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Tungsten in Hawaiian picrites: A compositional model for the sources of Hawaiian lavas

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Abstract

Concentrations of tungsten (W) and uranium (U), which represent two of the most highly incompatible elements during mantle melting, have been measured in a suite of Hawaiian picrites and primitive tholeiites from nine main-stage shield volcanoes. Tungsten abundances in the parental melts are estimated from correlations between sample W abundances and MgO contents, and/or by olivine correction calculations. From these parental melt determinations, along with independent estimates for the degree of partial melting at each volcanic center, we extrapolate the W content of the mantle sources for each shield volcano. The mantle sources of Hualalai, Mauna Loa, Kohala, Kilauea, Mauna Kea, Koolau and Loihi contain 9 ± 2 (2σ), 11 ± 5, 10 ± 4, 12 ± 4, 10 ± 5, 8 ± 7 and 11 ± 5 ng/g, respectively. When combined, the mean Hawaiian source has an average of 10 ± 3 ng/g W, which is three-times as enriched as the Depleted MORB Mantle (DMM; 3.0 ± 2.3 ng/g).

The relatively high abundances of W in the mantle sources that contribute to Hawaiian lavas may be explained as a consequence of the recycling of W-rich oceanic crust and sediment into a depleted mantle source, such as the depleted MORB mantle (DMM). However, this scenario requires varying proportions of recycled materials with different mean ages to account for the diversity of radiogenic isotope compositions observed between Kea- and Loa-trend volcanoes. Alternatively, the modeled W enrichments may also reflect a primary source component that is less depleted in incompatible trace elements than the DMM. Such a source would not necessarily require the addition of recycled materials, although the presence of some recycled crust is permitted within our model parameters and likely accounts for some of the isotopic variations between volcanic centers.

The physical admixture of $\leqslant$0.5 wt.% outer core material with the Hawaiian source region would not be resolvable via W source abundances or W/U ratios; however, W isotopes may provide a more sensitive to this mixing process. Recent W isotopic studies show no indication of core–mantle interaction, indicating that either such a process does not occur, or that mechanisms other than physical mixing may operate at the core–mantle boundary.

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1. INTRODUCTION

The distinct geochemical behaviour of tungsten (W) makes this element particularly suitable for addressing a range of geologic phenomena, including constraining the proportion of recycled crustal materials in mantle source regions and identifying potential core–mantle interactions in ocean island basalts (OIB). Tungsten behaves as a moderately siderophile (iron-loving) element under reducing conditions, which has resulted in the sequestration of $\geqslant$90% of the terrestrial W budget into the core (Jagoutz et al., 1979; Sun, 1982; Newsom and Palme, 1984; Newsom et al., 1996; McDonough, 2003). Under the more oxidized conditions prevalent in the silicate portion of the Earth, however, W behaves as a highly incompatible element and strongly partitions into liquid phases during mantle melting. Consequently, core–mantle segregation and the production of oceanic and continental crust has depleted the mantle in W. Due to the large contrast in W abundances between the mantle and both the crust and core, W concentrations and elemental ratios may provide useful geochemical tracers of physical mixing between these reservoirs (Arevalo and McDonough, 2008).

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The Hawaiian source, which represents the greatest mantle buoyancy flux (Sleep, 1990) and hottest potential temperature (e.g., Putirka, 2008) of any modern intraplate ocean island, serves as an archetype of OIB volcanism. Consequently, primitive Hawaiian lavas may provide new insight to the utility of W as a geochemical tracer for both crustal recycling and core–mantle interactions. There is abundant geochemical support for the incorporation of recycled oceanic crustal materials into the mantle sources of the Hawaiian main-shield stage volcanoes (e.g., Eiler et al., 1996; Bennett et al., 1996; Hauri, 1996; Hofmann and Jochum, 1996; Lassiter and Hauri, 1998; Blichert-Toft and Albarede, 1999; Sobolev et al., 2000, 2005). The source region of the Hawaiian shield volcanoes has also been suggested to extend as deep as the core–mantle boundary, based on geophysical evidence (e.g., Russell et al., 1998; Zhao, 2001; Courtillot et al., 2003; Montelli et al., 2004), as well as geochemical evidence based on Os isotopes and Fe/Mn ratios (e.g., Brandon et al., 1999; Humayun et al., 2004). Tungsten isotopes have been implicated as a useful proxy to assess a potential core contribution to the Hawaiian source (Scherstén et al., 2004; Hawkesworth and Scherstén, 2007). Although W studies have not identified a core signature in Hawaiian lavas, an important aspect of W isotopic modeling is the accurate estimation of W abundances in the mantle sources.

Traditionally, the budget of W in mantle reservoirs (e.g., Newsom and Palme, 1984; Newsom et al., 1986; Sims et al., 1990; Arevalo and McDonough, 2008) and the continental crust (e.g., Rudnick and Gao, 2003; Hu and Gao, 2008) has hinged on relating well-established lithophile element abundances (e.g., Ba, Th and U) to W via relatively constant concentration ratios in mid-ocean ridge basalts (MORB), mantle peridotites and crustal samples. Here, we report W and U concentrations for a suite of Hawaiian picritic lavas that represent primitive melts from the Hawaiian source region. As both W and U are highly incompatible elements, the relative abundances of these elements in a partial melt of the mantle reflect the composition of the source. The main objective of this study is to constrain the abundance of W in the mantle sources that feed the Hawaiian main-stage shield volcanoes by relating sample W concentrations to that of an estimated parental melt for each volcanic center. By establishing the mantle source abundances of W, we seek to evaluate the processes that may have contributed to these sources.

2. SAMPLES AND METHODS

The suite of picrites ($\geqslant 13$ wt.% MgO; $n = 22$) and associated tholeiitic basalts (9–12 wt.% MgO; $n = 4$) examined here include some of the most primitive melts from the Hawaiian source region and spans a wide range in MgO, indicative of both olivine removal (low-MgO) and accumulation (high-MgO; Norman and Garcia, 1999). The picrites were derived from high density melts that erupted on the flanks of the main-stage shield volcanoes and bypassed the summit reservoirs (Garcia et al., 1995). Hence, these lavas are less likely to have been affected by fractionation and/or assimilation processes that may operate in high-level magma chambers (Norman and Garcia, 1999), and thus are the best samples available to constrain the abundances of highly incompatible elements (e.g., W and U) in the mantle sources of Hawaiian lavas. Samples were obtained from submersible dives and submarine dredge hauls that sampled the flanks of the Hawaiian volcanoes, as well as from subaerial collection (Table 1). Nine volcanic centers are represented here, including Mauna Kea, Mauna Loa, Hualalai, Loihi, Kilauea, Koolau, Kohala, Lanai and Molokai. Two high-MgO alkalic basalts (186-5 and 187-1) and a basanitoid (186-11) from Loihi were also analyzed in this study for comparison.

In order to obtain precise concentrations of W and U, glassy and/or microcrystalline sample sections were analyzed via laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) following the analytical procedures of Arevalo and McDonough (2008). The utility and reliability of in situ laser ablation methods for measuring trace elements in geologic materials have been previously validated through numerous analytical studies (e.g., Pearce et al., 1997; Eggins et al., 1998; Norman et al., 1998; Jochum et al., 2005, 2006, 2007). Additionally, LA–ICP-MS methods allow for: (i) the identification and analysis of unaltered sample surfaces; (ii) low analytical blanks; (iii) minimal sample destruction; and, (iv) spatially resolved concentration measurements with typical lower limits of detection in the sub-ng/g range. The rocks examined in this study were analyzed using a New Wave frequency-quintupled Nd-YAG laser (213 nm light) coupled to a Thermo Finnigan Element2 single-collector ICP-MS at the University of Maryland.

Spectral matrix effects, particularly isobaric interferences from potential diatomic oxides, were limited by implementing a standard tuning procedure that maximized the elemental signal (based on ^{43}Ca and ^{232}Th spectra) and minimized oxide production ($^{232}\mathrm{Th}^{16}\mathrm{O}/^{232}\mathrm{Th} < 0.15\%$). Our method monitored four W isotope mass stations (^{182}W, ^{183}W, ^{184}W and ^{186}W) and the ratios of these isotopes in order to ensure that no isobaric interferences hindered our concentration measurements. Non-spectral matrix effects resulting from differences in chemical compositions between the analyte and a standard reference material were accounted for by externally calibrating our W measurements to multiple tholeiitic basalts and our U analyses to a suite of silicate reference glasses spanning a range in concentration. The basaltic standards were measured via solution ICP-MS, including both isotope dilution and high-precision standard addition analyses. Details on the calibration of our trace element analyses and the specific laser and mass spectrometer parameters utilized for the measurements of this study are reported in Arevalo and McDonough (2008).

Following determination of trace element abundances in the glassy and/or microcrystalline matrices, data were corrected to whole rock values by accounting for the dilutional effect of olivine, the only major phenocryst phase present. Olivine phenocrysts analyzed in this study had W and U concentrations at or below our analytical limits of detection (<1.0 ng/g). The modal fraction of olivine in each sample was independently determined by point counting of thin

Table 1
W and U abundance data for Hawaiian picrites.

Volcano	Sample name	MgO_{wr} (wt.%)[e]	W_{glass} (ng/g)	$2\sigma_{\text{m}}$	U_{glass} (ng/g)	$2\sigma_{\text{m}}$	W/U	%ol calc[g]	%ol point count	# points	W_{wr} (ng/g)[h]	$2\sigma_{\text{m}}$	U_{m} (ng/g)	$2\sigma_{\text{m}}$
Mauna Kea														
	MK-1-6[a]	17.24	170	2	307	1	0.55	27	23	500	124	3	225	4
Mauna Loa														
	ML-2-50[a]	19.92	121	3	182	5	0.66	33			81	2	122	4
	ML KAH-1	21.66	171	10	297	26	0.57		34	500	113	10	196	21
	ML 1868-9	21.48	162	3	248	7	0.65		36	1000	103	5	159	8
Hualalai[a]														
	H-2	13.63	114	4	178	5	0.64	20	19	500	91	4	142	5
	H-7[b]	11.23	107	3	177	7	0.60	13	13	500	93	4	155	7
	H-9[b]	11.30	125	5	194	7	0.65	12	14	500	110	5	170	8
	H-11	13.67	113	2	161	4	0.70	18	18	500	92	3	132	4
	H-27	14.91	108	3	165	4	0.65	21			85	3	130	4
	H-P	23.19	102	3	161	5	0.63	40	44	1000	61	2	97	3
	Average olivine[f]	47.73												
Loihi[a]														
	LO-02-02	24.21	265	4	337	11	0.79	40			158	4	202	7
	LO-02-04	26.58	313	6	365	7	0.86	56			139	3	162	4
	158-9	16.57	414	8	763	31	0.54	23			320	9	589	27
	186-5[c]	19.52	352	4	480	10	0.73		30	1000	247	12	336	18
	186-11[d]	13.76	572	11	739	13	0.77		21	1000	452	32	584	37
	187-1[c]	25.16	223	3	308	7	0.72	46			121	3	167	5
	average olivine[f]	46.80												
Kilauea														
	KIL-1-18[a]	13.80	165	5	361	9	0.46		15	1000	140	11	307	24
	KIL-2-3[a]	22.36	184	2	317	4	0.58		40	500	110	6	190	11
	KIL-2-4[a]	22.55	213	3	373	7	0.57	40			127	3	373	8
	KIL-3-1[a]	19.24	230	6	429	8	0.54	33			155	5	288	7
	KIL 1840-2	14.27	230	6	406	16	0.57		21	500	182	17	321	30
	Average olivine[f]	48.15												
Koolau														
	K98-08	17.78	36	4	164	16	0.22		29	500	25	3	116	14
	S497-6[a]	21.55	198	24	306	22	0.65		42	500	115	15	177	16
	S500-5B	21.22	109	2	170	1	0.64	39			67	2	104	2

(*continued on next page*)

Table 1 (*continued*)

Volcano	Sample name	MgO_{wr} (wt.%)[e]	W_{glass} (ng/g)	$2\sigma_m$	U_{glass} (ng/g)	$2\sigma_m$	W/U	%ol calc[g]	%ol point count	# points	W_{wr} (ng/g)[h]	$2\sigma_m$	U_m (ng/g)	$2\sigma_m$
Kohala														
	KO-1-10	13.54	164	4	262	3	0.62		20	500	131	12	210	19
	KO-1-20[b]	9.60	199	10	316	16	0.63	10	10	500	180	11	286	17
	KOH-1-28	20.52	157	5	254	12	0.62	35			102	4	165	8
	Average olivine[f]	47.53												
Lanai														
	LWAW-4	14.48	62	5	121	6	0.51		15	1000	53	6	103	9
	LWAW-7[b]	11-69	79	4	174	7	0.45		9	1000	72	8	158	17
Molokai[a]														
	S501-2	28.96	98	3	212	12	0.46	52	51	500	47	2	102	6

[a] Submarine sample.

[b] Tholeiitic basalt (MgO $<$ 13 wt.%).

[c] Alkali basalt.

[d] Basanitoid.

[e] MgO contents from Ireland et al. (2009) and references therein.

[f] Average olivine MgO content from Ireland et al. (2009).

[g] See Table S1 for correction procedure.

[h] *Example correction calculation:* The matrix for MK-1-6 contains 170 ng/g W and olivine comprises 27% of this sample. The matrix concentration was converted to a whole rock concentration by accounting for the olivine present using the following formula: W(wr) = W(matrix) * (1 − ol%). Following this calculation, the whole rock W concentration for MK-1-6 is 124 ng/g.

sections (between 500 and 1000 points each) and/or mass balance of MgO abundances in the matrix, olivine and whole rock. To test the robustness of these methods, both techniques were applied to several samples with consistent results (see Supplemental Table 1).

The precision of the matrix W and U concentrations were not limited by counting statistics and are typically reported with ⩽5% uncertainty ($2\sigma_m$; external reproducibility), which translates to uncertainties of ⩽6% and ⩽10% in the whole rock calculations via mass balance and point counting respectively. Major element abundances, as well as average olivine compositions, were previously reported by Ireland et al. (2009). The current study includes samples previously examined by Brandon et al. (1999; ML 2-50, ML 1868-9, Lo-02-02, Lo-02-04, H-11, Kil 1-18, KOH 1-28) for which a core contribution was inferred based on coupled enrichments of ^{186}Os and ^{187}Os, as well as three samples analyzed by Scherstén et al. (2004) for their W isotopic compositions.

3. TUNGSTEN IN HAWAIIAN PICRITES

Tungsten and U concentration data and W/U ratios for samples from nine Hawaiian shield volcanoes are presented in Table 1. The calculated whole-rock abundances of W in the Hawaiian picrites range from as low as 25 ng/g (Koolau sample K98-08) up to 452 ng/g (Loihi sample 186-11). The highest W (and U) concentrations were observed in the alkalic basalt (186-5 and 187-1), pre-shield picrite (158-9) and basanitoid (186-11) samples from Loihi, which are representative of the pre-shield stage of volcanism and likely represent different sources and lower degrees of melting than the later shield stage volcanics (Garcia et al., 1995). Koolau sample S500-5B was reported to have been affected by Mn-crust alteration by Ireland et al. (2009); however, the rock section analyzed in this present study was carefully selected to avoid the obvious alteration and no apparent effect was noticed. A duplicate measurement of the matrix of sample H-11, which was previously analyzed by Arevalo and McDonough (2008), was found to be statistically indistinguishable from the previously reported value.

Although the calculated whole-rock W concentrations of the entire Hawaiian picrite suite appear to show no correlation with MgO (a proxy for crystal–liquid fractionation processes), data for several individual volcanic centers show linear trends (Fig. 1a; 2). In general, W abundances decrease with increasing MgO content at each main-stage shield volcano, reflecting the highly incompatible nature of W; Mauna Loa and Koolau appear to serve as exceptions, although each of these volcanoes are represented by only three samples that span a narrow range in MgO.

The W/U ratio of the silicate Earth (0.65 ± 0.45, 2σ) has been demonstrated to be invariant between mantle and crustal sources and is independent of bulk rock MgO, indicating analogous behaviour of these elements during mantle melting and crystal–liquid fractionation (Arevalo and McDonough, 2008). The average W/U ratio of our suite of primitive Hawaiian lavas is 0.62 ± 0.19 (2σ; Fig. 1b), consistent with the terrestrial average. However, Koolau sample K98-08, which has the lowest W concentration (25 ng/g) of the samples analyzed here but a typical U content (115 ng/g), has an anomalously low W/U ratio (W/U = 0.22). This value is outside of the range of our picritic dataset, and is suggestive of a preferential loss of W, perhaps due to alteration effects. Hualalai lavas, in general, have the lowest W abundances (average of 90 ng/g; $n = 6$), but possess normal W/U ratios (0.65 ± 0.06). Conversely, Loihi lavas are characterized by the highest W concentrations (up to 452 ng/g; $n = 6$) and W/U ratios (0.74 ± 0.21), although they reside within the range of variance defined by mantle-derived rocks.

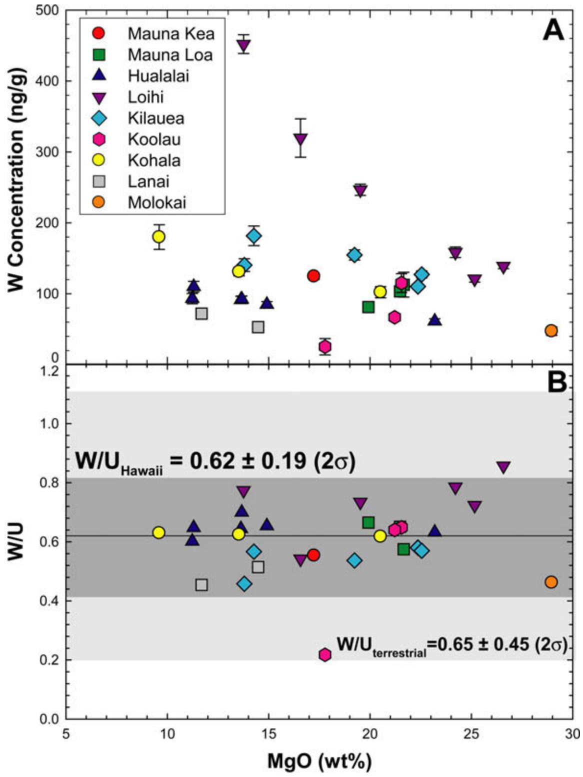

Fig. 1. (A) Tungsten versus MgO content for the primitive Hawaiian lavas analyzed in this study. Tungsten concentrations were determined by high-precision laser ablation ICP-MS following the analytical protocol of Arevalo and McDonough (2008). In general, W abundances decrease with increasing MgO content at each individual volcanic center with ⩾3 samples (with the exception of Koolau). (B) The average W/U ratio of primitive Hawaiian melts (0.62 ± 0.19; dark shaded area) does not vary as a function of MgO and is identical to the terrestrial value established by Arevalo and McDonough (2008; 0.65 ± 0.45; lightly shaded area).

Although visibly fresh rock chips were selected for analysis, several samples show evidence for alteration. Lanai samples LWAW-4 and LWAW-7, and Molokai sample S501-2 have high LOI values, as well as low alkali abundances (Ireland et al., 2009), which are indicative of fluid-rock reactions involving the breakdown of igneous minerals (Crocket, 2000). These three samples also have low W concentrations and W/U ratios, suggesting that W may be affected by this alteration process to a slightly greater extent than U. Sample K98-08 may have been affected by a similar alteration process, although it is not reflected in the LOI or alkali abundances for this sample. Norman and Garcia (1999) noted high LOI contents for Lo-02-02 and Lo-02-04, but concluded that this feature was not due to alteration because Pb isotope, trace element and alkali characteristics were similar to other lavas from Loihi.

4. THE W CONTENT OF HAWAIIAN MANTLE SOURCE REGIONS

To model the mantle source W composition for each volcanic center considered here, various critical parameters must be estimated, including a suitable bulk crystal/melt partition coefficient (*D*) for W during mantle melting, the W content of the parental melts from each volcanic center and the degree of partial melting (*F*). As mentioned previously, W partitions in a similar manner to U during mantle melting, so a bulk crystal/melt partition coefficient of 0.001 is used. This estimate is similar to that determined for U in basaltic melts and partitioning experiments (0.001–0.0001; e.g., http://www.earthref.org/GERM). Sections 4.1 and 4.2 document our procedures for estimating the parental melt compositions for the Hawaiian shield volcanoes, and the degree of partial melting.

4.1. W content of Hawaiian parental melts

Parental melts are primary magmas produced from a mantle source region with minimal fractionation or contamination, and thus, can be used to place constraints on the composition of the source. Based on whole rock MgO and Al_2O_3 relationships of the samples analyzed in this study, in addition to olivine-melt equilibria, the parental melts for all of the Hawaiian shield volcanoes have been established to contain 16 ± 1 (2σ) wt.% MgO (Norman and Garcia, 1999; Ireland et al., 2009). Two different techniques were used to constrain the W content of the Hawaiian parental melts. The first method utilizes a linear regression of the MgO-W trends, as well as the average olivine composition for each volcanic center, to interpolate the W content at the primary MgO content of 16 ± 1 wt.%. The second approach is to individually correct each sample for olivine accumulation or removal to a MgO content of 16 wt.% and take an average of the samples at each volcanic center. The second technique is independent of the shape of the MgO-W trends and is more appropriate for those volcanic centers that do not show a linear correlation or are represented by few samples. For these estimations, it is essential that only those picritic and tholeiitic samples that are most likely to represent a parental melt of similar initial composition are used; therefore, the alkali basalts (186-5 and 187-1), pre-shield picrite (158-9) and the basanitoid (186-11) from Loihi that likely represent a different source from the Loihi shield picrites, as well as samples that may have experienced alteration (i.e., LWAW-4, LWAW-7 and S501-2) are not considered in the following exercise.

4.1.1. *Linear regression of MgO-W trends*

Although the MgO content of Hawaiian picrites vary, primarily as a result of olivine accumulation and/or removal, the W content of the parental melts can be estimated by the intersection between the linear regressions of the MgO-W data and the determined parental melt MgO content of 16 ± 1 wt.% (Fig. 2). Since olivine is the only major phenocryst phase present, these regressions represent olivine control lines and the average composition of co-existing olivine for each volcanic center is also plotted as part of the trend (Fig. 2 and Table 1). As mentioned previously, olivine contains negligible concentrations of W (and U), so the linear regressions should intersect the MgO axis at an equivalent MgO content as the average olivine. This method was employed for four of the Hawaiian shield volcanoes, with the parental melts from Hualalai, Kohala, Kilauea and Loihi estimated to contain 85 ± 6 (2σ), 133 ± 20, 155 ± 21 and 214 ± 10 ng/g W, respectively (Table 2).

4.1.2. *Olivine correction to 16 wt.% MgO*

A second way to determine the W abundance of a Hawaiian parental melt is to individually correct each sample for olivine accumulation or removal to 16 wt.% MgO (e.g., Garcia et al., 1995; Hauri, 1996; Danyushevsky et al., 2000; Huang and Frey, 2003). For samples that have lost olivine (MgO < 16 wt.%), equilibrium olivine was mathematically added in 0.1% increments until the calculated whole rock MgO content reached 16 wt.% MgO following the procedure of Danyushevsky et al. (2000). Likewise, for samples with accumulated olivine, Fo_{90} olivine (corresponding to the most magnesian olivine present in the sample suite) was subtracted from the sample until the whole rock MgO content reached 16 wt.% MgO. In this manner, an average W content for each volcanic center is calculated at an MgO content of 16 wt.%, which is presumed to be representative of the parental melt (Table 2).

The main advantage of this calculation is that it is independent of the shape of the MgO-W trends, so it can be used for those volcanic centers with poor correlations between W and MgO (Mauna Loa, Koolau) and for those volcanic centers with small datasets (Mauna Kea). Following the olivine correction, the parental melts for Hualalai, Mauna Loa, Kohala, Kilauea, Mauna Kea, Koolau and Loihi are determined to contain 83 ± 18 (2σ), 111 ± 40, 129 ± 39, 149 ± 42, 127 ± 46, 104 ± 84 and 185 ± 20 ng/g W, respectively. The parental melt for Mauna Kea, based upon one data point, is estimated to contain 127 ± 46, using the same relative error from Mauna Loa (40%).

Both parental melt estimation techniques were utilized for Hualalai, Kohala, Kilauea and Loihi, with the results of each method producing statistically indistinguishable estimates. Due to the smaller uncertainties on the W content from the MgO-W linear regression method, we use these values for the calculation of source composition.

4.2. Degree of partial melting

The degree of partial melting of the mantle source regions of the Hawaiian shield volcanoes is a key parameter for calculating the W contents of these sources; however, such estimations are far from straightforward and often require making significant assumptions about the initial source composition and/or mineralogy (Feigenson et al.,

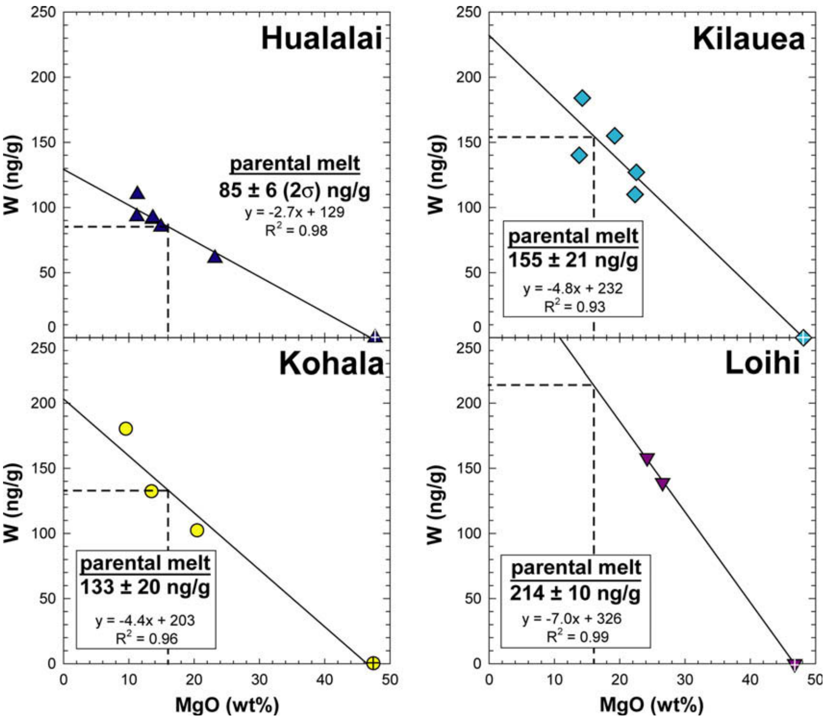

Fig. 2. Estimated concentrations of W (in ng/g) in parental melts from the Hualalai, Kilauea, Kohala and Loihi main-stage shield volcanoes. Tungsten abundances were determined from the intersection of the linear regressions of the data with 16 ± 1 wt.% MgO, the parental melt MgO content as determined by Norman and Garcia (1999) and Ireland et al. (2009). Co-existing olivine, which contains negligible W, is also plotted as part of the MgO-W trends and is denoted by the crossed symbols.

Table 2
Estimates of the source composition of Hawaii from various shield volcano parental melts.

Hawaiian shield volcano	Hualalai	Mauna Loa	Kohala	Kilauea	Mauna Kea	Koolau	Loihi
Method 1							
Parental melt W (ng/g)	85 ± 6	—	133 ± 20	155 ± 21	—	—	214 ± 10
Degree of Partial Melting (F)	7.5–12.5	—	5–10	5–10	—	—	2.5–7.5
Mantle source W (ng/g)	9 ± 2	—	10 ± 4	12 ± 4	—	—	11 ± 5
Linear regression results							
Slope	−2.7 ± 0.2	—	−4.4 ± 0.6	−4.8 ± 0.7	—	—	−7.0 ± 0.1
y-Intercept	129 ± 4	—	203 ± 16	232 ± 18	—	—	326 ± 4
Parental melt U (ng/g)	132 ± 10	—	212 ± 30	290 ± 30	—	—	263 ± 31
Degree of Partial Melting (F)	7.5–12.5	—	5–10	5–10	—	—	2.5–7.5
Mantle source U (ng/g)	13 ± 3	—	16 ± 6	22 ± 8	—	—	13 ± 7
Linear regression results							
Slope	−4.3 ± 0.3	—	−6.9 ± 0.9	−9.2 ± 0.9	—	—	−8.6 ± 0.8
y-Intercept	200 ± 7	—	324 ± 25	437 ± 24	—	—	400 ± 26
Method 2							
Parental Melt W (ng/g)	83 ± 18	111 ± 40	129 ± 39	149 ± 42	127 ± 46	104 ± 84	185 ± 20
Degree of partial melting (F)	7.5–12.5	7.5–12.5	5–10	5–10	5–10	5–10	2.5–7.5
Mantle source W (ng/g)[a]	8 ± 3	11 ± 5	10 ± 4	11 ± 5	10 ± 5	8 ± 7	9 ± 5
Parental melt U (ng/g)	129 ± 27	178 ± 40	206 ± 60	276 ± 77	231 ± 83	161 ± 127	225 ± 51
Degree of partial melting (F)	7.5–12.5	7.5–12.5	5–10	5–10	5–10	5–10	2.5–7.5
Mantle source U (ng/g)[a]	13 ± 4	13 ± 4	15 ± 7	21 ± 9	17 ± 9	12 ± 10	13 ± 7
Averages[b]							
Mantle source W (ng/g)[b]	10 ± 3						
Mantle source U (ng/g)[b]	15 ± 7						

[a] A bulk crystal/melt partition coefficient (*D*) of 0.001 was assumed for both W and U mantle source calculations.

[b] Averages calculated using *Method 1* for Hualalai, Kohala, Kilauea and Loihi and *Method 2* for Mauna Loa, Mauna Kea and Koolau.

2003). The assumptions inherent to melting models introduce a potentially large source of error into our calculations of source W contents, so an appropriate model must be carefully chosen. Several melting models have been suggested for Hawaii, based on different geochemical arguments, including incompatible element abundances (Norman and Garcia, 1999), rare each element (REE) systematics (Feigenson et al., 1996, 2003) and U-series disequilibria (Sims et al. 1995, 1999; Pietruszka et al., 2006).

Norman and Garcia (1999) used relationships between incompatible trace element ratios that are sensitive to the partial melting process, such as La/Yb, Sm/Nd and Lu/Hf, to infer that the degree of partial melting for the Hawaiian picrites was between 4% and 10%. These authors also indicated that the average degree of partial melting increases in the sequence: Loihi < Koolau < Kilauea < Mauna Kea < Kohala ⩽ Hualalai ⩽ Mauna Loa. However, a significant assumption of their melting model involves a common source composition for all the picrites, which they modeled as a mixed spinel and garnet lherzolite source.

In a similar fashion, Feigenson et al. (1996, 2003) used REE inverse modeling to estimate the degree of partial melting necessary to produce Mauna Kea basalts, ranging from alkalic to tholeiitic in composition, in the HSDP drill cores. The primary magmas at Mauna Kea were determined to result from 8% to 15% partial melting of the mantle source for alkalic and tholeiitic basalts, respectively, based on equilibrium and accumulated fractional melting models of calculated primary magmas. Their primary magma for Mauna Kea was estimated to contain 19–21 wt.% MgO, which is higher than other estimates for Hawaiian primary magmas which suggest that Hawaiian primary magmas contain ~16 wt.% MgO (e.g., Hauri, 1996; Norman and Garcia, 1999).

Sims et al. (1995, 1999) examined U-series disequilibria in Hawaiian basalts, ranging from basanitic to tholeiitic in composition, to determine melting zone porosity and mantle upwelling rates in the Hawaiian system. Their modeling indicates that total melt fractions range from 3% for alkali basalts up to 15% for tholeiitic basalts. In a similar study of U-series disequilibria, Pietruszka et al. (2006) modeled Kilauean basalts as a result of an average of 10% partial melting. These melting models assume a constant melt productivity rate, and are reliant on the thickness of the melting zone. U-series disequilibria studies also require an accurate knowledge of eruption age and suitable partition coefficients for U, Th, Ra and Pa in a presumed source mineralogy.

Despite different analytical and theoretical methods, the three melting models outlined above all provide similar estimates of the maximum degrees of partial melting (10–15%). For the purposes of our study, we use the relative degrees of partial melting outlined by Norman and Garcia (1999), coupled with conservative melting ranges (a 5% melting window) for each volcanic center (Table 2). The Norman and Garcia (1999) melting model best describes our picritic sample suite for several reasons: (i) several samples from Norman and Garcia (1999) are included in our current work; (ii) we estimate a similar parental melt MgO content of 16 wt.% (Ireland et al., 2009); and (iii) La/Yb, Lu/Hf and Sm/Nd ratios for each volcanic center (our data; Norman and Garcia, 1999; Gurriet, 1988; see Supplemental Table 2) mirror the trends observed by Norman and Garcia (1999). Accordingly, we model Hualalai and Mauna Loa from 7.5% to 12.5% partial melting, Kohala, Kilauea, Mauna Kea and Koolau from 5% to 10% partial melting and Loihi from 2.5% to 7.5% partial melting.

4.3. W abundances of Hawaiian mantle source regions

To infer the W content for the mantle source regions of the Hawaiian shield volcanoes, an equilibrium batch melting model is employed (e.g., Shaw, 1970):

$$\left(\frac{C_I}{C_o} = \frac{1}{D + (1 - D)F}\right)$$

with the parameters for the bulk partition coefficient (D), parental melt concentration and degree of partial melting (F) outlined above, where C_i and C_o are the parental melt composition and mantle source composition, respectively. Since W behaves incompatibly during mantle melting, aggregated fractional melting and equilibrium melting models yield essentially identical results. Following the equilibrium melting model described above, we generate estimates for the W content of the Hawaiian mantle source regions of 9 ± 2 (2σ), 11 ± 5, 10 ± 4, 12 ± 4, 10 ± 5, 8 ± 7 and 11 ± 5 ng/g for Hualalai, Mauna Loa, Kohala, Kilauea, Mauna Kea, Koolau and Loihi, respectively (Fig. 3 and Table 2).

Overall, the mean W contents of the mantle sources for the Hawaiian shield volcanoes show a limited range of 8–12 ng/g with all calculated source compositions within statistical uncertainty of each other. The similar W concentrations in the mantle sources of each individual Hawaiian shield volcano suggest that the mantle components that contribute to each shield volcano have comparable absolute abundances of W, as well as analogous W/U ratios. Accordingly, the mean Hawaiian source region is determined to have 10 ± 3 (2σ) ng/g W, which is three-times more enriched than the Depleted MORB Mantle (DMM; 3.0 ± 2.3 ng/g W), but comparable to the Primitive Mantle (PM: 13 ± 10 ng/g W; Arevalo and McDonough, 2008). The mean W abundance of the Hawaiian source, as determined in this study, is also consistent with the approximation by Hawkesworth and Scherstén (2007), who estimated the Hawaiian source to contain between 8 and 12 ng/g W based on Th/W ratios of similar picritic samples.

Similarly, the U abundances for the mantle sources of each volcanic center were calculated following the same modeling parameters as outlined above. This calculation not only provides an estimate for mantle source U abundance, but is also an independent test of the consistency of our W modeling. The estimated U abundances for the mantle source regions of Hualalai, Mauna Loa, Kohala, Kilauea, Mauna Kea, Koolau and Loihi are 13 ± 3 (2σ), 13 ± 4, 16 ± 6, 22 ± 8, 17 ± 9, 12 ± 10 and 13 ± 7 ng/g U, respectively, with a mean value of 15 ± 7 ng/g U. These results demonstrate excellent agreement with those derived from W abundances, with the mean Hawaiian mantle source having a W/U ratio of ≈0.65 and an U abundance three-times greater than DMM (4.7 ± 1.4 ng/g U; Salters and Stracke, 2004), but similar to PM (20 ± 8 ng/g U; McDonough and Sun, 1995).

5. ORIGIN OF W IN THE HAWAIIAN SOURCE REGIONS

5.1. Source components in the Hawaiian plume

Typically, three source components are invoked to explain the range of isotopic variations amongst the Hawaiian shield volcanoes (Staudigel et al., 1984; West et al., 1987; Kurz et al., 1996; Eiler et al., 1996). These three end-members are best expressed by lavas from Mauna Kea, Loihi and Koolau (Makapuu-stage lavas). The Kea component is characterized by relatively low ^{87}Sr/^{86}Sr and ^{187}Os/^{188}Os, as well as high ^{143}Nd/^{144}Nd, ^{176}Hf/^{177}Hf and Pb isotopic ratios (Lassiter et al., 1996; Blichert-Toft and Albarede, 1999). Conversely, the Loihi component, which may represent a relatively undepleted deep mantle reservoir, is defined by more radiogenic Sr and Os, and less-radiogenic Nd, Hf and Pb isotopes relative to the Kea component. This end-member is also distinguished by high ^{3}He/^{4}He ratios (Kurz et al., 1983; Mukhopadhyay et al., 2003). The Koolau (Makapuu) component, which is not characterized by any of the samples analyzed here, occupies the isotopic extreme with the highest ^{87}Sr/^{86}Sr and ^{187}Os/^{188}Os, coupled with lowest ^{143}Nd/^{144}Nd, ^{176}Hf/^{177}Hf and Pb isotopic ratios seen in Hawaiian lavas (West et al., 1987; Roden et al., 1994; Hauri, 1996; Lassiter and Hauri, 1998; Blichert-Toft and Albarede, 1999; Huang and Frey, 2005). A fourth component, which may not significantly contribute to the shield stage volcanoes analyzed here, may be required to explain Pb characteristics of some post-shield stage Hawaiian lavas (Abouchami et al., 2000; Mukhopadhyay et al., 2003).

The surface manifestation of the three dominant components of the Hawaiian source region is expressed as two geographically parallel, but geochemically distinct trends, commonly referred to as the Kea- and Loa-trends (e.g., Frey and Rhodes, 1993; Hauri, 1996; Lassiter et al., 1996; Ren et al., 2005). Huang et al. (2005) suggested that the Kea-trend volcanoes (Mauna Kea, Kilauea, Kohala) are dominated by the Kea and Loihi source components with negligible contribution from the Koolau component. The Loa-trend volcanoes (Mauna Loa, Loihi, Hualalai, Lanai, Koolau), on the other hand, are controlled by the Loihi and Koolau components with insignificant contribution from the Kea component. In the following sections, we model the origin of the apparent W enrichment observed in the composite Hawaiian source region.

5.2. Recycled oceanic crust and sediment in Hawaiian mantle sources

5.2.1. Tungsten mobility during subduction

To consider if recycled oceanic crust and sediment may influence the W content of the Hawaiian mantle source regions, the mobility of W during subduction must be addressed. Although Kishida et al. (2004) and Arnórsson and Óskarsson (2007) illustrate that W abundances are positively correlated with highly fluid-mobile elements (e.g., B) and are enriched in hydrothermal fluids relative to ambient seawater, Noll et al. (1996) found that W/Th ratios in a suite of subduction-related magmas: (i) overlap with those of typical OIB and MORB; (ii) do not decrease systematically with distance from the back-arc; and (iii) are independent of B/La ratios (a tracer of fluid flux), suggesting limited (if any) mobilization of W by hydrothermal fluids during subduction. Further, data from Noll (1994) indicate that W/Ba ratios in some arc lavas are actually depleted due to the preferential fluid-mobility of Ba compared to W in hydrothermal systems, and the continental crust is not enriched in W relative to Ba, Th or U, as would be expected if W was significantly more fluid-mobile (such as B, Pb, As and Sb).

König et al. (2008) have recently asserted that W behaves as a fluid-mobile species in hydrothermal systems based on the significant scatter seen in W/Th ratios in a representative sample suite of subduction-related volcanic rocks from the Solomon Islands and Cyprus, but the average W/U ratio of these samples is statistically indistinguishable from typical MORB samples. Additionally, the Cyprus samples show a similar magnitude of scatter in Nb/U and Ba/Th ratios but constant Th/U ratios that are within the realm of typical MORB rocks, indicating variable fluid mobility between all high field strength elements, which are generally considered immobile in fluid systems. Thus,

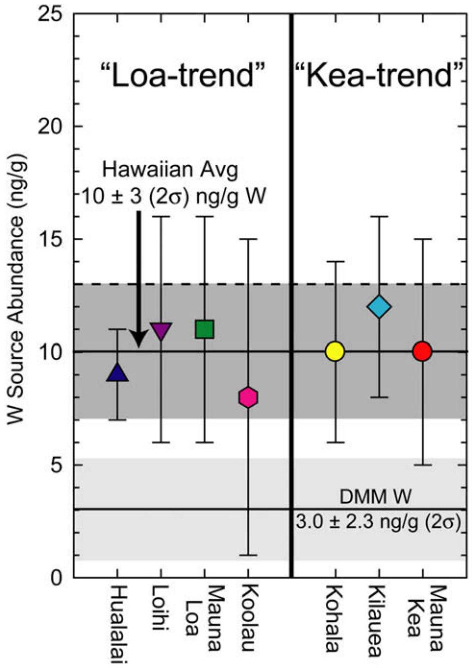

Fig. 3. The estimated W abundances for the mantle source regions of Hualalai, Mauna Loa, Kohala, Kilauea, Mauna Kea, Koolau and Loihi are estimated to be 9 ± 2 (2σ), 11 ± 5, 10 ± 4, 12 ± 4, 10 ± 5, 8 ± 7 and 11 ± 5 ng/g W, respectively. The average W source abundance is 10 ± 3 ng/g (dark shaded area), which is similar to that of PM (13 ± 10 ng/g W, dashed line), but three-times greater than DMM (3.0 ± 2.3 ng/g W; lightly shaded area).

W/U may be selectively fractionated to some degree by fluid systems, but systematic variations have yet to be documented and, thus, the fluid mobility of W, particularly when compared to U, has yet to be resolved. For the purposes of our modeling, it is assumed that W is conserved during the subduction process.

5.2.2. Addition of recycled crust to the Hawaiian mantle source regions

The recycling of oceanic crust, including associated pelagic sediment, into the deep mantle is one of the dominant paradigms for the introduction of chemical heterogeneities into the source region of OIB (e.g., Hofmann and White, 1982; Hofmann, 1997, 2003 and references therein). For Hawaii, there is abundant geochemical support for the incorporation of recycled oceanic crustal materials in the Koolau component, as well as in the mantle sources of Loa-trend volcanoes (e.g., Bennett et al., 1996; Eiler et al., 1996; Hauri, 1996; Hofmann and Jochum, 1996; Lassiter and Hauri, 1998; Blichert-Toft and Albarede, 1999; Sobolev et al., 2000, 2005). The presence of variable proportions and types of recycled materials may explain the trace element and isotopic characteristics of the Hawaiian shields and the variations between individual volcanic centers. Crustal recycling is also consistent, to a first order, with the W (and U) enrichment of the Hawaiian sources relative to the DMM.

Typical oceanic crust contains on the order of ~30 ng/g W, consistent with 8–12% partial melting of a DMM source (3 ng/g W; Arevalo and McDonough, 2008). Sediment is generally more enriched in W than oceanic crust, reaching concentrations in excess of ~1400 ng/g W for upper crustal-derived sediments (Rudnick and Gao, 2003; Hu and Gao, 2008). Pelagic sediments contain even higher concentrations of W than upper continental crust, with an average of ~2700 ng/g W (Strekopytov, 1998). The recycled component in the Hawaiian source region may contain as much as 3% sediment derived from the upper crust without resulting in anomalous Nb/U ratios outside the variance seen in the Hawaiian lavas analyzed in this study. Here, we model a hypothetical recycled package containing 97% oceanic crust and 3% upper crustal sediment resulting in a subducted package with ~70 ng/g W, consistent with the crust-to-sediment proportions estimated in the Koolau mantle end-member based on O and Os isotopes (Bennett et al., 1996; Lassiter and Hauri, 1998), presuming W is conserved during subduction (Fig. 4).

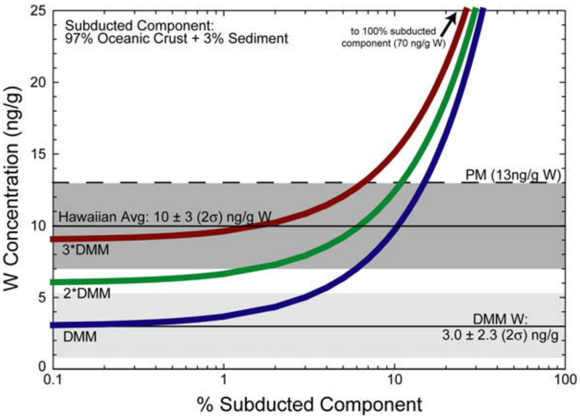

Fig. 4. Addition of a model subducted component to various mantle reservoirs. The subducted package consists of 97% oceanic crust (30 ng/g W) and 3% continental sediment (1400 ng/g W), resulting in a recycled package containing ~70 ng/g W. Adding such a recycled package to DMM (3 ng/g W) requires 5–20% of a subducted component to produce the average Hawaiian source W abundance. However, if a more enriched reservoir (e.g., 3∗DMM) is involved, no recycled material may be required to explain the estimated W source characteristics. With this second scenario, the addition of some recycled material is still permissible within the uncertainties of the model, which may explain the isotopic differences between Loa- and Kea-trend volcanoes. The dark shaded area represents the average W source abundance (10 ± 3 ng/g W), while the lightly shaded area shows the composition of DMM (3.0 ± 2.3 ng/g W).

If the Hawaiian source region ultimately originates from a depleted end-member, modeled here to be DMM, that is variably contaminated by a recycled component similar to our model recycled package, two-component mixing calculations require the addition of between 3% and 20% recycled materials to the DMM to satisfy the estimated W concentration in the sources of the individual shield volcanoes, and between 5% and 20% recycled material to satisfy the mean W budget of the composite Hawaiian source region. The distinct isotopic signatures displayed by Kea-trend and Loa-trend volcanics, however, require either different proportions of recycled components, or incorporation of recycled components of different ages. Given the comparable W concentrations among the Hawaiian shield sources, the isotopic differences between volcanic centers may best be interpreted as the result of recycled materials with different mean ages. For example, the compositions of the Kea-trend volcanic centers can be satisfied by recycling 10–15% of young oceanic crust and sediment, whereas the Loa-trend trend volcanics would require similar proportions of an ancient (>1.8 Ga) crust + sediment package in order to account for the relatively high Sr and Os isotopic compositions, and the relatively low Nd, Hf and Pb isotopic ratios (Bennett et al., 1996; Lassiter and Hauri, 1998).

An alternative explanation for the apparent W enrichment of the Hawaiian source region is that the Hawaiian source does not originate from a depleted end-member like DMM, but rather from an end-member that is less depleted in incompatible elements prior to crustal recycling. This scenario is consistent with some isotopic studies which have suggested that the DMM is not directly involved in producing Hawaiian magmas (Bennett et al., 1996; Lassiter and Hauri, 1998; Blichert-Toft and Albarede, 1999). If the Hawaiian source samples a primary component that is less depleted in incompatible trace elements relative to DMM, then the incorporation of recycled material in the Hawaiian source is not necessary to account for the observed enrichment of W (Fig. 4). However, for this scenario, the addition of variable proportions of recycled crust (up to 10–12%) to account for the isotope characteristics associated with each volcanic center is permitted because this addition would not be resolvable within the W abundance uncertainties reported for the volcanic centers. For example, although the abundance of W in the sources of Mauna Loa and Loihi lavas (11 ± 5 ng/g) is within uncertainty of the rest of the shield volcanoes, the addition of as much as 11% recycled material to an undepleted source with ~9 ng/g W could be accommodated within the uncertainty of the estimated source composition. This scenario is consistent with the suggestion that Loa-trend volcanoes may involve some recycled material (i.e., the Koolau component), while the Kea-trend volcanoes may have incorporated little to none (Huang et al., 2005).

The ultimate origin of this hypothetical, less-depleted reservoir is uncertain. It would most likely represent a reservoir that has experienced little prior melt depletion, thereby preserving high incompatible element concentrations (McKenzie and O'Nions, 1995). If such a reservoir exists, it would likely be located in the deep mantle in order to avoid mixing and/or processing in the upper mantle over geologic time and may be related to the FOZO mantle component (FOcused ZOne; Hart et al., 1992; Hofmann, 2003). To account for the isotopic characteristics of Kea-trend volcanoes, this reservoir would have to be isotopically similar to the Kea end-member. Huang et al. (2005) showed that the Loihi end-member component is similar to the Kea end-member in terms of $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$, albeit slightly more enriched. If this hypothetical reservoir is related to the Loihi end-member, the isotopic constraints of both Kea- and Loa-trend volcanoes can be satisfied.

5.3. Core–mantle interaction?

A role for core–mantle interaction in the Hawaiian plume has been suggested based on observed coupled enrichments in ^{186}Os–^{187}Os isotopes in Hawaiian picrites (Brandon et al., 1999), as well as elevated Fe/Mn ratios in Hawaiian basalts (Humayun et al., 2004). These authors proposed that the enrichments may result from the incorporation of small amounts ($\leqslant$0.5 wt.%) of outer core material to the sources of some Hawaiian volcanoes. However, a lack of corresponding enrichments in the highly siderophile element abundances of the Hawaiian sources (Bennett et al., 2000; Ireland et al., 2009), recent thermal models for the core suggesting the relatively late inception of inner core crystallization (Buffett et al., 1996; Labrosse et al., 2001), and the discovery of other possible mechanisms to create coupled ^{186}Os–^{187}Os enrichments (Smith, 2003; Hawkesworth and Scherstén, 2007; Luguet et al., 2008), have cast doubt on this hypothesis. Tungsten isotopes have been suggested as a more robust tracer of core–mantle interactions (Scherstén et al., 2004; Brandon and Walker, 2005; Hawkesworth and Scherstén, 2007; Takamasa et al., 2009) because the silicate portion of the Earth is isotopically enriched in ^{182}W (the decay product of ^{182}Hf) relative to chondrites. Consequently, mass balance arguments suggest that Earth's core has approximately 2 parts in 10,000 (ε_W units) less ^{182}W than the silicate Earth (Kleine et al., 2002).

The addition of core material to the Hawaiian source could, therefore, lead to a modest depletion in ^{182}W in lavas relative to the ambient upper mantle. Towards this end, Scherstén et al. (2004) observed no difference in W isotopic compositions between a terrestrial standard and three Hawaiian samples (H-11, Lo-02-02 and Lo-02-04) that had previously been suggested to record a core component (Brandon et al., 1999), leading these authors to conclude that no core material is involved in the Hawaiian source regions. The Scherstén et al. (2004) model, however, was strongly dependent on the assumed concentration of W in the mantle source that would have been contaminated with W from the outer core.

Our current study suggests that the W content of the mean Hawaiian source region (10 ± 3 ng/g) is most consistent with the "preferred" model of Scherstén et al. (2004) that assumed an initial W concentration of 8 ng/g. The addition of 0.5 wt.% of outer core material to the average Hawaiian source would raise the source W concentration by only ~2 ng/g, which is unresolvable within the uncertainty on the mantle source W estimates. Arevalo and McDonough (2008) also showed that the incorporation of 0.5 wt.% core material would not have a resolvable effect on the W/U ratios.

However, the physical addition of this amount of outer core material would result in a ε_W of -0.45, which should be resolvable by W isotopes. The lack of an outer core W signature in the Hawaiian rocks suggests that either core–mantle interaction does not occur, or that mechanisms other than physical mixing may operate at the core–mantle boundary (Puchtel and Humayun, 2000; 2005; Humayun et al., 2004).

6. CONCLUSIONS

(1) The concentration of W in Hawaiian picrites is highly variable, but within most individual shield volcanoes, linear trends are observed between W and MgO. The W/U ratios for Hawaiian picrites have an average of 0.62 ± 0.19 (2σ), which is indistinguishable from the W/U ratio for the sampled silicate Earth.

(2) Estimates of the W content of the parental melts for the Hawaiian shield volcanoes were obtained by two different techniques, which yield statistically indistinguishable results. The parental melts for Hualalai, Mauna Loa, Kohala, Kilauea, Mauna Kea, Koolau and Loihi are determined to contain 85 ± 6 (2σ), 111 ± 40, 133 ± 20, 155 ± 21, 127 ± 46, 104 ± 84 and 214 ± 8 ng/g W, respectively.

(3) Correspondingly, the W abundances for the Hawaiian mantle sources are estimated to contain 9 ± 2 (2σ), 11 ± 5, 10 ± 4, 12 ± 4, 10 ± 5, 8 ± 7 and 11 ± 5 ng/g for Hualalai, Mauna Loa, Kohala, Kilauea, Mauna Kea, Koolau and Loihi, respectively. As a result, the mean Hawaiian source region contains 10 ± 3 (2σ) ng/g W, about three-times more than the DMM (3.0 ± 2.3 ng/g W), but comparable to the PM (13 ± 10 ng/g W). The estimated U abundances for the mantle sources of the Hawaiian volcanic centers are consistent with those derived from W abundances.

(4) Bulk addition of recycled oceanic material to the DMM alone can explain the enriched W composition of each individual Hawaiian shield volcano, but the mean age of the recycled material in Kea- and Loa-trend volcanoes would have to be fundamentally different to satisfy

isotopic constraints. However, if the Hawaiian source regions originate from a less depleted mantle reservoir, crustal recycling is not necessary to produce the estimated source W abundances, although the addition of some recycled oceanic crust can be accommodated within the uncertainties of our model source compositions.

(5) The incorporation of minor amounts ($\leqslant$0.5 wt.%) of outer core material is unresolvable within the uncertainty of our W source modeling and W/U ratios, however, this addition should be detectable via W isotopes. The lack of a core W signature suggests that either core–mantle interaction does not occur, or that mechanisms other than physical mixing may operate at the core–mantle boundary.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2009.04.016.

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