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## Sr, Nd, Hf and Pb isotope systematics of postshield-stage lavas at Kahoolawe, Hawaii



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#### ABSTRACT

We report high-precision Sr, Nd, Hf and Pb isotope compositions for twenty-one postshield-stage and two post-caldera lavas from Kahoolawe, a Loa-trend Hawaiian volcano. Kahoolawe postshield- and shield-stage lavas have overlapping though highly heterogeneous Sr, Nd, Hf and Pb isotope compositions, implying that the shield- and postshield-stage volcanism at Kahoolawe sampled the same isotopically heterogeneous mantle source. This differs from that of most other Hawaiian volcanoes, such as Haleakala, Mauna Kea, and Hualalai, whose shield-topostshield transitions are characterized by shifts to lower  $^{87}\text{Sr}/^{86}\text{Sr}$  and higher  $^{143}\text{Nd}/^{144}\text{Nd}$ . There are correlations between CaO, Sc and V contents and radiogenic isotope compositions within Kahoolawe postshield-stage lavas. For example, Sc abundance is negatively correlated with  $^{87}\text{Sr}/^{86}\text{Sr}$ , and positively correlated with  $\epsilon_{Nd}$  and  $\epsilon_{Hf}$ ; V abundance is positively correlated with  $\epsilon_{Nd}$ ,  $\epsilon_{Hf}$ , and  $^{206}\text{Pb}/^{204}\text{Pb}$ . Element-isotope correlations are also observed in Mauna Kea postshield-stage lavas: Sc and V abundances are negatively correlated with  $\epsilon_{Hf}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$ , and positively correlated with  $\epsilon_{Nd}$ . These trends may be due to magma–magma mixing. That is, in addition to clinopyroxene fractionation to account for the low CaO, Sc and V contents in some postshield-stage lavas, partial melts of eclogite/garnet pyroxenite, characterized by low CaO, Sc and V contents, may also be part of the petrogenesis of Kahoolawe postshield-stage lavas.

It is well established that lavas erupted at the geographically defined Loa- and Kea-trend volcanoes have different isotopic and geochemical compositions. Specifically, compared to the Kea-trend lavas, Loa-trend lavas have higher <sup>208</sup>Pb/<sup>204</sup>Pb at a given <sup>206</sup>Pb/<sup>204</sup>Pb. However, cases exist of both shield- and postshield-stage volcanism where Kea-type isotopic signatures are present in Loa-trend volcanoes and the reverse. We propose that Loa- and Kea-type source components are present beneath both Loa- and Kea-trend volcanoes in such a way that the average source compositions of Loa-trend volcanoes have a Loa-type isotopic signature, and that of the Kea-trend volcanoes have a Kea-type isotopic signature. When the size of the magma capture zone is much larger than that of the source components, the erupted lavas have the average compositions of the source. If the size of the magma capture zone is comparable to that of the source components, the erupted lavas could have either Loa- or Kea-type isotopic signatures.

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#### 1. Introduction

Studies of shield lavas forming the Hawaiian islands at the southeast end of the 6000-km long, age-progressive hotspot track provide constraints on their magma source, presumably a plume, i.e., ascending buoyant mantle which partially melts. Large isotopic and compositional variations are observed in Hawaiian lavas, with lavas from the uppermost shield-stage of Koolau (Makapuu-stage), Lanai and Kahoolawe defining the highest  $^{87} {\rm Sr}/^{86} {\rm Sr}$  and  $^{208} {\rm Pb}^*/^{206} {\rm Pb}^*$ , and the lowest  $\epsilon_{\rm Nd}$ ,  $\epsilon_{\rm Hf}$  and  $^{206} {\rm Pb}/^{204} {\rm Pb}$  end of the isotopic spectrum. These distinctive isotopic

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characteristics have been interpreted to reflect an important role of recycled ancient oceanic crustal material, including sediments, in the petrogenesis of Hawaiian lavas (e.g., Lassiter and Hauri, 1998; Blichert-Toft et al., 1999; Huang and Frey, 2005; Sobolev et al., 2005, 2007; Huang et al., 2009, 2011a; Pietruszka et al., 2013). Specifically, this recycled component may be sampled by Hawaiian volcanism in the form of melts from eclogite or garnet pyroxenite (Lassiter and Hauri, 1998; Huang and Frey, 2005; Sobolev et al., 2007).

Modern Hawaiian volcanoes form two *en echelon* tracks, the socalled Loa- and Kea-trends named after the largest volcanoes at the southern end of each track (Fig. 1; Jackson et al., 1972). There are important geochemical differences between shield lavas erupted on the Loa- and Kea-trend volcanoes (Abouchami et al., 2005), which have been used to constrain the spatial distribution of geochemical

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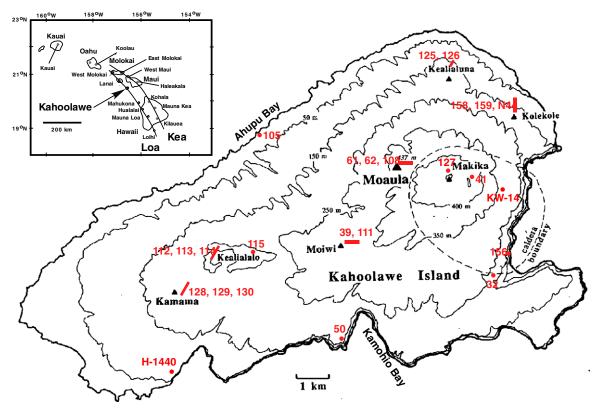


Fig. 1. Map of Kahoolawe Island. The locations of the postshield lavas analyzed in this study, as well as the two "rejuvenated-stage" lavas, are indicated. The inset shows a map of the modern Hawaiian islands and their volcanoes with the Loa- and Kea-trends traced with the slightly curved solid lines.

heterogeneities within the Hawaiian plume (e.g., Lassiter and Hauri, 1998; Bryce et al., 2005; Blichert-Toft and Albarède, 2009; Farnetani and Hofmann, 2010; Weis et al., 2011; Farnetani et al., 2012; Nobre Silva et al., 2013). Such bimodal trends may be a common feature of all Pacific hotspot volcanism (Huang et al., 2011b). Two primary types of plume structure have been proposed to explain the two-trend phenomena: a bilaterally zoned plume (Abouchami et al., 2005) and a concentrically zoned plume (Lassiter et al., 1996; DePaolo et al., 2001). Variants of these two types of models have also been proposed (see Fig. 2 of Xu et al., 2007 for a summary).

A typical Hawaiian volcano has four growth stages, namely preshield, shield, postshield and rejuvenated (e.g., Clague and Dalrymple, 1987), though not all Hawaiian volcanoes evolved through all four stages. The first three growth stages, preshield- to postshieldstage volcanism, are continuous in time, and usually occur within 1 Myrs. Each of these three growth stages lasts for several hundred kyrs (e.g., Fig. 1 of Frey et al., 1990). Preshield-stage volcanism is dominated by alkalic lavas and accounts for only 1-2% of the total volcanic volume. Shield-stage volcanism is dominated by tholeiitic lavas, and the majority (97-98%) of the volcanic mass is erupted during this growth stage. Similar to preshield-stage volcanism, postshield-stage volcanism also is dominated by alkalic lavas and accounts for no more than ~1% of the volcano. Rejuvenated-stage volcanism occurs in only some volcanoes, ~0.6 to 2 Ma after the shield-stage volcanism seized (e.g., Ozawa et al., 2005). The rejuvenated-stage volcanism is characterized by highly alkalic lavas and accounts for a very small (<<1%) portion of a volcano (e.g., Garcia et al., 2010).

According to the plume hypothesis, postshield-stage volcanism occurs when a volcano moves away from the mantle plume and samples the plume edge (e.g., Frey et al., 1990, 1991). Relative to shield-stage volcanism, postshield-stage volcanism is characterized by a significantly reduced eruption rate and lavas produced by a lower degree of partial

melting. Despite its relative small volume, postshield volcanism records a substantial part of the temporal history of any one of the volcanoes in the Hawaiian-Emperor chain (e.g., Fig. 1 of Frey et al., 1990). Among the three volcanoes (Makapuu-stage of Koolau which is the youngest shield building stage of Koolau volcano, Lanai and Kahoolawe) that define the isotopically enriched endmember, i.e., high  $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$  and low 143Nd/144Nd, at Hawaii, only Kahoolawe (Fig. 1; Fodor et al., 1992) displays postshield-stage volcanism with at least seven vents erupting postshield lavas. Sampling lavas on Kahoolawe has been restricted because of military and preservation policies, but limited visits were granted to G. R. Bauer, R. V. Fodor, and M. O. Garcia in the early 1980s (West et al., 1987; Fodor et al., 1992; Leeman et al., 1994) during which they recovered more than 200 samples from the surface of Kahoolawe volcano. Elemental and isotope compositions of its shield-stage lavas have since been thoroughly documented in a number of studies (West et al., 1987; Fodor et al., 1992; Leeman et al., 1994; Blichert-Toft et al., 1999; Abouchami et al., 2005; Huang et al., 2005a) and recently have been reviewed in detail by Fodor and Bauer (2010). However, only major and trace element abundances have been reported for the postshield-stage Kahoolawe lavas (Fodor et al., 1992; Fodor and Bauer, 2012), and precise isotopic data for Sr, Nd, Hf and Pb are not available.

In order to constrain the petrogenesis of the Kahoolawe postshield-stage lavas, we measured their Sr, Nd, Hf and Pb isotope compositions. With these data we also test whether the Loa-Kea geochemical differences (e.g., Abouchami et al., 2005; Weis et al., 2011) persist during the transition from the shield- to the postshield-stage (e.g., Xu et al., 2007; Hanano et al., 2010).

#### 2. Samples and analytical techniques

Twenty-one postshield-stage Kahoolawe lavas (Fig. 1), including tholeiites, alkalic lavas and hawaiites, which were measured for major

**Table 1**Sr, Nd, Hf and pb isotopic ratios of Kahoolawe postshield stage and two shield stage lavas.

SAMPLE	Rock Type <sup>a</sup>	$^{87}$ Sr/ $^{86}$ Sr	$2 \sigma$	$^{143} Nd / ^{144} Nd$	$2\sigma$	$^{176}\text{Hf}/^{177}\text{Hf}$	$2\sigma$	$^{206}\text{Pb}/^{204}\text{Pb}$	$2\sigma$	$^{207}\text{Pb}/^{204}\text{Pb}$	$2\sigma$	$^{208}\text{Pb}/^{204}\text{Pb}$	$2\sigma$	$^{208}Pb^{*}/^{206}Pb^{*c}$
Postshield	stage													
Kealialuna														
KAH 125	Tholeiite	0.703950	0.000008		0.000009	0.283050	0.000004			15.4448	0.0006	37.8242	0.0018	0.9591
KAH 126	Tholeiite	0.703948	0.000006	0.512842	0.000019	0.283045	0.000004	18.0197	0.0004	15.4453	0.0004	37.8294	0.0010	0.9588
Kolekole														
KAH 158 <sup>b</sup>	Tholeiite	0.703826	0.000007	0.512921	0.000003	0.283078	0.000004	18.2317	0.0004	15.4591	0.0005	37.9914	0.0015	0.9542
KAH 159	Tholeiite	0.703854	0.000007	0.512921	0.000009	0.283081	0.000004	18.2511	0.0003	15.4605	0.0003	38.0074	0.0009	0.9539
KAH N44	Tholeiite	0.703837	0.000007	0.512910	0.000009	0.283079	0.000004	18.1917	0.0005	15.4578	0.0005	37.9669	0.0014	0.9557
Makika														
KAH 41 <sup>b</sup>	Tholeiite	0.704025	0.000007	0.512866	0.000007	0.283040	0.000004	18.1496	0.0004	15.4590	0.0004	37.9439	0.0012	0.9577
KAH 127	Tholeiite		0.000008		0.000006		0.000004			15.4601		37.9512		0.9577
	morence	0.70 1015	0.000000	0.012001	0.000000	0.203001	0.000001	1011070	0.0001	1011001	0.0001	37.0012	0.0012	0.0077
Kamama	Harraiita	0.704172	0.000007	0.513000	0.000005	0.202005	0.000004	10.0145	0.0002	15 4570	0.0002	27.0021	0.0010	0.0022
KAH 128 <sup>b</sup>	Hawaiite	0.704173	0.000007		0.000005	0.282995	0.000004			15.4572	0.0003	37.8631		0.9633
KAH 129	Hawaiite	0.704545		0.512799	0.000007	0.282994	0.000004			15.4562	0.0003	37.8657	0.0011	0.9639
KAH 130	Hawaiite	0.704358	0.000008	0.512795	0.000006	0.282986	0.000004	18.0107	0.0002	15.4561	0.0003	37.8665	0.0008	0.9641
Kealialalo														
KAH 112	Alkalic basalt	0.704593	0.000005	0.512840	0.000006	0.283019	0.000004	18.0560	0.0005	15.4661	0.0005	37.8237	0.0013	0.9542
KAH 113	Tholeiite	0.703783	0.000007	0.512915	0.000014	0.283084	0.000003	18.3125	0.0004	15.4698	0.0004	38.0372	0.0012	0.9507
KAH 114 <sup>b</sup>	Tholeiite	0.703890	0.000013	0.512913	0.000002	0.283084	0.000004	18.3094	0.0005	15.4683	0.0005	38.0305	0.0016	0.9503
KAH 115	Alkalic basalt	0.704090	0.000008	0.512799	0.000007	0.283003	0.000004	18.0780	0.0004	15.4738	0.0004	37.8681	0.0012	0.9569
Moiwi														
KAH 39	Transitional	0.703724	0.000007	0.512034	0.000008	0.283081	0.000004	18 2702	0.0003	15.4703	0.0003	37.9912	0.0008	0.9501
IVIII JJ	basalt	0.703724	0.000007	0.512554	0.000000	0.285081	0.000004	10,2702	0.0003	13,4703	0.0003	37.3312	0.0008	0,3301
KAH 111	Transitional	0.703737	0.000007	0.512923	0.000008	0.283081	0.000004	18 2625	0.0004	15.4656	0.0004	37.9747	0.0011	0.9491
10 11 11 1	basalt	0.703737	0.000007	0.512525	0.000000	0.203001	0.000001	10.2025	0.0001	13.1030	0.0001	37.37 17	0.0011	0.5 15 1
Moaula	411 12 1 1	0.70.44.07	0.000000	0.540000	0.00004.4	0.000000	0.000000	40.0005	0.0004	45 4505	0.0004	27.7057	0.0040	0.0500
KAH 61	Alkalic basalt		0.000008			0.282989		18.0295		15.4707		37.7957	0.0012	
KAH 62	Alkalic basalt		0.000008		0.000008	0.282992	0.000003			15.4734		37.7935		0.9539
KAH 108	Alkalic basalt	0.704085	0.000008	0.512829	0.000029	0,282995	0.000004	18.0232	0.0003	15.4722	0.0004	37.7924	0.0011	0.9542
Аһири Вау														
KAH 105	Alkalic basalt	0.703752	0.000007	0.512916	0.000009	0.283081	0.000004	18.0406	0.0004	15.4536	0.0004	37.7876	0.0011	0.9518
Kamohio B	'av													
Karnonio B KAH 50	<i>uy</i> Tholeiite	0.70/172	0.000007	0.512781	0.000006	0.282975	0.000004	17 0/67	0.0004	15.4474	0.0004	37.8266	0.0011	0.9666
KAH 30	Holente	0./041/3	0.000007	0.312/01	0.000000	0,202973	0.000004	17,9407	0.0004	13,44/4	0.0004	37.0200	0.0011	0.3000
Shield stage	е													
KAH 32	Tholeiite	0.703945	0.000009	0.512869	0.000011	0.283050	0.000004	18.1695	0.0005	15.4560	0.0004	37.9580	0.0013	0.9571
KAH 156	Tholeiite	0.703729	0.000008	0.512937	0.000008	0.283096	0.000004	18.4052	0.0004	15.4696	0.0004	38.1171	0.0011	0.9498

<sup>&</sup>lt;sup>a</sup> . From Fodor et al. (1992).

and trace elements by Fodor et al. (1992), were analyzed for Sr, Nd, Hf and Pb isotope compositions (Table 1). We also included two supposedly "rejuvenated-stage" tholeiitic lavas, KAH-32 and -156 (Fig. 1). These two samples were collected from two different outcrops on the steep slope above Kanapou Bay that Stearns (1940) and Macdonald (1940) believed to represent the final growth stage (i.e., rejuvenated-stage, termed "post-erosional" by Stearns (1940) and Macdonald (1940)) of volcanism on Kahoolawe. However, geochronological data (Sano et al., 2006) indicate that these two samples belong to the Kahoolawe shield-stage.

Isotope compositions of Sr, Nd and Pb were determined at the Geochemistry Division, National High Magnetic Field Laboratory, Florida State University (FSU). Between 0.2 and 0.4 g of rock chips were step-leached in 6 N HCl at room temperature following the leaching procedure described in Huang et al. (2005b) until the acid was colorless or pale yellow. The leached chips were then dissolved in concentrated HF-HNO<sub>3</sub>. Strontium and rare earth elements (REEs) were separated from the matrix using cation-exchange resin (AG50W-X12), and Nd was further separated from the other REEs on Ln-Spec columns. Isotope

compositions of Sr and Nd were measured on a Finnigan® MAT 262 TIMS in dynamic mode. The E&A Sr standard gave an average of  $0.708002 \pm 0.000011$  (2  $\sigma$ , n=8) for  $^{87}\text{Sr}/^{86}\text{Sr}$  and the LaJolla Nd standard gave an average of 0.511846  $\pm$  0.000011 (2  $\sigma\!,\,n=10)$  for <sup>143</sup>Nd/<sup>144</sup>Nd during the course of this study. Neodymium isotope compositions of KAH-41, -114, -128 and -158 were measured on a ThermoFinnigan Neptune® MC-ICP-MS with an ESI Apex® nebulizer following the procedure outlined in Huang et al. (2009). Instrumental mass fractionation was corrected relative to  $^{146}$ Nd/ $^{144}$ Nd = 0.7219 using the exponential law. The LaJolla Nd standard was analyzed regularly in between samples to monitor instrument performance, and yielded an average  $^{143}\text{Nd}/^{144}\text{Nd}$  of 0.511837  $\pm$  0.000010 (2  $\sigma$  $n=50).\ ^{143}\mbox{Nd}/^{144}\mbox{Nd}$  of the analyzed samples are reported relative to  $^{143}\mbox{Nd}/^{144}\mbox{Nd}_{\mbox{\scriptsize LaJolla}} = 0.511850$  using our average LaJolla Nd value. In order to estimate the external reproducibility of MC-ICP-MS  $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$  measurements, a SPEX Nd standard solution was analyzed as an unknown sample and yielded an average of 0.511714  $\pm$  0.000008  $(2 \sigma, n = 7)$ . The total procedural Sr and Nd blanks were less than 100 pg and 10 pg, respectively.

b . Nd isotopic ratios of these samples were obtained on Neptune MC-ICP-MS. See text for details.

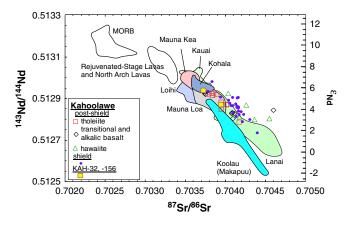
 $<sup>^{\</sup>circ}$  .  $^{208}\text{Pb}^*/^{206}\text{Pb}^* = [(^{208}\text{Pb}/^{204}\text{Pb})^{\circ}\text{sample-29.475}]/[(^{206}\text{Pb}/^{204}\text{Pb})^{\circ}\text{sample-9.307}].$ 

Lead was separated from the matrix solution using anion-exchange resin (AG1-X8) with HBr and HCl. The Pb isotope compositions were measured on a ThermoFinnigan Neptune® MC-ICP-MS with the above instrument configuration using the Tl-doping technique and sample-standard bracketing (White et al., 2000; Albarède et al., 2004). The detailed analytical procedure is described in Huang et al. (2009). Mass fractionation was corrected using  $^{203}\text{Tl}/^{205}\text{Tl} = 0.418922$ . The NIST SRM-981 standard was analyzed every 4-5 samples in order to monitor instrument performance and bracket the unknown samples. The sample Pb isotope compositions are reported relative to the average Pb isotope compositions of the NIST SRM-981 standard obtained at the Max-Planck-Institüt using the triple spike technique  $(^{206}\text{Pb}/^{204}\text{Pb}_{SRM981} = 16.9432, \ ^{207}\text{Pb}/^{204}\text{Pb}_{SRM981} = 15.5015 \ \text{and}$  $^{208}$ Pb/ $^{204}$ Pb<sub>SRM981</sub> = 36.7313) (Abouchami et al., 2005; Huang et al., 2009). The Pb isotopic results from Tl-doping (FSU) and triple spike (Max-Planck) are within 0.2% per amu (see Huang et al., 2009 for details). The total procedural Pb blank was less than 50 pg.

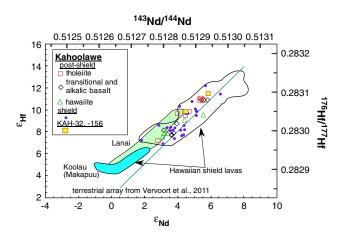
Hafnium isotope compositions were determined on unleached rock chips at the Ecole Normale Supérieure in Lyon (ENSL) using a Nu Plasma® 500 HR MC-ICP-MS coupled with a DSN-100 desolvating nebulizer and following the procedure of Blichert-Toft et al. (1997). Instrumental mass bias was corrected relative to  $^{179}\mathrm{Hf}/^{177}\mathrm{Hf}=0.7325$  using the exponential law. The Hf standard JMC-475 was analyzed every two to four samples and gave an average  $^{176}\mathrm{Hf}/^{177}\mathrm{Hf}=0.282160\pm0.000010$  (2  $\sigma$ , n = 10). Since this is identical to the accepted value of 0.282163  $\pm$  0.000009 (Blichert-Toft et al., 1997) for JMC-475, no corrections were applied to the measured Hf isotope data. The total procedural Hf blank was less than 20 pg.

#### 3. Results

The isotope compositions of Sr, Nd, Hf and Pb for 21 postshield-stage lavas and 2 shield-stage lavas, KAH-32 and -156, from Kahoolawe volcano are listed in Table 1. Kahoolawe shield- and postshield-stage lavas are highly heterogeneous, covering over 70% of the total Sr, Nd, Hf and Pb isotopic variations in Hawaiian shield-stage lavas (Figs. 2–5). In general, most Loa-trend volcanoes, such as Koolau, Lanai and



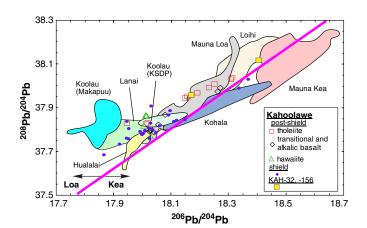
**Fig. 2.** <sup>87</sup>Sr/<sup>86</sup>Sr vs. <sup>143</sup>Nd/<sup>144</sup>Nd for Kahoolawe lavas. Fields for other Hawaiian shields, Hawaiian rejuvenated-stage lavas and MORB are shown for comparison. Data sources: Kahoolawe lavas: West et al., 1987; Huang et al., 2005a; this study; Koolau (Makapuu): Roden et al., 1984, 1994; Lanai: West et al., 1987; Basu and Faggart, 1996; Gaffney et al., 2005; Mauna Kea: Lassiter et al., 1996; Bryce et al., 2005; Blichert-Toft and Albarède, 2009; Mauna Loa: Cohen et al., 1996; Kurz et al., 1995; Kauai: Mukhopadhyay et al., 2003; Loihi: Garcia et al., 1993, 1995, 1998; Kohala: Hofmann et al., 1987; rejuvenated stage lavas: Stille et al., 1983; Roden et al., 1984; Chen and Frey, 1985; Tatsumoto et al., 1987; West et al., 1987; Frey et al., 2000; Lassiter et al., 2000; EPR MORB: Niu et al., 1999; Regelous et al., 1999; Castillo et al., 2000.



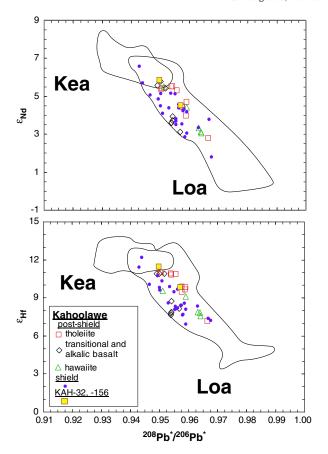
**Fig. 3.** ε<sub>Nd</sub> vs. ε<sub>Hf</sub> for Kahoolawe lavas. ε<sub>Hf</sub> = [(<sup>176</sup>Hf)<sup>177</sup>Hf)<sub>sample</sub>/(<sup>176</sup>Hf)<sup>177</sup>Hf)<sub>CHUR</sub> - 1] × 10,000 and ε<sub>Nd</sub> = [(<sup>143</sup>Nd/<sup>144</sup>Nd)<sub>sample</sub>/(<sup>143</sup>Nd/<sup>144</sup>Nd)<sub>CHUR</sub> - 1] × 10,000 with (<sup>176</sup>Hf)<sup>177</sup>Hf)<sub>CHUR</sub> = 0.282772 (Blichert-Toft and Albarède, 1997) and (<sup>143</sup>Nd/<sup>144</sup>Nd)<sub>CHUR</sub> = 0.512638. Fields for other Hawaiian shield lavas (Blichert-Toft et al., 1999; Gaffney et al., 2005; Huang et al., 2005a; Salters et al., 2006; Blichert-Toft and Albarède, 2009), as well as the terrestrial array (Vervoort et al., 2011), are shown for comparison.

Kahoolawe, are more isotopically heterogeneous than Kea-trend volcanoes (e.g., Fig. 15 of Huang et al., 2009; Fig. 2 of Weis et al., 2011).

In an <sup>87</sup>Sr/<sup>86</sup>Sr-<sup>143</sup>Nd/<sup>144</sup>Nd plot, Kahoolawe postshield lavas form a negative array, overlapping the array defined by the isotopically heterogeneous Kahoolawe shield lavas (Fig. 2). KAH-32 and -156 plot on the same array as Kahoolawe shield and postshield lavas, and are distinct from the dominantly depleted isotope compositions of the Hawaiian rejuvenated-stage lavas from Koloa, Honolulu, Lahaina and Hana volcanics (Fig. 2). The isotopic data for KAH-32 and -156 together with the geochronological data for the outcrops they come from (Sano et al., 2006) indicate that these samples *do not* belong to the rejuvenated-stage volcanism.



**Fig. 4.** <sup>208</sup>Pb/<sup>204</sup>Pb vs. <sup>206</sup>Pb/<sup>204</sup>Pb for Kahoolawe lavas. Fields for other Hawaiian shields are shown for comparison. The Loa-Kea dividing line (in pink) is from Abouchami et al. (2005). Data sources: Makapuu-stage Koolau: Roden et al., 1994; Abouchami et al., 2005; Koolau (KSDP): Fekiacova et al., 2007; Lanai: Gaffney et al., 2005; Kahoolawe: West et al., 1987; Abouchami et al., 2005; Huang et al., 2005a; this study; Mauna Loa: Kurz et al., 1995; Cohen et al., 1996; Abouchami et al., 2000; Loihi: Garcia et al., 1995, 1998; Hualalai: Cousens et al., 2003; Mauna Kea: Abouchami et al., 2000; Blichert-Toft et al., 2003; Eisele et al., 2003; Blichert-Toft and Albarède, 2009; Kohala: Abouchami et al., 2005.



**Fig. 5.**  $^{208}$ Pb\*/ $^{206}$ Pb\* vs.  $^{176}$ Hf/ $^{177}$ Hf for Kahoolawe lavas.  $^{208}$ Pb\*/ $^{206}$ Pb\* = [( $^{208}$ Pb/ $^{204}$ Pb)<sub>sample</sub>-29.475]/[( $^{206}$ Pb/ $^{204}$ Pb)<sub>sample</sub>-9.307] (Galer and O'Nions, 1985). Fields for Loa- and Kea-trend lavas are shown for comparison. Data sources: see captions to Figs. 2–4.

Compared to Makapuu-stage Koolau lavas, shield- and postshield-stage lavas from Kahoolawe have higher  $^{87}{\rm Sr}/^{86}{\rm Sr}$  at a given  $^{143}{\rm Nd}/^{144}{\rm Nd}$  (Fig. 2).

Kahoolawe shield- and postshield-stage lavas have overlapping Nd and Hf isotope compositions (Fig. 3). Hawaiian lavas, as a whole, define an  $\epsilon_{Nd}\text{-}\epsilon_{Hf}$  array shallower than the global terrestrial array. This shallower Hawaiian array is mostly controlled by Makapuu-stage Koolau lavas. The Kahoolawe  $\epsilon_{Nd}\text{-}\epsilon_{Hf}$  array has a slope of 1.22  $\pm$  0.20 (2  $\sigma$ ), slightly shallower than the terrestrial array, which has a slope of 1.549  $\pm$  0.016 (2  $\sigma$ ) (Fig. 3; Vervoort et al., 2011).  $\epsilon_{Hf}$  and  $\epsilon_{Nd}$  measure the  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  deviations from their chondritic reference reservoirs, respectively, and are defined caption to Fig. 3.

Loa-trend shield-stage lavas have higher <sup>208</sup>Pb/<sup>204</sup>Pb at a given <sup>206</sup>Pb/<sup>204</sup>Pb, i.e., higher <sup>208</sup>Pb\*/<sup>206</sup>Pb\* (where \* stands for radiogenic Pb, see caption to Fig. 5 for definition), than Kea-trend shield-stage lavas (Eisele et al., 2003; Abouchami et al., 2005; Huang et al., 2011b; Weis et al., 2011). Kahoolawe postshield- and shield-stage lavas have overlapping Pb isotope compositions, and they both plot on the Loaside in a <sup>206</sup>Pb/<sup>204</sup>Pb-<sup>208</sup>Pb/<sup>204</sup>Pb diagram, with two exceptions among the shield lavas that fall just barely into the Kea field and one sample plotting on the Loa-Kea divide (Fig. 4).

In plots of  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  vs.  $\epsilon_{\text{Hf}}$  and  $\epsilon_{\text{Nd}}$ , Loa-trend shield-stage lavas form steep negative arrays, while Kea-trend shield-stage lavas form nearly horizontal arrays (Abouchami et al., 2005; Huang et al., 2005a, 2011b; Weis et al., 2011). Shield- and postshield-stage lavas of Kahoolawe also define a negative  $^{208}\text{Pb}^*/^{206}\text{Pb}^*-\epsilon_{\text{Hf}}$  array plotting within the field defined by other Loa-trend shield-stage lavas (Fig. 5).

#### 4. Discussion

4.1. Isotopic variations during the shield-to-postshield transition at Kahoolawe

The shield-to-postshield transitions at several Hawaiian volcanoes, such as Haleakala, Kohala and Mauna Kea (both Kea-trend volcanoes) and Hualalai (a Loa-trend volcano), have been thoroughly documented (e.g., Chen and Frey, 1985; Frey et al., 1990; Chen et al., 1991; Frey et al., 1991; Yang et al., 1996; Cousens et al., 2003; Hanano et al., 2010). Systematic isotopic shifts have been observed, with lower <sup>87</sup>Sr/<sup>86</sup>Sr and higher 143Nd/144Nd for the postshield-stage lavas relative to the shield-stage lavas (e.g., Fig. 10 of Chen et al., 1991 for Haleakala; Fig. 8 of Huang and Frey, 2003 for Mauna Kea with data from Bryce et al., 2005; Fig. 7a of Cousens et al., 2003 and Fig. 2d of Yamasaki et al., 2009 for Hualalai). This implies that during the shield-to-postshield transition at most Hawaiian volcanoes, the volcanoes started sampling more of a depleted source component, but still retained their respective Kea-type or Loa-type Pb isotopic signatures (Abouchami et al., 2005; Xu et al., 2005). The shield-to-postshield transitions of Pb isotopes are more complicated: it is coupled with increasing  $^{206}\text{Pb}/^{204}\text{Pb}$  at Kohala (Keatrend) and Mahukona (Loa-trend), but decreasing 206Pb/204Pb at Mauna Kea (Kea-trend) and Hualalai (Loa-trend) (Fig. 7 of Hanano et al., 2010).

The shield-to-postshield transition at Kahoolawe is coupled with an increase in La/Yb, reflecting decreasing degree of partial melting (Fig. 6). However, Kahoolawe postshield- and shield-stage lavas have overlapping Sr, Nd, Hf and, to a lesser extent, Pb isotope compositions (Figs. 2–5) with no systematic isotopic shift between the two stages (Fig. 6). This suggests that at Kahoolawe, a Loa-trend volcano, shield and postshield volcanism sampled a common, but isotopically heterogeneous source, and retained a Loa-type Pb isotopic signature during postshield volcanism.

#### 4.2. Correlations between element abundances and isotope compositions

Detailed geochemical studies of postshield-stage lavas at Mauna Kea (Hamakua and Laupahoehoe volcanics) have shown that at MgO contents less than 7%, the abundances of CaO, Sc and V decrease with decreasing MgO content (e.g., Frey et al., 1990). Such correlations have been interpreted as the result of clinopyroxene fractionation during postshield-stage volcanism, in contrast to the dominant role of olivine fractionation/accumulation during shield-stage volcanism (e.g., Frey et al., 1990). At Mauna Kea, the basaltic postshield-stage (Hamakua Volcanics) is followed by the hawaiitic postshield-stage (Laupahoehoe Volcanics), which is more enriched in alkalis (LeBas et al., 1986). This temporal trend has been interpreted to be the result of a decreased magma supply rate during postshield-stage volcanism (Frey et al., 1990). The low magma supply rate led to the closing of the shallow magma chamber that formed during the shield-stage volcanism. Consequently, magmas evolved at a greater depth, perhaps at the crust-mantle boundary, and hawaiites formed as a result of the high-pressure crystal fractionation involving clinopyroxene.

Similar correlations are also observed for the Kahoolawe postshield-stage lavas (Fig. 7). In detail, Kahoolawe shield-stage lavas with MgO contents greater than 6% form slightly negative trends in plots of MgO vs. CaO, Sc and V contents, consistent with olivine fractionation/accumulation, as typically observed in other Hawaiian shield lavas. In contrast, Kahoolawe postshield-stage lavas, most of which have MgO contents less than 7%, form weak positive trends in the CaO, Sc and V plots, with hawaiites defining the low MgO end. Each of these elements is compatible in clinopyroxene (e.g., Hart and Dunn, 1993). In addition, CaO, Sc, and V display weak correlations with some radiogenic isotope compositions (Fig. 8). For example,  $^{87}{\rm Sr}/^{86}{\rm Sr}$  is the highest and  $^{206}{\rm Pb}/^{204}{\rm Pb}$  the lowest in the samples with lowest CaO, Sc, and V abundances, which are largely hawaiites. Also,  $\epsilon_{\rm Nd}$  and  $\epsilon_{\rm Hf}$  generally decrease

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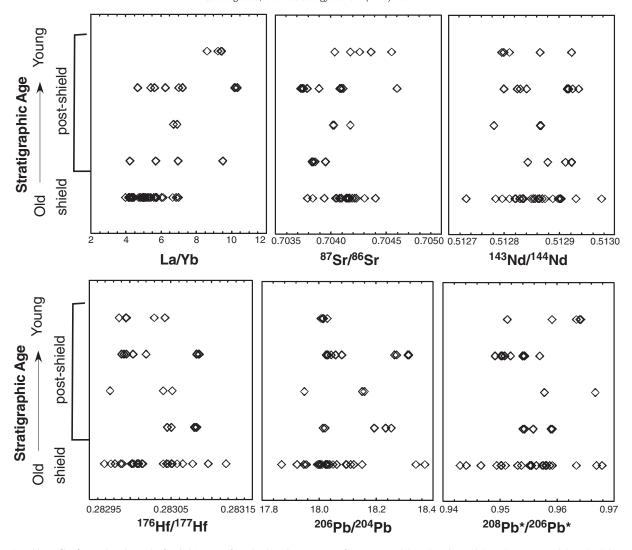


Fig. 6. Stratigraphic profiles for La/Yb and Sr, Nd, Hf and Pb isotopes for Kahoolawe lavas. Data are from West et al. (1987), Fodor et al. (1992), Leeman et al. (1994), Blichert-Toft et al. (1999), Huang et al. (2005a), this study.

with decreasing CaO, Sc, and V, but the hawaiites have somewhat scattered Sr, Nd and Hf though uniform Pb isotope compositions (Fig. 8). The <sup>87</sup>Sr/<sup>86</sup>Sr ratios in the postshield lavas generally show a slight increase with decreasing elemental concentrations (Fig. 8). While these elemental variations may be attributed to a closed system process, such as magma chamber fractionation, the isotopic variations require changes in the source of these magmas, such as an open system process like magma-magma mixing. The observed element-isotope correlations could reflect a similar process invoked at Mauna Kea by Frey et al. (1990, 1991): The transition to postshield-stage volcanism is coupled with transitions in isotope compositions and a decrease in magma supply, which led to a larger degree of clinopyroxene fractionation. However, there are no clear secular changes in isotope compositions during the postshield-stage volcanism at Kahoolawe (Fig. 6).

While the observed element-isotope correlations at Kahoolawe (Fig. 8) are weak in some cases, it is nonetheless worth noting that where element-isotope correlations have been observed for some other Hawaiian volcanoes, the interpretations are usually that magma mixing was involved between melts from garnet pyroxenites/eclogites and from peridotites. For example, Hauri (1996) showed that after

adjustment for olivine fractionation/accumulation, the major element contents of Hawaiian shield-stage lavas are correlated with Nd and Os isotope compositions, an observation later confirmed by Jackson et al. (2012) with a much larger data set. Huang and Frey (2005) applied this approach on Koolau lavas, and also identified significant major element abundance-isotope composition correlations. Lassiter et al. (2000) observed correlations between <sup>187</sup>Os/<sup>188</sup>Os and abundances of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Sr in the Honolulu Volcanics (rejuvenated-stage volcanism at Koolau) and Koloa Volcanics (rejuvenated-stage volcanism at Kauai). These correlations have all been interpreted to reflect magmamagma mixing, implying that this process has been identified in the three major growth stages of Hawaiian volcanism. In all three cases, melts from eclogite or garnet pyroxenite were invoked (Hauri, 1996; Lassiter et al., 2000; Huang and Frey, 2005; Jackson et al., 2012).

Element-isotope correlation is not a feature unique to Hawaii. Reiners (2002) showed that this type of correlation is also observed at the Canary Islands, the Pisgah and Amboy craters in southern California and the Fort Selkirk volcanic complex at Yukon, Canada. Similarly to Hawaii, these trends have been interpreted as magma-magma mixing lines, with the involvement of melts from eclogite or garnet pyroxenite and peridotite.

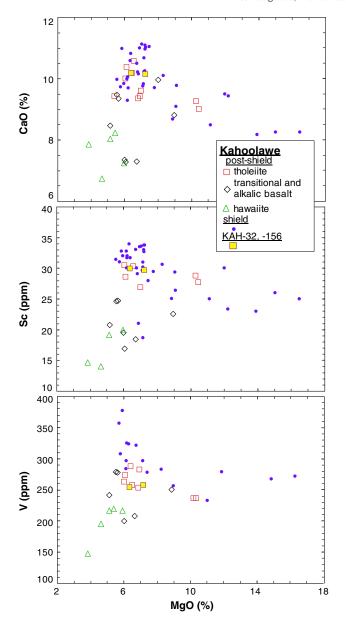


Fig. 7. MgO (%) vs. CaO (%), Sc (ppm) and V (ppm) for Kahoolawe shield- and postshield-stage lavas. Data are from Fodor et al. (1992), Leeman et al. (1994), Huang et al. (2005a), this study.

The above models require partial melts of garnet pyroxenite/eclogite to have distinctive geochemical signatures, such as low CaO and high SiO<sub>2</sub> contents, which in turn entail that garnet pyroxenite/eclogite cannot melt to a large degree (e.g., Pertermann and Hirschmann, 2003). Garnet pyroxentes/eclogites have large ranges in their solidus temperatures, with some refractory ones having solidus temperatures similar to that of peridotites (e.g., Fig. 1 of Phipps Morgan, 2001). However, some eclogites have melting points much lower than that of peridotite. When peridotite begins to melt, these eclogites therefore may have completely melted, and their melts would not have the distinctive geochemical signatures. In order to solve this problem, Sobolev et al. (2005, 2007) proposed a two-stage model for sampling eclogite. During the first stage, low-degree partial melting of eclogite forms SiO<sub>2</sub>-rich eclogite melts, which react with ambient peridotite and replace olivine with pyroxene to form a secondary pyroxenite. During the second stage, mixtures of different proportions of partial melt of this secondary pyroxenite and partial melt of peridotite form the parental magmas of erupted lavas. Alternatively, partial melting of eclogite and peridotite could occur at different parts of a mantle plume. If there is a large thermal gradient within the Hawaiian plume, (e.g., ~200 °C, Ribe and Christensen, 1999), then partial melting of eclogite can occur near the plume edge, where the temperature is low, while partial melting of peridotite takes place near the plume center, where the temperature is higher. Subsequently, partial melts of eclogite and peridotite can mix in a shallow magma chamber at variable proportions.

Based on these observations among various Hawaiian volcanoes and stages of their development, we surmise that the correlations observed for Kahoolawe postshield-stage lavas, albeit weak in some cases, suggest that they, too, reflect mixing between tholeiitic basaltic magmas and partial melts of clinopyroxene-rich mantle source material, such as eclogite/garnet pyroxenite. In support of this argument are the observations that partial melts of eclogite or garnet pyroxenite are characterized by distinctively low contents of Sc and V because of the large proportions of residual clinopyroxene and garnet (e.g., Pertermann and Hirschmann, 2003; Pertermann et al., 2004; Sobolev et al., 2005; Herzberg, 2006; Sobolev et al., 2007). Therefore, the origin of Kahoolawe postshield-stage lavas may have involved more than clinopyroxene segregation (e.g., Fodor and Bauer, 2012) to account for their relatively low MgO, CaO, Sc, and V abundances, particularly for strongly alkali lavas, such as hawaiites. Specifically, we suggest that the low MgO, CaO, Sc, and V endmember in Fig. 8 may represent partial melts from pyroxenite.

The isotope-element expressions at Kahoolawe can be compared with those at the well-studied postshield-stage volcanism at Mauna Kea, for which weak correlations are also apparent, though generally in opposite directions (Fig. 9). For example, Mauna Kea postshield-stage lavas form negative <sup>206</sup>Pb/<sup>204</sup>Pb vs. CaO, Sc and V trends. Additionally, no apparent correlations are observed between <sup>87</sup>Sr/<sup>86</sup>Sr and element abundances. We suggest that these correlations as well may reflect magma-magma mixing, where the low-Sc, -V endmember represents partial melts from eclogite or garnet pyroxenite.

### 4.3. Geochemical structure of the Hawaiian plume: Constraints from Kahoolawe postshield-stage lavas

The geochemical differences between shield lavas erupted by the Loa- and Kea-trend volcanoes (Abouchami et al., 2005) have been used to constrain the spatial distribution of these geochemical heterogeneities within the Hawaiian plume, and may reflect the geochemical heterogeneity at the core-mantle boundary (e.g., Blichert-Toft and Albarède, 2009; Farnetani and Hofmann, 2010; Huang et al., 2011b; Weis et al., 2011; Farnetani et al., 2012). Two primary types of plume structure have been proposed to explain the two-trend phenomena: a bilaterally zoned plume (Abouchami et al., 2005) and a concentrically zoned plume (Lassiter et al., 1996; DePaolo et al., 2001). Variants of these two types of models have also been proposed. Bryce et al. (2005) suggested a radially zoned plume model where a concentrically zoned plume was dragged downstream by the Pacific lithosphere (see Fig. 2 of Xu et al., 2007 for details). Because of plume-lithosphere interaction, the ideal concentrically zoned plume (Lassiter et al., 1996; DePaolo et al., 2001) may not exist. Rather, the radially zoned plume model (Bryce et al., 2005), which takes into account the effect of lithospheric drag, is more realistic. In a variant of the bilaterally zoned plume model, the plume is partially ordered (Fig. 12 of Kurz et al., 2004; Herzberg, 2005). Loa- and Kea-type geochemical heterogeneities are randomly distributed within the plume, but the Loa- and Kea-parts of the plume are statistically different, Lastly, Tanaka et al. (2008) attributed the Loa-trend volcanism to the transient incorporation of an enriched component best sampled by Makapuu-stage Koolau lavas into the upwelling plume; it is yet another variant of the bilaterally zoned plume model.

These models of plume structure are primarily based on shield-stage lava geochemistry, and they can be tested using postshield-stage lavas

(e.g., Xu et al., 2007). Specifically, the concentrically zoned plume model (Lassiter et al., 1996; DePaolo et al., 2001) predicts that both Loa- and Kea-trend postshield-stage lavas have Kea-type isotope compositions (Fig. 2 and Table 7a of Xu et al., 2007). The radially zoned plume model (Bryce et al., 2005) and the bilaterally zoned plume model (Abouchami et al., 2005) predict that Loa-trend postshield-stage lavas have Loa-type isotope compositions and Kea-trend postshield-stage lavas have Kea-type isotope compositions (Fig. 2 and Table 7a of Xu et al., 2007).

This question can be addressed by our new Kahoolawe postshield data along with published data from postshield-stage lavas of several Loa- and Kea-trend volcanoes: Mauna Kea, Kohala, Haleakala, West Maui and East Molokai from the Kea-trend, and Hualalai, Mahukona,

Kahoolawe and West Molokai from the Loa-trend. The isotopic characteristics of these postshield-stage lavas are summarized in Table 2, an updated summary following Xu et al. (2007). The Loa- and Kea-affinities are based on the  $^{208}\text{Pb}/^{204}\text{Pb}-^{206}\text{Pb}/^{204}\text{Pb}$  criterion of Abouchami et al. (2005), with a Loa-Kea discriminator of  $^{208}\text{Pb}*/^{206}\text{Pb}*=0.95$ . Two critical observations can be made:

Overall, Loa- and Kea-trend volcanoes retain their respective Pb isotopic characteristics during their transitions to postshield volcanism (Abouchami et al., 2005; Xu et al., 2005, 2007; Huang et al., 2009; Hanano et al., 2010) even though most volcanoes, such as Haleakala and Mauna Kea from the Kea-trend and Hualalai from the Loa-trend, show a shift toward lower <sup>87</sup>Sr/<sup>86</sup>Sr and higher <sup>143</sup>Nd/<sup>144</sup>Nd.

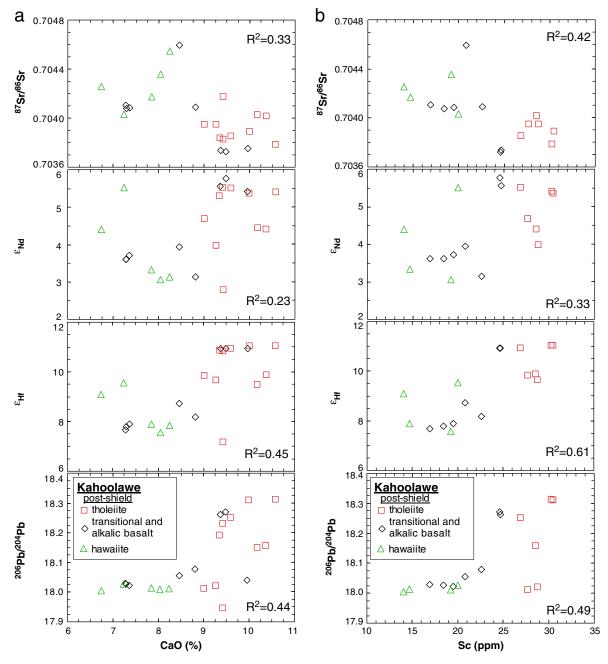


Fig. 8. CaO (%), Sc (ppm) and V (ppm) vs.  $^{87}$ Sr/ $^{86}$ Sr,  $\epsilon_{Nd}$ ,  $\epsilon_{Hf}$  and  $^{206}$ Pb/ $^{204}$ Pb for Kahoolawe postshield-stage lavas. Linear correlation coefficients,  $R^2$ , are given in each panel. Data source: see Fig. 6 caption.

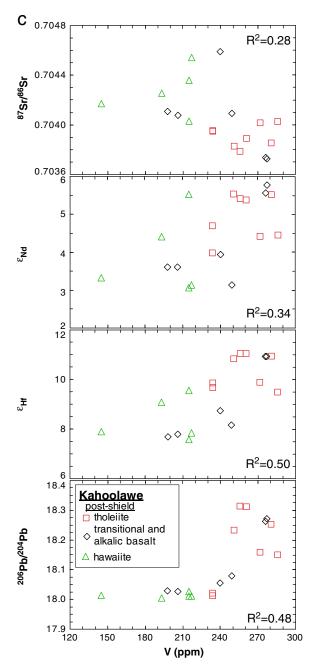


Fig. 8. (continued).

Kahoolawe is an example of shield-to-postshield consistency where its shield- and postshield-stage lavas have overlapping although highly heterogeneous Sr, Nd, Pb and Hf isotope compositions.

2. In the shield- and postshield-stages of some Hawaiian volcanoes, there are examples of mixed Pb isotopic signatures, where the Loatype isotopic signatures are present at Kea-trend volcanoes and the Kea-type isotopic signatures are present at Loa-trend volcanoes (Table 2). Specifically, at Mauna Kea, the HSDP2 low-SiO<sub>2</sub> tholeiitic lavas (Huang and Frey, 2003; Rhodes and Vollinger, 2004) have Loa-type Pb isotope compositions (Eisele et al., 2003; Abouchami et al., 2005). Late shield-stage to postshield-stage lavas (Honomanu lavas) from Haleakala, a Kea-trend volcano (Fig. 1), exhibit both Loa- and Kea-type Pb isotope compositions (Chen et al., 1991; Abouchami and Frey, 2006). Shield-stage lavas from West Molokai

and Mahukona, both Loa-trend volcanoes (Fig. 1), show both Loaand Kea-type Pb isotopic signatures (Xu et al., 2007; Huang et al., 2009; Garcia et al., 2012), while West Molokai postshield-stage lavas clearly show Kea-type isotopic signatures (Xu et al., 2007). Marske et al. (2007) observed co-variations in Sr, Nd and Pb isotope compositions in lavas erupted at Kilauea (Kea-trend volcano) and Mauna Loa (Loa-trend volcano) in the brief period from AD 250 to 1400. Within this period, Kilauea lavas become more Loa-like, and Mauna Loa lavas become more Kea-like.

The observations that Loa-type isotopic signatures are present at Kea-trend volcanoes and Kea-type isotopic signatures are present at Loa-trend volcanoes cannot be explained by any of the proposed plume zoning models, whether concentrically zoned, radially zoned or bilaterally zoned (Fig. 2 and Table 7a of Xu et al., 2007). One explanation for the presence of the Loa-type isotopic signatures in Kea-trend volcanoes and vice versa is vertical heterogeneity within the Hawaiian plume (e.g., Blichert-Toft et al., 2003; Abouchami et al., 2005; Bryce et al., 2005; Blichert-Toft and Albarède, 2009).

Here we present an alternative interpretation, using a stochastic approach similar to that presented by Jacobsen and Yu (2012). Specifically, the plume is composed of two components, Loa-type and Kea-type. Both components are present throughout the plume, but statistically the southern side of the plume contains more of the Loa-type components and the northern side more of the Kea-type components. This is a variant of the partially ordered plume model (Kurz et al., 2004; Herzberg, 2005; Fig. 2d of Xu et al., 2007).

The isotope compositions of erupted lavas are controlled by the relative sizes of the magma capture zone (DePaolo et al., 2001; Farnetani et al., 2012) and the Kea- and Loa-type components (Fig. 10). Here we present a simple example to show how a Loa-trend volcano yields both Loa- and Kea-type lavas, and a dominant Loa-type isotopic signature. The Kea- and Loa-type components have the same size,  $l_h$ , the same Pb abundances, and <sup>208</sup>Pb\*/<sup>206</sup>Pb\* of 1.00 and 0.92, respectively, corresponding to the extreme <sup>208</sup>Pb\*/<sup>206</sup>Pb\* found in Hawaiian lavas (Fig. 12 of Huang et al., 2005a). The plume source contains equal amounts of Loa- and Kea-type components, and an average <sup>208</sup>Pb\*/ <sup>206</sup>Pb\* of 0.96; this is the mantle source for a Loa-trend volcano. Note that, among all geochemical parameters (e.g, Xu et al., 2007) that separate Loa- vs. Kea-type signatures, Pb isotopes are the most telling (Abouchami et al., 2005; Weis et al., 2011). Here we therefore focus on Pb isotopes to best illustrate our model. We use a Monte Carlo simulation approach to investigate the relationship between the <sup>208</sup>Pb\*/  $^{206}\text{Pb}^*$  of the erupted magma and the ratio of  $l_s/l_h$ , where  $l_s$  is the size of the magma capture zone (Fig. 10a). At Hawaii,  $l_s/l_h$  is usually much greater than one (e.g., Farnetani et al., 2012). For example, the magma capture zone usually has a radius of 25-30 km (e.g., DePaolo et al., 2001; Farnetani et al., 2012), and the eclogite body sampled by Koolau lavas may have a size of up to 10 km (Takahashi and Nakajima, 2002; Huang and Frey, 2005). For a given  $l_s/l_h$ , the magma capture zone contains  $(l_s/l_h)^2$  source components (Fig. 10a). Each of these  $(l_s/l_h)^2$  source components is randomly assigned to be Loa- or Kea-type, and the average  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  of these  $(l_s/l_h)^2$  source components is then calculated. We simulated 2000 cases for a given  $l_s/l_h$ , and three  $l_s/l_h$  ratios are considered. The results are given in the <sup>208</sup>Pb\*/<sup>206</sup>Pb\* histograms (Fig. 10b). If the size of the magma capture zone of a volcano is much larger than that of the Kea- and Loa-type components (e.g., the case of  $l_s/l_h = 25$  in Fig. 10b), the compositions of erupted lavas are close to the average composition of the source region. That is, the Loa-trend volcanoes yield lavas with the Loa-type isotopic signature. If the size of the magma capture zone is comparable to that of the Kea- and Loa-type components (e.g., the cases of  $l_s/l_h = 10$  and 6 in Fig. 10b), the erupted lavas could have both Loa- and Kea-type isotopic signatures. That is, lavas with Kea-type isotopic signatures can erupt at Loa-trend volcanoes, but lavas from a Loa-trend volcano have dominantly Loa-type signature.

In our model, we assumed that both Loa- and Kea-type components contribute equally to the melts. However, the Loa-type component with high <sup>208</sup>Pb\*/<sup>206</sup>Pb\* has been argued to be an eclogite/garnet pyroxenite component (e.g., Hauri, 1996; Lassiter and Hauri, 1998; Huang and Frey, 2005; Sobolev et al., 2005; Fekiacova et al., 2007). If it has a lower solidus temperature than the Kea-component, it may contribute proportionally more to the erupted melts than the Kea-component. In this case, all the distributions in Fig. 10b would skew toward higher <sup>208</sup>Pb\*/<sup>206</sup>Pb\*, and the average composition of the erupted melts would have higher <sup>208</sup>Pb\*/<sup>206</sup>Pb\* than the source average. However, this would not significantly affect our conclusion that lavas with Keatype isotopic signatures can erupt at Loa-trend volcanoes. Our model calculation is shown for a Loa-trend volcano, and the same conclusion can be reached for a Kea-trend volcano by changing the proportions of Kea- to Loa-type components in the source.

Therefore, in our model, the long-term geochemical difference between Loa- and Kea-trend volcanoes implies that their magma capture zones are much larger than the sizes of Loa- and Kea-type components for most of their volcanic history. When the size of the magma capture zone is comparable to that of the Loa- and Kea-type components, Loatrend volcanoes can yield lavas with the Kea-type isotopic signature, and vice versa. Although our discussion is based on a bilaterally zoned plume model (Abouchami et al., 2005), it also applies to a radially zoned plume model (Bryce et al., 2005).

#### 5. Conclusions

Unlike some Hawaiian volcanoes, such as Haleakala, Mauna Kea and Hualalai, where the postshield-stage lavas have lower  $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$  and higher  $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$  than the shield-stage lavas, Kahoolawe shield- and

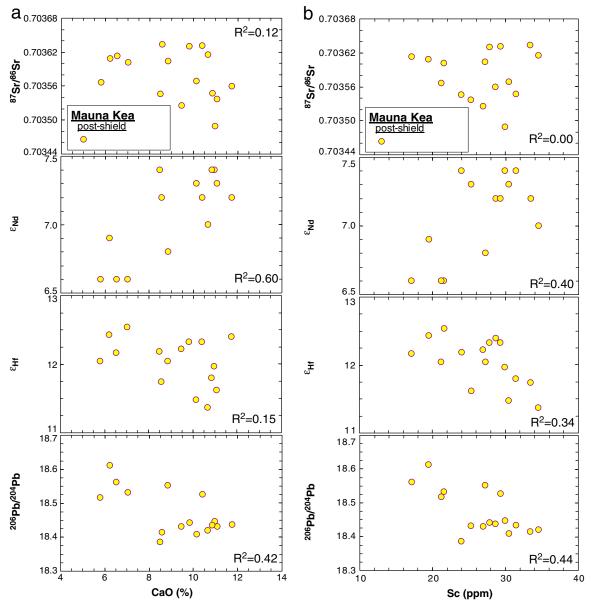


Fig. 9. CaO (%), Sc (ppm) and V (ppm) vs.  $^{87}$ Sr/ $^{86}$ Sr,  $\epsilon_{Nd}$ ,  $\epsilon_{Hf}$  and  $^{206}$ Pb/ $^{204}$ Pb for Mauna Kea postshield-stage lavas recovered by the Hawaii Scientific Drilling Project. Linear correlation coefficients,  $R^2$ , are given in each panel. Data are from: Blichert-Toft et al. (2003), Huang and Frey (2003), Rhodes and Vollinger (2004), Bryce et al. (2005).

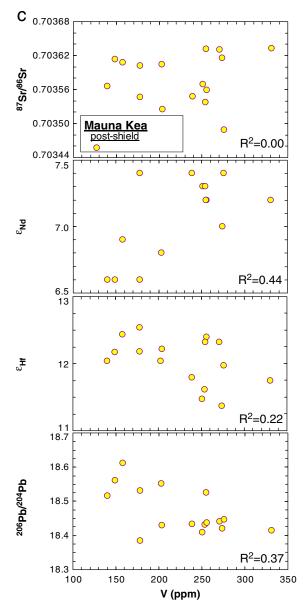


Fig. 9. (continued).

postshield-stage lavas have overlapping Sr, Nd, Hf and Pb isotope compositions, implying that shield and postshield volcanism at Kahoolawe sampled the same isotopically heterogeneous mantle source.

The Kahoolawe tholeiitic "rejuvenated-stage" lavas, which were classified as such by Stearns (1940) and Macdonald (1940), have Sr, Nd, Hf and Pb isotope compositions similar to those of the Kahoolawe shield and postshield lavas. In addition, there is no observable or measurable eruptive hiatus between Kahoolawe postshield lavas and these "rejuvenated-stage" lavas (Sano et al., 2006).

Kahoolawe postshield-stage lavas trend to lower contents of CaO, Sc and V, and these elemental abundances are correlated, albeit weak in some cases, with Sr, Nd, Pb and Hf isotope compositions. Correlations between element abundances and isotope compositions are also observed for Mauna Kea postshield lavas recovered by the Hawaii Scientific Drilling Project. In addition to the traditional interpretation that the lower abundances of CaO, Sc and V of postshield-stage lavas reflect extensive clinopyroxene fractionation, we suggest that partial melts from eclogite or garnet pyroxenite may also have been involved in the petrogenesis of these postshield-stage lavas.

Despite the first-order long-term geochemical difference between Loa- and Kea-trend volcanoes, a small number of Loa-trend lavas are characterized by Kea-type isotopic signatures and vice versa. This could reflect vertical heterogeneity within the Hawaiian plume. Alternatively, it may reflect the relationship between the size of the magma capture zone and that of Loa- and Kea-type components in the Hawaiian plume. Specifically, the Loa- and Kea-type components are distributed throughout the Hawaiian plume to form a partially ordered plume, such that the average source composition of a given volcano is characterized by the isotopic signature of its corresponding trend. When the magma capture zone of a volcano is much larger than the sizes of Loa- and Kea-type components, lavas characterized by the average source compositions are erupted. When the magma capture zone has a size comparable to that of the source components, the erupted lavas could yield both Loa- and Kea-type isotopic signatures. In this scenario, Loa-trend volcanoes may yield lavas with Kea-type isotopic signatures and vice versa.

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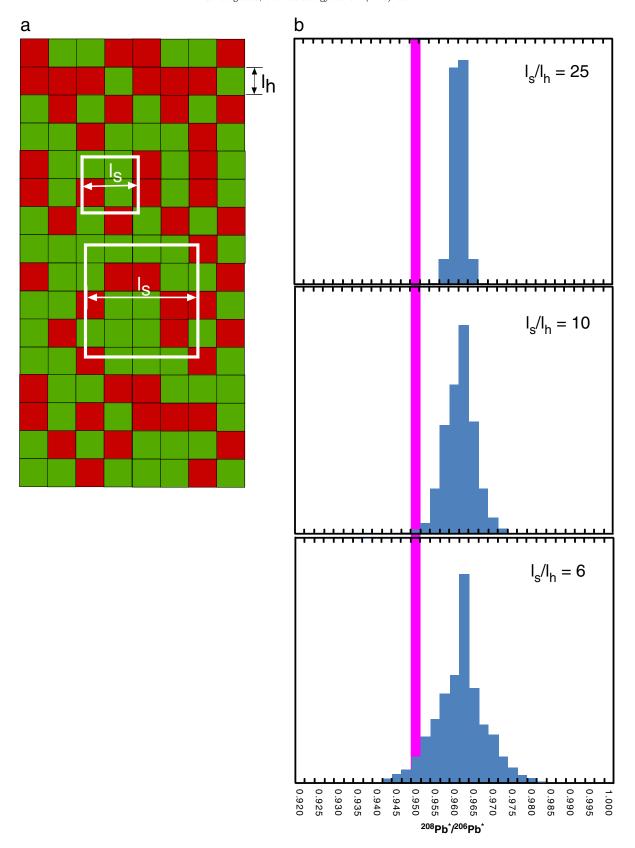
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**Table 2**Observed geochemical characteristics of shield and postshield stage lavas in Hawaiian volcanoes.<sup>a</sup>

	Observed geochemical of	characteristics	Source					
	Shield	Postshield						
Loa-Trend volcanoes								
West Molokai	t Molokai Loa and Kea		Xu et al. (2007)					
Kahoolawe	oolawe Loa		Abouchami et al. (2005), Huang et al. (2005a), this study					
Mahukona	kona Loa and Kea		Huang et al. (2009), Garcia et al. (2012)					
Hualalai	Loa	Loa	Cousens et al. (2003), Yamasaki et al. (2009)					
Kea-Trend volcanoes								
East Molokai	Kea	Kea	Xu et al. (2005)					
West Maui	st Maui Kea		Gaffney et al. (2004)					
Haleakala	Kea	Loa and Kea	Chen et al. (1991), Ren et al. (2006), Abouchami and Frey (2006)					
Kohala	Kea	Kea	Abouchami et al. (2005)					
Mauna Kea Loa and Kea		Kea	Eisele et al. (2003), Abouchami et al. (2005)					

 $<sup>^{\</sup>rm a}\,$  . Updated from Table 7a of Xu et al. (2007).

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**Fig. 10.** (a) Cartoon showing sampling of the mantle source components (red and green squares) with a size of  $l_h$  by a magma capture zone (white rectangle) with a size of  $l_s$ . (b) Histograms of  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  in the erupted magmas simulated by a Monte Carlo method. See text for details. The vertical red line shows  $^{208}\text{Pb}^*/^{206}\text{Pb}^*$  of 0.95, the Loa–Kea discriminator following Abouchami et al. (2005).

#### References

- Abouchami, W., Frey, F.A., 2006. Temporal Evolution of Pb Isotopes in Shield Lavas from Haleakala Volcano. EGU General Assembly.
- Abouchami, W.W., Galer, S.J.G., Hofmann, A.W., 2000. High precision lead isotope systematics of lavas from the Hawaiian Scientific Drilling Project. Chem. Geol. 169, 187–209.
- Abouchami, W., Hofmann, A.W., Galer, S.J.G., Frey, F.A., Eisele, J., Feigenson, M., 2005. Lead isotopes reveal bilateral asymmetry and vertical continuity in the Hawaiian mantle plume. Nature 434, 851–856. http://dx.doi.org/10.1038/nature03402.
- Albarède, F., Télouk, P., Blichert-Toft, J., Boyet, M., Agranier, A., Nelson, B.K., 2004. Precise and accurate isotopic measurements using multiple-collector ICPMS. Geochim. Cosmochim. Acta 68, 2725–2744.
   Basu, A.R., Faggart, B.E., 1996. Temporal isotopic variations in the Hawaiian mantle
- Basu, A.R., Faggart, B.E., 1996. Temporal isotopic variations in the Hawaiian mantle plume: the Lanai anomaly, the Molokai Fracture Zone and a seawater-altered lithospheric component in Hawaiian volcanism. In: Basu, A.R., Hart, S.R. (Eds.), Earth Processes: Reading the Isotopic Code. Geophys. Monogr. Ser., vol. 95. AGU, Washington, D. C., pp. 149–159.Blichert-Toft, J., Albarède, F., 1997. The Lu–Hf isotope geochemistry of chondrites and the
- Blichert-Toft, J., Albarède, F., 1997. The Lu–Hf isotope geochemistry of chondrites and the evolution of the mantle–crust system. Earth Planet. Sci. Lett. 148, 243–258.
- Blichert-Toft, J., Albarède, F., 2009. Mixing of isotopic heterogeneities in the Mauna Kea plume conduit. Earth Planet. Sci. Lett. 282, 190–200. http://dx.doi.org/10.1016/j.epsl.2009.03.015.
- Blichert-Toft, J., Chauvel, C., Albarède, F., 1997. Separation of Hf and Lu for high-precision isotope analysis of rock samples by magnetic sector-multiple collector ICP-MS. Contrib. Mineral. Petrol. 127, 248–260.
- Blichert-Toft, J., Frey, F.A., Albarede, F., 1999. Hf isotope evidence for pelagic sediments in the source of Hawaiian basalts. Science 285 (5429), 879–882.
- Blichert-Toft, J., Weis, D., Maerschalk, C., Agranier, A., Albarède, F., 2003. Hawaiian hot spot dynamics as inferred from the Hf and Pb isotope evolution of Mauna Kea volcano. Geochem. Geophys. Geosyst. 4( (2), 8704. http://dx.doi.org/10.1029/2002GC000340.
- Bryce, J.G., DePaolo, D.J., Lassiter, J.C., 2005. Geochemical structure of the Hawaiian plume: Sr, Nd, and Os isotopes in the 2.8 km HSDP-2 section of Mauna Kea volcano. Geochem. Geophys. Geosyst. 6, Q09G18. http://dx.doi.org/10.1029/2004GC000809.
- Castillo, P.R., Klein, E., Bender, J., Langmuir, C., Shirey, S., Batiza, R., White, W., 2000. Petrology and Sr, Nd, and Pb isotope geochemistry of mid-ocean ridge basalt glasses from the 11°45′N to 15°00′N segment of the East Pacific Rise. Geochem. Geophys. Geosyst. 1. http://dx.doi.org/10.1029/1999GC000024.
- Chen, C.-Y., Frey, F.A., 1985. Trace element and isotope geochemistry of lavas from Haleakala Volcano, East Maui: implications for the origin of Hawaiian basalts. J. Geophys. Res. 90 (B10), 8743–8768.
- Chen, C.-Y., Frey, F.A., Garcia, M.O., Dalrymple, G.B., Hart, S.R., 1991. The tholeiitie to alkalic basalt transition at Haleakala Volcano, Maui, Hawaii. Contrib. Mineral. Petrol. 106, 183–200.
- Clague, D.A., Dalrymple, G.B., 1987. The Hawaiian-Emperor volcanic chain part 1: geologic evolution. In: Decker, R.W., et al. (Eds.), Volcanism in Hawaii. U.S. Geol. Surv. Prof. Pap., 1350, pp. 5–54.
- Cohen, A.S., O'Nions, R.K., Kurz, M.D., 1996. Chemical and isotopic variations in Mauna Loa tholeiites. Earth Planet. Sci. Lett. 143, 111–124.
- Cousens, B.L., Clague, D.A., Sharp, W.D., 2003. Chronology, chemistry, and origin of trachytes from Hualalai Volcano, Hawaii. Geochem. Geophys. Geosyst. 4 (9), 1078. http://dx.doi.org/10.1029/2003GC000560.
- DePaolo, D.J., Bryce, J.G., Dodson, A., Shuster, D.L., Kennedy, B.M., 2001. Isotopic evolution of Mauna Loa and the chemical structure of the Hawaiian plume. Geochem. Geophys. Geosyst. 2 (7). http://dx.doi.org/10.1029/2000GC000139.
- Eisele, J., Abouchami, W., Galer, S.J.G., Hofmann, A.W., 2003. The 320 kyr Pb isotope evolution of Mauna Kea lavas recorded in the HSDP-2 drill core. Geochem. Geophys. Geosyst. 4 (5), 8710. http://dx.doi.org/10.1029/2002GC000339.
- Geosyst. 4 (5), 8710. http://dx.doi.org/10.1029/2002GC000339.

  Farnetani, C.G., Hofmann, A.W., 2010. Dynamics and internal structure of the Hawaiian plume. Earth Planet. Sci. Lett. 295, 231–240.
- Farnetani, C.G., Hofmann, A.W., Class, C., 2012. How double volcanic chains sample geochemical anomalies from the lowermost mantle. Earth Planet. Sci. Lett. 359-360, 240-247. http://dx.doi.org/10.1016/j.epsl.2012.09.057.
- Fekiacova, Z., Abouchami, W., Galer, S.J.G., Garcia, M.O., Hofmann, A.W., 2007. Origin and temporal evolution of Ko'olau volcano, Hawai'i: inferences from isotope data on the Ko'olau Scientific Drilling Project (KSDP), the Honolulu Volcanics and ODP Site 843. Earth Planet. Sci. Lett. 261, 65–83.
- Fodor, R.V., Bauer, G.R., 2010. Kahoolawe Island, Hawaii: the role of an "inaccessible" shield volcano in the petrology of the Hawaiian islands and plume. Chem. Erde. http://dx.doi.org/10.1016/j.chemer.2010.01.001.
- Fodor, R.V., Bauer, G.R., 2012. Did Kahoolawe volcano, Hawaii, evolve to alkalic composition magmatism? J. Geol. 120, 191–202.
- Fodor, R.V., Frey, F.A., Bauer, G.R., Clague, D.A., 1992. Ages, rare-earth element enrichment, and petrogenesis of tholeitic and alkalic basalts from Kahoolawe Island, Hawaii. Contrib. Mineral. Petrol. 110, 442–462.
- Frey, F.A., Wise, W.S., Garcia, M.O., West, H., Kwon, S.-T., Kennedy, A., 1990. Evolution of Mauna Kea Volcano, Hawaii: petrologic and geochemical constrains on postshield volcanism. J. Geophys. Res. 95, 1271–1300.
  Frey, F.A., Garcia, M.O., Wise, W.S., Kennedy, A., Gurriet, P., Albarède, F., 1991. The evolu-
- Frey, F.A., Garcia, M.O., Wise, W.S., Kennedy, A., Gurriet, P., Albarède, F., 1991. The evolution of Mauna Kea Volcano, Hawaii: petrogenesis of tholeitic and alkalic basalts. J. Geophys. Res. 96, 14347–14375.
- Frey, F.A., Clague, D.A., Mahoney, J.J., Sinton, J.M., 2000. Volcanism at the edge of the Hawaiian plume; petrogenesis of submarine alkalic lavas from the North Arch volcanic field. J. Petrol. 41 (5), 667–691.
- Gaffney, A.M., Nelson, B.K., Blichert-Toft, J., 2004. Geochemical constraints on the role of oceanic lithosphere in intra-volcano heterogeneity at West Maui. Hawaii. J. Petrol. 45, 1663–1687.

- Gaffney, A.M., Nelson, B.K., Blichert-Toft, J., 2005. Melting in the Hawaiian plume at 1–2 Ma as recorded at Maui Nui: the role of eclogite, peridotite, and source mixing. Geochem. Geophys. Geosyst. 6, Q10L11. http://dx.doi.org/10.1029/2005GC000927.
- Galer, S.J.G., O'Nions, R.K., 1985. Residence time of thorium, uranium and lead in the mantle with implications for mantle convection. Nature 316, 778–782.
- Garcia, M.O., Jorgenson, B.A., Mahoney, J.J., Ito, E., Irving, A.J., 1993. An evaluation of temporal geochemical evolution of Loihii summit lavas: results from Alvin submersible dives. J. Geophys. Res. 98, 535–550.
- Garcia, M.O., Foss, D.J.P., West, H.B., Mahoney, J.J., 1995. Geochemical and isotopic evolution of Loihi Volcano, Hawaii. J. Petrol. 36, 1647–1671.
- Garcia, M.O., Rubin, K.H., Norman, M.D., Rhodes, J.M., Graham, D.W., Muenow, D.W., Spencer, K., 1998. Petrology and geochronology of basalt breccia from the 1996 earthquake swarm of Loihi Seamount, Hawaii; magmatic history of its 1996 eruption. Bull. Volcanol. 59, 577–592.
- Garcia, M.O., Swinnard, L., Weis, D., Greene, A.R., Tagami, T., Sano, H., Gandy, C.E., 2010. Petrology, geochemistry and geochronology of Kaua'l lavas over 4.5 Myr: implications for the origin of rejuvenated volcanism and the evolution of the Hawaiian plume. J. Petrol. 51 (7), 1507–1540. http://dx.doi.org/10.1093/petrology/egq027.
- Garcia, M.O., Hanano, D., Flinders, A., Weis, D., Ito, G., Kurz, M.D., 2012. Age, geology, geophysics, and geochemistry of Mahukona Volcano, Hawai'i. Bull. Volcanol. 74, 1445–1463. http://dx.doi.org/10.1007/s00445-012-0602-4.
- Hanano, D., Weis, D., Scoates, J.S., Aciego, S., DePaolo, D.J., 2010. Horizontal and vertical zoning of heterogeneities in the Hawaiian mantle plume from the geochemistry of consecutive postshield volcano pairs: Kohala-Mahukona and Mauna Kea-Hualalai. Geochem. Geophys. Geosyst. 11, Q01004. http://dx.doi.org/10.1029/ 2009GC002782.
- Hart, S.R., Dunn, T., 1993. Experimental cpx/melt partitioning of 24 trace elements. Contrib. Mineral. Petrol. 113, 1–8.
- Hauri, E.H., 1996. Major-element variability in the Hawaiian mantle plume. Nature 382, 415–419.
- Herzberg, C., 2005. Mantle geochemistry: big lessons from little droplets. Nature 436, 789–790.
- Herzberg, C., 2006. Petrology and thermal structure of the Hawaiian plume from Mauna Kea volcano. Nature 440, 605–609.
- Hofmann, A.W., Feigenson, M.D., Raczek, I., 1987. Kohala revisited. Contrib. Mineral. Petrol. 95, 114–122.
- Huang, S., Frey, F.A., 2003. Trace element abundances of Mauna Kea basalt from Phase 2 of the Hawaii Scientific Drilling Project: petrogenetic implications of correlations with major element content and isotopic ratios. Geochem. Geophys. Geosyst. 4 (6), 8711. http://dx.doi.org/10.1029/2002GC000322.
- Huang, S., Frey, F.A., 2005. Recycled oceanic crust in the Hawaiian plume: evidence from temporal geochemical variations within the Koolau shield. Contrib. Mineral. Petrol. 149, 556–575. http://dx.doi.org/10.1007/s00410-005-0664-9.
- Huang, S., Frey, F.A., Blichert-Toft, J., Fodor, R.V., Bauer, G.R., Xu, G., 2005a. Enriched components in the Hawaiian plume: evidence from Kahoolawe Volcano, Hawaii. Geochem. Geophys. Geosyst. 6, Q11006. http://dx.doi.org/10.1029/2005GC001012.
- Huang, S., Regelous, M., Thordarson, T., Frey, F.A., 2005b. Petrogenesis of lavas from Detroit Seamount: geochemical differences between Emperor Chain and Hawaiian volcanoes. Geochem. Geophys. Geosyst. 6, Q01L06. http://dx.doi.org/10.1029/ 2004GC000756.
- Huang, S., Abouchami, W., Blichert-Toft, J., Clague, D.A., Cousens, B.L., Frey, F.A., Humayun, M., 2009. Ancient carbonate sedimentary signature in the Hawaiian plume: evidence from Mahukona volcano, Hawaii. Geochem. Geophys. Geosyst. 10, Q08002. http://dx.doi.org/10.1029/2009GC002418.
- Huang, S., Farkaš, J., Jacobsen, S.B., 2011a. Stable calcium isotopic compositions of Hawaiian shield lavas: evidence for recycling of ancient marine carbonates into the mantle. Geochim. Cosmochim. Acta 75, 4987–4997. http://dx.doi.org/10.1016/ j.gca.2011.06.010.
- Huang, S., Hall, P.S., Jackson, M.G., 2011b. Geochemical zoning of volcanic chains associated with Pacific hotspots. Nat. Geosci. 4, 874–878. http://dx.doi.org/10.1038/ngeo1263.
- Jackson, E.D., Silver, E.A., Dalrymple, G.B., 1972. Hawaiian-Emperor chain and its relation to Cenozoic circumpacific tectonics. Geol. Soc. Am. Bull. 83, 601–617.Jackson, M.G., Weis, D., Huang, S., 2012. Major element variations in Hawaiian shield
- Jackson, M.G., Weis, D., Huang, S., 2012. Major element variations in Hawaiian shield lavas: source features and perspectives from global ocean island basalt (OIB) systematic. Geochem. Geophys. Geosyst. 13, Q09009. http://dx.doi.org/10.1029/ 2012GC004268.
- Jacobsen, S.B., Yu, G., 2012. Extinct isotope heterogeneities in the mantles of Earth and Mars: implications for mantle stirring rates. Lunar Planet. Sci. Conf. 43rd Abstract #2210.
- Kurz, M.D., Kenna, T.C., Kammer, D.P., Rhodes, J.M., Garcia, M.O., 1995. Isotopic evolution of Mauna Loa volcano: a view from the submarine southwest rift Mauna Loa: a decade volcano. In: Rhodes, J.M., Lockwood, J.P. (Eds.), Mauna Loa Revealed. Geophys. Monogr. Ser., vol. 92. AGU, Washington, D.C., pp. 289–306.
- Kurz, M.D., Curtice, J., Lott III, D.E., Solow, A., 2004. Rapid helium isotopic variability in Mauna Kea shield lavas from the Hawaiian Scientific Drilling Project. Geochem. Geophys. Geosyst. 5, Q04G14. http://dx.doi.org/10.1029/2002GC000439.Lassiter, J.C., Hauri, E.H., 1998. Osmium-isotope variations in Hawaiian lavas: evidence for
- Lassiter, J.C., Hauri, E.H., 1998. Osmium-isotope variations in Hawaiian lavas: evidence for recycled oceanic lithosphere in the Hawaiian plume. Earth Planet. Sci. Lett. 164, 483-496
- Lassiter, J.C., DePaolo, D.J., Tatsumoto, M., 1996. Isotopic evolution of Mauna Kea volcano: results from the initial phase of the Hawaiian Scientific Drilling Project. J. Geophys. Res. 101, 11,769–11,780.
- Lassiter, J.C., Hauri, E.H., Reiners, P.W., Garcia, M.O., 2000. Generation of Hawaiian posterosional lavas by melting of a mixed lherzolite/pyroxenite source. Earth Planet. Sci. Lett. 178 (3–4), 269–284.

- LeBas, M.J., Lemaitre, R.W., Streckeisen, A., Zanettin, B., 1986. A chemical classification of volcanic-rocks based on the total alkali silica diagram. J. Petrol. 27 (3), 745–750.
- Leeman, W.P., Gerlach, D.C., Garcia, M.O., West, H.B., 1994. Geochemical variation in lavas from Kahoolawe volcano, Hawaii: evidence for open system evolution of plumederived magmas. Contrib. Mineral. Petrol. 116, 62–77.
- Macdonald, G.A., 1940. Petrography of Kahoolawe. Hawaii Div. Hydrogr. Bull. 6, 149–173.
  Marske, J.P., Pietruszka, A.J., Weis, D., Garcia, M.O., Rhodes, J.M., 2007. Rapid passage of a small-scale mantle heterogeneity through the melting regions of Kilauea and Mauna Loa Volcanoes. Earth Planet. Sci. Lett. 259, 34–50. http://dx.doi.org/10.1016/iensl.2007.04.026
- Mukhopadhyay, S., Lassiter, J.L., Farley, K.A., Bogue, S.W., 2003. Geochemistry of Kauai shield-stage lavas: implications for the chemical evolution of the Hawaiian plume. Geochem. Geophys. Geosyst. 4 (1), 1009. http://dx.doi.org/10.1029/2002GC 000342.
- Niu, Y., Collerson, K.D., Batiza, R., Wendt, J.I., Regelous, M., 1999. Origin of enriched-type mid-ocean ridge basalt at ridges far from mantle plumes; the East Pacific Rise at 11 degrees 20'N. J. Geophys. Res. 104 (4), 7067–7087.
- Nobre Silva, I.G., Weis, D., Scoates, J.S., 2013. Isotopic systematics of the early Mauna Kea shield phase and insight into the deep mantle beneath the Pacific Ocean. Geochem. Geophys. Geosyst. 14, 659–676.
- Ozawa, A., Tagami, T., Garcia, M.O., 2005. Unspiked K-Ar ages of Honolulu rejuvenated and Koolau shield volcanism on Oahu. Hawaii. Earth Planet. Sci. Lett. 232. 1–11.
- Pertermann, M., Hirschmann, M.M., 2003. Anhydrous partial melting experiments on MORB-like eclogite: phase reactions, phase compositions and mineral-melt partitioning of major elements at 2–3 GPa. J. Petrol. 44, 2173–2201.
- Pertermann, M., Hirschmann, M.M., Hametner, K., Günther, D., Schmidt, M.W., 2004. Experimental determination of trace element partitioning between garnet and silicarich liquid during anhydrous partial melting of MORB-like eclogite. Geochem. Geophys. Geosyst. 5, Q05A01. http://dx.doi.org/10.1029/2003GC000638.
- Phipps Morgan, J., 2001. Thermodynamics of pressure release melting of a veined plum pudding mantle. Geochem. Geophys. Geosyst. 2 (paper number 2000GC000049).
- Pietruszka, A.J., Norman, M.D., Garcia, M.O., Marske, J.P., Burns, D.H., 2013. Chemical heterogeneity in the Hawaiian mantle plume from the alteration and dehydration of recycled oceanic crust. Earth Planet. Sci. Lett. 361, 298–309. http://dx.doi.org/10.1016/j.epsl.2012.10.030.
- Regelous, M., Niu, Y., Wendt, J.I., Batiza, R., Greig, A., Collerson, K.D., 1999. Variations in the geochemistry of magmatism on the East Pacific Rise at 10 degrees 30'N since 800 ka. Earth Planet. Sci. Lett. 168 (1–2), 45–63.
- Ren, Z.Y., Shibata, T., Yoshikawa, M., Johnson, K.T.M., Takahashi, E., 2006. Isotope compositions of submarine Hana Ridge lavas, Haleakala volcano, Hawaii: Implications for source compositions, melting process and the structure of the Hawaiian plume. J. Petrol. 47, 255–275.
- Reiners, P.W., 2002. Temporal-compositional trends in intraplate basalt eruption: implications for mantle heterogeneity and melting processes. Geochem. Geophys. Geosyst. 3 (2). http://dx.doi.org/10.1029/2001GC000250.
- Rhodes, J.M., Vollinger, M.J., 2004. Composition of basaltic lavas sampled by phase-2 of the Hawaii Scientific Drilling Project: geochemical stratigraphy and magma types. Geochem. Geophys. Geosyst. 5, Q03G13. http://dx.doi.org/10.1029/2002GC000434.
- Ribe, N.M., Christensen, U.R., 1999. The dynamical origin of Hawaiian volcanism. Earth Planet. Sci. Lett. 171, 517–531.
- Roden, M.F., Frey, F.A., Clague, D.A., 1984. Geochemistry of tholeitic and alkalic lavas from the Koolau Range, Oahu, Hawaii; implications for Hawaiian volcanism. Earth Planet. Sci. Lett. 69 (1), 141–158.
- Roden, M.F., Trull, T., Hart, S.R., Frey, F.A., 1994. New He, Sr, Nd and Pb isotopic constraints on the constitution of the Hawaiian plume: results from Koolau Volcano, Oahu, Hawaii. Geochim. Cosmochim. Acta 58, 1431–1440.

- Salters, V.J.M., Blichert-Toft, J., Fekiacova, Z., Sachi-Kocher, A., Bizimis, M., 2006. Isotope and trace element evidence for depleted lithosphere in the source of enriched Koolau basalts. Contrib. Mineral. Petrol. 151, 297–312.
- Sano, H., Sherrod, D.R., Tagami, T., 2006. Youngest volcanism about 1 million years ago at Kahoolawe Island, Hawaii. J. Volcanol. Geotherm. Res. 152, 91–96.
- Sobolev, A.V., Hofmann, A.W., Sobolev, S.V., Nikogosian, I.K., 2005. An olivine-free mantle source of Hawaiian shield basalts. Nature 434, 590–597.
- Sobolev, A.V., Hofmann, A.W., Kuzmin, D.V., Yaxley, G.M., Arndt, N.T., Chung, S.-L., Danyushevsky, L.V., Elliott, T., Frey, F.A., Garcia, M.O., Gurenko, A.A., Kamenetsky, V.S., Kerr, A.C., Krivolutskaya, N.A., Matvienkov, V.V., Nikogosian, I.K., Rocholl, A., Sigurdsson, I.A., Sushchevskaya, N.M., Teklay, M., 2007. The amount of recycled crust in source of mantle-derived melts. Nature 316, 412-417.
- Stearns, H.T., 1940. Geology and groundwater resources of the islands of Lanai and Kahoolawe, Hawaii. Hawaii Div. Hydrogr. Bull. 6 (3–95), 119–147.
- Stille, P., Unruh, D.M., Tatsumoto, M., 1983. Pb, Sr, Nd and Hf isotopic evidence of multiple sources for Oahu, Hawaii basalts. Nature 304 (5921), 25–29.
- Takahashi, E., Nakajima, K., 2002. Melting process in the Hawaiian Plume; an experimental study. In: Takahashi, E., Lipman, P.W., Garcia, M.O., Naka, J., Aramaki, S. (Eds.), Hawaiian volcanoes; deep underwater perspectivesGeophys. Monogr. Ser. 128, 403–418.
- Tanaka, R., Makishima, A., Nakamura, E., 2008. Hawaiian double volcanic chain triggered by an episodic involvement of recycled material: constraints from temporal Sr-Nd-Hf-Pb isotopic trend of the Loa-type volcanoes. Earth Planet. Sci. Lett. 265, 450-465.
- Tatsumoto, M., Hegner, E., Unruh, D.M., 1987. Origin of the West Maui volcanic rocks inferred from Pb, Sr, and Nd isotopes and a multicomponent model for oceanic basalt. In: Decker, R.W., Wright, T.L., Stauffer, P.H. (Eds.), Volcanism in Hawaii. U.S. Geological Survey Professional Paper, 1350, II, pp. 723–744.
- Vervoort, J.D., Plank, T., Prytulak, J., 2011. The Hf–Nd isotopic composition of marine sediments. Geochim. Cosmochim. Acta 75, 5903–5926.
- Weis, D., Garcia, M.O., Rhodes, J.M., Jellinek, M., Scoates, J.S., 2011. Role of the deep mantle in generating the compositional asymmetry of the Hawaiian mantle plume. Nat. Geosci. 4, 831–838.
- West, H.B., Gerlach, D.C., Leeman, William P., Garcia, Michael O., 1987. Isotopic constraints on the origin of Hawaiian lavas from the Maui volcanic complex, Hawaii. Nature 330 (6145), 216–220.
- White, W.M., Albarède, F., Télouk, P., 2000. High-precision analysis of Pb isotopic ratios using multi-collector ICP-MS. Chem. Geol. 167, 257–270.
- Xu, G., Frey, F.A., Clague, D.A., Weis, D., Beeson, M.H., 2005. East Molokai and other Kea-trend volcanoes: magmatic processes and sources as they migrate away from the Hawaiian hot spot. Geochem. Geophys. Geosyst. 6, 2Q05008. http:// dx.doi.org/10.1029/2004GC000830.
- Xu, G., Frey, F.A., Clague, D.A., Abouchami, W., Blichert-Toft, J., Cousens, B., Weisler, M., 2007. Geochemical characteristics of West Molokai shield-and postshield-stage lavas: constraints on Hawaiian plume models. Geochem. Geophys. Geosyst. 8, Q08G21. http://dx.doi.org/10.1029/2006GC001554.
- Yamasaki, S., Kani, T., Hanan, B.B., Tagami, T., 2009. Isotopic geochemistry of Hualalai shield-stage tholeiitic basalts from submarine North Kona region, Hawaii. J. Volcanol. Geotherm. Res. 185, 223–230. http://dx.doi.org/10.1016/ j.jvolgeores.2009.06.006.
- Yang, H.-J., Frey, F.A., Rhodes, J.M., Garcia, M.O., 1996. Evolution of Mauna Kea volcano: inferences from lava compositions recovered in the Hawaii Scientific Drilling Project. J. Geophys. Res. 101, 11,747–11,767.