb is positively correlated with Sr/Nb.

3.2.2. Zr and Nb

Because Zr and Nb are minimally affected by alteration, and their abundance can be accurately determined by X-ray fluorescence, Zr/Nb has been used extensively to provide petrogenetic constraints for basalt. They are high-field-strength elements whose extent of incompatibility differs substantially (Fig. 3). Both clinopyroxene and garnet can change the Zr/Nb ratio because for each phase, $D_{\text{Zr}}/D_{\text{Nb}} > 1$ (Fig. 5e); consequently, Zr/Nb varies with the extent of melting of peridotite. Nevertheless this ratio can be used to evaluate geochemical heterogeneity in the mantle sources of basalt. In particular Hawaiian shield lavas define inverse trends for Zr/Nb versus $^{206}\text{Pb}/^{204}\text{Pb}$ (Fig. 11 of Chen et al., 1996) and for Zr/Nb versus $^{143}\text{Nd}/^{144}\text{Nd}$ (Fig. 7a). The well defined intershield trends in Panels a and c show that Loa-trend lavas have high Sr/Nb and La/Nb but low Th/La as expected for cumulus plagioclase (Fig. 5b). In contrast Th/Nb, a ratio not controlled by plagioclase, is not correlated with Sr/Nb (Panel b).
The high ratios in the Loa-trend lavas are consistent with the LOA component forming as an adcumulate gabbro composed of cumulus plagioclase and clinopyroxene. Such rocks are common in the oceanic crust (e.g., Meyer et al., 1989; Elthon et al., 1992; Hart et al., 1999; Natland and Dick, 2001; Coogan et al., 2001). Moreover plagioclase and clinopyroxene in gabbros cored from the Atlantis Massif on the Mid Atlantic Ridge (Drouin et al., 2009) have incompatible element ratios consistent with equilibrium crystallization from a MORB melt (Fig. 5c, d). Increasing pressure during subduction converts the gabbro to eclogite. If metamorphism occurred in a closed system, the eclogite retains the Sr enrichment caused by cumulus plagioclase and the relatively high Zr/Nb caused by clinopyroxene.

3.2.3. Th, Nb and La

We focus on Th, Nb and La because these elements are highly incompatible during the petrogenesis of tholeitic basalt, and they are relatively immobile during post-magmatic alteration of Hawaiian shield lavas (e.g., Huang et al., 2016). Because few processes can change the ratios of highly incompatible elements, it is surprising that La/Nb, Th/La and Th/Nb ratios in Hawaiian shield lavas vary by factors of 1.9, 1.8 and 1.6, respectively (Figs. 8 and 9).

Ratios of La/Nb and Th/La, but not Th/Nb, are correlated with Zr/Nb and Sr/Nb and with radiogenic isotope ratios (Figs. 8 and 9). What process created these correlations? Equilibrium partial melting changes ratios only if the extent of melting is less than the (bulk solid)/melt partition coefficients (Appendix F). The low extent of melting required, <5%, to change La/Nb, Th/La and Th/Nb ratios is too low to generate tholeiitic basalt (e.g., Green and Ringwood, 1968).

In contrast, residues created by fractional melting will have very different incompatible element ratios than the source and these ratios are very sensitive to extent of melting (e.g., Johnson et al., 1990; Appendix H). However the fractional melting model is not realistic because it requires that solid-state diffusion is able to maintain a homogeneous residue as fractional melts are segregating instantaneously from the residue. More realistic melting models, such as dynamic melting that assume a critical proportion of melt is not removed from the residue, i.e., the residue is porous, are much less effective in changing abundance ratios of incompatible elements.

High Sr/Nb, La/Nb and La/Th are characteristic of plagioclase (Fig. 5a and Appendix I). For La the plagioclase partition coefficient at an appropriate An/Ab ratio is
~0.07 (Appendix G). The sensitivity of La/Nb and Th/La to extent of melting of a pyroxenite/eclogite is shown in Appendix E. A simple interpretation of the trends in Fig. 8a and c is mixing of Kea-trend melt with melt derived by high, >50%, extents of melting of pyroxenite/eclogite that formed as the plagioclase-rich adcumulate entered the mantle. If the system was closed during this reaction, the pyroxenite/eclogite inherited the incompatible elements in the plagioclase-rich adcumulate. Melts formed by high (>50%) extents of melting of the pyroxenite/eclogite are basaltic, and they would have the characteristic ratios of cumulus plagioclase, i.e. high Sr/Nb, La/Nb and low Th/La (Appendix E).

Both Loa and Kea components have (Th/Nb)PM and (Th/La)PM < 1 (Fig. 8b, c; Hofmann and Jochum, 1996); therefore the sources of all Hawaiian shield lavas are relatively depleted in Th. Depletion in Th is consistent with the high Ba/Th in both Loa- and Kea-trend lavas (Fig. 4e; Hofmann and Jochum, 1996). Plagioclase has high D_Ba/D_Th (Fig. 5a; Bindeman and Davis, 2000; Tepley et al., 2010). High Ba/Th has been attributed to accumulation of plagioclase and recycling of cumulate plagioclase-rich gabbros into the source of Hawaiian lavas (Hofmann and Jochum, 1996; Yang et al., 2003) and to reaction of basaltic magma with plagioclase-rich cumulates in the oceanic lithosphere (Saal et al., 2007). However Ba/Th is poorly correlated with Sr/Nd (Fig. 4e; Yang et al., 2003) possibly because of Ba mobility during alteration process (Huang et al., 2016).

3.3. The Origin of the LOA Component: The Role of Lower Oceanic Crust

Lavas from different shields define strong correlations between La/Nb, Th/La, Sr/Nb and Zr/Nb (Fig. 8). In a plot of plagioclase/(basaltic melt) partition coefficient versus atomic number the RREE define a negative slope, i.e., LREE are more compatible than HREE, and there are prominent peaks at Ba, Pb, Sr and Eu and valleys at Th, Nb, Zr and Hf (Fig. 5a). Appendix I shows that cumulus plagioclase is the explanation for the high Sr/Nd, Sr/Nb, La/Nb and low Th/La that characterize the LOA component. Acumulate gabbros with cumulus plagioclase and clinopyroxene are common in the oceanic lower crust (e.g., Natland and Dick, 2001). However the low 143Nd/144Nd of Loa-trend shield lavas relative to MORB is not explained by involving only the oceanic lower crust (Fig. 4c).

3.4. The Origin of the LOA component: an alternative approach to evaluating the role of lower oceanic crust

Pietruszka et al. (2013) evaluated the source of geochemical heterogeneity in the Hawaiian plume by assuming that the heterogeneity reflects processes at ancient subduction zones where oceanic crust was introduced into the upper mantle and subsequently incorporated into the Hawaiian hotspot. Instead of using the intershield differences in ratios of highly incompatible elements, which they described as enigmatic, Pietruszka et al. (2013) constrained the source of Hawaiian shield lavas by calculating a mass balance among partial melts of ambient Hawaiian mantle peridotite and two components of subducted oceanic crust, variably dehydrated upper crust of altered MORB and lower crust of unaltered gabbro. For parental Makapu'u-stage Koolau shield lavas, they concluded that the lava source was dominantly peridotite that included 8–10% altered MORB and 7–8% lower oceanic crust.

Previously we argued that the high La/Nb of the Loa-component reflects a deficiency in Nb caused by a small amount of sediment in the Loa-component (Jackson et al., 1999; Huang and Frey, 2003, 2005). This conclusion is consistent with Li, Ca, Nd, Hf and Os isotopic data for Makapu'u-stage lavas in Koolau volcano (Lassiter and Hauri, 1998; Blichert-Toft et al., 1999; Huang et al., 2011b; Harrison et al., 2015). However we now favor the interpretation that the high Sr/Nd and La/Nb that distinguish the LOA component were created by cumulus plagioclase.

Pietruszka et al. (2013) proposed a very different model; specifically that the high La/Nb of the LOA component indicates that rutile was not present in recycled oceanic crust that led to Loa-trend lavas. They inferred that the absence of rutile indicates that these slabs were not strongly dehydrated during subduction. We point out that Fig. 3e of Pietruszka et al. (2013) shows that the component with high Sr/Nd and La/Nb in their mass balance model is “fresh lower crustal gabbro”. We suggest that both high Sr/Nd and La/Nb in their gabbroic lower oceanic crust reflect cumulus plagioclase. Therefore their inference of less dehydration of the subducted oceanic crust for Loa-trend shields is not required.

Another difficulty with the less dehydration inference is that Hauri (2002) in a study of the volatile content of olivine-hosted melt inclusions concluded that the subducted slab component contributing to Koolau lavas “was efficiently devolatilized during ancient subduction”. This evidence for extensive dehydration is strengthened by the recent discovery that melt inclusions in olivine phenocrysts of Loa-trend magmas have lower H2O, F and Cl contents than those in Kea magmas (Marske et al., 2014).

3.5. The origin of the LOA component: the role of granulites in the lower continental crust

Our preceding discussion of incompatible element ratios led to the conclusion that the LOA component is rich in plagioclase. Although plagioclase-rich rocks are abundant in the lower oceanic crust (e.g., Natland and Dick, 2001), they also occur in the lower crust of arcs and in the lower continental crust as granulites (Rudnick and Gao, 2014). Could the LOA component have originated in a continental environment? McKenzie and O’Nions (1983) proposed that the continental lithosphere mantle could become detached and incorporated into the convecting mantle. Stern and Scholl (2010) suggested that there are three processes, subduction, subduction erosion and lower crust foundering (delamination) that transfer lower continental crust into the mantle. Consistent with deep recycling of continental crust, there are
several examples of ocean island basalt and MORB that are interpreted to have had a source component derived from continental lithosphere (e.g., Kamenetsky et al., 2001, 2009; O’Reilly et al., 2009; Regelous et al., 2009).

3.6. The Origin of the LOA Component: the role of cumulate rocks in the lower crust of arcs?

Volcanic arcs are a tectonic setting where mafic cumulates in the lower crust may delaminate and founder into the convecting mantle. Jagoutz and Schmidt (2013) estimated that worldwide the mass of delaminated lower crust in arcs is 1/3 to 1/2 of subducted oceanic crust. In order to achieve sufficient density for delamination, Jagoutz and Schmidt (2013) emphasized the important role of garnet-bearing cumulates. They calculated delaminate for the Kohistan arc; it has high ratios of Ba/Th, La/Nb, Sr/Nd, Sm/Zr and Pb/Ce and relative depletion in Zr and Nb. These are characteristics of plagioclase/melt partition coefficients (Fig. 5a). However, the high abundance of heavy REE in the calculated delaminate is not consistent with plagioclase as the only aluminous cumulus phase. Since HREE are compatible in garnet, the cumulate in the Kohistan arc may have contained both plagioclase and garnet.

3.7. Where did the Loa Component form? Can incompatible element ratios constrain the tectonic setting?

Rocks that formed as plagioclase-rich adcumulates occur in oceanic and continental lower crust and in deep sections of volcanic arcs. Examples are:

(1) The lower oceanic crust has been sampled by drill cores into gabbroic sections exposed on the seafloor. The 1508 m section recovered by the Ocean Drilling Program in Hole 735B near the Southwest Indian Ridge has been especially useful. For example, Natland and Dick (2001) emphasized that many of these gabbros formed as cumulates and commonly as adcumulates with very little trapped melt. However Loa-trend shield lavas with high Sr/Nd (>19) have $^{143}$Nd/$^{144}$Nd ratios less than 0.5128, distinctly lower than the mean value for normal MORB of 0.5131 (Fig. 4c). Although this result seems to preclude a relationship to MORB we calculated a mass balance (Fig. 11a) for an average lower oceanic crust (Hart et al., 1999).

(2) The lower continental crust is sampled by xenoliths in explosive eruptions of mafic magmas. For example at Lashaine, a tuff cone in Tanzania, there are xenoliths of garnet-clinopyroxene granulites. These xenoliths were originated as plagioclase-rich cumulates in the lower continental crust (LCC) at depths within the stability field of plagioclase; subsequently garnet formed during subsolidus metamorphic reactions (Jones et al., 1983; Mansur et al., 2014). Rudnick and Gao (2014) recognized the problems with using xenoliths to sample the lower crust and they favored a LCC composition that is based on seismic velocities of lower crust coupled with “typical” compositions of lower crust lithologies (Rudnick and Fountain, 1995).

In our subsequent mass balance calculations, we use estimates of LCC composition based on granulite xenoliths and a composition based on seismic velocities in the lower continental crust (Fig. 11a, b, e, h).

(3) The lower crust of volcanic arcs is sampled as xenoliths in arc magmas. It includes 1–2 km of hornblende- and garnet-granulite that are inferred to have formed as cumulates. Garnet was probably not a cumulus phase and probably formed during subsolidus metamorphic reaction (Jagoutz and Schmidt, 2013).

We used two simple end-member models (Fig. 10) to evaluate the suitability of lower crust in the three different tectonic areas to satisfy the mass balance equation:

\[ \text{Mauna Loa primary melt} = X\% \text{ Loa component} + (1 - X\%) \text{Kilauea primary melt}. \]

In this equation $X$ is unknown; the incompatible element contents of primary melt compositions are inferred from Mauna Loa and Kilauea glass compositions (Appendix D) and the LOA component is the composition of plagioclase-rich lower crust in the three different tectonic settings. We chose this simple mass balance because Loa-trend lavas have several geochemical characteristics indicating that their source contained recycled crust. For example, among Hawaiian shield lavas, they have: the highest $^{187}$Os/$^{188}$Os (Fig. 2 of Lassiter and Hauri, 1998) and the most anomalous (Sr/Nd)$_{PM}$ and (La/Nb)$_{PM}$ (1.28 and 1.38, respectively) in contrast to near PM ratios (1.04 and 0.89, respectively) for Kilauea lavas. Clearly the Loa-trend lavas have more unusual compositions than Kea-trend lavas. The simplest model is addition of an exotic component to Kilauea magma to make a Loa-trend magma. The goal of these calculations is to determine if the incompatible element content of plagioclase-rich gabbroic adcumulate in the lower crust in different tectonic settings or estimates of lower crust composition can satisfy such a mass balance for incompatible elements; if they do so such a model for Loa-trend lavas is plausible.

The first model is mixing of two melts that are created as mantle containing peridotite and eclogite (garnet pyroxenite) ascend in an upwelling plume (Fig. 10a). The eclogite (garnet pyroxenite) melts to a large extent, >60%, before the peridotite reaches its solidus (e.g., Hirschmann and Stolper, 1996; Pertermann and Hirschmann, 2003). In this model it is assumed that the melt derived from the eclogite (garnet pyroxenite) is insulated enabling ascent to a shallow magma accumulation zone where it mixes with the peridotite-derived melt (Pertermann and Hirschmann, 2003; Kogiso et al., 2004; Liang et al., 2010). Fig. 11a shows that a mixed melt consisting of 65% of Kilauea primary magma and 35% of the melt derived by large extent of melting the eclogite (garnet pyroxenite) (see Appendix E for details) matches the incompatible element content of Mauna...
Loa primary magma within 10% for 17 of the 19 elements; the largest discrepancy ~20% is for Th and Nb (Fig. 11f; note that Panels f and j use a linear vertical axis to compare the calculated results with the Mauna Loa composition). We view 10% as a satisfactory match because our choice of end-member LOA components from diverse localities is surely not the LOA component in Hawaiian Loa-trend basalt. Partial melting of peridotite occurs at shallower depth, as indicated by red rims on peridotite minerals. At this depth the pyroxenite is melted to a high extent, >50%. In this alternative the partial melts of pyroxenite and garnet peridotite are formed at different depths and mix within crustal magma chambers. In Case B, pyroxenite begins to melt deeper, ~150 km, than the peridotite. Then such melts wet both pyroxenite minerals and peridotite minerals, as indicated by the yellow lines (melts) linking pyroxenite and peridotite in the middle panel. If melt is in equilibrium with all minerals, this forces the garnet and clinopyroxene in peridotite have the same minerals compositions as those in pyroxenite. This effect is indicated by the same colors for garnet and clinopyroxene in both pyroxenite and peridotite in the upper panel, and the same color for melts wetting both pyroxenite and peridotite minerals. At this stage, it is equivalent to partial melting of a peridotite enriched by a pyroxenite. The effect of this alternative can also be interpreted using a slightly modified version of the Sobolev et al. (2005) model: pyroxenite begins to melt deeper. By the time peridotite begins to melt, pyroxenite melts to ~100%. At this stage, melt of pyroxenite reacts with peridotite to form an enriched peridotite. Then partial melts of this enriched peridotite contributes to a Hawaiian volcano. Calculation details are in Appendix J.

In contrast our choices of incompatible element abundances of the lower continental crust, two granulite xenoliths and an estimate that used seismic velocities, did not produce a reasonable mass balance (Fig. 11f).

A third possibility for the LOA component is delaminates of the lower crust in arcs. Estimated compositions of delaminates (Table 4 of Jagoutz and Schmidt, 2013) mixed with Kilauea basalt in a 35/65 proportion provides a fit to the mass balance equation comparable to that of the unaltered gabbro from the oceanic crust (Fig. 11d).

The second model is solid–solid mixing whereby peridotite and pyroxenite equilibrate. This is an end-member melt–rock reaction model whereby total melts of recycled eclogite (garnet pyroxenite) react with olivine in the peridotite to form a homogenous solid (Fig. 10b) that can be melted to different extents (Yaxley and Green, 1998;
Appendix J; Fig. 11 g, h, i). This calculation involves a mixing ratio for the two solids and an extent of melting of the homogeneous solid that fits most of the trace element abundances within 10%; exceptions are Th and Nb which deviate by 15–25% (Fig. 11 j).

In summary, plagioclase-rich cumulates transformed to eclogite (garnet pyroxenite) from all three tectonic locations can create melts with abundances of incompatible elements that are similar to the LOA component. Therefore it is not possible to use incompatible element abundance ratios to associate the LOA component with a particular tectonic location.

4. USING ISOTOPIC RATIOS OF O, SR, ND, HF, PB AND OS TO IDENTIFY THE SOURCE AND TECTONIC ENVIRONMENT OF THE LOA COMPONENT?

4.1. Oxygen

Eiler et al. (1996) found inter-shield differences in $\delta^{18}$O of olivine phenocrysts, relatively low in Kea-trend lavas and high in Loa-trend lavas. Among Hawaiian shield basalts the highest $\delta^{18}$O are in Makapuu-stage lavas erupted during late growth of the Koolau shield; speci-
cally, olivine from seven samples ranges in $\delta^{18}O$ from +5.71 to +5.98 and olivine from three Lanai samples ranges from 5.39 to 5.61 (Eiler et al., 1996). In contrast, olivines in Kea-trend lavas have $\delta^{18}O < 5.2$ (Eiler et al., 1996) and an average of historical Kilauea lavas is 5.11 ± 0.07 (Garcia et al., 2008). Most importantly, $\delta^{18}O$ is correlated with isotopic ratios such as $^{143}$Nd/$^{144}$Nd and $^{206}$Pb/$^{204}$Pb, the major element ratio CaO/Al$_2$O$_3$ and incompatible element ratios such as Sr/Nb (Wang et al., 2010). The important inference is that the high $\delta^{18}O$ of the Makapuu lavas is a source characteristic rather than one controlled by a process such as recent interaction of an ascending magma with plagioclase-rich lithosphere (Saal et al., 2007; Peterson et al., 2014). The inferred $\delta^{18}O = +6.4$ of coexisting Makapuu melt is well above that of MORB and similar to the $\delta^{18}O = +6.5 \pm 1$ of gabbro in the lower km of oceanic crust core recovered at ODP Hole 735B (Alt and Bach, 2006).

Granulite xenoliths from the lower continental crust also have high oxygen isotopic ratios. Fowler and Harmon (1990) found that 86 granulites from 7 locations have average $\delta^{18}O = +7.5$. If partial melts of granulites are mixed with melts derived from peridotite with $\delta^{18}O = +5.7$, a granulite component could also explain the high $\delta^{18}O$ of +6.4 in Koolau (Makapuu stage) lavas. The major conclusion is that oxygen isotope ratios of altered lower oceanic crust and continental crust are similar and not useful in constraining the source of the LOA component.

### 4.2. Osmium

Lassiter and Hauri (1998) determined that Makapuu stage lavas of the Koolau shield have high $^{187}$Os/$^{188}$O. They concluded that high Os ratios accompanied by high $\delta^{18}O$ indicate that the source of Loa-trend lavas contained recycled oceanic crust including up to 5% pelagic sediments. As we noted earlier a role for only recycled normal MORB is not consistent with the low $^{143}$Nd/$^{144}$Nd that accompanies the characteristic high Sr/Nd of Loa-trend shield basalt (Fig. 4c). The presence of pelagic sediment in the LOA component may explain why the LOA component has low $^{143}$Nd/$^{144}$Nd relative to MORB (Fig. 4c).

### 4.3. Lead

Previously we used the Pb isotopic ratios that are characteristic of the LOA component, i.e. relatively low $^{206}$Pb/$^{204}$Pb and high $^{208}$Pb*/$^{206}$Pb*, to conclude that ancient oceanic plagioclase-rich adcumulates formed from MORB magma could explain the Pb isotopic characteristics of the LOA component (Fig. 6a, b).

Lustrino (2005) emphasized that lower continental crust incorporated into the convecting mantle also results in distinctive isotopic signatures such as the low $^{206}$Pb/$^{204}$Pb and high $^{187}$Os/$^{188}$Os and unradiogenic Nd. Lower continental crust in arcs can also generate the Pb isotopic characteristic of the LOA component because
when Pb is lost from subducting slabs and incorporated into the source of arc lavas (Kelley et al., 2005), the delaminates in arc settings have very low U/Pb and Th/Pb; consequently, they retain their initial Pb isotopic ratios (Jagoutz and Schmidt, 2013; Huang et al., 2014). In summary the distinctive Pb isotopic characteristics of Loa-trend lavas can develop in each of the three tectonic settings.

4.4. Strontium and Neodymium

Hawaiian shield lavas, like most ocean island basalt define an inverse trend of $^{143}$Nd/$^{144}$Nd vs. $^{87}$Sr/$^{86}$Sr (Fig. 12a). At a given $\varepsilon$Nd, shield lavas increase in $^{87}$Sr/$^{86}$Sr from Koolau (Makapuu) to Lanai to Kahoolawe (Fig. 12a). There is no obvious correlation of $^{87}$Sr/$^{86}$Sr with Rb/Sr. In particular, even ancient oceanic crust of 3.5 Ga will not reach the lower range of $^{87}$Sr/$^{86}$Sr in Loa-trend basalts (Fig. 12c, d). The simplest explanation is that in addition to cumulus plagioclase, the Loa component includes a recent and variable addition of a high $^{87}$Sr/$^{86}$Sr component such as carbonate (Huang et al., 2009, 2011b), or seawater altered lithospheric mantle (Sobolev et al., 2011). Another possibility is loss of incipient, volatile-rich partial melt with high Rb/Sr as melting in the hotspot commenced (Roden et al., 1994).

4.5. Hafnium and Neodymium

Most oceanic island basalts have highly correlated $^{176}$Hf/$^{177}$Hf and $^{143}$Nd/$^{144}$Nd ratios because their parent/daughter ratios, Sm/Nd and Lu/Hf, are usually highly correlated. However because Lu is compatible in garnet (Fig. 5e), a petrogenetic role for garnet will decouple Hf and Nd isotope ratios. Jagoutz and Schmidt (2013) concluded that garnet-bearing delaminated lower crust in arcs would lead
to oceanic island basaltic lavas offset from the mantle array to high \(^{176}\text{Hf}/^{177}\text{Hf}\) at a given \(^{143}\text{Nd}/^{144}\text{Nd}\). Although garnet is a common mineral in granulites and delaminated lower crust, petrographic observations commonly conclude that garnet formed as a metamorphic mineral (e.g., Mansur et al., 2014). If garnet formed by solid state reaction in a closed system, ancient arc delaminates are unlikely to deviate from the highly correlated \(^{176}\text{Hf}/^{177}\text{Hf}-^{143}\text{Nd}/^{144}\text{Nd}\) terrestrial array. The Loa-trend lavas from Lanai, Kahoolawe and Koolau (Makapuu stage) deviate from the mantle array to high \(\varepsilon\text{Nd}\) at the low end of the array (Fig. 13). Garnet would cause deviation from the array at the high end of the array (Bizimis et al., 2004). The offset of Loa-trend lavas at the low end of the array has been interpreted to indicate that the LOA component includes a pelagic sediment component (Blichert-Toft et al., 1999), an inference that is consistent with the low \(^{143}\text{Nd}/^{144}\text{Nd}\) and high \(\delta^{18}\text{O}\) and \(^{187}\text{Os}/^{186}\text{Os}\) of Makapuu stage Koolau lavas (Lasserst and Hauri, 1998).

However, Salters et al. (2006) concluded that the incompatible element and radiogenic isotope ratios in Loa-trend lavas cannot be explained by adding only ancient pelagic sediments to the source. The slope of the Kahoolawe, Lanai and Koolau lavas in \(\varepsilon\text{Nd}-\varepsilon\text{Hf}\) (Fig. 13) is the shallowest observed for most rocks (Salters et al., 2006). Salters et al. (2006) proposed that the low \(\varepsilon\text{Nd}-\varepsilon\text{Hf}\) end of the Hawaiian trend that deviates from the terrestrial array is best explained if the LOA component contained ancient depleted oceanic lithosphere, and possibly pelagic sediment (Fig. 13) in addition to plagioclase-rich accumulates.

5. SUMMARY

5.1. Spatial distribution of LOA component

Volcanoes forming the Hawaiian Islands define two sub-parallel spatial trends known as the Loa-trend and Kea-trend. The Kea-trend volcanoes clearly end at East Molokai Volcano whereas the Loa-trend extends to Koolau Volcano and even perhaps to Kauai (Fig. 1, Weis et al., 2011; Garcia et al., 2015). Most lavas erupted at Loa-trend volcanoes are geochemically different from those erupted at Kea-trend volcanoes. These differences reflect the geochemical characteristics of the LOA component that is most abundant in the uppermost shield lavas of Kahoolawe, Lanai and Koolau volcanoes. Curiously at West Molokai, located between Koolau and Lanai (Fig. 1), only 1 of the 39 shield samples analyzed has a Loa-trend geochemical signature, such as high Sr/Nd (Xu et al., 2007).

5.2. What is the LOA component?

It is important to recognize the heterogeneity of the LOA component that created the distinctive geochemical characteristics of Loa-trend shield lavas. The most obvious geochemical signature of the LOA component is that of ancient gabbroic acummulate rich in cumulus plagioclase; such material is recognized by high Sr/Nd, La/Nb, low \(^{143}\text{Nd}/^{144}\text{Nd}\) and high Sr/\(^{208}\text{Pb}\)/\(^{206}\text{Pb}\) and low \(^{206}\text{Pb}/^{204}\text{Pb}\) (Figs. 4, 6, 9 and 12b); it is most prominent in the uppermost shield lavas of Koolau volcano. There is also a relatively enriched material with high \(^{87}\text{Sr}/^{86}\text{Sr}\) that is not supported by its Rh/Sm; it is most prominent in Kahoolawe volcano (Fig. 12a). A third geochemically distinct material is inferred from the offset of Koolau, Lanai and Kahoolawe shield lavas from the \(\varepsilon\text{Nd}-\varepsilon\text{Hf}\) terrestrial array to high \(^{176}\text{Hf}/^{177}\text{Hf}\) at low \(^{143}\text{Nd}/^{144}\text{Nd}\) (Fig. 13). This material has been interpreted modified pelagic sediment and recycled ancient depleted lithosphere (Salters et al., 2006).

5.3. Is the LOA component dominantly recycled oceanic lower crust?

Ratios of Sr/Nd and La/Nb in Loa-trend lavas exceed estimates of primitive mantle and indicate that a gabbroic
adcumulate with cumulus plagioclase is a major part of the Loa-component. Such rocks are abundant in the oceanic crust and their incompatible element content satisfies the mass balance equation Mauna Loa basalt = Kilauea basalt + LOA component.

Also the Pb isotope ratios of cumulate gabbros in the oceanic crust, i.e., low $^{206}\text{Pb}/^{204}\text{Pb}$ and high $^{208}\text{Pb}/^{206}\text{Pb}$, are consistent with the LOA component as unaltered gabbro formed from MORB as a plagioclase-rich adcumulate and aged for $>3$ Ga.

There are, however, geochemical characteristics of the LOA component that are not consistent with derivation from only igneous oceanic crust. Most obvious is the inverse trend between Sr/Nd and $^{143}\text{Nd}/^{144}\text{Nd}$ (Fig. 4c) that shows the high Sr/Nd material has lower $^{143}\text{Nd}/^{144}\text{Nd}$ than most MORB. Another component such as pelagic sediment is required to explain the low $^{143}\text{Nd}/^{144}\text{Nd}$. Also from nNd +2 to -2, $^{87}\text{Sr}/^{86}\text{Sr}$ increases from Koolau (Makapuu) to Lanai to Kahoolawe (Fig. 12a); this increase in $^{87}\text{Sr}/^{86}\text{Sr}$ is not related to normal MORB because the average Rb/Sr = 0.0016 of oceanic gabbro does not lead to the high $^{87}\text{Sr}/^{86}\text{Sr}$ of the Loa-trend lava (~0.7045) in 4.5 Ga (Fig. 12c,d).

Relative to the mantle array in $^{176}\text{Hf}/^{177}\text{Hf}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$, Loa-trend lavas define a shallower slope that reflects an ancient high Lu/Hf material that evolved to high $^{176}\text{Hf}/^{177}\text{Hf}$ at low ratios of $^{143}\text{Nd}/^{144}\text{Nd}$; this material was initially inferred to be ancient pelagic sediment consistent with Koolau (Makapuu stage) lavas having high $^{87}\text{Sr}/^{86}\text{Sr}$ and low $^{143}\text{Nd}/^{144}\text{Nd}$. An alternative interpretation for this component is ancient depleted oceanic lithosphere (Fig. 13; Salters et al., 2006).

5.4. Is the LOA component recycled lower continental crust (LCC) or as delaminated lower crust beneath volcanic arcs?

Samples of lower crust beneath continents and arcs include rocks that formed as adcumulates with abundant cumulus plagioclase. These rocks commonly occur as xenoliths in explosive volcanic eruptions on continents and rarely as exhumed basement beneath volcanic arcs such as Kohistan in Pakistan. The ratios of incompatible elements can be explained by the mass balance equation Mauna Loa basalt = Kilauea basalt + LOA component. However, some choices for the composition of LCC, such as xenoliths from Tanzania and the estimate for LCC composition by Rudnick and Fountain (1995) cannot be explained by mixing of two melts model presented in Fig. 10a, and evaluated in Fig. 11f.

Relative to MORB, continental rocks have lower $^{143}\text{Nd}/^{144}\text{Nd}$ and higher $^{87}\text{Sr}/^{86}\text{Sr}$. Therefore unlike igneous oceanic lower crust they do not have a problem in explaining the Nd and Sr ratios in the LOA component (Fig. 12). Also the Pb isotopic ratios estimated for LCC can explain the trend of Loa-trend lavas to low $^{206}\text{Pb}/^{204}\text{Pb}$ and high $^{208}\text{Pb}/^{206}\text{Pb}$ (Fig. 6). However, as with igneous oceanic lower crust, a process is needed to explain that Kahoolawe shield lavas have high $^{87}\text{Sr}/^{86}\text{Sr}$ at a given nNd (Fig. 12a).

5.5. Important role of cumulus plagioclase in creating the LOA component

Although we cannot make a compelling argument for a specific tectonic setting for origin of the LOA component, we conclude that regardless of tectonic setting there is a commonality in the sequence of processes that created the geochemical signature of cumulus plagioclase in the LOA component. They are: (a) ancient formation in the lower crust of gabbroic adcumulates with abundant cumulus plagioclase, that is, no melt was trapped; (b) recrystallization to eclogite-facies mineralogy in a closed system, i.e., there was no compositional change accompanying metamorphism; (c) incorporation into the convecting mantle via subduction, foundering or delamination; (d) addition of a component with a long-term high Lu/Hf ratio, such as residues from ancient melting processes; or pelagic sediment (e) during ascent of the buoyant Hawaiian plume melts formed by low extents of partial melting of peridotite and high extents of melting of pyroxenite/eclogite are mixed (Fig. 10a). Alternatively, the mineralogically heterogeneous peridotite and pyroxenite are homogenized, by melt-rock reaction, described as solid–solid mixing. This solid partially melts as the buoyant Hawaiian hotspot ascends (Fig. 10b).

Interestingly, Loa-trend Hawaiian volcanoes are not the only locality where cumulate gabbros rich in cumulus plagioclase are a source component for basalt. Acdumulate rocks have also been proposed as a source for depleted Iceland basalt (Chauvel and Hemond, 2000), for lavas erupted at the easternmost volcanoes in the Galapagos Archipelago (Saal et al., 2007; Peterson et al., 2014) and for basalt erupted in Sardinia derived from plagioclase-rich cumulates formed in oceanic plateaus (Gasperini et al., 2000) or recycled lower continental crust (Lustrino et al., 2000).

ACKNOWLEDGMENTS

We thank A. Saal, A. Hofmann, K. Purtirka, R. Rudnick and especially J. Natland for discussion and the geochemists who published the data that we use in this paper, M. Norman for providing the data for 21 Mauna Loa basalts from Jason Cruise and Pisces Dive 184 in TabI A5, and A. Hofmann, W. Abouchami and J. Blichert-Toft for isotopic data for Lanai basalts in Table A9 of Appendix. J. Bédard provided the calculated partition coefficients in Appendix G. The reviewers (anonymous and A. Pietruszka) and Guest Editor M. Garcia made numerous comments that improved the paper. GX thanks D. McCormick for useful comments. Fred thanks M. Garcia for insisting that I present a talk at the 2014 annual meeting that led to this GCA issue. SH acknowledges support from NSF EAR-1524387.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2016.04.010.
REFERENCES


*Associate editor:* Michael Garcia