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# Major element variations in Hawaiian shield lavas: Source features and perspectives from global ocean island basalt (OIB) systematics

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[1] Among volcanic hot spots globally, Hawaii has the highest magma flux, yet there is significant controversy surrounding the composition of the mantle sourcing Hawaiian lavas. In order to place constraints on the source lithologies of Hawaiian lavas, we explore relationships between major elements and radiogenic isotopes in tholeiitic, shield-building lavas. Olivine-fractionation corrected lava compositions reveal clear trends between radiogenic isotopes and major elements. Individual data points exhibit remarkable trends and there is no need to average the data by volcano. Data form arrays that are anchored by Koolau lava at one end (with high \*\*87sr'\*,\*\*86sr, \*\*187Os/\*188Os, \*\*SiO<sub>2</sub>, and Na<sub>2</sub>O/TiO<sub>2</sub>, and low \*\*143\*Nd/\*144\*Nd, \*\*206\*Pb/\*204\*Pb, TiO<sub>2</sub>, CaO and CaO/Al<sub>2</sub>O<sub>3</sub>) and by Kea and Loihi lavas at the other (with low \*\*87sr'\*,\*\*86sr, \*\*187Os/\*188\*Os, SiO<sub>2</sub>, and Na<sub>2</sub>O/TiO<sub>2</sub>, and high \*\*143\*Nd/\*144\*Nd, \*\*206\*Pb/\*204\*Pb, TiO<sub>2</sub>, CaO and CaO/Al<sub>2</sub>O<sub>3</sub>). FeO<sub>total</sub>, Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O concentrations do not correlate with radiogenic isotopes. The Hawaiian data set exhibits correlations that mirror the best correlations between major elements and radiogenic isotope in the global ocean island basalt (OIB) database. We suggest that the mechanism driving the correlations in Hawaii illustrates, in microcosm, a larger global process that generates major element variability in mantle plumes. Like the global arrays, the Hawaiian lavas with radiogenic Pb and SiO<sub>2</sub>-poor lavas are sourced by a SiO<sub>2</sub>-poor mafic component (pyroxenite) admixed with peridotite, while Hawaiian lavas with unradiogenic Pb and high SiO<sub>2</sub> are sourced by a SiO<sub>2</sub>-rich mafic component (eclogite). The variable SiO<sub>2</sub> in the mafic component may result from different degrees of SiO<sub>2</sub>-extraction from the slab during subduction.

Components: 14,700 words, 10 figures, 1 table.

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### 1. Introduction

[2] Oceanic plates—including mafic crust, depleted lithospheric peridotite, and a thin veneer of marine sediments—are sent into the mantle at subduction zones, thereby contributing to the compositional heterogeneity of Earth's mantle [Hofmann and White, 1982; White and Hofmann, 1982; Iwamori et al., 2010]. Buoyantly upwelling regions of the mantle are thought to return parts of these subducted oceanic plates to the shallow mantle, where they partially melt beneath hot spots like Hawaii. Lavas erupted at hot spots therefore reveal clues about the dynamic history and composition of the mantle [Zindler and Hart, 1986; Hofmann, 1997]. The compositions of hot spot lavas suggest that recycling of ancient subducted oceanic plates is a common process that has affected the geochemistry of the mantle over geologic time [e.g., Hofmann and White, 1982; Sobolev et al., 2005].

[3] However, significant controversy surrounds the final fate of recycled oceanic crust in the mantle [Eggins, 1992; Hauri, 1996; Wagner and Grove, 1998; Putirka, 1999; Sobolev et al., 2005, 2007; Gaffney et al., 2005; Huang and Frey, 2005; Huang et al., 2007; Herzberg, 2006, 2011; Putirka et al., 2011; Niu et al., 2012]. Following billion-year timescales of residence in the mantle, oceanic crust is likely stretched, thinned, and its geochemical signal is greatly attenuated [e.g., Ottino, 1989; Van Keken et al., 2004]. While distinct mafic lithologies may survive mantle convection to be melted beneath hot spots like Hawaii [Hauri, 1996; Sobolev et al., 2005, 2007, 2008; Huang and Frey, 2005; Huang et al., 2007; Herzberg, 2006, 2011], the survival of distinct mafic lithologies into the mantle beneath Hawaii has been questioned [*Putirka*, 1999; Salters et al., 2006; Putirka et al., 2011]. Putirka [1999] and Putirka et al. [2011] argue that peridotite melting can explain the geochemistry of Hawaiian lavas, and a distinct mafic lithology in the mantle source of Hawaiian lavas is not required.

[4] Hawaii is arguably the most-studied oceanic hot spot, and the abundance of geochemical data obtained from Hawaiian lavas makes it an ideal location for evaluating the presence of recycled oceanic crust in the mantle source. While a multitude of components

have been identified in the Hawaiian mantle, most of the isotopic variability in Hawaiian shield-building lavas can be described with just three components, as shown by principal component analysis [Hauri, 1996; Eiler et al., 1996a]. These components include the Koolau, Loihi and Kea components (Figure 2) [Stille et al., 1986; West and Leeman, 1987; Eiler et al., 1996b; Hauri, 1997; Gaffney et al., 2005; Huang et al., 2005; Weis et al., 2011]. The small volumes of low-degree melts sampled by post-shield and rejuvenated lavas require the presence of a fourth, depleted component, distinct from Pacific MORB [Mukhopadhyay et al., 2003; Frey et al., 2005; Fekiacova et al., 2007; Garcia et al., 2010; Hanano et al., 2010], but post-shield and rejuvenated-stage lavas are volumetrically insignificant compared to the shield-building lavas and these lavas are not considered here. Hawaii is the archetypal high <sup>3</sup>He/<sup>4</sup>He hot spot, and lavas from Loihi seamount define the Loihi component and host <sup>3</sup>He/<sup>4</sup>He ratios in excess of 30 Ra (ratio to atmosphere) [Kurz et al., 1982; Rison and Craig, 1983; Kurz et al., 1983; Staudigel et al., 1984; Sarda et al., 1988; Honda et al., 1993; Valbracht et al., 1997; Eiler et al., 1998; Jackson et al., 2008]. The Koolau component, defined by Koolau Makapuustage lavas, is a lower  ${}^3\text{He}/{}^4\text{He}$  end-member characterized by the lowest  ${}^{143}\text{Nd}/{}^{144}\text{Nd}$  and  ${}^{206}\text{Pb}/{}^{204}\text{Pb}$ and highest <sup>87</sup>Sr/<sup>86</sup>Sr in Hawaii and constitutes the enriched Loa trend volcanic end-member (see below) [Tanaka et al., 2008]. This end-member is sampled in diluted form at several Hawaiian volcanoes and likely hosts a component of recycled oceanic crust and sediment [e.g., Hauri, 1996; Lassiter and Hauri, 1998; Blichert-Toft et al., 1999; Norman et al., 2002; Sobolev et al., 2005; Huang et al., 2005, 2011a; Herzberg, 2011; Putirka et al., 2011]. The origin of the Kea component, best exemplified by lavas from Mauna Kea, W. Maui and Kilauea, is less clear. The Kea component, which hosts the highest <sup>143</sup>Nd/<sup>144</sup>Nd and <sup>206</sup>Pb/<sup>204</sup>Pb and the lowest <sup>87</sup>Sr/<sup>86</sup>Sr in Hawaii, is relatively homogeneous relative to the Koolau component, leading to models suggesting a MORB-source, Pacific oceanic lithosphere source or entrained asthenospheric source in Kea lavas, but recycled lower oceanic crust and mantle lithosphere also have been suggested [Chen and Frey, 1985; Frey and Rhodes, 1993; Hauri,



1996; Eiler et al., 1996a, 1996b; Lassiter and Hauri, 1998; Blichert-Toft et al., 2003; Gaffney et al., 2005]. The Kea component dominates the Kea volcanic trend (see below).

[5] The distribution of the Loa and Kea components is organized geographically along the hot spot (Figure 1). Hawaiian shield volcanoes erupted during the past 5 Ma tend to be oriented along two en echelon volcanic trends that exhibit distinct isotopic [e.g., Jackson et al., 1972; Tatsumoto, 1978; Abouchami et al., 2005; Tanaka et al., 2008; Farnetani and Hofmann, 2010; Weis et al., 2011; Huang et al., 2011b] and major element [Hauri, 1996; Greene et al., 2010] compositions. Volcanoes along the northern geographic trend erupt Kea-type lavas and southern-trend volcanoes tend to erupt Loa-type lavas. The origin of this geographic and geochemical separation is the source of significant discussion [e.g., Hieronymus and Bercovici, 1999; Abouchami et al., 2005; Ren et al., 2005; Marske et al., 2007; Weis et al., 2011; Huang et al., 2011b]. Understanding the origin of the different major element compositions of shield-stage lavas between the Loa and Kea trends [Hauri, 1996] may provide important clues about the structure of the Hawaiian plume, including the possible organization of lithologic heterogeneities within the plume conduit [Blichert-Toft et al., 2003; Abouchami et al., 2005] and in the deep mantle [Weis et al., 2011; Huang et al., 2011b].

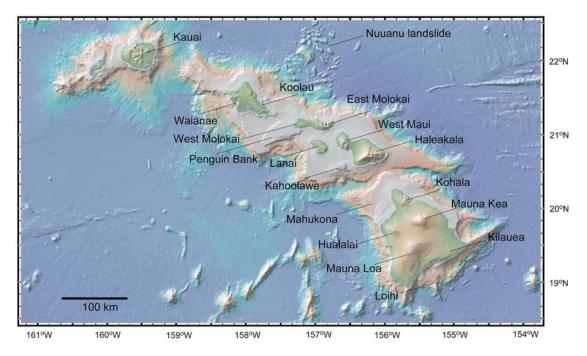
[6] Frey and Rhodes [1993] systematically documented major element variations among different Hawaiian shields and attributed them to mantle source variability. However, correlations between major elements and isotopes can strengthen conclusions that major element variations in hot spot lavas reflect mantle source lithological heterogeneity [Hauri, 1996; Sobolev et al., 2008; Jackson and Dasgupta, 2008]. Hauri [1996] showed correlated major element and isotopic variations in compositional and isotopic averages of Hawaiian volcanoes, and on this basis, argued for major element variability in the Hawaiian mantle and for the importance of eclogite in the petrogenesis of Hawaiian shield lavas. Jackson and Dasgupta [2008] extent such major element-isotope correlation to the global OIB data set. Here we show that the original element-isotope correlations observed by *Hauri* [1996] are "mirrored" by the global OIB data set [Jackson and Dasgupta, 2008]. These data document the major element variability in the Hawaiian plume, constrain source lithologies, and place the major element variability in the Hawaiian plume in the context of global OIB variability.

### 2. Treatment of Geochemical Data

[7] The geochemical data used in this study were obtained from the Georoc database (georoc.mpchmainz.gwdg.de/georoc) on December 26, 2011. Only tholeiitic lavas are considered. All nontholeiitic lavas [Macdonald and Katsura, 1964] are excluded, as are lavas that are explicitly described as post-shield or rejuvenated. Only lavas with a complete set of major elements (SiO2, TiO2, Al2O3, FeO<sub>total</sub>, MnO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>) are considered. A sample is excluded if it does not have at least one of the following isotopic measurements:  ${}^{87}\text{Sr/}^{86}\text{Sr}, {}^{143}\text{Nd/}^{144}\text{Nd}, {}^{206}\text{Pb/}^{204}\text{Pb} \text{ (and } {}^{207}\text{Pb/}^{204}\text{Pb} \text{ and } {}^{208}\text{Pb/}^{204}\text{Pb)}, {}^{187}\text{Os/}^{188}\text{Os}, {}^{176}\text{Hf/}^{177}\text{Hf, or }$ <sup>3</sup>He/<sup>4</sup>He. Compared to Sr, Nd and Pb isotopes, and Hf isotopes to a lesser extent, measurements of He and Os isotopes are still relatively rare. Lavas with low Os concentrations are susceptible to contamination by assimilation of materials with radiogenic Os. Therefore, Os-poor (Os < 40 ppt) lavas are excluded [Class et al., 2009]. Similarly, lavas with low helium concentrations are susceptible to reduction of <sup>3</sup>He/<sup>4</sup>He by post-eruptive radiogenic ingrowth of <sup>4</sup>He or crustal assimilation, and analyses of Hepoor olivines and glasses (less than  $2*10^{-8}$  cc/g STP <sup>4</sup>He) are excluded [Garcia et al., 1990; Hilton et al., 1995; Kurz et al., 2004; Class and Goldstein, 2005]. Only <sup>3</sup>He/<sup>4</sup>He measurements obtained by crushing olivines and glasses are used. Much of the helium isotopic data available for Hawaiian lavas are eliminated using the concentration filter, but we feel that the filter yields a data set that better reflects mantle <sup>3</sup>He/<sup>4</sup>He compositions. However, all <sup>3</sup>He/<sup>4</sup>He measurements are preserved in Data Set S1 in the auxiliary material, regardless of <sup>4</sup>He concentration, as long as the associated whole rock major element analyses do not indicate excessive alteration or magmatic evolution.1

[8] As a filter for alteration, samples with K<sub>2</sub>O/P<sub>2</sub>O<sub>5</sub> < 1, low dry totals (<97 wt.%) or high dry totals (>101 wt.%) were excluded [e.g., *Frey et al.*, 1994]. Leaching is necessary to reduce alteration components in lavas that most strongly influence Sr and Pb isotopic ratios but not Nd and Hf isotopic ratios [*Nobre Silva et al.*, 2009, 2010]. However, it is not always known which samples were leached in acid

<sup>&</sup>lt;sup>1</sup>Auxiliary material data sets are available at ftp://ftp.agu.org/apend/gc/2012gc004268. Other auxiliary materials are available in the HTML. doi:10.1029/2012GC004268.



**Figure 1.** Map of Hawaiian hot spot from Loihi to Kauai showing individual volcanoes (map made using GeoMapApp, http://www.geomapapp.org).

prior to isotopic analyses, as this is not consistently reported in the literature. Fortunately, Sr and Pb isotopic ratios show excellent correlations with Nd and Hf isotopic ratios in Hawaiian volcanoes (Figure 2). Owing to these correlations, we show Nd and Pb isotopic data, but not Sr and Hf isotopic data, in subsequent figures. Sr and Hf isotopic data, where available, are preserved in Data Set S1.

[9] Low MgO lavas (<6.5 wt.%) were not included in the filtered data set. Such lavas can suffer from clinopyroxene and plagioclase fractionation [e.g., *Rhodes and Vollinger*, 2004; *Rhodes et al.*, 2012]. Lavas with MgO > 6.5 wt.% are affected primarily by fractionation or accumulation of olivine  $\pm$  Cr-spinel [*Hauri*, 1996].

[10] The lavas remaining (n = 551) after these filtering steps were renormalized to 100 wt.% totals (on a dry basis) with all Fe reported as FeO<sub>total</sub> (see Data Set S1). The lavas were then corrected for olivine fractionation to a constant MgO of 16 wt.% by adding or subtracting equilibrium olivine in 0.01 wt.% increments, similar to *Langmuir et al.* [1992]. Equilibrium olivines were generated using the olivine-melt K<sub>d</sub> of 0.3 [*Roeder and Emslie*, 1970; *Ford et al.*, 1983] assuming 10% of the total iron is Fe<sup>3+</sup>. Correcting the lavas for olivine fractionation/addition until they are in equilibrium with a mantle olivine (forsterite 90) does not change our conclusions (see Table 1, Figure S1, and Data Set S1). An

olivine-melt  $K_d$  of 0.34 has been suggested for Mauna Kea lavas [e.g., *Matzen et al.*, 2011], which does not change our conclusions (see Figure S1 and Data Set S1). For cumulates (MgO > 20 wt.%), we follow the procedure of *Hauri* [1996] and subtract an olivine composition of forsterite 87 until the bulk lava has 16 wt.% MgO. All of the major element and isotopic data, and major element data corrected for olivine fractionation, are reported in Data Set S1 for individual samples and in Table 1 as volcano averages.

#### 3. Observations

#### 3.1. Radiogenic Isotopes

[11] The panels of Figure 2 show the variability in radiogenic isotopes in the lavas considered in this study. Every lava considered in this study has both major element data (n = 551) and at least one radiogenic isotope system measured (<sup>87</sup>Sr/<sup>86</sup>Sr [n = 444], <sup>143</sup>Nd/<sup>144</sup>Nd [n = 417], <sup>206</sup>Pb/<sup>204</sup>Pb (and <sup>207</sup>Pb/<sup>204</sup>Pb and <sup>208</sup>Pb/<sup>204</sup>Pb) [n = 452], <sup>176</sup>Hf/<sup>177</sup>Hf [n = 229], <sup>187</sup>Os/<sup>188</sup>Os [n = 86], <sup>3</sup>He/<sup>4</sup>He [n = 152 for all <sup>4</sup>He concentrations, or 48 for samples with <sup>4</sup>He > 2\*10<sup>-8</sup> cc STP/g]). The radiogenic isotopic data shown in Figure 2 are intended to show the isotopic variability in the freshest, least evolved Hawaiian shield lavas that we examined in this study, and therefore the data in the figures do not encompass the complete radiogenic isotopic variability in Hawaiian lavas.



Table 1 (Sample). Mean Isotopic and Major Element Compositions for Hawaiian Volcanoes Examined in This Study<sup>a</sup> [The full Table 1 is available in the HTML version of this article

		<sup>143</sup> Nd/ <sup>144</sup> Nd	$^{87}\mathrm{Sr/^{86}Sr}$	$^{206} Pb/^{204} Pb$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}{ m Pb}/^{204}{ m Pb}$	187Os/188Os
Volcano	Island	Average $\pm$ 2SD	Average $\pm$ 2SD	Average $\pm$ 2SD	Average $\pm$ 2SD	Average $\pm$ 2SD	Average $\pm$ 2SD
Loa-trend							
Loihi (tholeiitic)	Big Island	$0.512953 \pm 0.000070$	$0.703581 \pm 0.000131$	$18.376 \pm 0.133$	$15.468 \pm 0.030$	$38.118 \pm 0.122$	$0.1333 \pm 0.0046$
Mauna Loa	Big Island	$0.512906 \pm 0.000074$	$0.703809 \pm 0.000668$	$18.168 \pm 0.176$	$15.460 \pm 0.024$	$37.908 \pm 0.138$	$0.1356 \pm 0.0030$
Hualalai	Big Island	$0.512903 \pm 0.000051$	$0.703727 \pm 0.000086$	$18.182 \pm 0.132$	$15.459 \pm 0.025$	$37.951 \pm 0.159$	$0.1348 \pm 0.0016$
Mahukona	Big Island	$0.512962 \pm 0.000068$	$0.703639 \pm 0.000155$	$18.253 \pm 0.222$	$15.469 \pm 0.014$	$37.941 \pm 0.152$	NA
Kahoolawe	Maui Nui	$0.512848 \pm 0.000099$	$0.704120 \pm 0.000318$	$18.042 \pm 0.314$	$15.436 \pm 0.030$	$37.829 \pm 0.219$	0.1439
Lanai	Maui Nui	$0.512770 \pm 0.000121$	$0.704181 \pm 0.000316$	$17.922 \pm 0.098$	$15.437 \pm 0.016$	$37.753 \pm 0.057$	NA
West Molokai	Maui Nui	$0.512943 \pm 0.000216$	$0.703819 \pm 0.000394$	$18.253 \pm 0.445$	$15.460 \pm 0.025$	$37.939 \pm 0.254$	NA
Koolau (Makapuu)	Oahu	$0.512757 \pm 0.000077$	$0.704082 \pm 0.000315$	$17.854 \pm 0.074$	$15.438 \pm 0.026$	$37.773 \pm 0.071$	$0.1426 \pm 0.0075$
Koolau (KSDP)	Oahu	$0.512917 \pm 0.000083$	$0.703760 \pm 0.000173$	$18.063 \pm 0.081$	$15.453 \pm 0.007$	$37.837 \pm 0.051$	NA
Koolau (Nuuanu Landslide)	Oahu	$0.512972 \pm 0.000059$	$0.703568 \pm 0.000161$	$18.204 \pm 0.366$	$15.448 \pm 0.017$	$37.883 \pm 0.240$	$0.1337 \pm 0.0056$
Waianae	Oahu	$0.512975 \pm 0.000126$	$0.703648 \pm 0.000194$	$18.146 \pm 0.206$	$15.461 \pm 0.037$	$37.856 \pm 0.117$	NA
Kauai	Kauai	$0.512969 \pm 0.000056$	$0.703671 \pm 0.000229$	$18.228 \pm 0.166$	$15.451 \pm 0.015$	$37.939 \pm 0.098$	$0.1368 \pm 0.0038$
Kea-trend							
Kilauea	Big Island	$0.512958 \pm 0.000027$	$0.703584 \pm 0.000099$	$18.464 \pm 0.205$	$15.483 \pm 0.055$	$38.104 \pm 0.189$	$0.1310 \pm 0.0017$
Mauna Kea	Big Island	$0.512968 \pm 0.000036$	$0.703584 \pm 0.000094$	$18.497 \pm 0.181$	$15.483 \pm 0.025$	$38.104 \pm 0.171$	$0.1297 \pm 0.0011$
Kohala	Big Island	$0.513015 \pm 0.000000$	$0.703710 \pm 0.000087$	$18.170 \pm 0.276$	$15.460 \pm 0.041$	$37.845 \pm 0.148$	$0.1365 \pm 0.0115$
Haleakala	Maui Nui	$0.512958 \pm 0.000040$	$0.703645 \pm 0.000194$	$18.541 \pm 0.220$	$15.480 \pm 0.019$	$38.154 \pm 0.183$	$0.1304 \pm 0.0000$
West Maui	Maui Nui	$0.513025 \pm 0.000048$	$0.703550 \pm 0.000140$	$18.431 \pm 0.142$	$15.483 \pm 0.031$	$37.957 \pm 0.128$	$0.1321 \pm 0.0011$
East Molokai	Maui Nui	$0.512981 \pm 0.000083$	$0.703565 \pm 0.000207$	$18.437 \pm 0.410$	$15.480 \pm 0.032$	$38.060 \pm 0.255$	NA

corrected for olivine fractionation/addition to a constant MgO (16 wt.%) or to be in equilibrium with a forsterite 90 olivine composition (but the two different correction schemes yield similar major element compositions). An olivine-melt Kd of 0.30 is used for correction. Data for samples are excluded if the whole rock is altered, highly evolved, or if the major element data are incomplete or the analyses yields high or low totals (see text for filters applied). Helium and Os isotope data exist for many of the volcanoes listed as NA in the table, but in several cases, corresponding major element data does not exist, or indicates excessive magmatic evolution or post-eruptive alteration, and the He and Os data are not reported. Sr, Nd, Pb and Hf isotopes are not filtered based on trace element concentrations. In one column, helium isotopic ratios for samples with low helium concentrations (<2\*10-8 cc 4 He/g STP) are not reported ("High He conc"). However, helium isotopic ratios with lower concentration are preserved in the next column ("All He conc") and in Data Set SI. Os isotopes are excluded if the Os concentration is <40 ppt. <sup>a</sup>Means and the standard deviations (SD, 2 sigma) are from Data Set S1. If the standard deviation is not reported, it is because only a single measurement is available. Major element compositions are

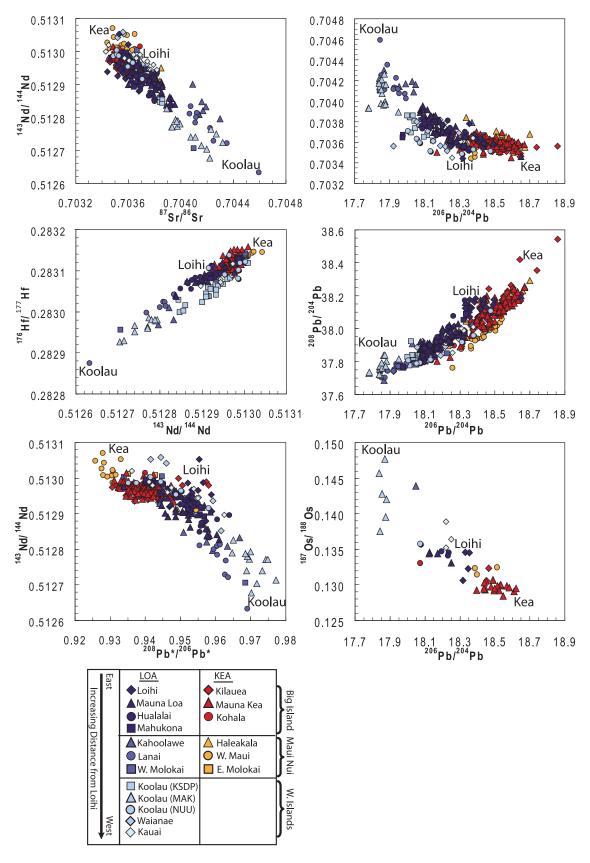


Figure 2



[12] The radiogenic isotopic compositions of Hawaiian shield lavas have been discussed at great length in the literature (for a recent review, see *Weis et al.* [2011]). We outline some of the most outstanding features of the radiogenic isotopic geochemistry of Hawaiian lavas in Figure 2. In general, Loa-trend lavas have lower <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>143</sup>Nd/<sup>144</sup>Nd and <sup>176</sup>Hf/<sup>177</sup>Hf and higher <sup>187</sup>Os/<sup>188</sup>Os, <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>208</sup>Pb\*/<sup>206</sup>Pb\* (<sup>208</sup>Pb\*/<sup>206</sup>Pb\* = (<sup>208</sup>Pb/<sup>204</sup>Pb - 29.475)/(<sup>206</sup>Pb/<sup>204</sup>Pb - 9.306) [*Hofmann*, 2003]) than Kea-trend lavas (Figure 2).

[13] In isotope space, Hawaiian lavas define clear arrays that resolve the Loa- and Kea-trends. For example, in <sup>208</sup>Pb/<sup>204</sup>Pb versus <sup>206</sup>Pb/<sup>204</sup>Pb isotope space (Figure 2), Kea-trend volcanoes tend to have more radiogenic <sup>206</sup>Pb/<sup>204</sup>Pb values than Loa-trend volcanoes. Kea-trend volcanoes—including Mauna Kea, Kilauea, Haleakala, E. Molokai and W. Mauidefine the most radiogenic Pb-isotopic compositions in Hawaii. By contrast, Loa-trend volcanoes tend to have less radiogenic <sup>206</sup>Pb/<sup>204</sup>Pb (and a higher <sup>208</sup>Pb/<sup>204</sup>Pb for a given <sup>206</sup>Pb/<sup>204</sup>Pb) than Kea-trend volcanoes. Koolau, Kahoolawe and Lanai, the Hawaiian volcanoes with the most geochemically enriched <sup>143</sup>Nd/<sup>144</sup>Nd and <sup>87</sup>Sr/<sup>86</sup>Sr, also have the least radiogenic <sup>206</sup>Pb/<sup>204</sup>Pb. However, Loihi, the youngest Loa-trend volcano, has depleted (high) <sup>143</sup>Nd/<sup>144</sup>Nd and (low) <sup>87</sup>Sr/<sup>86</sup>Sr signatures and radiogenic Pb-isotopic compositions, similar to Keatrend volcanoes. The Pb-isotopic compositions in Loihi lavas extend to values encountered only in the Kea trend volcanoes, including Mauna Kea and Kilauea (and the Hilina-stage of Kileaua in particular [Kimura et al., 2006]). However, Loihi generally has a higher <sup>208</sup>Pb/<sup>204</sup>Pb at a given <sup>206</sup>Pb/<sup>204</sup>Pb, and therefore higher <sup>208</sup>Pb\*/<sup>206</sup>Pb\*, than Kea-trend volcanoes. In general, all other Loa-trend volcanoes plot between Loihi and the geochemically extreme Koolau-component lavas from Koolau, Kahoolawe and Lanai.

#### 3.2. Major Element Variation Diagrams

[14] Plots of whole rock MgO concentrations versus the other major element oxides (Figure 3)—

including SiO<sub>2</sub>, TiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>, FeO<sub>total</sub> and Na<sub>2</sub>O—are useful for showing enrichments or depletions of these elements at various stages of magmatic evolution. The Loa- and Kea- trend volcanoes, which exhibit different isotopic characteristics, also tend to follow different trends in several of the major element variation diagrams.

[15] At a given MgO content, Loa-trend volcanoes tend to have higher SiO<sub>2</sub> and lower TiO<sub>2</sub> and CaO contents than Kea-trend volcanoes. However, Loihi seamount, another Loa-trend volcano, has among the lowest SiO<sub>2</sub> and the highest TiO<sub>2</sub> and CaO concentrations in Hawaii. Loihi lavas overlap compositionally with the major element compositions found in the extreme Kea-component volcanoes, Mauna Kea and Kilauea. Al<sub>2</sub>O<sub>3</sub> exhibits little variability among volcanoes at a given MgO. It is possible that the Loa-trend volcanoes with the lowest 143Nd/144Nd—Koolau, Lanai and Kahoolawe—have slightly higher Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O and lower FeOtotal contents than Loihi and the Kea-trend volcanoes, but the differences, if real, are small (See Section 3.3).

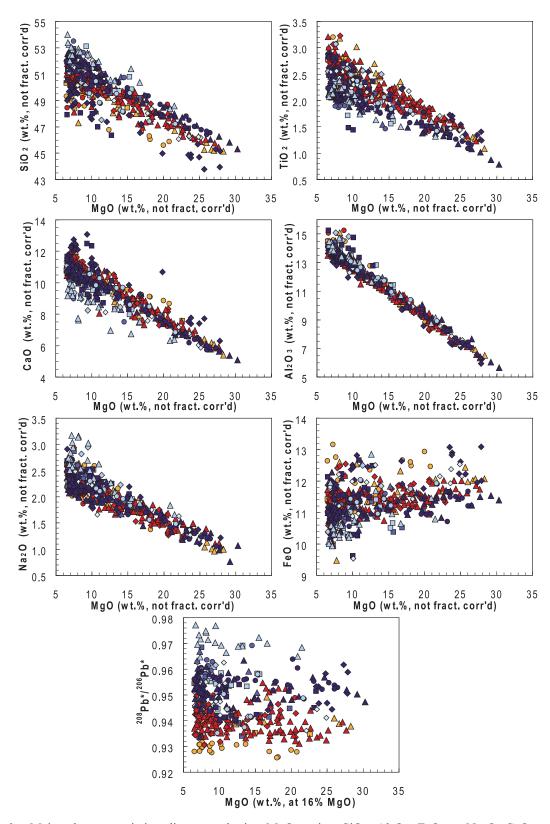
[16] In Figure 3, we show that <sup>208</sup>Pb\*/<sup>206</sup>Pb\* exhibits no relationship with MgO. This suggests that magma evolution and crustal assimilation, which can modify MgO abundances, are not responsible for generating the variability in <sup>208</sup>Pb\*/<sup>206</sup>Pb\*, which is a source feature [e.g., *Hofmann*, 2003]. This observation is important, as several major element oxides (SiO<sub>2</sub>, CaO, TiO<sub>2</sub>) exhibit clear relationships with <sup>208</sup>Pb\*/<sup>206</sup>Pb\* (See Section 3.3, Figure 4) after corrections for olivine fractionation/addition are made.

#### 3.3. Major Elements Versus Isotopes

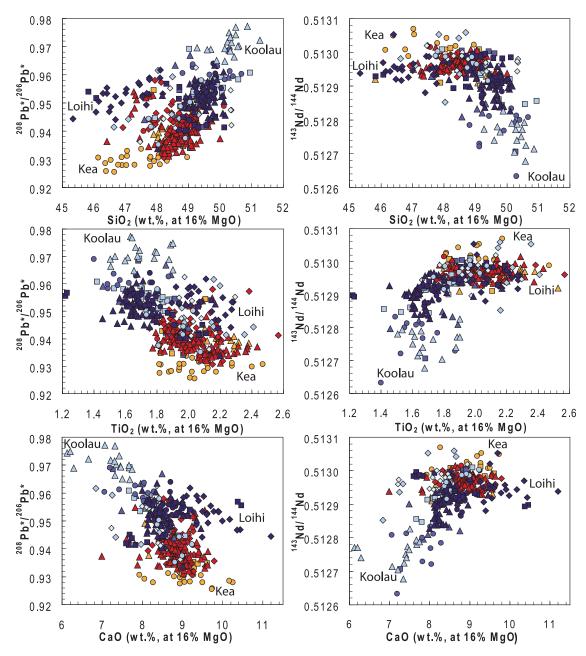
[17] The Loa- and Kea-trend volcanoes exhibit isotopic (Section 3.1) and major element (Section 3.2) differences. The isotopic variations in Hawaiian shield lavas also exhibit clear relationships with olivine fractionation-corrected major element oxide abundances.

[18] Fractionation-corrected SiO<sub>2</sub>, CaO and TiO<sub>2</sub> concentrations and Nd and Pb isotopic ratios show

**Figure 2.** Plots of radiogenic isotope ratios for data included in this study. Note that the radiogenic isotope data in the figures includes only samples with the major element data indicating that the lavas are not highly evolved or altered. Koolau lavas are divided into three groups: Makapuu (MAK), Koolau scientific drilling project (KSDP), and the Nuuanu landslide (NUU). The approximate isotopic composition of the 3 geochemical components in Hawaii (as identified in lavas) are labeled in the figure: Koolau, Loihi and Kea. Many lavas have only one of the radiogenic isotope data and do not appear in any of the panels (but lavas with a single radiogenic isotope ratio do appear in the other data figures). Similarly, lavas that do not possess the full suite of radiogenic isotopic compositions appear in some, but not all, of the panels.



**Figure 3.** Major element variation diagrams plotting MgO against SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO<sub>total</sub>, Na<sub>2</sub>O, CaO and TiO<sub>2</sub>. A plot of MgO versus  $^{208}$ Pb\*/ $^{206}$ Pb\* is also shown. The major elements in the panels of this figure have not been corrected for olivine fractionation or addition. Lavas with MgO lower than 6.5 wt.% are not considered in this study, and are not shown in the diagrams. K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> and MnO are not shown, but data are available in Data Set S1. Colors and data symbols as in Figure 2.

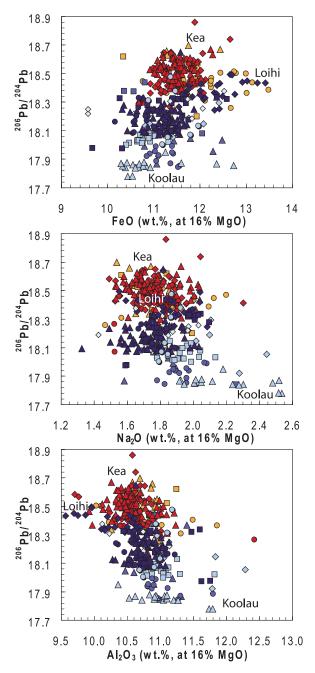


**Figure 4.** Olivine fractionation-corrected SiO<sub>2</sub>, TiO<sub>2</sub>, and CaO oxide abundances are plotted against  $^{143}$ Nd/ $^{144}$ Nd and  $^{208}$ Pb\*/ $^{206}$ Pb\*. SiO<sub>2</sub>, TiO<sub>2</sub>, and CaO exhibit similar relationships with  $^{87}$ Sr/ $^{86}$ Sr and  $^{176}$ Hf/ $^{177}$ Hf (not shown). An olivine-melt K<sub>d</sub> of 0.30 is used for olivine fractionation/addition to 16 wt.% MgO. See Table 1, Figure S1, and Data Set S1 for alternative olivine fractionation/addition schemes. Colors and data symbols as in Figure 2.

the clearest relationships, and define arrays in the Hawaiian data set [*Hauri*, 1996] (Figure 4). Lavas from the Makapuu-stage of Koolau, Lanai and Kahoolawe anchor one extreme of the arrays, and have the lowest <sup>143</sup>Nd/<sup>144</sup>Nd, <sup>206</sup>Pb/<sup>204</sup>Pb, CaO and TiO<sub>2</sub> and the highest SiO<sub>2</sub> and <sup>208</sup>Pb\*/<sup>206</sup>Pb\*. The other end of the Hawaiian array is anchored by Loihi and the extreme Kea-trend volcanoes,

Mauna Kea and Kilauea, which define the highest  $^{143}$ Nd/ $^{144}$ Nd,  $^{206}$ Pb/ $^{204}$ Pb, CaO and TiO<sub>2</sub> and the lowest  $^{208}$ Pb\*/ $^{206}$ Pb\* and SiO<sub>2</sub> (Figure 4).

[19] Contrary to the findings of *Hauri* [1996], the other fractionation-corrected major element oxides—  $FeO_{total}$ ,  $Al_2O_3$  and  $Na_2O$ —do not exhibit clear relationships with Nd and Pb-isotopic compositions (Figure 5). When plotted against  $^{206}Pb/^{204}Pb$ , the

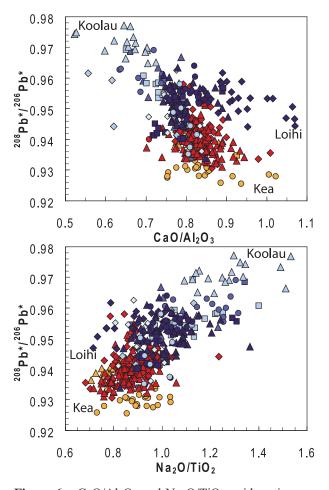


**Figure 5.** Olivine fractionation-corrected FeO<sub>total</sub>, Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O abundances are plotted against  $^{206}\text{Pb}/^{204}\text{Pb}$ . The correlations (if any) are poor.  $^{143}\text{Nd}/^{144}\text{Nd},~^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  also fail to exhibit clear relationships with FeO<sub>total</sub>, Al<sub>2</sub>O<sub>3</sub>, and Na<sub>2</sub>O (not shown). An olivine-melt K<sub>d</sub> of 0.30 is used for olivine fractionation/addition to 16 wt.% MgO. See Table 1, Figure S1, and Data Set S1 for alternative olivine fractionation/addition schemes. Colors and data symbols as in Figure 2.

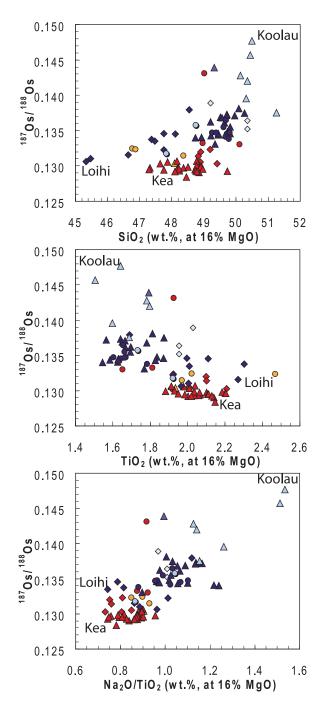
fractionation-corrected FeO<sub>total</sub> concentrations of the extreme low <sup>143</sup>Nd/<sup>144</sup>Nd Loa-trend lavas—all from Koolau, Kahoolawe and Lanai—appear to be shifted to slightly lower values than Kea-trend volcanoes

and Loihi. Fractionation-corrected Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O concentrations appear to be offset to somewhat higher values in most of Loa-trend lavas, while Hawaiian lavas with the highest <sup>143</sup>Nd/<sup>144</sup>Nd, including Loihi and Kea-trend volcanoes, tend to have slightly lower Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O abundances. However, care must be taken when generalizing about relationships between radiogenic isotopes and FeO<sub>total</sub>, Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O, as there is significant scatter in the data and the trends (if any) are not as clear as with SiO<sub>2</sub>, CaO and TiO<sub>2</sub>.

[20] Two major element ratios not affected by olivine fractionation, CaO/Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O/TiO<sub>2</sub>, exhibit striking relationships with Nd and Pb-isotopic compositions (Figure 6), as noted previously [*Hauri*, 1996; *Putirka*, 1999]. CaO/Al<sub>2</sub>O<sub>3</sub> ratios are lowest and Na<sub>2</sub>O/TiO<sub>2</sub> ratios are highest in the most extreme low <sup>143</sup>Nd/<sup>144</sup>Nd Loa-trend lavas from



**Figure 6.** CaO/Al $_2$ O $_3$  and Na $_2$ O/TiO $_2$  oxide ratios are plotted against  $^{208}$ Pb\*/ $^{206}$ Pb\*.  $^{143}$ Nd/ $^{144}$ Nd,  $^{87}$ Sr/ $^{86}$ Sr and  $^{176}$ Hf/ $^{177}$ Hf exhibit similar relationships with CaO/Al $_2$ O $_3$  and Na $_2$ O/TiO $_2$  (not shown). Colors and data symbols as in Figure 2.



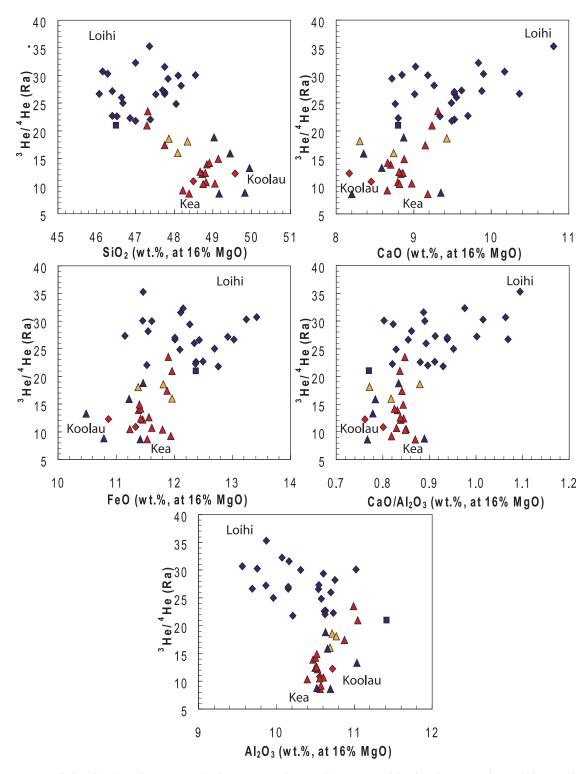
**Figure 7.** Olivine fractionation-corrected SiO<sub>2</sub> and TiO<sub>2</sub> oxide abundances and Na<sub>2</sub>O/TiO<sub>2</sub> ratios are plotted against <sup>187</sup>Os/<sup>188</sup>Os. Olivine fractionation corrected FeO<sub>total</sub>, Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub> and CaO oxide abundances and CaO/Al<sub>2</sub>O<sub>3</sub> ratios also exhibit relationships with <sup>187</sup>Os/<sup>188</sup>Os, but are not shown here. An olivine-melt K<sub>d</sub> of 0.30 is used for olivine fractionation/addition to 16 wt.% MgO. See Table 1, Figure S1, and Data Set S1 for alternative olivine fractionation/addition schemes. Colors and data symbols as in Figure 2.

Koolau, Kahoolawe and Lanai. Loihi lavas and extreme Kea-trend lavas from Mauna Kea and Kilauea have the highest CaO/Al<sub>2</sub>O<sub>3</sub> and the lowest Na<sub>2</sub>O/TiO<sub>2</sub>.

[21] Helium and Os isotopic ratios show clear relationships with fractionation-corrected major element compositions and major element ratios. <sup>3</sup>He/<sup>4</sup>He exhibits trends with SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>, CaO/Al<sub>2</sub>O<sub>3</sub> and FeOtotal [Kurz et al., 2004; Herzberg, 2011; Hauri, 1996], but not with TiO2 and Na2O abundances or with Na<sub>2</sub>O/TiO<sub>2</sub> ratios (Figure 8). High <sup>3</sup>He/<sup>4</sup>He lavas from Loihi anchor the low-SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and high-CaO, CaO/Al<sub>2</sub>O<sub>3</sub> and FeO<sub>total</sub> portions of the arrays. When plotted against olivine fractionation corrected major element abundances and major element ratios, extreme Loa-component lavas with the highest <sup>187</sup>Os/<sup>188</sup>Os (and high SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and Na<sub>2</sub>O/TiO<sub>2</sub>, and low TiO<sub>2</sub>, FeO<sub>total</sub>, CaO, and CaO/Al<sub>2</sub>O<sub>3</sub>) anchor one portion of the array and Loihi and the extreme Kea-component lavas with low <sup>187</sup>Os/<sup>188</sup>Os (and low SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and Na<sub>2</sub>O/TiO<sub>2</sub> and high TiO<sub>2</sub>, FeO<sub>total</sub>, CaO and CaO/  $Al_2O_3$ ) anchor the other extreme of the arrays.

### 4. Origin of Major Element Variability in Hawaiian Lavas

[22] While assimilation of oceanic crust has been suggested to modify the isotopic compositions of oxygen [Wang et al., 2003], heavy noble gases [e.g., Kent et al., 1999] and  $^{187}$ Os/ $^{188}$ Os (in Os-poor lavas [e.g., Martin et al., 1994]) in some Hawaiian lavas, shallow processes operating in the oceanic crust are not likely to be responsible for the observed relationships between radiogenic isotopes and fractionation-corrected major element abundances in the filtered data set. First, highly evolved lavas, which are most susceptible to being modified by assimilation, are not considered in this study. Second, radiogenic isotopes exhibit no relationship with MgO (Figure 3), a proxy for magmatic evolution. This suggests that crustal assimilation is not responsible for generating variability in radiogenic isotopes and major elements. Third, the Sr-Nd-Pb-Hf isotopic compositions of altered oceanic crust and oceanic sediment in the Hawaiian region are unlike Hawaiian lavas or geochemical end-member compositions sampled by Hawaiian lavas [Hauri, 1996; Lassiter and Hauri, 1998; Blichert-Toft et al., 1999; Hanano et al., 2010]. Therefore, assimilation of local oceanic crust and sediments is not the mechanism responsible for driving relationships between major elements and radiogenic isotopes in Hawaiian lavas. Consequently, the observed major element-isotope



**Figure 8.** Olivine fractionation-corrected SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub> and FeO<sub>total</sub> oxide abundances and CaO/Al<sub>2</sub>O<sub>3</sub> ratios are plotted against  ${}^{3}\text{He}/{}^{4}\text{He}$ . Olivine fractionation corrected Na<sub>2</sub>O and TiO<sub>2</sub> oxide abundances and Na<sub>2</sub>O/TiO<sub>2</sub> ratios exhibit no relationships with  ${}^{3}\text{He}/{}^{4}\text{He}$  and are not shown here. An olivine-melt  $K_d$  of 0.30 is used for olivine fractionation/addition to 16 wt.% MgO. See Table 1, Figure S1, and Data Set S1 for alternative olivine fractionation/addition schemes. Colors and data symbols as in Figure 2.



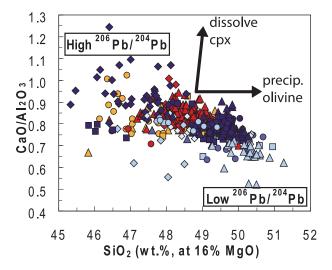
correlations in Hawaiian shield lavas (Figures 4 and 6–8) reflect mantle source heterogeneity. Here we examine each of the three Hawaiian components in turn—Koolau, Loihi and Kea—and evaluate the origin of the major element variability and discuss possible mechanisms that drive the observed relationships between radiogenic isotopes and olivine-fractionation corrected major element compositions.

### 4.1. The Koolau Component: The Enigmatic Eclogite

### 4.1.1. Bulk Lava Major Element Compositions From Peridotite or Eclogite Melts?

- [23] Makapuu stage lavas from Koolau volcano exhibit the most enriched <sup>143</sup>Nd/<sup>144</sup>Nd in Hawaii and sample the end-member Koolau-component compositions [Roden et al., 1994], and they anchor the low CaO, high SiO<sub>2</sub> portion of the arrays formed in major element versus isotope space in Figure 4. Makapuu-stage Koolau lavas play a central role in the debate on the role of eclogite melting in the Hawaiian plume [e.g., Hauri, 1996; Huang and Frey, 2005; Salters et al., 2006; Huang et al., 2007; Sobolev et al., 2005, 2007; Herzberg, 2011; Putirka et al., 2011], and we explore the arguments surrounding eclogite versus peridotite melting.
- [24] One argument against the generation of Makapuustage Koolau melts by peridotite melting hinges on high pressure and temperature experiments performed on a Kilauea high-MgO glass composition. Eggins [1992] and Wagner and Grove [1998] showed experimentally that the major element compositions of the high MgO Kilauea glasses cannot be in equilibrium with both garnet and olivine (i.e., garnet peridotite). This is important because Hawaiian shield lavas exhibit heavy rare earth element (HREE) depletions and, after correction for olivine fractionation, relatively constant concentrations of HREE [Hofmann et al., 1984], which require residual garnet in the mantle source of the lavas [Hofmann et al., 1984; Huang and Frey, 2005]. Instead, Eggins [1992] and Wagner and Grove [1998] found that Kilauea glasses are in equilibrium with a harzburgite (olivine + orthopyroxene) residue, but this phase assemblage will not generate the residual garnet signature observed in Hawaiian lavas.
- [25] The SiO<sub>2</sub> contents of Kilauea glasses are also too high to be melts of garnet peridotite [*Hauri*, 1996; *Wagner and Grove*, 1998], and Koolau Makapuu-stage lavas have even higher SiO<sub>2</sub> than the Kilauea lavas, which excludes garnet peridotite

- as a source for the Koolau component (Figure 4). Similarly, the FeO<sub>total</sub> versus SiO<sub>2</sub> systematics of Makapuu-stage Koolau lavas are inconsistent with experimentally derived partial melts of peridotite at garnet stability field pressures [Hauri, 1996]. While low pressure (1–1.5 GPa) partial melts of peridotites can yield the high SiO<sub>2</sub> contents found in these lavas, the FeO<sub>total</sub> of low pressure partial melts is too low. There are at least two reasons why such low pressures of melting are not feasible. First, low pressures of melting (1–1.5 GPa) are below those of the field of garnet stability and will not generate the residual garnet signature observed in Hawaiian lavas [Hofmann et al., 1984; Huang and Frey, 2005]. Second, the lithosphere beneath Hawaii is too thick to permit such shallow melting (<45 km) [Hauri, 1996].
- [26] Water addition to peridotite can increase the SiO<sub>2</sub> content of melts at low pressures of melting [Parman and Grove, 2004]. However, wet melting of garnet peridotite does not increase the melt SiO<sub>2</sub> concentration [Tenner et al., 2012], and existing wet melting experiments of garnet peridotite cannot explain the high SiO<sub>2</sub> in Koolau lavas.
- [27] Nonetheless, Putirka et al. [2011] suggest that eclogite/garnet pyroxenite are not required for the petrogenesis of Hawaiian lavas, and that peridotite melting can generate the entire observed compositional range. Using a compilation of experimental melt data generated from a range of peridotitic compositions at different pressure and temperature conditions, they argue that the major element compositions of parental magmas of Makapuustage Koolau lavas can be explained by mixing of partial melts from different peridotite melting experiments. However, there is no single experimental melt that matches the extreme composition of Makapuu-stage Koolau lavas (i.e., high SiO<sub>2</sub>, low FeO and CaO). While Putirka et al. [2011] argued that the primary magma composition of Makapuu-stage Koolau lavas can be reproduced by mixing three experimental melts [see Putirka et al., 2011, equation 6], the three experimental melts (i.e., H154 from Kinzler and Grove [1992], T-762 from Falloon et al. [1988], and T-3572 from Falloon and Danyushevsky [2000]) are all lowpressure melts (1–2 GPa) and have only olivine and orthopyroxene as residual phases. Consequently, these experiments are inconsistent with REE concentrations and patterns in Hawaiian lavas, which require garnet as a residual phase during melting.
- [28] In summary, existing experimental peridotite melt data and melt-rock reaction models do not



**Figure 9.** CaO/Al<sub>2</sub>O<sub>3</sub> versus SiO<sub>2</sub> in the Hawaiian magmatic suite considered in this study. Melt-rock reaction between the shallow mantle lithosphere and a mantle melt tends to increase SiO<sub>2</sub> in the melt as clinopyroxene from the mantle lithosphere is dissolved into the melt while olivine from the melt is precipitated. This melt-rock reaction would be manifested as a positive trend in SiO<sub>2</sub> versus CaO/Al<sub>2</sub>O<sub>3</sub> space. However, Hawaiian lavas with the highest SiO<sub>2</sub> have the lowest CaO/Al<sub>2</sub>O<sub>3</sub>, a signature that is inconsistent with melt rock reaction. The lavas in the figure have been corrected for olivine fractionation to a constant MgO of 16 wt.%. An olivine-melt K<sub>d</sub> of 0.30 is used for olivine fractionation/addition. Lavas with high <sup>206</sup>Pb/<sup>204</sup>Pb have low SiO<sub>2</sub> and high CaO/Al<sub>2</sub>O<sub>3</sub>, and lavas with high low <sup>206</sup>Pb/<sup>204</sup>Pb have high SiO<sub>2</sub> and low CaO/Al<sub>2</sub>O<sub>3</sub>. Colors and data symbols as in Figure 2.

explain the composition of Makapuu-stage Koolau lavas. While we cannot exclude the possibility that future peridotite melting experiments may match the unusual major element compositions of Makapuustage Koolau, we note that eclogite melting in the Hawaiian mantle source may provide a mechanism for generating the highest SiO<sub>2</sub> Hawaiian lavas. Eclogite has been invoked to explain the combined residual garnet signature and high SiO<sub>2</sub> content of Makapuu-stage Koolau lavas [Hauri, 1996; Huang and Frey, 2005; Sobolev et al., 2005, 2007]. The low CaO contents of Makapuu-stage Koolau lavas are also consistent with partial melting of eclogite [Huang and Frey, 2005; Herzberg, 2006]. Herzberg [2006] parameterized the peridotite melting experiments of Walter [1998] and argued that most Hawaiian shield lavas have CaO contents that are too low to be partial melts of peridotite [Pertermann and Hirschmann, 2003]. Since Makapuu-stage Koolau lavas have the lowest CaO contents at a given MgO content among Hawaiian lavas [Frey et al., 1994] (Figures 3 and 4), Huang and Frey [2005] and Sobolev et al. [2005] suggested that they contain the largest contribution from partial melts of eclogite/garnet pyroxenite. Additionally, Makapuu-stage lavas and olivines have the lowest MnO contents among Hawaiian lavas [Huang et al., 2007; Sobolev et al., 2007], consistent with partial melting of eclogite [Pertermann and Hirschmann, 2003], as MnO is relatively compatible in garnet. Finally, Makapuu-stage lavas have the among lowest TiO<sub>2</sub> contents in the Hawaiian tholeiitic suite [Frey et al., 1994] (Figures 3 and 4). Such low magmatic TiO<sub>2</sub> is distinctive feature of dacitic melts of eclogite with residual rutile [Pertermann and Hirschmann, 2003, Figure 9].

## 4.1.2. High SiO<sub>2</sub> Lavas From Melt-Rock Reaction Between Peridotite Melts and Peridotite Mantle?

[29] Melt-rock reaction between peridotite melts and harzburgite/peridotite (i.e., assimilation of orthopyroxene+clinopyroxene and precipitation of olivine [Kelemen et al., 1992]) has also been proposed as a model to explain the high SiO<sub>2</sub>content in Hawaiian lavas [Eggins, 1992; Wagner and Grove, 1998; Stolper et al., 2004; Putirka et al., 2011]. The peridotite reacting with the melt could be a melt-residue of the rising mantle plume [Wagner and Grove, 1998, Figure 5a] or in situ lithospheric mantle [Wagner and Grove, 1998, Figure 5b]. *Hauri* [1996] noted that, if the elevated SiO<sub>2</sub> in Koolau were a result of melt-rock reaction with the mantle lithosphere, it would be reflected by a lithospheric imprint on the Koolau lavas, including unradiogenic <sup>187</sup>Os/<sup>188</sup>Os and high <sup>143</sup>Nd/<sup>144</sup>Nd ratios typical of the oceanic mantle lithosphere [e.g., Shirey and Walker, 1998; Warren et al., 2009]. This is not observed. Koolau Makapuu-state lavas have radiogenic <sup>187</sup>Os/<sup>188</sup>Os and low <sup>143</sup>Nd/<sup>144</sup>Nd (Figure 2), an observation that is inconsistent with extensive melt-rock reaction in the oceanic mantle lithosphere. Further, a meltmantle reaction predicts that CaO/Al<sub>2</sub>O<sub>3</sub> will increase with SiO2 as pyroxene is dissolved and olivine is precipitated: olivine precipitation from the melt will drive up melt SiO<sub>2</sub>, and clinopyroxene (and/or orthopyroxene) dissolution from the mantle will increase melt SiO<sub>2</sub> and CaO/Al<sub>2</sub>O<sub>3</sub>. However, this is inconsistent with the negative relationship observed between CaO/Al<sub>2</sub>O<sub>3</sub> and high SiO<sub>2</sub> in Hawaiian lavas (Figure 9), indicating that a mechanism other than melt-rock reaction is responsible for the increased SiO<sub>2</sub> in Koolau lavas.



[30] Melt-rock reaction with the mantle plume also fails to explain the observed residual garnet signature. i.e., and relatively constant HREE contents (after correction for olivine fractionation or accumulation) in Hawaiian tholeiites [e.g., Hofmann et al., 1984; Huang and Frey, 2005]. This is because melt-rock reaction is likely to generate variable HREE abundances. Previous studies invoking melt-rock reaction considered high LREE/HREE ratios alone to reflect a residual garnet signature [e.g., Eggins, 1992; Wagner and Grove, 1998; Putirka et al., 2011], but the variable HREE abundances resulting from melt-rock reaction do not match the relatively constant abundances in Hawaiian lavas. Therefore, a melt-mantle reaction occurring within the plume, proposed to explain the high SiO<sub>2</sub> content in Hawaiian lavas, cannot explain the observed residual garnet signature.

### 4.1.3. Peridotite Versus Eclogite Melting: Evidence From Ni in Olivine?

- [31] Ni concentrations in olivines play a key role in the debate surrounding eclogite melting in the Hawaiian plume, particularly beneath Koolau volcano. Olivines in Makapuu-stage Koolau lavas have unusually high Ni abundances [e.g., *Clague et al.*, 1991; *Garcia*, 2002]. *Sobolev et al.* [2005, 2007] and *Herzberg* [2011] argued that the high Ni contents in Hawaiian olivines and lavas imply an olivine-free, secondary garnet pyroxenite source for Hawaiian lavas. *Wang and Gaetani* [2008] suggest that the high olivine Ni contents are caused by high  $D_{\rm Ni}^{\rm Ol/melt}$  that results from a melt with a high SiO<sub>2</sub> content, which implies an important role of eclogite in the petrogenesis of Hawaiian lavas.
- [32] However, *Putirka et al.* [2011] and *Rhodes et al.* [2012] suggest that there are large uncertainties in the model predicted D<sub>Ni</sub><sup>ol/melt</sup> values and Ni variations in peridotites. They argued that Ni concentrations in olivines and lavas may not be used as discriminators between eclogite melting and peridotite melting. *Putirka et al.* [2011] argue that, at high temperature, D<sub>Ni</sub><sup>ol/melt</sup> is low, and hot peridotite melting yields Ni-rich melts. Following transport to shallower depths, D<sub>Ni</sub><sup>ol/melt</sup> is higher owing to lower ambient temperatures, and crystallizing olivines are Ni-rich. Further experiments parameterizing the effects of temperature, pressure and melt composition on Ni partitioning between olivine and melt are needed to evaluate these contrasting hypotheses.
- [33] In summary, there is active debate surrounding the interpretation of the elevated Ni abundances in Hawaiian magmatic olivines and whole rocks, and

further experiments parameterizing the effects of temperature, pressure and melt composition on Ni partitioning between olivine and melt are needed to evaluate the contrasting hypotheses. However, the distinctive geochemical characteristics of Makapuustage Koolau lavas—high SiO<sub>2</sub>, low CaO, TiO<sub>2</sub> and MnO, and REE patterns showing residual garnet signature—are consistent with partial melting of eclogite [Hauri, 1996; Pertermann and Hirschmann, 2003; Herzberg, 2006; Dasgupta et al., 2010], but are not matched by melt compositions from existing experimental peridotite melting studies.

### 4.2. The Loihi Component: The Paradoxical Pyroxenite

#### 4.2.1. Lithology of the Loihi Mantle Source

- [34] Lavas from the Hawaiian Loa-trend describe arrays that suggest binary mixing between two extreme compositions (Figures 2 and 4-8): Makapuustage Koolau lavas anchor the low <sup>143</sup>Nd/<sup>144</sup>Nd and <sup>206</sup>Pb/<sup>204</sup>Pb portion of the Loa array, and high <sup>3</sup>He/<sup>4</sup>He lavas from Loihi define the portion with depleted <sup>143</sup>Nd/<sup>144</sup>Nd and <sup>87</sup>Sr/<sup>86</sup>Sr signatures and radiogenic <sup>206</sup>Pb/<sup>204</sup>Pb. While Koolau lavas have high SiO<sub>2</sub> and low TiO<sub>2</sub>, CaO and CaO/Al<sub>2</sub>O<sub>3</sub>, Loihi lavas exhibit the lowest SiO<sub>2</sub> and highest TiO<sub>2</sub>, CaO and CaO/Al<sub>2</sub>O<sub>3</sub> in the Loa-trend suite. Unlike the Koolau Makapuu source, which is likely to contain an eclogite component, the Loihi mantle source is generally agreed to be peridotitic [e.g., Sobolev et al., 2005, 2007; Putirka et al., 2011; Herzberg, 2006, 2011]. Nonetheless, there are key geochemical features of high <sup>3</sup>He/<sup>4</sup>He Loihi lavas suggesting that the source peridotite is enriched as a result of the addition a mafic component [e.g., Sobolev et al., 2005; Putirka et al., 2011; Herzberg, 2011]—likely a SiO<sub>2</sub>-poor pyroxenite—and the final, hybrid mixture is still a peridotite.
- [35] Evidence that a mafic component was added to the Loihi peridotite source comes from elevated TiO<sub>2</sub> contents in fractionation-corrected Loihi lavas, which are too high to be generated by peridotite melting at the degrees of melting inferred for Hawaiian shield lavas. *Prytulak and Elliot* [2007] showed that, after correcting lavas to 16 wt.% MgO, the fractionation-corrected TiO<sub>2</sub> abundances of lavas from many Hawaiian volcanoes (>1.8 wt%) can only be generated by low degrees (<3%) of partial melting of a primitive peridotite (840–1200 ppm Ti) [*McDonough and Sun*, 1995; *Carlson and Boyet*, 2008] or a depleted mantle source (657–798, ppm Ti) [*Workman and Hart*, 2005; *Salters and Stracke*,



2004]. Such low degrees of partial melting are inconsistent with their tholeitic bulk compositions, and there is evidence that Hawaiian lavas are generated at higher degrees of melting (≥5%) [McKenzie and O'Nions, 1991; Watson and McKenzie, 1991; Garcia et al., 1995]. Therefore, Prytulak and Elliot [2007] concluded that the mantle sources beneath these Hawaiian volcanoes have been enriched by the addition of a Ti-rich component, and the most likely material to host sufficient Ti is a recycled mafic component. Loihi tholeiites have among the highest  $TiO_2$  concentrations— $\sim$ 2.1 wt. %  $TiO_2$  at 16 wt.% MgO—in the Hawaiian tholeiite suite (Figures 3 and 4) [Garcia et al., 1995; Hauri, 1996] indicating that the dominantly peridotitic Loihi source has incorporated a mafic lithology during its history in the mantle.

[36] Pb isotopic compositions offer a second line of evidence for the addition of a mafic component to the peridotitic Loihi mantle source. Loihi lavas have the highest <sup>206</sup>Pb/<sup>204</sup>Pb and <sup>208</sup>Pb/<sup>204</sup>Pb among Loa trend volcanoes, and only extreme Kea-trend lavas have more radiogenic Pb isotopic ratios. The Pbisotopic compositions of Loihi lavas plot well to the right of the geochron, which has been attributed to the presence of a mafic material [*Lassiter and Hauri*, 1998; *Jackson et al.*, 2010; *Jackson and Carlson*, 2011] with high U/Pb following seafloor alteration (U addition) and subduction zone processing (Pb loss) [*Hofmann and White*, 1982; *Kelley et al.*, 2005].

[37] A third line of evidence supporting a mafic component in the Loihi mantle source comes from elevated <sup>187</sup>Os/<sup>188</sup>Os ratios (up to 0.138) in Loihi lavas. Roy-Barman et al. [1998] identified a positive correlation between <sup>3</sup>He/<sup>4</sup>He and <sup>187</sup>Os/<sup>188</sup>Os in Loihi, which led the authors to suggest that the mantle beneath Loihi hosts a component with radiogenic Os that is somehow related to the endmember component found in Makapuu-stage Koolau lavas. (A similar correlation between <sup>3</sup>He/<sup>4</sup>He and <sup>187</sup>Os/<sup>188</sup>Os is Iceland led *Brandon et al.* [2007] to suggest the presence of a mafic component admixed with high <sup>3</sup>He/<sup>4</sup>He peridotite in the source of high <sup>3</sup>He/<sup>4</sup>He Icelandic lavas.) However, owing to the much higher <sup>3</sup>He/<sup>4</sup>He and more depleted <sup>87</sup>Sr/<sup>86</sup>Sr and 143Nd/144Nd ratios in Loihi lavas compared to Koolau lavas, we consider it unlikely that the high <sup>187</sup>Os/<sup>188</sup>Os mafic components in Loihi and Koolau lavas are the same.

[38] The radiogenic Os and Pb, and high Ti concentration in Loihi lavas are consistent with the presence of a mafic component added to the

peridotitic mantle source of Loihi lavas, yet petrologic models for the Loihi source indicate that peridotite melting is occurring [e.g., Putirka et al., 2011; Herzberg, 2011]. This raises an important question, which relates to the paradox of pyroxenite in the Loihi mantle source: How can the mixture of the peridotite and pyroxenite result in a mantle source that generates melts that appear petrologically to have been sourced by a peridotite? Owing to the high TiO<sub>2</sub> in Loihi lavas, Putirka et al. [2011] invoked the Prytulak and Elliot [2007] Ti model to suggest the incorporation of a mafic component in the Loihi source, but argued that it no longer exists as a distinct lithology. Putirka et al. [2011] suggested that the mafic source has been mixed completely into the peridotite, so that the final lithology is an enriched peridotite. If true, the final mixture, a peridotite, would inherit elevated TiO<sub>2</sub> and radiogenic Os and Pb from the mafic lithology. However, mixing of the pyroxenite into the peridotite might not take place in the solid state. Gaffney et al. [2005] proposed a model for melting a mafic component in the presence of peridotite, while keeping the petrologic signature of the mafic component "hidden." They suggested that the eclogite melt would infiltrate and react with the peridotite and generate a fertile peridotite, similar to that observed in eclogiteperidotite "sandwich" experiments [Yaxley and Green, 1998; Takahashi and Nakajima, 2002]. The resulting fertile peridotite will be rich in orthopyroxene, as a result of eclogite melt reaction with olivine in the peridotite. Gaffney et al. [2005] suggested that melting of the fertilized peridotite will yield melts with a major element composition that reflects peridotite melting [Hirschmann et al., 2003], even though they possess isotopic and trace element geochemical signatures that reflect a contribution from a mafic component. The *Putirka et al.* [2011] and Gaffney et al. [2005] models may help explain the paradox of a mafic component in the Loihi mantle source that is essentially "invisible" to petrologic models that suggest derivation of Loihi lavas from a peridotitic source.

### 4.2.2. Mantle Source Lithological Differences Between the Loa-Trend Extremes: Comparing the Loihi Mantle Source to the Koolau Makapuu Mantle

[39] The association of high <sup>3</sup>He/<sup>4</sup>He with a mantle source that hosts a mafic component at Loihi is paradoxical. Owing to the highly incompatible nature of U and Th during mantle melting, mafic materials should in general have higher U and Th than peridotitic materials. Therefore, over time,

mafic materials will generate more <sup>4</sup>He than peridotites, resulting in lower <sup>3</sup>He/<sup>4</sup>He in the former relative to the latter. As a result, a mafic component added to the peridotitic source should result in low <sup>3</sup>He/<sup>4</sup>He in Loihi lavas, not high <sup>3</sup>He/<sup>4</sup>He. However, if the SiO<sub>2</sub>-undersaturated pyroxenite inferred to have been added to the peridotitic Loihi source suffered melt extraction in a paleo-subduction zone, then incompatible elements like U and Th will have been effectively removed from the pyroxenite, thus reducing its potential to generate <sup>4</sup>He over time. Jackson et al. [2008] observed that <sup>3</sup>He/<sup>4</sup>He ratios correlate with the magnitude of positive Ti, Ta and Nb (TITAN) anomalies (where anomalies of the TITAN elements—calculated relative to elements of similar compatibility in peridotite on a primitive mantle normalized spidergram—are not to be confused with the absolute concentrations of these elements) in Hawaiian lavas, where Loihi exhibits the largest Ti anomalies and highest <sup>3</sup>He/<sup>4</sup>He ratios. Owing to the ubiquitous presence of rutile in eclogite, trace elements compatible in rutile, including the TITAN elements, are residually enriched relative to other trace elements during melt extraction from and dehydration of the downing-going slab; incompatible elements not sequestered into rutileincluding the radiogenic helium-producing elements, U and Th-will be lost from the slab, together with SiO<sub>2</sub>. For such a model to explain the radiogenic Pb isotopes in Loihi lavas, Pb would have to be preferentially removed from the slab relative to U and Th, which is likely [Kelley et al., 2005]. The residual SiO<sub>2</sub>-poor mafic material—a pyroxenite—is TITANenriched and depleted in U and Th, and will contribute little <sup>4</sup>He to the peridotite with which it mixes, including high <sup>3</sup>He/<sup>4</sup>He peridotites. Such a model might explain the association of TITAN enrichment and high <sup>3</sup>He/<sup>4</sup>He in SiO<sub>2</sub>-poor Loihi lavas.

[40] By contrast, Makapuu-stage Koolau lavas have higher SiO<sub>2</sub>, lower <sup>3</sup>He/<sup>4</sup>He and less radiogenic Pb. These lavas sample a SiO<sub>2</sub>-rich eclogite (Section 4.1) that has not suffered severe SiO<sub>2</sub> and incompatible element depletion in a subduction zone, as evidenced by the silica-rich character of Koolau lavas. Such an eclogite will have retained its complement of U and Th (and Pb, thereby preserving a low U/Pb ratio) and will produce more <sup>4</sup>He over time that will "infect" the surrounding peridotite mantle-including the lithologic reservoir hosting high <sup>3</sup>He/<sup>4</sup>He peridotite [e.g., Parman et al., 2005; Albarède, 2008; Hart et al., 2008; Jackson et al., 2008]-with low <sup>3</sup>He/<sup>4</sup>He. A host of possible mafic lithologies exist in nature, and the presence of two distinct mafic components—a SiO<sub>2</sub>-poor pyroxenite and a SiO<sub>2</sub>- rich eclogite—in the Hawaiian plume might reconcile the geochemical differences between the two Loa-trend mantle components, Loihi and Koolau-Makapuu.

### 4.3. The Kea Component

[41] A third major isotopic end-member observed in Hawaiian shield lavas—the Kea component—is sampled by volcanoes that define the Kea en echelon volcanic trend. The Kea-trend volcanoes have more homogeneous Sr, Nd and Hf isotopes that are also generally more depleted [e.g., Stille et al., 1986] than their Loa-trend equivalents [DePaolo et al., 2001; Weis et al., 2011]. This has led to models suggesting a depleted peridotite source— MORB-source, Pacific oceanic lithosphere, entrained asthenosphere, or recycled mantle lithosphere—for Kea-component lavas [West et al., 1987; Chen and Frey, 1985; Hauri, 1996; Eiler et al., 1996a, 1996b; Lassiter et al., 1996]. However, the low <sup>176</sup>Hf/<sup>177</sup>Hf of the Kea end-member suggests that asthenospheric or lithospheric materials are not present in the source of Kea-type lavas [Blichert-Toft et al., 1999]. Recycled lower oceanic crust has also been suggested to source Kea-component lavas, but only in combination with recycled lithospheric peridotite [Lassiter and Hauri, 1998].

[42] With the exception of  ${}^{3}\text{He}/{}^{4}\text{He}$  and  ${}^{208}\text{Pb*}/{}^{206}\text{Pb*}$ . Kea- and Loihi-component lavas are more similar to each other than to Koolau-component lavas, and the fractionation-corrected major element compositions of Kea lavas are remarkably similar to Loihi-component lavas, as observed previously [Hauri, 1996]. In fact, the Kea-component exhibits several geochemical similarities with the Loihi-component that suggest that the former also hosts a mafic component in its mantle source. For example, Kea-component lavas host high TiO<sub>2</sub> contents, consistent with the addition of a pyroxenite component in the source of Keacomponent lavas (Mauna Kea and Kilauea have >2 wt.% TiO<sub>2</sub> at 16 wt.% MgO (Table 1) [Prytulak and Elliot, 2007]). However, information from radiogenic isotopes does not permit a clear resolution of the debate over source lithologies contributing to the Kea mantle source. On the one hand, Pb isotopic compositions in Kea-component lavas are among the most radiogenic in Hawaii. If radiogenic Pb is associated with a recycled mafic component, then Kilauea lavas should host a significant mafic component. This is contradicted by the generally unradiogenic \$^{187}Os/^{188}Os\$ in Kea-trend lavas (<0.133, with the exception of a single Kohala lava; Figure 7). One possible explanation for this apparent



disagreement is that there is a greater contribution of recycled sediment to the Loa-trend mantle than to the Kea-trend source: Sediment generally has higher <sup>187</sup>Os/<sup>188</sup>Os than mafic lithologies, so it is possible for a mantle source with a sediment and a mafic component (like the Loa-trend mantle) to have a higher <sup>187</sup>Os/<sup>188</sup>Os than the a mantle source with just a mafic component (like the Kea-trend mantle) [*Lassiter and Hauri*, 1998; *Huang et al.*, 2005].

### 5. Major Element Versus Isotope Correlations in Hawaii in the Context of Global OIBs

[43] The broad correlations between major elements and isotopes in Hawaiian lavas form arrays anchored by Loihi and Kea-component lavas (with high  $^{143}{\rm Nd/}^{144}{\rm Nd,}~^{176}{\rm Hf/}^{177}{\rm Hf}$  and  $^{206}{\rm Pb/}^{204}{\rm Pb}$  and low  $^{87}$ Sr/ $^{86}$ Sr) at one end and by Koolau lavas (with low  $^{143}$ Nd/ $^{144}$ Nd,  $^{176}$ Hf/ $^{177}$ Hf and  $^{206}$ Pb/ $^{204}$ Pb and high <sup>87</sup>Sr/<sup>86</sup>Sr) at the other. Information from olivinefractionation corrected major element data suggests that the correlations in the Hawaiian data set are anchored on both ends by different types of mafic component that coexist (and interact) with peridotite in the Hawaiian plume: a silica-poor pyroxenite anchors the Loihi and Kea-component portion of the Hawaiian array (Section 4.2 and 4.3), and a silicarich eclogite anchors the enriched portion (Koolau) of the Hawaiian array (Section 4.1). A host of possible mafic lithologies exist in nature, and the SiO<sub>2</sub> content of the mafic materials in the source of the Loihi, Kea and Koolau components may be the defining difference among these components. However, in order to understand the origin of these contrasting mafic sources, they must first be placed in the context of global OIB geochemical variability.

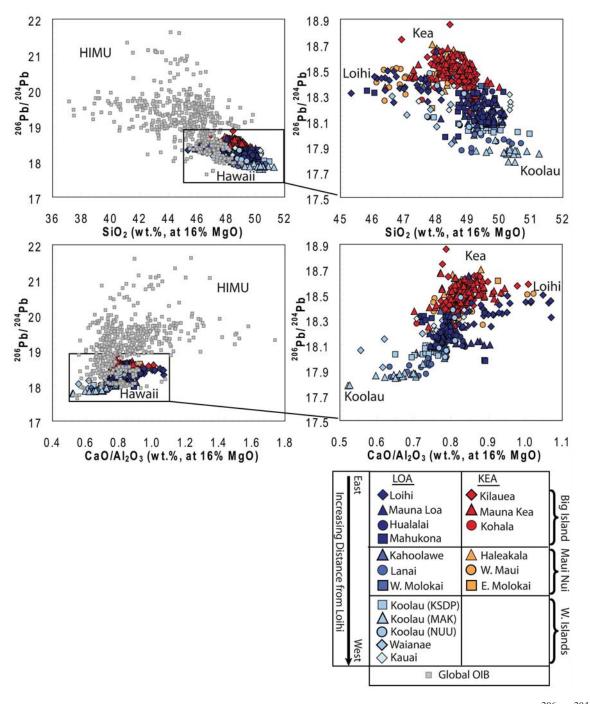
[44] Broad relationships between major elements and radiogenic isotopes in the global OIB data set may help constrain the mantle source compositions of the Loihi, Kea and Koolau components. Jackson and Dasgupta [2008] show that global OIB lavas with the most radiogenic Pb have the lowest SiO<sub>2</sub> and the highest CaO/Al<sub>2</sub>O<sub>3</sub> (Figure 10). SiO<sub>2</sub> and CaO/Al<sub>2</sub>O<sub>3</sub> also exhibit some of the clearest correlations with <sup>206</sup>Pb/<sup>204</sup>Pb in Hawaiian lavas, and these correlations mimic the global trend (Figure 10). Like the global OIB data set, FeO<sub>total</sub>, Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O abundances in Hawaii exhibit little or no correlation with radiogenic isotopes. In summary, the correlations between Pb isotopes and major elements in Hawaii appear to broadly reflect the global trends, and we suggest that the mechanism that drives the correlations between major elements and isotopes in Hawaii illustrates, in microcosm, a larger global process.

[45] Hauri [1996] suggested that SiO<sub>2</sub>-rich (~50 wt.%) Koolau lavas resulted from melting of SiO<sub>2</sub>-saturated mafic material (which we refer to above as eclogite), while the mantle sources of the low SiO<sub>2</sub> lavas (~40 wt.%) in the Pacific Islands with the most radiogenic Pb are thought to host SiO<sub>2</sub>-poor mafic material (which we refer to as pyroxenite) [Hirschmann et al., 2003; Kogiso et al., 2003; Kogiso and Hirschmann, 2006; Dasgupta et al., 2006; Jackson and Dasgupta, 2008]. Applying this model to the Hawaiian magmatic suite, we infer that Loihi and Kea-component lavas, which exhibit the most radiogenic Pb compositions and the lowest SiO<sub>2</sub> concentrations in Hawaiian shield lavas, are derived from a peridotitic mantle source that incorporated a small portion of a SiO<sub>2</sub>-poor mafic component with radiogenic Pb.

[46] Subduction zone processes can modify the composition of the downgoing oceanic crust by variably removing SiO<sub>2</sub> (and fractionating trace element ratios, such as U, Th and Pb) [Hauri, 1996; Jackson and Dasgupta, 2008]. As a result, SiO<sub>2</sub>-rich and SiO<sub>2</sub>-poor mafic lithologies exist in the mantle that are likely to host distinct time-integrated isotopic ratios. Low SiO2 lavas from Mangaia and Tubuaii and the high SiO<sub>2</sub> lavas from Hawaii's Koolau Makapuu-stage anchor the high <sup>206</sup>Pb/<sup>204</sup>Pb and low <sup>206</sup>Pb/<sup>204</sup>Pb portions of the global array, respectively (Figure 10) [Jackson and Dasgupta, 2008]. SiO<sub>2</sub>-deficient eclogites suggested for the source of SiO<sub>2</sub>-poor OIB lavas with radiogenic Pb must have somehow attained higher U/Pb ratios, likely via Pb-loss from the slab [Kellev et al., 2005] (i.e., the same subduction zone processes reduced the SiO<sub>2</sub> of the downgoing crust and increased U/Pb). The variability within the Hawaiian array may be generated in a similar manner, where the Hawaiian plume hosts both SiO2-rich eclogites (with low <sup>206</sup>Pb/<sup>204</sup>Pb) and SiO<sub>2</sub>-poor pyroxenites (with high <sup>206</sup>Pb/<sup>204</sup>Pb) that mix in the peridotite matrix of the plume to generate the correlations between major elements and radiogenic isotopes in Hawaii. Thus, processes operating in subduction zones that modify the downgoing oceanic crust may be responsible for generating much of the major element variability observed in Hawaii and in OIBs in general [Hauri, 1996].

### 6. Conclusions

[47] From this review study, we draw the following conclusions:



**Figure 10.** Olivine fractionation-corrected SiO<sub>2</sub> concentrations and CaO/Al<sub>2</sub>O<sub>3</sub> ratios are plotted against  $^{206}$ Pb/ $^{204}$ Pb for Hawaiian lavas and the global OIB data set. The correlations in the Hawaiian data set mimics, in microcosm, the larger global correlation. The global OIB data set is from *Jackson and Dasgupta* [2008] and includes only lavas with MgO > 8 wt.% MgO, as many non-Hawaiian OIB lavas experience clinopyroxene fractionation at lower MgO abundances (see Data Set S1 for compositions). An olivine-melt  $K_d$  of 0.30 is used for olivine fractionation/addition to 16 wt.% MgO. HIMU (or high- $\mu$ , or  $^{238}$ U/ $^{204}$ Pb) represents the mantle reservoir with radiogenic Pb-isotopes [e.g., *Hauri and Hart*, 1993; *Woodhead*, 1996; *Hanyu et al.*, 2011].

[48] 1. Data for tholeiitic Hawaiian shield lavas form arrays in plots of radiogenic isotopes versus olivine-corrected major element oxides. Individual

data points exhibit remarkable trends and there is no need to average the data by volcano.

[49] 2. The trends are anchored by Koolau lavas at one end (with high  $^{87}{\rm Sr}/^{86}{\rm Sr},~^{187}{\rm Os}/^{188}{\rm Os},~{\rm SiO_2},$ 



- and Na<sub>2</sub>O/TiO<sub>2</sub>, and low <sup>143</sup>Nd/<sup>144</sup>Nd, <sup>176</sup>Hf/<sup>177</sup>Hf, <sup>206</sup>Pb/<sup>204</sup>Pb, TiO<sub>2</sub>, CaO and CaO/Al<sub>2</sub>O<sub>3</sub>) and by Kea and Loihi lavas at the other (low <sup>87</sup>Sr/<sup>86</sup>Sr, <sup>187</sup>Os/<sup>188</sup>Os, SiO<sub>2</sub>, and Na<sub>2</sub>O/TiO<sub>2</sub>, and high <sup>143</sup>Nd/<sup>144</sup>Nd, <sub>176</sub>Hf/<sub>177</sub>Hf, <sup>206</sup>Pb/<sup>204</sup>Pb, TiO<sub>2</sub>, CaO and CaO/Al<sub>2</sub>O<sub>3</sub>). FeO<sub>total</sub>, Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O concentrations do not correlate with Sr, Nd, Pb or Hf isotope compositions.
- [50] 3. In Hawaiian tholeiitic lavas, <sup>3</sup>He/<sup>4</sup>He shows a remarkably good relationship with SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>, CaO/Al<sub>2</sub>O<sub>3</sub> and FeO<sub>total</sub>. High <sup>3</sup>He/<sup>4</sup>He lavas from Loihi anchor the low SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and high CaO, CaO/Al<sub>2</sub>O<sub>3</sub> and FeO<sub>total</sub> portions of the arrays. <sup>3</sup>He/<sup>4</sup>He exhibits no clear relationships with TiO<sub>2</sub> and Na<sub>2</sub>O abundances or with Na<sub>2</sub>O/TiO<sub>2</sub> ratios.
- [51] 4. The Loihi source is likely peridotitic, but has been infused with a SiO<sub>2</sub>-poor mafic component such that the final mixture is an enriched peridotite. Loihi and Kea-component lavas exhibit similar major element characteristics (low SiO<sub>2</sub> and Na<sub>2</sub>O/TiO<sub>2</sub> and high TiO<sub>2</sub>, CaO and CaO/Al<sub>2</sub>O<sub>3</sub>), which may suggest lithologically similar mantle sources. The composition of SiO<sub>2</sub>-rich Koolau-component lavas is not easily explained by available data for peridotite melting experiments (wet or dry) or by melt-rock reaction of peridotite melts with the oceanic mantle lithosphere. Instead, Koolau-component lavas are likely derived from melts of a SiO<sub>2</sub>-rich eclogite that has variably interacted with peridotite.
- [52] 5. Correlations between major elements and radiogenic isotopes in Hawaiian lavas mimic the best correlations observed in the global OIB data set between Pb isotopic ratios and SiO<sub>2</sub> and CaO/Al<sub>2</sub>O<sub>3</sub>. We suggest that the mechanism that drives the correlations between major elements and isotopes in Hawaii illustrates, in microcosm, a larger global process. Variable processing of slabs in subduction zones yields SiO<sub>2</sub>-poor pyroxenites (with high U/Pb) and SiO<sub>2</sub>-rich eclogites (with low U/Pb) that evolve radiogenic and unradiogenic Pb isotopic compositions, respectively. These two endmember mafic components interact variably with peridotite and anchor the extreme ends (i.e., high SiO<sub>2</sub> and low SiO<sub>2</sub>) of the global array (Figure 10).

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