Excesses of seawater-derived ^{234}U in volcanic glasses from Loihi Seamount due to crustal contamination

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ABSTRACT

The effects of crustal contamination on the chemistry of oceanic basalts are commonly assumed to be negligible due to the compositional similarity between the erupted basalt and the underlying oceanic crust or volcanic edifice. Here we evaluate this assumption with high-precision measurements of the ^{234}U–^{238}U and ^{230}Th–^{238}U disequilibria, Cl/K$_2$O ratios, and ^{87}Sr/^{86}Sr ratios of volcanic glasses from Loihi Seamount, a submarine Hawaiian volcano with an active hydrothermal system. The samples, including one from the volcano's 1996 eruption, have small to moderate amounts of excess ^{234}U (~0.2–1.0%) and variable, elevated Cl/K$_2$O ratios. These excesses of ^{234}U and enrichments in Cl are thought to result from contamination with seawater-derived U and Cl, but neither of these signatures can be explained by syn- or post-eruptive interaction between lava and seawater. Instead, mantle-derived magmas at Loihi appear to be variably contaminated with two distinct crustal materials: hydrothermal brines (which create enrichments in Cl) and U-enriched hydrothermally altered rocks (which create excesses of ^{234}U). Both of these materials are expected to be found within the volcanic edifice as complementary parts of the volcano's hydrothermal system. The Loihi glasses display a wide measured range in the amount of excess ^{230}Th from ~1 to 7% (due to the addition of seawater-derived U) that overlaps with lavas from Kilauea Volcano (~2% excess ^{230}Th). We correct the ^{230}Th–^{238}U disequilibria of the Loihi glasses back to their original pre-contamination values using their ^{234}U–^{238}U disequilibria and a simple mass-balance calculation. This correction suggests that mantle-derived magmas at Loihi have a narrow range of ~6–9% excess ^{230}Th, which is significantly larger than observed for lavas from the neighboring volcano, Kilauea. This difference is consistent with the idea that Loihi is tapping mantle that is upwelling slowly (~5–6 cm/yr) on the margin of the Hawaiian plume.

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1. Introduction

The effects of crustal contamination on the chemistry of oceanic basalts are commonly assumed to be negligible due to the compositional similarity between the erupted basalt and the underlying oceanic crust or volcanic edifice. However, the well-known depletion of ^{18}O in some Hawaiian and Icelandic lavas and their olivine crystals (e.g., Bindeman et al., 2008; Eiler et al., 2000; Garcia et al., 1998a; Hémond et al., 1993; Wang and Eiler, 2008) suggests that mantle-derived magmas at these ocean-island volcanoes may assimilate hydrothermally altered rocks on their way to the surface. Furthermore, volcanic glasses from both mid-ocean ridges and the submarine portions of Hawaiian volcanoes display the telltale signs of crustal interaction between magma and a seawater-derived contaminant. Strong evidence for this process comes from enrichments of Cl (up to 1.7 wt.% at Kilauea Volcano) and high Cl/K$_2$O ratios in fresh volcanic glasses and melt inclusions in olivine (e.g., Clague et al., 1995; Coombs et al., 2004; Davis et al., 2003; Kent et al., 1999a,b; le Roux et al., 2006; Michael and Cornell, 1998; Michael and Schilling, 1989), which could result from the assimilation of hydrothermal brines, altered oceanic crust or volcanic edifice, and/or Cl-rich minerals (e.g., halite). Unraveling the significance and mechanism(s) of crustal contamination is vital for studies of the mantle source and melting processes at mid-ocean ridge and ocean-island volcanoes.

Measurements of radioactive disequilibria between ^{238}U and its short-lived daughter isotopes (e.g., ^{230}Th) in basaltic lavas provide key estimates of the time scales of magmatic processes, such as the rates of mantle upwelling and melting (e.g., Russo et al., 2009; Sims et al., 1999). This approach requires that the (^{230}Th/^{238}U) ratio of a given sample of volcanic glass reflects the composition of its mantle-derived parental magma (parentheses around nuclides indicate activities, or decay rates). Crustal

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contamination is known to modify the ^{230}Th–^{238}U disequilibria of many evolved lavas, such as andesites and dacites from Hekla Volcano of Iceland (Sigmarsson et al., 1992) or Ruapehu Volcano of the Taupo Volcanic Zone of New Zealand (Price et al., 2007). In contrast, only a few studies (e.g., Elkins et al., in revision; Sims et al., 2002) have addressed the possibility that the (^{230}Th/^{238}U) ratios of oceanic basalts can be affected by crustal contamination. These effects can be particularly significant if hydrothermal fluids (e.g., Pietruszka et al., 2009) or seawater are involved. For example, primary magmas delivered from the mantle are expected to be in radioactive equilibrium for ^{234}U and ^{238}U, whereas seawater has an elevated (^{234}U/^{238}U) ratio of 1.146 (e.g., Chen et al., 1986a; Cheng et al., 2000). Thus, contamination of a mantle-derived magma with seawater-derived hydrothermal fluids (i.e., brines) or hydrothermally altered rocks within the oceanic crust or volcanic edifice, as proposed for mid-ocean ridge basalts (MORB) and submarine volcanic glasses from Hawaii, might lead to a measurable excess of ^{234}U in oceanic basalts. If this contamination involves the bulk addition of seawater-derived U and it occurred recently relative to the ~75.7 ka half-life of ^{230}Th, any increase in the (^{234}U/^{238}U) ratio of a contaminated volcanic glass would be accompanied by a concomitant decrease in its (^{230}Th/^{238}U) ratio.

Evidence for modification of the (^{234}U/^{238}U) or (^{230}Th/^{238}U) ratios of oceanic basalts due to crustal contamination is sparse. Most of the confirmed "zero-age" MORB with high-precision measurements of their (^{234}U/^{238}U) ratios are within error of radioactive equilibrium for ^{234}U and ^{238}U (e.g., Rubin et al., 2005; Sims et al., 2002). Rarely, however, strongly elevated (^{234}U/^{238}U) ratios (possibly due to secondary Fe–Mn oxide coatings) have been discovered in some MORB glasses (up to ~6.5% excess ^{234}U; Peate et al., 2001; Tepley et al., 2004). These signatures and the slightly more common moderate (~1%) excesses of ^{234}U in MORB are usually attributed to post-eruptive alteration and the ^{230}Th–^{238}U disequilibria of the affected samples are rejected from consideration when evaluating mantle processes. Nevertheless, it remains possible that contamination of mantle-derived magmas with seawater-derived U occurs in the crust beneath spreading centers (e.g., Elkins et al., in revision). Similarly, crustal contamination has been inferred to affect the (^{230}Th/^{238}U) and (^{238}U/^{232}Th) ratios of historical lavas from Piton de la Fournaise, a frequently active ocean-island volcano on Réunion Island (Pietruszka et al., 2009). Some of these lavas have anomalously low (^{230}Th/^{238}U) and high (^{238}U/^{232}Th) ratios, which are thought to result from the assimilation of U-enriched hydrothermally altered rocks within the volcanic edifice. However, the (^{234}U/^{238}U) ratios of these subaerial lavas from Piton de la Fournaise are nearly within error of unity.

In this study, we present high-precision measurements of the ^{234}U–^{238}U disequilibria, Cl/K$_2$O ratios, and ^{87}Sr/^{86}Sr ratios of volcanic glasses from Loihi Seamount, a submarine Hawaiian volcano with an active hydrothermal system (Davis and Clague, 1998; Karl et al., 1988; Malahoff et al., 1982). Each of these geochemical parameters is expected to be a sensitive tracer of crustal contamination. In addition, the Th and U abundances, (^{230}Th/^{232}Th) ratios, and ^{230}Th–^{238}U disequilibria of the Loihi glasses were measured to compare with the geochemical tracers of crustal contamination. Our major goals are to (1) evaluate the role of crustal contamination at Loihi, building upon the results of Kent et al. (1999a,b), (2) propose a model for crustal contamination at Loihi that incorporates the complementary parts of the volcano's hydrothermal system (i.e., both fluids and altered rocks), and (3) discuss the potential effects of the assimilation of hydrothermally altered rocks on the ^{230}Th–^{238}U disequilibria of Loihi glasses and other oceanic basalts.

2. Sample description and analytical methods

Sixteen tholeiitic to mildly alkalic volcanic glasses were collected from Loihi's summit platform and south rift zone using the *Alvin* (Garcia et al., 1993), *Pisces V* (Garcia et al., 1998b) and *Shinkai 6500* submersibles. The major- and volatile-element abundances and a summary of the sample locations are provided in Table 1. All of the samples were also analyzed for Th and U concentrations, (^{230}Th/^{232}Th), (^{234}U/^{238}U) and ^{87}Sr/^{86}Sr ratios, and ^{230}Th–^{238}U disequilibria (Table 2). Exact ages for the samples are unknown except for P286-1F, which is thought to have erupted in 1996 based on ^{210}Po–^{210}Pb dating (Garcia et al., 1998b; Rubin et al., 2005). All of the other samples are thought to be young relative to the half-life of ^{230}Th because they were collected from surface flows or from the wall of a summit pit crater at relatively shallow depths (i.e., the 1801 series of samples). Thus, no age corrections were applied to the Th isotope ratios or ^{230}Th–^{238}U disequilibria.

All analyses were performed on fresh volcanic glasses that were handpicked under a binocular microscope to avoid any fragments with signs of post-eruptive alteration. The volatile element abundances (H$_2$O, CO$_2$, F, S, and Cl) were measured by secondary ion mass spectrometry at the Department of Terrestrial Magnetism (DTM) of the Carnegie Institution of Washington using the methods of Hauri et al. (2002). For the isotopic analyses, the samples were treated with ultra-pure reagents prior to dissolution. The glasses for dissolutions #1 and #2 were cleaned sequentially in 2 M HCl and H$_2$O. We verified that this procedure did not significantly fractionate Th from U by measuring the abundances of these elements in an aliquot of sample 1804-1 that was cleaned only in H$_2$O (Table 2). The Th/U ratios of the two analyses of 1804-1 agree to ~0.3%. For the leached dissolution, the glasses were cleaned sequentially in H$_2$O, 6 M HCl, a 1 M HCl–2% H$_2$O$_2$ solution, a 0.05 M oxalic acid–2% H$_2$O$_2$ solution, 0.2 M HCl, and H$_2$O. During each cleaning step, the reagent was applied for 10 min in an ultrasonic bath followed by two rinses with H$_2$O. The ^{87}Sr/^{86}Sr ratios were measured on a VG Sector 54 thermal ionization mass spectrometer at San Diego State University (SDSU) using analytical methods described by Marske et al. (2007). The (^{230}Th/^{232}Th) ratios, isotope dilution Th and U abundances, and ^{230}Th–^{238}U disequilibria were measured on a P54-30 multiple collector inductively coupled plasma mass spectrometer (MC–ICP–MS) at DTM. The (^{234}U/^{238}U) ratios were measured either on the P54-30 or a Nu Plasma 1700 MC–ICP–MS at SDSU. The measurements at DTM were conducted using the techniques described by Pietruszka et al. (2002), whereas a new technique was developed for the (^{234}U/^{238}U) measurements at SDSU (see Supplementary materials for a detailed description of the analytical method). A summary of results for the (^{234}U/^{238}U) ratios of relevant standards analyzed over the course of this study is presented in Table 2. Full details for the (^{230}Th/^{232}Th) and (^{234}U/^{238}U) ratios, Th and U abundances, and ^{230}Th–^{238}U disequilibria of these and other standards measured at DTM (all of which were performed concurrently with the DTM analyses of the Loihi glasses in Table 2) are described by Pietruszka et al. (2002). All uncertainties in this paper are given as $\pm 2\sigma$ (± 2 standard deviations) unless otherwise noted, and all literature data has been corrected to the same values of the decay constants (Table 2).

3. Accuracy of the (^{234}U/^{238}U) ratios

The (^{234}U/^{238}U) ratio of a sample is determined by multiplying its atomic ^{234}U/^{238}U ratio by the quotient of the decay constants (λ) for ^{234}U and ^{238}U (λ^{234}U/λ^{238}U). Thus, the accuracy of the calculated (^{234}U/^{238}U) ratio depends partly on the ^{234}U and ^{238}U the decay constants, which are currently known to a precision of 0.20% for ^{234}U (Cheng et al., 2000) and 0.11% for ^{238}U (Jaffey et al., 1971). For a sample in radioactive equilibrium, these decay constants lead to an expected ^{234}U/^{238}U ratio of 5.489×10^{-5}. We compare this value, converted to a (^{234}U/^{238}U) ratio of 1.0000 ± 23, with our results for both rock standards and samples that are anticipated to be in radioactive equilibrium for ^{234}U and ^{238}U to determine the accuracy of the U isotopic data presented in this study. In addition, the (^{234}U/^{238}U) ratios of the Loihi glasses were measured on two different instruments, so the possibility of inter-laboratory bias is also evaluated.

Table 1
Sampling locations, basalt types, and major and volatile element abundances of volcanic glasses from Loihi Seamount.

Sample	Basalt type	Depth (m)	Location	Lat. (°N)	Long. (°W)	SiO_2 (wt.%)	TiO_2	Al_2O_3	FeO^T	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O	Total	CO_2 (ppm)	F	S	Cl
P286-1F[a]	Thol.	1050	S			48.75	2.63	13.70	11.80	0.14	6.91	12.05	2.53	0.45	0.24	0.60	99.80	17	385	1553	249
1801-1[b]	Thol.	1305	S			48.77	2.64	13.63	11.73	0.20	6.82	11.90	2.36	0.44	0.21	0.60	99.30	14	386	1585	239
1801-11[b]	Thol.	1248	S			49.49	2.44	13.55	11.94	0.18	6.93	11.45	2.40	0.38	0.21	0.49	99.46	28	342	1813	293
1801-16[b]	Thol.	1110	S			49.13	2.82	13.86	11.67	0.16	6.49	11.53	2.56	0.60	0.25	0.68	99.75	14	462	1474	371
1801-19[b]	Thol.	1062	S			48.67	2.87	13.75	11.74	0.21	6.71	11.69	2.58	0.57	0.24	0.65	99.68	14	452	1381	353
1801-22[b]	Thol.	987	S			49.31	2.61	13.84	11.84	0.18	6.80	11.65	2.41	0.42	0.20	0.57	99.83	11	365	1452	194
1802-22[a]	Thol.	998	S			49.20	2.61	13.71	12.00	0.18	6.80	11.72	2.48	0.42	0.27	0.60	99.99	13	380	1445	199
1803-14[b]	Alk.	1140	S			47.12	3.88	14.17	13.10	0.18	5.49	11.10	3.31	0.84	0.38	0.91	100.48	12	750	1696	613
1803-16[b]	Thol.	977	S			49.69	2.48	13.26	11.52	0.18	7.50	11.72	2.33	0.36	0.18	0.45	99.67	31	329	1333	246
1804-1[b]	Thol.	1357	R			49.19	2.46	13.35	11.40	0.19	7.29	12.21	2.40	0.49	0.21	0.55	99.74	39	381	1698	447
1804-10[b]	Thol.	1320	R			49.20	2.56	12.93	11.46	0.16	8.01	12.02	2.35	0.44	0.21	0.43	99.77	53	370	911	443
1804-19[b]	Alk.	1020	S			48.73	3.76	13.82	12.75	0.19	5.17	10.21	3.33	0.89	0.34	0.69	99.88	31	698	872	932
6K490-1[c]	Alk.	4684	R	18.7415	155.1904	47.62	2.96	14.07	11.49		6.56	11.76	2.97	0.76	0.31	0.89	99.38	258	579	1847	723
6K490-2[c]	Thol.	4657	R	18.7427	155.1898	47.96	2.92	13.93	11.19		6.31	11.50	2.77	0.53	0.25	2.61	99.96	58	600	1658	1193
6K491-2[c]	Trans.	4300	R	18.7652	155.1618	48.45	2.91	14.26	11.24		6.47	11.48	3.03	0.64	0.30	0.76	99.55	217	483	1861	531
6K494-6[c]	Thol.	2323	R	18.8422	155.2295	49.06	2.68	13.99	12.05		6.40	11.56	2.53	0.44	0.25	0.69	99.66	53	388	1693	275

Note: Lat. = latitude; Long. = longitude; Thol. = tholeiitic; Alk. = alkalic; Trans. = transitional; FeO^T = total Fe expressed as Fe^{2+}; S = summit platform; R = south rift zone. The classification of the basalts is based on the scheme of Macdonald and Katsura (1964). Detailed locations for P286-1F, which is thought to have erupted in 1996, and the 1800-series samples may be found in Garcia et al. (1993, 1998b).
[a] Major element abundances from Garcia et al. (1998b).
[b] Major element abundances from Garcia et al. (1993).
[c] Major element abundances determined by electron microprobe at the University of Hawaii using the methods described by Garcia et al. (1995).

Nearly all of the ($^{234}U/^{238}U$) ratios of the Loihi glasses for dissolution #1 (except sample 1801-11) were measured on the P54-30 MC–ICP–MS at DTM. Concurrently, we analyzed the Table Mountain Latite (TML) rock standard at DTM (Pietruszka et al., 2002), which is expected to be in radioactive equilibrium for ^{234}U and ^{238}U due it its Pliocene age (Williams et al., 1992). The average ($^{234}U/^{238}U$) ratio for 27 analyses of TML was 1.0005 ± 4 ($\pm 2\sigma_m$, or ± 2 standard deviations of the mean). This result is within error of the expected value for radioactive equilibrium. In addition, a Hawaiian in-house rock standard (Kil1919, collected from the same 1919 Kilauea lava flow as the BHVO-1 and -2 rock standards) was analyzed at DTM. Unaltered subaerial basalts are generally expected to be in radioactive equilibrium for ^{234}U and ^{238}U. However, the average ($^{234}U/^{238}U$) ratio of Kil1919 (n = 33) at DTM was 1.0016 ± 3 ($\pm 2\sigma_m$), which appears to be distinct from TML and slightly enriched in ^{234}U. A similar, small apparent excess of ^{234}U (relative to the $\pm 2\sigma_m$ error of multiple analyses) was obtained at DTM for nine lavas from the Puu Oo eruption of Kilauea Volcano [($^{234}U/^{238}U$) = 1.0011 ± 3; n = 9] by Pietruszka et al. (2006) and 15 subaerial lavas from historical eruptions of Piton de la Fournaise Volcano [($^{234}U/^{238}U$) = 1.0014 ± 2] by Pietruszka et al. (2009).

The ($^{234}U/^{238}U$) ratios of the other Loihi glasses were measured on the Nu Plasma 1700 MC–ICP–MS at SDSU. Concurrently, Kil1919 and an in-house Hawaiian volcanic glass standard called Menehune (quenched from an active Puu Oo lava flow of Kilauea on June 24, 2006) were analyzed at SDSU. The average ($^{234}U/^{238}U$) ratio of Kil1919 (n = 10) was 1.0009 ± 7 ($\pm 2\sigma_m$), whereas the average ($^{234}U/^{238}U$) ratio for Menehune (n = 12) was 1.0008 ± 6 ($\pm 2\sigma_m$). These results lie within the $\pm 2\sigma_m$ errors of the ($^{234}U/^{238}U$) ratios of all of the subaerial basalts and rock standards analyzed at DTM, including TML. Furthermore, the SDSU value for the CRM112 standard agrees within $\pm 2\sigma_m$ of the value for this standard measured at DTM (Table 2). Thus, no correction for inter-laboratory bias on the ($^{234}U/^{238}U$) ratios was performed for the Loihi glasses analyzed in this study.

The average ($^{234}U/^{238}U$) ratio for all of the subaerial basalts that were measured in both laboratories (n = 79) is 1.0013 ± 2 ($\pm 2\sigma_m$), which is slightly distinct from TML. There are two potential explanations for this difference: (1) the average ($^{234}U/^{238}U$) ratio of the subaerial basalts might reflect an actual excess of ^{234}U in lavas from Kilauea and Piton de la Fournaise (relative to TML and the expected value for radioactive equilibrium), or (2) these samples are truly in radioactive equilibrium and the results, including our analyses

of the Loihi glasses, might be slightly inaccurate due to an unknown analytical artifact. Neither scenario will significantly affect any of our interpretations because the difference between the average subaerial basalts and TML is only 0.08%. This difference probably cannot result from a non-spectral matrix effect in the MC–ICP–MS because the $^{234}U/^{238}U$ ratios measured at both DTM and SDSU were corrected for instrumental mass-dependent isotopic fractionation during each analysis using the measured $^{238}U/^{235}U$ ratio relative to an assumed $^{238}U/^{235}U = 137.88$ (Table 2). On the other hand, we cannot completely rule out the possibility that the apparent excess of ^{234}U in the subaerial basalts results from an unidentified sample-derived spectral (molecular) interference on mass 234, which might affect TML less significantly due to the factor of ~20 greater dilution used for the analyses of this U-enriched rock standard. Nevertheless, we view this possibility as unlikely and tentatively suggest that the subaerial basalts have a slight (~0.1%) excess of ^{234}U. In any case, all of the subaerial basalts and rock standards lie within error of radioactive equilibrium based on the precision of the decay constants. For simplicity, therefore, we assume a ($^{234}U/^{238}U$) ratio of unity for radioactive equilibrium.

4. Results

All of the Loihi glasses have small to moderate amounts of excess ^{234}U (~0.2–1.0%). Although these signatures are not more than a factor of ~5 larger than our maximum analytical uncertainty (Table 2), the distribution of the ($^{234}U/^{238}U$) ratios of the samples on a histogram (Fig. 1A) is clearly distinct from the subaerial lavas (Fig. 1B). With two exceptions, the ($^{234}U/^{238}U$) ratios of the Loihi glasses are identical within error for replicate dissolutions, including the subset of leached samples (Table 2). Sample 1804-19 gave a significantly larger amount of excess ^{234}U for dissolution #2 (1.0%) compared to both dissolution #1 and the leached dissolution (~0.3–0.4% excess ^{234}U). For sample 1804-10, the leached dissolution gave a slightly higher ($^{234}U/^{238}U$) ratio (~0.6% excess ^{234}U) compared to dissolutions #1 and 2 (~0.3–0.4% excess ^{234}U). A different sample of volcanic glass from the 1996 Loihi eruption was previously analyzed by Rubin et al. (2005). The ($^{234}U/^{238}U$) ratio for their single analysis of this sample was 1.000 ± 0.006, which lies within error of our analyses of P286-1F (Table 2). The ($^{234}U/^{238}U$) ratios of the Loihi glasses display a strong negative correlation ($R^2 = 0.85$) with their $^{230}Th–^{238}U$ disequilibria (Fig. 2A), a weak positive correlation ($R^2 = 0.30$) with

Table 2
Isotope ratios and trace element abundances of volcanic glasses from Loihi Seamount.

Sample	Dissolution #1 measured						Dissolution #1 corrected		Dissolution #2		Leached
	Th (ppm)[a]	U (ppm)[a]	$(^{230}Th/^{232}Th)$[a]	$(^{230}Th/^{238}U)$[a]	$(^{234}U/^{238}U)$	$^{87}Sr/^{86}Sr$[b]	U (ppm)[c]	$(^{230}Th/^{238}U)$[c]	$(^{234}U/^{238}U)$	$^{87}Sr/^{86}Sr$[b]	$(^{234}U/^{238}U)$
P286-1F	0.8262	0.2565	0.9827	1.0432	1.0036 ± 9[d]	0.703494 ± 14	0.2502 ± 17	1.069 ± 8	1.0038 ± 7[e]	0.703490 ± 3	1.0035 ± 10[e]
1801-1	0.8497	0.2650	0.9874 ± 3	1.0434	1.0040 ± 3[e]	0.703498 ± 15	0.2577 ± 7	1.073 ± 5	1.0052[e]	0.703499 ± 7	
1801-11	0.8090	0.2516	0.9545 ± 18	1.0114	1.0061 ± 5[d]	0.703581 ± 2	0.2410 ± 10	1.056 ± 6	1.0055 ± 15[e]	0.703575 ± 2	1.0059 ± 20[e]
1801-16	1.011	0.3107	0.9751	1.0458	1.0036 ± 9[d]	0.703523 ± 3	0.3029 ± 20	1.073 ± 8	1.0029[e]	0.703530 ± 3	
1801-19	1.047	0.3221	0.9775 ± 12	1.0471	1.0036 ± 12[d]	0.703525 ± 11	0.3141 ± 27	1.074 ± 10	1.0020[e]	0.703521 ± 6	
1801-22	0.8213	0.2585	0.9878 ± 11	1.0344	1.0042 ± 9[d]	0.703526 ± 8	0.2511 ± 17	1.065 ± 8	1.0047[e]	0.703521 ± 2	
1802-22	0.7794	0.2455	0.9850 ± 7	1.0305	1.0044 ± 9[d]	0.703516 ± 6	0.2382 ± 16	1.062 ± 8	1.0043[e]	0.703519 ± 12	
1803-14	1.595	0.4927	0.9629 ± 6	1.0273	1.0058 ± 15[d]	0.703594 ± 9	0.4732 ± 51	1.070 ± 12	1.0069 ± 5[e]	0.703606 ± 2	1.0064 ± 25[e]
1803-16	0.7523	0.2347	0.9568 ± 21	1.0106	1.0080 ± 10[d]	0.703656 ± 1	0.2219 ± 16	1.069 ± 9	1.0067 ± 1[e]	0.703653 ± 25	1.0076 ± 5[e]
1804-1	0.8163	0.2492	0.9548 ± 16	1.0307	1.0063 ± 19[d]	0.703561 ± 6	0.2384 ± 33	1.078 ± 16	1.0062 ± 5[e]	0.703562 ± 22	1.0065 ± 12[e]
1804-1[f]	0.8075	0.2474									
1804-10	0.8519	0.2640	0.9767 ± 6	1.0387	1.0034 ± 3[d]	0.703597 ± 9	0.2577 ± 8	1.064 ± 5	1.0038 ± 6[e]	0.703597 ± 4	1.0063 ± 5[e]
1804-19	1.744	0.5233	0.9699 ± 27	1.0652	1.0028 ± 9[d]	0.703568 ± 6	0.5133 ± 35	1.086 ± 8	1.0101 ± 2[e]	0.703566 ± 2	1.0036 ± 8[e]
6K490-1	1.365	0.3964	0.9376 ± 8	1.0642	1.0021 ± 5[d]	0.703594 ± 14	0.3907 ± 15	1.080 ± 6	1.0024 ± 1[e]	0.703590 ± 5	1.0039 ± 15[e]
6K490-2	0.7779	0.2377	0.9728 ± 26	1.0493	1.0026 ± 6[d]	0.703586 ± 13	0.2334 ± 11	1.068 ± 7	1.0029[e]	0.703579 ± 5	
6K491-2	1.127	0.3433	0.9801 ± 7	1.0604	1.0019 ± 6[d]	0.703557 ± 7	0.3389 ± 16	1.074 ± 6	1.0025[e]	0.703551 ± 11	
6K494-6	0.7638	0.2420	0.9847	1.0244	1.0060 ± 13[d]	0.703522 ± 8	0.2321 ± 22	1.068 ± 11	1.0052[e]	0.703522 ± 9	

Note: The uncertainties of the Th, U, and Sr isotope ratios of the samples are the $\pm 2\sigma_m$ ($n > 2$) or total range ($n = 2$) of the replicate analyses reported in the Supplementary materials. The overall $\pm 2\sigma$ precision of the Th (~0.3%), U (~0.2%), and Sr (± 0.000020) isotope ratios for samples that were analyzed only once is based on repeated measurements of standards. The $\pm 2\sigma$ precision of the Th and U abundances is ~0.2%. The $(^{230}Th/^{232}Th)$, $(^{234}U/^{238}U)$, and $(^{230}Th/^{238}U)$ ratios were calculated using the decay constants summarized by Pietruszka et al. (2002). All uncertainties in this caption are given as $\pm 2\sigma$ unless otherwise noted.

[a] The $(^{230}Th/^{232}Th)$ ratios, Th and U abundances, and ^{230}Th–^{238}U disequilibria of the samples were measured on the P54-30 multiple collector inductively coupled plasma mass spectrometer (MC–ICP–MS) at the Department of Terrestrial Magnetism (DTM) of the Carnegie Institution of Washington. The analytical methods for these measurements at DTM, and a summary of results for standards analyzed concurrently with the Loihi glasses, are presented by Pietruszka et al. (2002).

[b] The Sr isotope ratios were measured on a VG Sector 54 thermal ionization mass spectrometer at San Diego State University (SDSU) over two periods of time separated by a major instrument upgrade using analytical methods described by Marske et al. (2007). Analyses of the NBS987 standard during each period gave $^{87}Sr/^{86}Sr$ ratios of 0.710245 ± 19 ($n = 38$) and 0.710255 ± 17 ($n = 60$). These values for NBS987 are distinct at the $\pm 2\sigma_m$ level. Thus, the Sr isotope ratios of the samples were normalized to $^{87}Sr/^{86}Sr = 0.710250$ for NBS987 to correct for this small offset.

[c] The U abundances and $(^{230}Th/^{238}U)$ ratios of the Loihi glasses from dissolution #1 were corrected for the addition of seawater-derived U due to crustal contamination as described in the text. The propagated errors were calculated from the $\pm 2\sigma_m$ error of the $(^{234}U/^{238}U)$ ratio for each sample, and the overall $\pm 2\sigma$ precision of the Th isotope ratios and Th and U concentrations.

[d] U isotope ratios measured on the P54-30 MC–ICP–MS at DTM using the methods of Pietruszka et al. (2002). The data are normalized to $^{234}U/^{238}U = 5.3525 \times 10^{-5}$ for the CRM112 standard (Pietruszka et al., 2002), which was analyzed as a bracketing standard. Two rock standards were analyzed at DTM during this study: a radioactive equilibrium standard (TML-3) and an in-house standard (Kil1919) collected from the same 1919 lava flow of Kilauea Volcano as the BHVO-1 and -2 rock standards. Analyses of the rock standards gave $(^{234}U/^{238}U)$ ratios of 1.0005 ± 20 ($n = 27$) for TML-3 and 1.0016 ± 16 ($n = 33$) for Kil1919 (Pietruszka et al., 2002).

[e] U isotope ratios measured on the Nu Plasma 1700 MC–ICP–MS at SDSU using a new technique described in the Supplementary materials. Briefly, the $(^{234}U/^{238}U)$ ratios of the samples were measured in sample-standard bracketing mode with ^{234}U on the ion-counting detector and ^{235}U and ^{238}U on the Faraday detectors in a single static sequence. The measured $^{234}U/^{238}U$ ratio of each sample was corrected for instrumental mass-dependent isotopic fractionation using its measured $^{238}U/^{235}U$ ratio, an assumed "true" $^{238}U/^{235}U$ ratio of 137.88, and the exponential fractionation law of Russell et al. (1978). CRM112-A (previously called SRM960) was analyzed as a bracketing standard before and after each sample to correct its fractionation-corrected $^{234}U/^{238}U$ ratio for the bias between the ion-counting and Faraday detectors. This correction was performed using a linear interpolation between the bracketing CRM112-A standards and an assumed "true" $^{234}U/^{238}U$ ratio of 5.2860×10^{-5} for this standard from Cheng et al. (2000). Three standards were analyzed at SDSU during this study: a new in-house volcanic glass standard (called "Menehune") that was prepared from a Puu Oo lava flow of Kilauea Volcano that was quenched on June 24, 2006, Kil1919, and the CRM112 standard (which has a different $^{234}U/^{238}U$ ratio from SRM960/CRM112-A). Analyses of the rock standards gave $(^{234}U/^{238}U)$ ratios of 1.0009 ± 21 ($n = 10$) for Kil1919 and 1.0008 ± 19 ($n = 12$) for Menehune. The average $^{234}U/^{238}U$ ratio of CRM112 was $5.3530 \pm 96 \times 10^{-5}$ ($n = 18$). The SDSU values for Kil1919 and CRM112 lie within $\pm 2\sigma_m$ of the values for these standards measured at DTM, so no corrections for inter-laboratory differences were applied to the $(^{234}U/^{238}U)$ ratios of the samples.

[f] Replicate dissolution that was cleaned only in H_2O.

their $(^{238}U/^{232}Th)$ ratios (Fig. 2B), and no correlation with their $(^{230}Th/^{232}Th)$ ratios. The $^{87}Sr/^{86}Sr$ ratios of the samples display a range (0.70349–0.70366) that is similar to previous analyses of Loihi glasses (e.g., Garcia et al., 1995). The $^{87}Sr/^{86}Sr$ ratios of dissolutions #1 and #2 agree within error, but do not correlate with the $(^{234}U/^{238}U)$ ratios of the samples (Fig. 3A). Similarly, there is no systematic relationship between the $(^{234}U/^{238}U)$ ratios of the glasses and their Cl/K_2O ratios (Fig. 3B), which lie within the range of previous studies of Loihi samples (Kent et al., 1999a,b).

5. Origin of the excess ^{234}U in Loihi glasses

Seawater is the most likely source of excess ^{234}U in volcanic glasses from Loihi Seamount. There are at least three possible mechanisms to incorporate seawater-derived U into the samples: (1) post-eruptive alteration with seawater, (2) syn-eruptive interaction between molten lava and seawater, or (3) crustal contamination with hydrothermal brines or hydrothermally altered rocks within the oceanic crust or volcanic edifice. Each of these possibilities is considered in the following discussion.

5.1. A lack of syn- or post-eruptive alteration

Chemical exchange between molten lava and seawater has been documented for MORB lava flows and pillars, which display a notable increase in the Cl content (and Cl/K_2O ratio) of the affected volcanic glass (Perfit et al., 2003; Schiffman et al., 2010; Soule et al., 2006). This type of contamination (like post-eruptive alteration) would most likely be concentrated within ~1–2 mm of the lava–seawater interface, although there is some evidence for irregular stirring of Cl-enriched melt and seawater vapor bubbles to depths of up to ~1 cm within the lava during flow on the seafloor (Soule et al., 2006). The highest Cl/K_2O ratio observed in Loihi glasses is ~0.3 (Kent et al., 1999a,b), which would require the addition of ~6% seawater to an uncontaminated lava with an assumed initial Cl/K_2O of 0.03 [using Cl and K_2O abundances from Kent et al. (1999b)]. Even if this amount of seawater was mixed evenly throughout the lava, it would have no measurable effect on the $(^{234}U/^{238}U)$ ratio of the volcanic glass (Fig. 3B). In other words, the U content of seawater is insufficient to create a significant excess of ^{234}U in a volcanic glass without elevating its Cl/K_2O ratio far beyond the observed maximum of ~0.3 (via bulk seawater addition during or after eruption). Syn- or post-eruptive
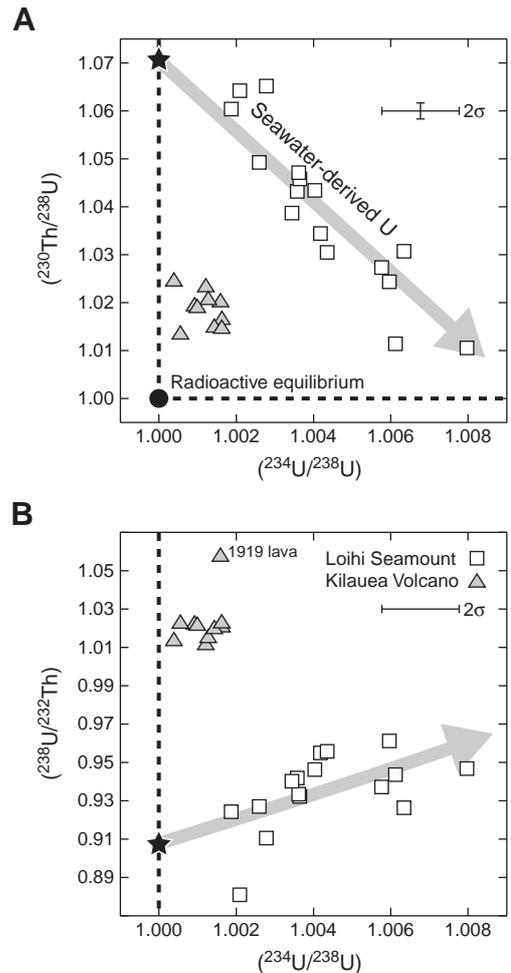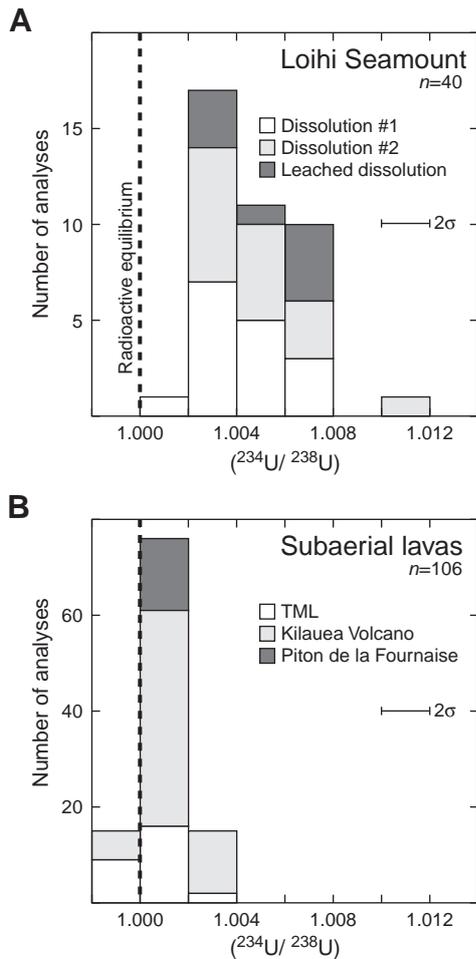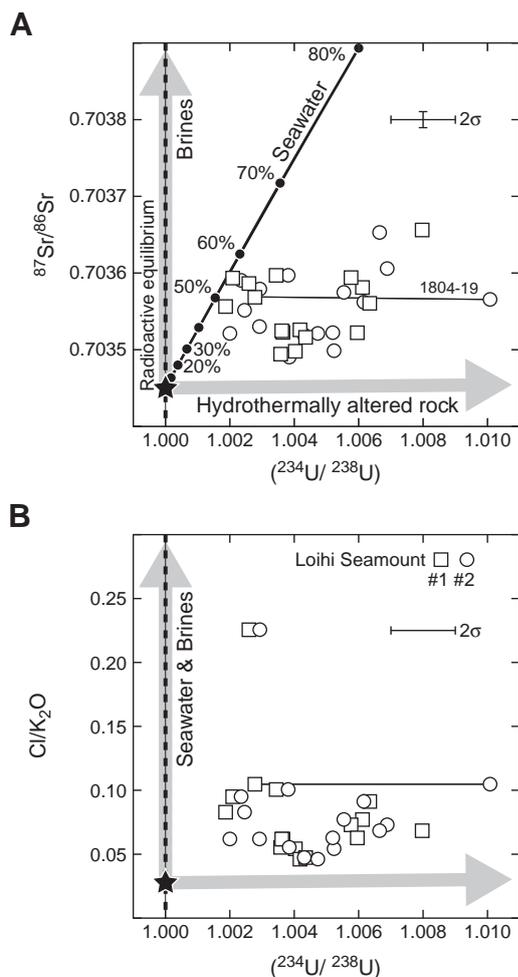
Fig. 1. Histograms of the $(^{234}U/^{238}U)$ ratios of (A) volcanic glasses from Loihi Seamount and (B) subaerial lavas. Samples in radioactive equilibrium for ^{234}U and ^{238}U should plot within error of the vertical dashed lines. TML stands for the Table Mountain Latite rock standard (Williams et al., 1992). The data from Kilauea Volcano include nine analyses of lavas from the Puu Oo eruption (Pietruszka et al., 2006) and numerous ($n = 55$) individual measurements of the Kil1919 and Menehune rock standards from Pietruszka et al. (2002) and Table 2. The $(^{234}U/^{238}U)$ ratios of TML and the Kilauea lavas are similar to subaerial lavas from historical eruptions of Piton de la Fournaise Volcano on Réunion Island (Pietruszka et al., 2009). The maximum error bar is shown on each plot. The uncertainty of the measurements for samples that were analyzed multiple times (Table 2) is expected to be smaller than this maximum.

addition of seawater in bulk to the Loihi glasses is also inconsistent with the combined $(^{234}U/^{238}U)$ and $^{87}Sr/^{86}Sr$ ratios of the samples. Loihi lavas are expected to show a range of $^{87}Sr/^{86}Sr$ ratios due to compositional heterogeneities in the mantle source region tapped by the volcano (e.g., Garcia et al., 1995). However, seawater has a much higher $^{87}Sr/^{86}Sr$ ratio (~0.7092; Palmer and Edmond, 1989) than any Hawaiian lavas. Assuming that U and Sr are added to the glass in proportion to their abundance in seawater, lava–seawater interaction during or after eruption should produce a strong correlation between the $(^{234}U/^{238}U)$ and $^{87}Sr/^{86}Sr$ ratios of the samples, which is not observed (Fig. 3A). These observations require that U is fractionated from Sr and Cl, and is preferentially concentrated in the seawater-derived component that is ultimately contaminating the Loihi glasses.

There are no studies of the relative U and Sr enrichment of volcanic glass when molten lava interacts with seawater. This interaction is known to occur on a time scale of minutes at magmatic temperatures, and is characterized mostly by the coalescence of microscopic (<100 μm) bubbles of seawater vapor in small patches near the lava–seawater interface (e.g., Soule et al., 2006), and by the formation of microfractures (as the lava is quenched) that are penetrated by seawater vapor (e.g., Schiffman et al., 2010). Even if U is preferentially

Fig. 2. A plot of the $(^{234}U/^{238}U)$ vs. (A) $(^{230}Th/^{238}U)$ and (B) $(^{238}U/^{232}Th)$ ratios of volcanic glasses from Loihi Seamount and lavas from Kilauea Volcano. Samples in radioactive equilibrium for ^{234}U and ^{238}U or ^{230}Th and ^{238}U should plot within error of the vertical or horizontal dashed lines, respectively. The black circle marks the position of a sample in radioactive equilibrium for all three isotopes. The white squares represent dissolution #1 of the Loihi glasses. The gray arrows trend along mixing lines between a hypothetical uncontaminated parental magma composition for Loihi (black star) and pure U derived from seawater. The Loihi parental magma is assumed to have $(^{234}U/^{238}U) = 1.0000$, $(^{230}Th/^{238}U) = 1.0705$, $(^{238}U/^{232}Th) = 0.9077$, [Th] = 1.00 ppm, and [U] = 0.30 ppm, whereas the seawater-derived U is assumed to have a $(^{234}U/^{238}U) = 1.1458$ from Cheng et al. (2000). The trajectory of the mixing line is not affected by the concentration of U in the contaminant. The data from Kilauea Volcano (gray triangles) include nine analyses of lavas from the Puu Oo eruption (Pietruszka et al., 2006) and the average Kil1919 value from Pietruszka et al. (2002). The maximum error bar is shown on each plot unless it is smaller than the size of the symbols.

removed from the seawater into the outer margin of the lava flow via diffusion or precipitation, the rapid and small-scale nature of this lava–seawater interaction provides little opportunity to generate even a modest increase in the $(^{234}U/^{238}U)$ ratio of a Loihi glass. For example, an enormous amount of seawater (>50%) would have to be added to a typical Loihi glass with 0.30 ppm U to match even the smallest amount of excess ^{234}U (~0.2%) due to the relatively low U concentration of seawater [3.2 ppb from Li (1982)]. An even higher water/rock ratio of ~7 would be required to match the Loihi glass with the largest ^{234}U excess (~1%). At magmatic temperatures (>900 °C), the seawater vapor is expected to be a single phase with a total salinity identical to the seawater from which it is derived, but filling a volume that is larger by a factor of ~20 (Perfit et al., 2003). Thus, the U concentration of the seawater vapor is likely to be less than cold seawater, and the required water/rock ratios even higher than calculated above. Thus, we conclude that the elevated $(^{234}U/^{238}U)$

A

B

Fig. 3. A plot of the (^{234}U/^{238}U) vs. (A) ^{87}Sr/^{86}Sr and (B) Cl/K$_2$O (wt.%/wt.%) ratios of volcanic glasses from Loihi Seamount. Samples in radioactive equilibrium for ^{234}U and ^{238}U should plot within error of the vertical dashed line. The white squares represent dissolution #1 and the white circles represent dissolution #2 of the Loihi glasses. The black star marks a hypothetical uncontaminated Loihi parental magma delivered from the mantle with [Sr] = 380 ppm and [U] = 0.30 ppm, a low Cl/K$_2$O ratio (0.03) using Cl and K$_2$O abundances from Kent et al. (1999b), and a low ^{87}Sr/^{86}Sr ratio (0.70345) within the range of Loihi basalts (Garcia et al., 1995). Relatively low ^{87}Sr/^{86}Sr and Cl/K$_2$O ratios were chosen to represent a magma that was least affected by any potential contamination with seawater-derived Sr or Cl. Seawater is assumed to have 8.0 ppm Sr and 3.2 ppb U (Li, 1982), ^{87}Sr/^{86}Sr = 0.7092 (Palmer and Edmond, 1989), and (^{234}U/^{238}U) = 1.1458 (Cheng et al., 2000). Mixing between this parental magma and seawater is shown in (A) by the solid line with small circles in 10% increments of bulk seawater addition. The trajectory of this magma–seawater mixing line in (B) is not shown because it is nearly indistinguishable from the vertical gray arrow that delineates mixing between the parental magma and hydrothermal brines. The brines are assumed to have a high Sr concentration [360 ppm from Coombs et al. (2004)], a low U concentration [0.1 ppb for pure high salinity hydrothermal fluid from Seyfried et al. (2003)], a seawater-like (^{234}U/^{238}U) ratio, and the range of Cl and K$_2$O abundances from Kent et al. (1999b). The ^{87}Sr/^{86}Sr ratio of the brine is poorly constrained, but is likely to be intermediate between seawater and volcanic glasses from Loihi due to interaction between seawater-derived hydrothermal fluids and the volcanic edifice (e.g., Coombs et al., 2004). However, an assumed range of ^{87}Sr/^{86}Sr ratios between a seawater-like value (as used for the mixing calculation) and ~0.7040 will have virtually no effect on the trajectory of the vertical arrow in (A) with respect to the scale of the plot. Bulk contamination of the parental magma with hydrothermally altered rocks that have been enriched in U, Sr, and Cl from seawater will lead to an elevated (^{234}U/^{238}U) ratio with little or no effect on the ^{87}Sr/^{86}Sr or Cl/K$_2$O ratios (nearly horizontal gray arrows). The U and Sr abundances and (^{234}U/^{238}U) and ^{87}Sr/^{86}Sr ratios of the altered rocks were calculated by adding seawater to the parental magma composition. The water/rock (W/R) ratio for the hydrothermal alteration was assumed to be ~400 with 100% precipitation of the U, although a similar trend is observed for a wide range of W/R ratios (e.g., 10–1000). The efficiency of Sr precipitation from seawater was assumed to be a factor of ~100 less than U (on a % enrichment basis) as discussed in the text. This leads to hydrothermally altered rocks with [Sr] = 400 ppm, [U] = 1.6 ppm, (^{234}U/^{238}U) = 1.118, and ^{87}Sr/^{86}Sr = 0.70369. The Cl and K$_2$O abundances assumed for the altered rock are from Kent et al. (1999b). The two analyses of sample 1804–19 are connected by a tie line. The maximum error bar is shown on each plot.

ratios of the Loihi glasses do not result from syn-eruptive addition of seawater U.

Post-eruptive seawater alteration at low temperature is well known to increase the U and Sr abundances and (^{234}U/^{238}U) and ^{87}Sr/^{86}Sr ratios of ancient MORB (e.g., Macdougall et al., 1979; Staudigel et al., 1995). Unfortunately, there are no controlled studies of the chemical and isotopic effects of incipient seawater alteration on young, visually unaltered volcanic glasses similar to those from Loihi. However, a detailed study of two pairs of "unaltered" MORB volcanic glasses and the corresponding heavily seawater-altered flow interiors (from individual samples erupted ~22 Ma ago) provides a guide to the expected behavior of U and Sr during an extended period of low-temperature interaction between basalt and seawater (Krolikowska-Ciaglo et al., 2007). Specifically, the average U abundances of the flow interiors were enriched relative to the glass by a factor of ~24 (from ~0.02 to 0.55 ppm). No Sr concentrations were presented, but the increases in the ^{87}Sr/^{86}Sr ratios of the samples (0.0011 on average) from ~0.70251 (glass) to 0.70366 (interior) implies a mere 20% enrichment of Sr (assuming that the contaminating seawater had a modern ^{87}Sr/^{86}Sr ratio). Thus, U appears to be more strongly absorbed into the basalt than Sr (by a factor of ~100 on a % enrichment basis) during low-temperature alteration by seawater. This process could potentially account for the inference that the Loihi glasses are preferentially contaminated with U from seawater (relative to Sr and Cl).

None of the analyzed Loihi glasses appear to have experienced significant post-eruptive alteration based on careful examination and hand-picking under a binocular microscope. Some of the samples had extremely thin, shiny, and transparent vesicle coatings or films (similar to those observed in some quenched subaerial volcanic glasses from Kilauea) that disappeared completely during the cleaning process. Nevertheless, incipient low-temperature seawater alteration might still have affected the outermost surfaces of the Loihi glasses. If U from seawater was significantly incorporated into any of the samples, chemical leaching prior to dissolution might be expected to at least partially remove the excess ^{234}U. Accordingly, we performed a leaching experiment on a subset of eight samples that display the full range of (^{234}U/^{238}U) ratios, including the glass that erupted in 1996 (P286-1F). This historical sample is particularly important because it was collected within ~6 months of eruption onto the seafloor (Garcia et al., 1998b; Rubin et al., 2005), and thus, had minimal time for post-eruptive alteration to occur. However, leaching failed to reduce the elevated (^{234}U/^{238}U) ratios of any of the Loihi glasses (Table 2). Thus, we conclude that the excesses of ^{234}U in volcanic glasses from Loihi do not result from post-eruptive alteration. Instead, these signatures probably derive from contamination of Loihi magmas with U-enriched hydrothermally altered rocks within the volcanic edifice.

5.2. Crustal contamination within the volcanic edifice

Hydrothermal brines are thought to form from the downward convection of seawater to the deep, hot "reaction zone" that overlies the melt lens or crystal-mush zone beneath the axis of a mid-ocean ridge (e.g., Alt, 1995). A similar process of brine formation probably occurs above the magmatic plumbing system of the submarine portion of a Hawaiian volcano (Fournier, 1987). Assimilation of these hydrothermal brines, rather than seawater-altered rock, is thought to be the most likely cause of the enrichments of Cl in fresh volcanic glasses from mid-ocean ridge and submarine Hawaiian eruptions (Coombs et al., 2004; Kent et al., 1999a,b; le Roux et al., 2006). Based on inferences from the Kilauea glasses with the most extreme Cl contents, these hydrothermal brines are expected to be strongly enriched in Sr (~360 ppm) and other trace elements (e.g., Rb, Ba, and Pb) due to processes such as boiling of seawater, separation of a highly saline phase, and chemical reactions between seawater-derived hydrothermal fluids and basalts or gabbros within the volcanic edifice

(Coombs et al., 2004). No estimates for the U content of these brines beneath Kilauea are available, but studies of active hydrothermal systems on mid-ocean ridges show that high-temperature, saline vent fluids are variably enriched in Sr but strongly depleted in U (~0.1 ppb) compared to seawater (e.g., Chen et al., 1986b; Michard et al., 1983; Seyfried et al., 2003). Assimilation of hydrothermal brines with this type of composition probably cannot account for the seawater-derived excesses of ^{234}U in Loihi glasses. For example, addition of ~1.3% brine with a NaCl concentration of 15% to a typical Loihi magma will match the highest observed Cl/K$_2$O ratio (~0.3) with no measurable increase in the ($^{234}U/^{238}U$) ratio (Fig. 3B). This is because the low (inferred) U concentration of the brine limits any significant increase in the ($^{234}U/^{238}U$) ratio of the contaminated magma, even though hydrothermal brine is expected to have a seawater-like ~14.6% excess of ^{234}U. This interpretation is also supported by the lack of correlation between the Cl/K$_2$O and ($^{234}U/^{238}U$) ratios of the Loihi glasses (Fig. 3B).

The nearly complete (~98%) depletion of U in hydrothermal fluids from mid-ocean ridges is thought to result from a change in the oxidation state of U from soluble U^{6+} to insoluble U^{4+}, which may be absorbed onto mineral or rock surfaces in the reaction zone (Chen et al., 1986b). This process would potentially create a region of U-enriched hydrothermally altered rocks with seawater-like ($^{234}U/^{238}U$) ratios in the area lying above Loihi's magmatic plumbing system (Fig. 4). In contrast, the fixed valence Sr^{2+} would be unaffected by this process of reduction, although precipitation of Sr or formation of secondary Sr-bearing minerals may still occur. By analogy with MORB altered by seawater at low temperature, a much smaller proportion of seawater Sr with a high $^{87}Sr/^{86}Sr$ ratio would presumably be added to the rock (compared to U). Assimilation of these seawater-altered rocks into mantle-derived magmas could easily account for the variable, elevated ($^{234}U/^{238}U$) ratios of the Loihi glasses. For example, mass-balance calculations show that for a water/rock ratio of ~400 (and 100% U removal from the deeply circulating seawater), less than 2% bulk assimilation would be required to account for the Loihi glass with the largest amount of excess ^{234}U (~1%). Even less assimilation and/or a smaller water/rock ratio would be required if the U enrichment is focused on the fractured surfaces of the altered rock, which would be the most likely scenario. If U is preferentially enriched in the altered rocks compared to Sr by a factor of ~100 (on a % enrichment basis) based on the analyses of Krolikowska-Ciaglo et al. (2007), then the $^{87}Sr/^{86}Sr$ ratio of the contaminated Loihi glass would

Fig. 4. Cross section of Loihi Seamount and a possible mechanism for crustal contamination. Mantle-derived magmas (black) at Loihi may be stored in a deep (~8–9 km) and/or shallow (~3–4 km) summit reservoir, or intrude into the volcano's north and south rift zones (dashed lines), prior to eruption. In region A, seawater convects downwards towards the magmatic plumbing system (arrows). This seawater may form a brine layer (gray area), or may recirculate upwards as hydrothermal fluids that vent on the seafloor in areas like Pele's Pit Crater (Davis and Clague, 1998). During this process, the rocks that lie above Loihi's magmatic plumbing system probably become enriched in seawater-derived U. In region B, magma in the shallow reservoir may become contaminated with the hydrothermally altered rocks, which leads to excess ^{234}U in the erupted lava. A similar process is inferred to occur along the volcano's rift zones. The cross section is modified from Garcia et al. (2006).

increase negligibly by 0.000004 (assuming a water/rock ratio of ~400 and 100% U removal). Similarly, the estimated Cl/K$_2$O ratio and Cl and K$_2$O abundances of altered basalt (e.g., Kent et al., 1999b) are probably insufficient to significantly increase the Cl/K$_2$O ratio of the contaminated Loihi glass (Fig. 3B). Thus, a small amount of assimilation of hydrothermally altered rock within the volcanic edifice is unlikely to significantly affect either the Sr isotope ratio (Fig. 3A) or Cl/K$_2$O ratio (Fig. 3B) of even the most contaminated Loihi glass.
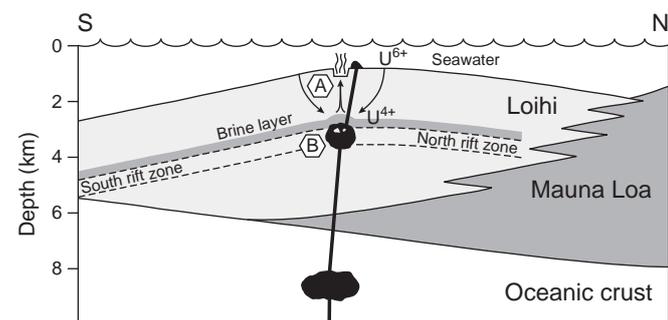
In summary, mantle-derived magmas at Loihi appear to be variably contaminated with two distinct materials (Fig. 4): hydrothermal brines (which create enrichments in Cl) and hydrothermally altered rocks (which create excesses of ^{234}U). The rocks may have been altered (and enriched in U) at low temperature after eruption, but we prefer the interpretation that they were hydrothermally altered given the anticipated efficiency of U enrichment from deeply circulating seawater. Both of these materials (brines and hydrothermally altered rocks) are expected to be found within the volcanic edifice as complementary parts of the volcano's active hydrothermal system (Fig. 4). However, the lack of correlation between the ($^{234}U/^{238}U$) and Cl/K$_2$O ratios of the glasses (Fig. 3B) suggests that variable proportions of brine and altered rock may be assimilated. Most of the Loihi glasses display consistent ($^{234}U/^{238}U$) ratios for each of the replicate dissolutions (Table 2). In most cases, therefore, the contamination probably occurred within the volcano's deep magmatic plumbing system and/or a relatively long time prior to eruption, which allowed the magma to homogenize completely. Triplicate dissolutions of two samples, however, gave variable excesses of ^{234}U (1804-19 and possibly 1804-10) that were not improved by leaching. Thus, the seawater-derived U component appears to be heterogeneously distributed in these samples. This might be explained if these magmas were contaminated immediately prior to eruption during flow towards the surface, which could prevent the magma from mixing thoroughly.

6. What are the mantle-derived ($^{230}Th/^{238}U$) and ($^{238}U/^{232}Th$) ratios?

Crustal contamination of a basaltic magma with hydrothermally altered U-enriched rocks might be expected to obscure a sample's mantle-derived ($^{230}Th/^{238}U$) and ($^{238}U/^{232}Th$) ratios. For example, the increase in the ($^{234}U/^{238}U$) ratios of the Loihi glasses during the contamination process may occur either by isotopic exchange (which would not necessarily be expected to raise the U concentration of the sample) or by bulk addition of seawater-derived U to the sample. The strong negative correlation between the ($^{234}U/^{238}U$) and ($^{230}Th/^{238}U$) ratios of the glasses (Fig. 2A) is consistent with the idea of variable amounts of bulk addition of seawater-derived U to the samples, rather than U isotopic exchange. This process has likely increased the ($^{238}U/^{232}Th$) ratios of the contaminated glasses as well (Fig. 2B).

Fortunately, the measured ($^{230}Th/^{238}U$) and ($^{238}U/^{232}Th$) ratios of a sample of volcanic glass that has been recently contaminated with seawater-derived U (in bulk) may be corrected back to their original pre-contamination values using a simple mass-balance calculation because the end-member ($^{234}U/^{238}U$) ratios of both seawater (1.146) and mantle-derived magma (1.000) are known. Assuming that the mass of the contaminant is negligible (i.e., it is dominated by the U alone rather than melted rock), the following equation provides a first-order estimate of the sample's original mantle-derived U concentration [U$_{Corr.}$]:

$$[U_{Corr.}] = [U_{Meas.}] \times \left\{ \frac{\left(\frac{^{234}U}{^{238}U}\right)_{Meas.} - \left(\frac{^{234}U}{^{238}U}\right)_{Seawater}}{\left(\frac{^{234}U}{^{238}U}\right)_{Equil.} - \left(\frac{^{234}U}{^{238}U}\right)_{Seawater}} \right\},$$

where "Meas." refers to the measured U concentration, [U], or (^{234}U/^{238}U) ratio, and "Equil." refers to the (^{234}U/^{238}U) ratio for radioactive equilibrium. This corrected U concentration may then be used to calculate the mantle-derived (^{230}Th/^{238}U) and (^{238}U/^{232}Th) ratios of the sample. For a small to moderate increase in the (^{234}U/^{238}U) ratio of a sample (≤1%), the enrichment of U is actually a factor of ~7 greater than the amount of excess ^{234}U. Thus, a (^{234}U/^{238}U) ratio of 1.01 implies ~7% addition of U from seawater, which would lead to an underestimate of the sample's mantle-derived (^{230}Th/^{238}U) ratio [and an overestimate of its (^{238}U/^{232}Th) ratio] by a similar amount. For comparison, this corresponds to approximately one-fifth of the entire range of ^{230}Th–^{238}U disequilibria for MORB (e.g., Bourdon et al., 1996) and Hawaiian lavas (Sims et al., 1999).

This type of correction may be especially important for future studies of mantle processes using submarine lavas because the ^{230}Th–^{238}U disequilibria of volcanic glasses can now be measured with much higher precision than was previously possible (e.g., Luo et al., 1997; Pietruszka et al., 2002). Unfortunately, the correction magnifies the analytical uncertainty of the U concentration, and thus, the uncertainty of the (^{230}Th/^{238}U) and (^{238}U/^{232}Th) ratios. For example, the propagated error on the corrected U concentration of a sample with (^{234}U/^{238}U) = 1.010 ± 0.002 is ~1.5%, which is a factor of ~7 worse than the precision of the measured U concentration (~0.2% in this study). Most of the error magnification comes from the analytical uncertainty of the (^{234}U/^{238}U) ratios. Thus, high-precision measurements of the (^{234}U/^{238}U) ratios of submarine lavas that have potentially been contaminated with seawater-derived U are absolutely critical in order to determine precisely their mantle-derived (^{230}Th/^{238}U) and (^{238}U/^{232}Th) ratios. Future studies can improve upon the correction by (1) obtaining a higher precision on the measured (^{234}U/^{238}U) ratios than is currently possible using MC–ICP-MS (e.g., Luo et al., 1997; Pietruszka et al., 2002) or TIMS (e.g., Yokoyama et al., 2001), and (2) evaluating our assumption that the mass of the contaminant is negligible.

We applied the mass-balance correction to the U abundances and the (^{230}Th/^{238}U) and (^{238}U/^{232}Th) ratios of the Loihi glasses to estimate the mantle-derived values for each sample (Table 2). On an equiline diagram (Fig. 5A), the measured (^{238}U/^{232}Th) and (^{230}Th/^{232}Th) ratios of the Loihi samples display a weak positive correlation ($R^2 = 0.43$). This correlation improves significantly after correction of the (^{238}U/^{232}Th) ratios ($R^2 = 0.86$), which suggests that the mass-balance correction is valid to a first order. Similarly, the samples display a wide measured range in the amount of excess ^{230}Th from ~1.1–6.5% with an average of 3.9% (Fig. 5B), which extends the ~3.9–7.3% range (avg. 4.8%) for previous analyses of four Loihi samples (Rubin et al., 2005; Sims et al., 1999). Interestingly, the measured (^{230}Th/^{238}U) ratios of some of the Loihi glasses are similar to or lower than lavas from Kilauea (Fig. 5B). After correction, however, the range in amount of excess ^{230}Th for the Loihi glasses decreases by a factor of ~2 to higher values of ~5.6–8.6% with an average of 7.0% (Fig. 5B). In the absence of high-precision measurements of the (^{234}U/^{238}U) ratios, the relatively large measured range in the ^{230}Th–^{238}U disequilibria and the inverse correlation between the (^{230}Th/^{238}U) and (^{238}U/^{232}Th) ratios of the samples would likely have been misinterpreted. Instead, we argue that the corrected values represent the best estimates for the mantle-derived (^{230}Th/^{238}U) and (^{238}U/^{232}Th) ratios of volcanic glasses from Loihi.

7. Mantle source and melting conditions at Loihi Seamount

The corrected (^{230}Th/^{238}U) and (^{238}U/^{232}Th) ratios (Table 2) can be used to compare the mantle source and melting conditions beneath Loihi with the neighboring shield volcano, Kilauea. The (^{238}U/^{232}Th) ratios of the Loihi glasses (0.91 on average) are lower than Kilauea lavas (1.04 on average) by ~14% (Fig. 5A). Since both Th and U are highly incompatible during partial melting of the mantle (and thus,
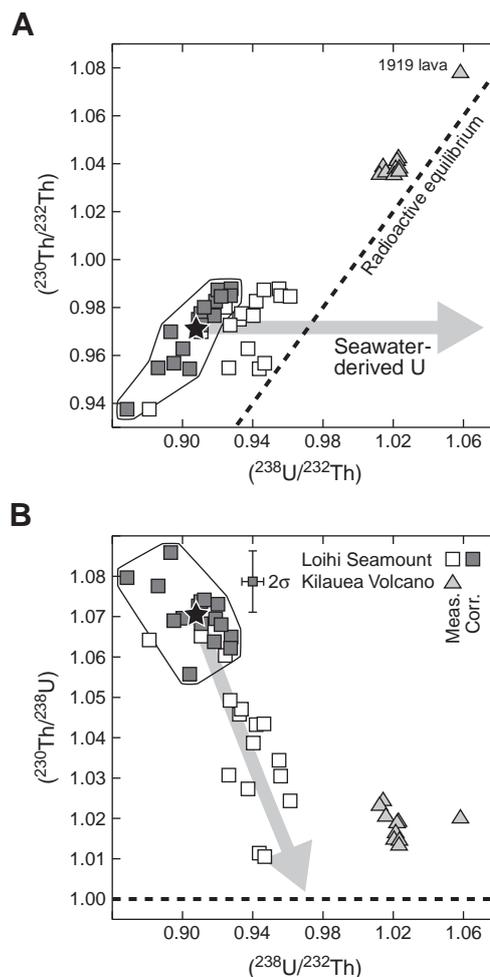
Fig. 5. A plot of the (^{238}U/^{232}Th) vs. (A) (^{230}Th/^{232}Th) and (B) (^{230}Th/^{238}U) ratios of volcanic glasses from Loihi Seamount and lavas from Kilauea Volcano. Samples in radioactive equilibrium for ^{230}Th and ^{238}U should plot within error of the diagonal or horizontal dashed lines. The white squares are the measured values for dissolution #1 of the Loihi glasses, whereas the gray squares are the values that have been corrected for the addition of seawater-derived U due to crustal contamination. The gray arrows trend along mixing lines between a hypothetical uncontaminated parental magma composition for Loihi (black star) and pure U derived from seawater. The assumed compositions for the parental magma and seawater-derived U are described in the caption to Fig. 2 [the (^{230}Th/^{232}Th) ratio of the parental magma is assumed to be 0.9717]. The trajectory of the mixing line is not affected by the concentration of U in the contaminant. The data sources of the Kilauea lavas (gray triangles) are listed in the caption to Fig. 2. The maximum error bars are smaller than the size of the symbols, except for the corrected (^{238}U/^{232}Th) and (^{230}Th/^{238}U) ratios of the Loihi glasses.

not significantly fractionated from their relative abundances in the mantle source region except at low degrees of partial melting), the difference in the (^{238}U/^{232}Th) ratios of lavas from these volcanoes indicates that Loihi and Kilauea magmas are derived from compositionally distinct sources (e.g., Garcia et al., 1998b). The overall correlation between the (^{238}U/^{232}Th) and (^{230}Th/^{232}Th) ratios of the Kilauea and Loihi samples suggests that the composition of the mantle source region, rather than ingrowth of ^{230}Th during partial melting (e.g., Spiegelman and Elliott, 1993), is the dominant control on the Th isotopic composition of magmas from both volcanoes. A mantle source control on the relatively low (^{238}U/^{232}Th) and (^{230}Th/^{232}Th) ratios of the Loihi glasses is consistent with the observation that this volcano erupts lavas with relatively high ^{208}Pb/^{206}Pb ratios (Abouchami et al., 2005). However, the overlapping ^{87}Sr/^{86}Sr ratios of the Loihi glasses (Table 2) and historical Kilauea lavas (Pietruszka and Garcia, 1999) suggest that any differences in the composition of their mantle sources are relatively small compared to the overall range for Hawaiian volcanoes.

Loihi is thought to have nearly completed its transition from alkalic to tholeiitic volcanism (Garcia et al., 1995), although both rock types have probably erupted recently based on the youthful appearance of several alkalic cones on the volcano's south rift zone (Garcia et al., 2006). One of these alkalic glasses (1804-19) has the largest amount of excess ^{230}Th observed in this study, although the average of the alkalic Loihi glasses (7.8 ± 1.6% excess ^{230}Th) is only slightly larger than the tholeiitic glasses (6.8 ± 1.2% excess ^{230}Th). This suggests that the process of melt generation at Loihi leads to similar (^{230}Th/^{238}U) ratios for both alkalic and tholeiitic magmas, despite the fact that the alkalic glasses might be expected to be produced by significantly lower degrees of partial melting. For example, the higher Th abundances of the alkalic glasses (Table 2) suggest that they were produced by up to a factor of ~2 lower degree of partial melting than the tholeiitic glasses (since Th is a highly incompatible element during partial melting of the mantle). In contrast, the range in the degree of partial melting for the tholeiitic Loihi glasses (Table 2) is probably similar to historical Kilauea lavas (~5–10%; Pietruszka and Garcia, 1999) because they have overlapping Th abundances (Pietruszka et al., 2001). Nevertheless, all of the Loihi glasses have a larger amount of excess ^{230}Th than observed in Kilauea lavas (Fig. 5B). This suggests that ingrowth of ^{230}Th (e.g., Spiegelman and Elliott, 1993) rather than net Th–U fractionation (e.g., Sims et al., 1995) during partial melting, is the dominant control on the ^{230}Th–^{238}U disequilibria of Loihi and Kilauea magmas. Thus, a simple explanation for the higher (^{230}Th/^{238}U) ratios of the Loihi glasses is that they formed by relatively low rates of mantle upwelling because this would provide more time for the ingrowth of ^{230}Th (e.g., Spiegelman and Elliott, 1993).

Estimates for the rate of mantle upwelling beneath Kilauea based on modeling of the U-series isotope disequilibria of its historical lavas range from ~40 to 1000 cm/yr (Pietruszka et al., 2001; Sims et al., 1999). The upwelling rate of the mantle tapped by Loihi can be quantified using a similar approach. Although it is possible to perform this modeling with only the ^{230}Th–^{238}U disequilibria of the Loihi glasses, the results are better constrained if the ^{226}Ra–^{230}Th disequilibria are also used. Accordingly, we use the ingrowth model of Spiegelman and Elliott (1993) with a source that lies in radioactive equilibrium prior to melting to match the average (^{226}Ra/^{230}Th) = 1.11 from measurements of two samples from the 1996 Loihi eruption (Rubin et al., 2005) and the average (^{230}Th/^{238}U) = 1.070 from all of the Loihi glasses in Table 2. In order to compare directly with our previous melting model results for Kilauea, the same mineralogy for Loihi's mantle source is assumed (60% olivine, 15% clinopyroxene, 15% orthopyroxene, and 10% garnet). In addition, we use a melt-column height of 55 km, the numerical solution of Spiegelman (2000), a 2.5–10% range in the degree of partial melting, and the Ra, Th and U partition coefficients that were optimized for partial melting of the mantle beneath Kilauea from Pietruszka et al. (2001). The target (^{226}Ra/^{230}Th) and (^{230}Th/^{238}U) ratios of the Loihi glasses can be matched by a narrow ~5–6 cm/yr range in the rate of mantle upwelling (and a melt-zone porosity of ~2%), which is at least an order of magnitude lower than the 50–1000 cm/yr range of upwelling rates inferred for the mantle beneath Kilauea using similar model parameters (Pietruszka et al., 2001). These model results are consistent with the idea that Loihi is tapping mantle that is upwelling slowly (e.g., Sims et al., 1999) on the margin of the Hawaiian plume (e.g., Garcia et al., 1995).

8. Conclusions

Volcanic glasses collected from Loihi Seamount, including one from the volcano's 1996 eruption, have small to moderate amounts of excess ^{234}U (~0.2–1.0%). These signatures cannot be explained by syn- or post-eruptive interaction between lava and seawater. Instead, mantle-derived magmas at Loihi appear to be variably contaminated with two distinct crustal materials: hydrothermal brines (which create enrich-

ments in Cl) and U-enriched hydrothermally altered rocks (which create excesses of ^{234}U). Both of these materials are expected to be found within the volcanic edifice as complementary parts of the volcano's hydrothermal system. The Loihi glasses display a wide measured range in the amount of excess ^{230}Th from ~1 to 7% (due to the addition of seawater-derived U) that overlaps with lavas from Kilauea Volcano (~2% excess ^{230}Th). We correct the ^{230}Th–^{238}U disequilibria of the Loihi glasses back to their original pre-contamination values using their ^{234}U–^{238}U disequilibria and a simple mass-balance calculation. This correction suggests that mantle-derived magmas at Loihi have a narrow range of ~6–9% excess ^{230}Th, which is significantly larger than the neighboring volcano, Kilauea. This difference is consistent with the idea that Loihi is tapping mantle that is upwelling slowly (~5–6 cm/yr) on the margin of the Hawaiian plume.

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References

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.

Alt, J.C., 1995. Subseafloor processes in mid-ocean ridge hydrothermal systems. In: Humphris, S.E., Zierenberg, R.A., Mullineaux, L.S., Thomson, R.E. (Eds.), Seafloor Hydrothermal Systems: Physical, Chemical, Biological, and Geological Interactions: AGU Geophys. Monogr., vol. 91, pp. 85–114.

Bindeman, I., Gurenko, A., Sigmarsson, O., Chaussidon, M., 2008. Oxygen isotope heterogeneity and disequilibria of olivine crystals in large volume Holocene basalts from Iceland: evidence for magmatic digestion and erosion of Pleistocene hyaloclastites. Geochim. Cosmochim. Acta 72, 4397–4420.

Bourdon, B., Zindler, A., Elliott, T., Langmuir, C.H., 1996. Constraints on mantle melting at mid-ocean ridges from global ^{238}U–^{230}Th disequilibrium data. Nature 384, 231–235.

Chen, J.H., Edwards, R.L., Wasserburg, G.J., 1986a. ^{238}U, ^{234}U and ^{232}Th in seawater. Earth Planet. Sci. Lett. 80, 241–251.

Chen, J.H., Wasserburg, G.J., von Damm, K.L., Edmond, J.M., 1986b. The U–Th–Pb systematics in hot springs on the East Pacific Rise at 21°N and Guaymas Basin. Geochim. Cosmochim. Acta 50, 2467–2479.

Cheng, H., Edwards, R.L., Hoff, J., Gallup, C.D., Richards, D.A., Asmerom, Y., 2000. The half-lives of uranium-234 and thorium-230. Chem. Geol. 169, 17–33.

Clague, D.A., Moore, J.G., Dixon, J.E., Friesen, W.B., 1995. Petrology of submarine lavas from Kilauea's Puna Ridge, Hawaii. J. Petrol. 36, 299–349.

Coombs, M.L., Sisson, T.W., Kimura, J.-I., 2004. Ultra-high chlorine in submarine Kilauea glasses: evidence for direct assimilation of brine by magma. Earth Planet. Sci. Lett. 217, 297–313.

Davis, A.S., Clague, D.A., 1998. Changes in the hydrothermal system at Loihi Seamount after the formation of Pele's pit in 1996. Geology 26, 399–402.

Davis, M.G., Garcia, M.O., Wallace, P., 2003. Volatiles in glasses from Mauna Loa Volcano, Hawaii: implications for magma degassing and contamination, and growth of Hawaiian volcanoes. Contrib. Mineral. Petrol. 144, 570–591.

Eiler, J.M., Grönvold, K., Kitchen, N., 2000. Oxygen isotope evidence for the origin of chemical variations in lavas from Theistareykir volcano in Iceland's northern volcanic zone. Earth Planet. Sci. Lett. 184, 269–286.

Elkins, L.J., Sims, K.W.W., Prytulak, J., Mattielli, N., Elliott, T., Blichert-Toft, J., Blusztajn, J., Dunbar, N., Devey, C., Mertz, D., Schilling, J.-G., in revision. Melt generation beneath the slow-spreading Kolbeinsey Ridge from ^{238}U, ^{230}Th, and ^{231}Pa excesses. Geochim. Cosmochim. Acta.

Fournier, R.O., 1987. Conceptual models of brine evolution in magmatic-hydrothermal systems. In: Decker, R.W., Wright, T.L., Stauffer, P.H. (Eds.), Volcanism in Hawaii: US Geol. Surv. Prof. Pap., vol. 1350, pp. 1487–1506.

Garcia, M.O., Jorgenson, B.A., Mahoney, J.J., 1993. An evaluation of temporal geochemical evolution of Loihi summit lavas: results from *Alvin* submersible dives. J. Geophys. Res. 98, 537–550.

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., Ito, E., Eiler, J.M., Pietruszka, A.J., 1998a. Crustal contamination of Kilauea Volcano magmas revealed by oxygen isotope analyses of glass and olivine from Puu Oo eruption lavas. J. Petrol. 39, 803–817.

Garcia, M.O., Rubin, K.H., Norman, M.D., Rhodes, J.M., Graham, D.W., Muenow, D.W., Spencer, K., 1998b. 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., Caplan-Auerbach, J., De Carlo, E.H., Kurz, M.D., Becker, N., 2006. Geology, geochemistry and earthquake history of Loihi Seamount, Hawaii's youngest volcano. Chem. Erde 66, 81–108.

Hauri, E., Wang, J., Dixon, J.E., King, P.L., Mandeville, C., Newman, S., 2002. SIMS analysis of volatiles in silicate glasses, 1: calibration, matrix effects and comparisons with FTIR. Chem. Geol. 183, 99–114.

Hémond, C., Arndt, N.T., Lichtenstein, U., Hofmann, A.W., Oskarsson, N., Steinthorsson, S., 1993. The heterogeneous Iceland plume: Nd–Sr–O isotopes and trace element constraints. J. Geophys. Res. 98, 15833–15850.

Jaffey, A.H., Flynn, K.F., Glendenin, L.E., Bentley, W.C., Essling, A.M., 1971. Precision measurement of half-lives and specific activities of ^{235}U and ^{238}U. Phys. Rev. 4, 1889–1906.

Karl, D.M., McMurtry, G.M., Malahoff, A., Garcia, M.O., 1988. Loihi Seamount, Hawaii: a mid-plate volcano with a distinctive hydrothermal system. Nature 335, 532–535.

Kent, A.J.R., Clague, D.A., Honda, M., Stolper, E.M., Hutcheon, I.D., Norman, M.D., 1999a. Widespread assimilation of a seawater-derived component at Loihi Seamount, Hawaii. Geochim. Cosmochim. Acta 63, 2749–2761.

Kent, A.J.R., Norman, M.D., Hutcheon, I.D., Stolper, E.M., 1999b. Assimilation of seawater-derived components in an oceanic volcano: evidence from matrix glasses and glass inclusions from Loihi seamount, Hawaii. Chem. Geol. 156, 299–319.

Krolikowska-Ciaglo, S., Deyhle, A., Hauff, F., Hoernle, K., 2007. Boron isotope geochemistry and U–Pb systematics of altered MORB from the Australian Antarctic Discordance (ODP Leg 187). Chem. Geol. 242, 455–469.

le Roux, P.J., Shirey, S.B., Hauri, E.H., Perfit, M.R., Bender, J.F., 2006. The effects of variable sources, processes and contaminants on the composition of northern EPR MORB (8–10°N and 12–14°N): evidence from volatiles (H_2O, CO_2, S) and halogens (F, Cl). Earth Planet. Sci. Lett. 251, 209–231.

Li, Y.-H., 1982. A brief discussion on the mean oceanic residence time of elements. Geochim. Cosmochim. Acta 46, 2671–2675.

Luo, X., Rehkämper, M., Lee, D.-C., Halliday, A.N., 1997. High precision ^{230}Th/^{232}Th and ^{234}U/^{238}U measurements using energy-filtered ICP magnetic sector multiple collector mass spectrometry. Int. J. Mass Spectrom. Ion Processes 171, 105–117.

Macdonald, G.A., Katsura, T., 1964. Chemical composition of Hawaiian lavas. J. Petrol. 5, 82–133.

Macdougall, J.D., Finkel, R.C., Carlson, J., Krishnaswami, S., 1979. Isotope evidence for uranium exchange during low-temperature alteration of oceanic basalt. Earth Planet. Sci. Lett. 42, 27–34.

Malahoff, A., McMurtry, G.M., Wiltshire, J.C., Yeh, H.-W., 1982. Geology and chemistry of hydrothermal deposits from active submarine volcano Loihi, Hawaii. Nature 298, 234–239.

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.

Michael, P.J., Cornell, W.C., 1998. Influence of spreading rate and magma supply on crystallization and assimilation beneath mid-ocean ridges: evidence from chlorine and major element chemistry of mid-ocean ridge basalts. J. Geophys. Res. 103, 18325–18356.

Michael, P.J., Schilling, J.-G., 1989. Chlorine in mid-ocean ridge magmas: evidence for assimilation of seawater-derived components. Geochim. Cosmochim. Acta 53, 3131–3143.

Michard, A., Albarède, F., Michard, G., Minster, J.F., Charlou, J.L., 1983. Rare-earth elements and uranium in high-temperature solutions from East Pacific Rise hydrothermal vent field (13°N). Nature 303, 795–797.

Palmer, M.R., Edmond, J.M., 1989. The strontium isotope budget of the modern ocean. Earth Planet. Sci. Lett. 92, 11–26.

Peate, D.W., Hawkesworth, C.J., van Calsteren, P.W., Taylor, R.N., Murton, B.J., 2001. ^{238}U–^{230}Th constraints on mantle upwelling and plume-ridge interaction along the Reykjanes Ridge. Earth Planet. Sci. Lett. 187, 259–272.

Perfit, M.R., Cann, J.R., Fornari, D.J., Engels, J., Smith, D.K., Ridley, W.I., Edwards, M.H., 2003. Interaction of sea water and lava during submarine eruptions at mid-ocean ridges. Nature 426, 62–65.

Pietruszka, A.J., Garcia, M.O., 1999. A rapid fluctuation in the mantle source and melting history of Kilauea Volcano inferred from the geochemistry of its historical summit lavas (1790–1982). J. Petrol. 40, 1321–1342.

Pietruszka, A.J., Rubin, K.H., Garcia, M.O., 2001. ^{226}Ra–^{230}Th–^{238}U disequilibria of historical Kīlauea lavas (1790–1982) and the dynamics of mantle melting within the Hawaiian plume. Earth Planet. Sci. Lett. 186, 15–31.

Pietruszka, A.J., Carlson, R.W., Hauri, E.H., 2002. Precise and accurate measurement of ^{226}Ra–^{230}Th–^{238}U disequilibria in volcanic rocks using plasma ionization multi-collector mass spectrometry. Chem. Geol. 188, 171–191.

Pietruszka, A.J., Hauri, E.H., Carlson, R.W., Garcia, M.O., 2006. Remelting of recently depleted mantle within the Hawaiian plume inferred from the ^{226}Ra–^{230}Th–^{238}U disequilibria of Puu Oo eruption lavas. Earth Planet. Sci. Lett. 244, 155–169.

Pietruszka, A.J., Hauri, E.H., Blichert-Toft, J., 2009. Crustal contamination of mantle-derived magmas within Piton de la Fournaise Volcano, Réunion Island. J. Petrol. 50, 661–684.

Price, R.C., George, R., Gamble, J.A., Turner, S., Smith, I.E.M., Cook, C., Hobden, B., Dosseto, A., 2007. U–Th–Ra fractionation during crustal-level andesite formation at Ruapehu volcano, New Zealand. Chem. Geol. 244, 437–451.

Rubin, K.H., van der Zander, I., Smith, M.C., Bergmanis, E.C., 2005. Minimum speed limit for ocean ridge magmatism from ^{210}Pb–^{226}Ra–^{230}Th disequilibria. Nature 437, 534–538.

Russell, W.A., Papanastassiou, D.A., Tombrello, T.A., 1978. Ca isotope fractionation on the Earth and other solar system materials. Geochim. Cosmochim. Acta 42, 1075–1090.

Russo, C.J., Rubin, K.H., Graham, D.W., 2009. Mantle melting and magma supply to the Southeast Indian Ridge: the roles of lithology and melting conditions from U-series disequilibria. Earth Planet. Sci. Lett. 278, 55–66.

Schiffman, P., Zierenberg, R., Chadwick Jr., W.W., Clague, D.A., Lowenstern, J., 2010. Contamination of basaltic lava by seawater: evidence found in a lava pillar from Axial Seamount, Juan de Fuca Ridge. Geochem. Geophys. Geosyst. 11, Q04004. doi:10.1029/2009GC003009.

Seyfried Jr., W.E., Seewald, J.S., Berndt, M.E., Ding, K., Foustoukos, D.I., 2003. Chemistry of hydrothermal vent fluids from the Main Endeavour Field, northern Juan de Fuca Ridge: geochemical controls in the aftermath of June 1999 seismic events. J. Geophys. Res. 108, 2429. doi:10.1029/2002JB001957.

Sigmarsson, O., Condomines, M., Fourcade, S., 1992. A detailed Th, Sr and O isotope study of Hekla: differentiation processes in an Icelandic Volcano. Contrib. Mineral. Petrol. 112, 20–34.

Sims, K.W.W., DePaolo, D.J., Murrell, M.T., Baldridge, W.S., Goldstein, S.J., Clague, D.A., 1995. Mechanisms of magma generation beneath Hawaii and mid-ocean ridges: uranium/thorium and samarium/neodymium isotopic evidence. Science 267, 508–512.

Sims, K.W.W., DePaolo, D.J., Murrell, M.T., Baldridge, W.S., Goldstein, S., Clague, D., Jull, M., 1999. Porosity of the melting zone and variations in the solid mantle upwelling rate beneath Hawaii: inferences from ^{238}U–^{230}Th–^{226}Ra and ^{235}U–^{231}Pa disequilibria. Geochim. Cosmochim. Acta 63, 4119–4138.

Sims, K.W.W., Goldstein, S.J., Blichert-Toft, J., Perfit, M.R., Keleman, P., Fournari, D.J., Michael, P., Murrell, M.T., Hart, S.R., DePaolo, D.J., Layne, G., Ball, L., Jull, M., Bender, J., 2002. Chemical and isotopic constraints on the generation and transport of magma beneath the East Pacific Rise. Geochim. Cosmochim. Acta 66, 3481–3504.

Soule, S.A., Fornari, D.J., Perfit, M.R., Ridley, W.I., Reed, M.H., Cann, J.R., 2006. Incorporation of seawater into mid-ocean ridge lava flows during emplacement. Earth Planet. Sci. Lett. 252, 289–307.

Spiegelman, M., 2000. UserCalc: a web-based uranium series calculator for magma migration problems. Geochem. Geophys. Geosyst. 1, 1016. doi:10.1029/1999GC000030.

Spiegelman, M., Elliott, T., 1993. Consequences of melt transport for uranium series disequilibrium in young lavas. Earth Planet. Sci. Lett. 118, 1–20.

Staudigel, H., Davies, G.R., Hart, S.R., Marchant, K.M., Smith, B.M., 1995. Large scale isotopic Sr, Nd and O isotopic anatomy of altered oceanic crust: DSDP/ODP sites 417/418. Earth Planet. Sci. Lett. 130, 169–185.

Tepley III, F.J., Lundstrom, C.C., Sims, K.W.W., Hékinian, R., 2004. U-series disequilibria in MORB from the Garrett Transform and implications for mantle melting. Earth Planet. Sci. Lett. 223, 79–97.

Wang, Z., Eiler, J.M., 2008. Insights into the origin of low-δ^{18}O basaltic magmas in Hawaii revealed from in situ measurements of oxygen isotope compositions of olivines. Earth Planet. Sci. Lett. 269, 377–387.

Williams, R.W., Collerson, K.D., Gill, J.B., Deniel, C., 1992. High Th/U ratios in subcontinental lithospheric mantle: mass spectrometric measurement of Th isotopes in Gaussberg lamproites. Earth Planet. Sci. Lett. 111, 257–268.

Yokoyama, T., Makishima, A., Nakamura, E., 2001. Precise analysis of ^{234}U/^{238}U ratio using UO$_2^+$ ion with thermal ionization mass spectrometry for natural samples. Chem. Geol. 181, 1–12.