

Oxygen Isotope Evidence for Chemical Interaction of Kīlauea Historical Magmas with Basement Rocks

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RECEIVED JANUARY 30, 2007; ACCEPTED JUNE 13, 2007
ADVANCE ACCESS PUBLICATION 19 JULY 2007

Kīlauea historical summit lavas have a wide range in matrix $\delta^{18}\text{O}_{\text{VSMOW}}$ values (4.9–5.6‰) with lower values in rocks erupted following a major summit collapse or eruptive hiatus. In contrast, $\delta^{18}\text{O}$ values for olivines in most of these lavas are nearly constant (5.1 ± 0.1‰). The disequilibrium between matrix and olivine $\delta^{18}\text{O}$ values in many samples indicates that the lower matrix values were acquired by the magma after olivine growth, probably just before or during eruption. Both Mauna Loa and Kīlauea basement rocks are the likely sources of the contamination, based on O, Pb and Sr isotope data. However, the extent of crustal contamination of Kīlauea historical magmas is probably minor (<12%, depending on the assumed contaminant) and it is superimposed on a longer-term, cyclic geochemical variation that reflects source heterogeneity. Kīlauea's heterogeneous source, which is well represented by the historical summit lavas, probably has magma $\delta^{18}\text{O}$ values within the normal mid-ocean ridge basalt mantle range (5.4–5.8‰) based on the new olivine $\delta^{18}\text{O}$ values.

KEY WORDS: Hawaii; Kīlauea; basalt; oxygen isotopes; crustal contamination

INTRODUCTION

Kīlauea volcano has undergone dramatic changes over the last ~320 years varying from continuous effusion to explosive eruptions with major summit collapses (>100 m) (Macdonald *et al.*, 1983; Holcomb 1987; Garcia *et al.*, 2003). The 1924 summit explosions and collapse were

accompanied by a reversal in the temporal trend in lava composition (including incompatible trace element abundances and Pb, Sr and Nd isotope ratios) that was interpreted to reflect changes in melting processes and compositional heterogeneity in the source (Pietruszka & Garcia, 1999a; Garcia *et al.*, 2003). The additional effects of crustal contamination were superimposed on the compositions of lavas erupted just after the collapse (Pietruszka & Garcia, 1999a). Kīlauea's historical period has been punctuated by numerous collapses (1823, 1832, 1840, 1868, 1924; Table 1). Here we evaluate the role of crustal contamination during the entire historical period using O isotopes, which have been shown to be a sensitive indicator of crustal contamination (e.g. Taylor, 1974).

Crustal contamination has been documented at various oceanic islands (e.g. Pitcairn; Eiler *et al.*, 1995; Canary, Thirlwall *et al.*, 1997; Hawai'i, Gaffney *et al.*, 2005) including the current eruption of Kīlauea, where magmas were stored for many years in the rift zone prior to eruption (Garcia *et al.*, 1998). It should also be noted that $\delta^{18}\text{O}$ variations could also reflect source heterogeneity (e.g. Eiler 2001). To unravel the potentially offsetting influences of source heterogeneity vs crustal contamination, we analyzed O isotopes in coexisting olivine and matrix material from well-characterized historical lavas from Kīlauea volcano (20 eruptions during ~400 years; Pietruszka & Garcia, 1999a; Garcia *et al.*, 2003). These results provide a detailed time series of O isotopes, which are compared

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Table 1: Historical Kīlauea summit geological events

Date	Event
~1670	Explosions and circumferential fissure lava eruption
~1790	Violent, phreatomagmatic explosions and summit collapse
1832	>100 m caldera collapse
1840	~100 m caldera collapse and large east rift zone eruption
1868	90–180 m caldera collapse following M7.8 earthquake
1924	~300 m collapse, violent phreatic explosions and caldera-rim eruption
1924–1982	Infrequent, short-term effusion (<1 day to few months) at summit and along rift zones (1955–1980)
1983–present	Prolonged rift zone eruption at Pu'u'Ō'ō

Sources: Bingham (1909); Macdonald *et al.* (1983); Dvorak & Dzurisin (1993); Garcia *et al.* (2003); Swanson *et al.* (2006).

with those for another active hotspot volcano, Grimsvötn in Iceland, where 800 years of volcanic activity (including the Laki flood basalt) have been investigated (Bindeman *et al.*, 2006). After evaluating the effects of crustal contamination on Kīlauea historical lavas, we examine the issue of $\delta^{18}\text{O}$ values for the Hawaiian plume source feeding this volcano.

KĪLAUEA ERUPTIVE HISTORY SUMMARY

Kīlauea's historical activity (~1790 to present) includes prolonged periods of quiescent lava effusion, interrupted by major collapses (≥ 100 m) of the caldera floor, rare violent explosions, and brief to prolonged rift zone eruptions (Table 1). The most dramatic event occurred in ~1790, when violent explosions killed ~80 Hawaiians (McPhie *et al.*, 1990). This event was accompanied by a major lower east rift zone eruption (Macdonald *et al.*, 1983). It was preceded by several explosive eruptions dating back to AD ~1670 (Swanson *et al.*, 2006) and followed, sometime between 1820 and 1823, by high lava fountaining within the caldera (Sharp *et al.*, 1987). In 1823, a 'great' crack extending 22 km down the SW rift produced a large lava flow causing the summit lava lake to drain and a summit collapse of >100 m (Brigham, 1909; Macdonald *et al.*, 1983). Eruptive activity resumed until 1832, when cracks formed on the NE rim of the caldera producing a small lava flow, which was followed by the summit lava lake draining and a >100 m collapse of the caldera floor (Brigham, 1909). Lava-lake activity restarted a few months later and persisted until 1840, when the caldera floor sank ~100 m during a major east rift zone eruption (Dana, 1891). Halema'uma'u Crater, in the SW corner of the caldera (Fig. 1), was the focus of subsequent lava lake activity until a M ~7.9 earthquake in 1868 caused the caldera floor to sink ~90 m

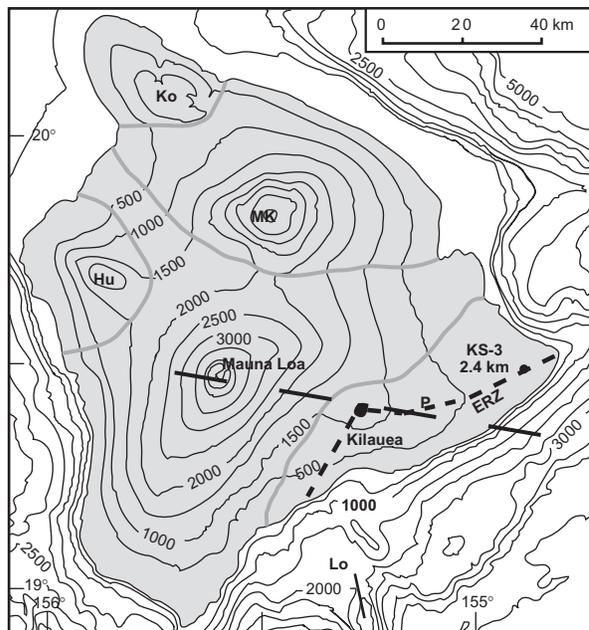


Fig. 1. Topographic map of the island of Hawai'i showing the five shield volcanoes that form the island [from youngest to oldest; Kīlauea, Mauna Loa, Hualalai (Hu), Mauna Kea (MK), Kohala (Ko)] and the young submarine volcano Loihi (Lo). Thick gray lines separate the shield volcanoes. Bold long-dashed line marks the location of the schematic cross-section (Fig. 6). Also shown as bold short-dashed lines are Kīlauea's two rift zones, including the east rift zone (ERZ) where the current Pu'u'Ō'ō eruption is occurring (P) and the 2.4 km deep KS-3 well is located (spot). Contour interval is 500 m.

to ~180 m (Brigham, 1909; Wyss & Koyanagi, 1992). Vigorous activity resumed immediately in Halema'uma'u and continued until 1894, when the lava lake drained. For the next 13 years, eruptive activity was episodic with a 5.5 year hiatus (Brigham, 1909). Lava-lake activity returned to Halema'uma'u in 1907, with major overflows and fissure eruptions from 1918 to 1921, covering large portions of the caldera floor.

In 1924, the Halema'uma'u lava lake drained, its crater floor collapsed ~300 m, and numerous violent phreatic explosions ensued (Jaggard, 1924). This event marked a reversal in Kīlauea's lava compositional trend that has persisted for >80 years (Pietruszka & Garcia, 1999a; Garcia *et al.*, 2003) and a major change in its eruptive style. Summit eruptions became short and infrequent (seven brief eruptions during the next 10 years; Jaggard, 1924; Finch, 1940). From 1934 to 1952, the volcano remained quiet. The next 30 years (1952–1982) witnessed mostly short-lived eruptions from fissures in and near Halema'uma'u crater (Fig. 1) and the more frequent east and SW rift zone eruptions, following a 115 year hiatus in rift zone eruptive activity (Macdonald *et al.*, 1983). There have been no summit eruptions since the start of the current east rift zone, Pu'u'Ō'ō eruption in 1983 (e.g. Garcia *et al.*, 2000).

SAMPLES

Well-dated and chemically characterized summit flow and tephra samples were utilized for this study [see Pietruszka & Garcia (1999a) and Garcia *et al.* (2003) for locations, petrography and compositional information (all for XRF major and trace elements, and many for Pb, Sr and Nd isotopes)]. This sample suite spans ~310 years of Kīlauea's eruptive history (~1670 to September 1982) and includes two young prehistoric samples [dates of 1790 were given by Pietruszka & Garcia (1999a) based on the work of McPhie *et al.* (1990); however, subsequent ^{14}C dating shows these samples are ~120 years older (Swanson *et al.*, 2006) than previously thought]. Unfortunately, only one sample (1832) is available for the period 1832–1865, during which two major collapse events occurred (1832 and 1840). Kīlauea erupted just prior to the 1832 collapse. Subsequent major collapses (1868 and 1924) and eruptive gaps (1897–1902 and 1934–1954) are well bracketed by the sample suite (Table 2). A previous study determined $\delta^{18}\text{O}$ values on whole-rocks for five historical summit samples, including samples from three of the same eruptions examined in our study (1885, 1954 and 1971), obtaining $\delta^{18}\text{O}$ values (all values in this paper are reported relative to Vienna Standard Mean Ocean Water, VSMOW), of 5.5–5.6‰ (Kyser *et al.*, 1982). Another study of O isotopes of olivine in 10 SOH-4 drill-core lavas from Kīlauea's east rift zone yielded $\delta^{18}\text{O}$ values of 4.9–5.2‰, averaging $5.1 \pm 0.1\%$ (Eiler *et al.*, 1996), consistent with the Kyser *et al.* (1982) summit results. In contrast, olivines from the current Pu'u'Ō'ō eruption are more variable, ranging in $\delta^{18}\text{O}$ values from 4.4 to 4.9‰ for 16 samples, with low values during the first 2 years of episodic eruptions ($4.8 \pm 0.1\%$), followed by even lower values for the continuous effusion phase ($4.64 \pm 0.2\%$; Garcia *et al.*, 1998). The matrix for these and other Pu'u'Ō'ō lavas (24 total) also ranges widely in $\delta^{18}\text{O}$ values (4.56–5.25‰), averaging $4.8 \pm 0.2\%$ for the early lavas and $5.1 \pm 0.1\%$ for later lavas (Garcia *et al.*, 1998).

Most of the summit samples are simple in mineralogy, consisting of rare to common olivine crystals (0.1–4.7 vol.%) in a glass matrix. Insufficient olivine was present in samples erupted between 1929 and 1934 to allow for O isotope analyses of olivine in these samples. Glass is present in most samples; in those samples where it is absent, matrix material was used for $\delta^{18}\text{O}$ determinations. Olivine elemental compositions for many of the summit samples were reported by Garcia *et al.* (2003). Most are in equilibrium with the whole-rock composition, except a few crystals from prehistoric samples (1790-1) and the early 19th century samples (1820 and 1832). The 1790 and 1820 samples contain a few lower forsterite crystals (Fo 84–85) that are weakly reversely zoned and the 1832 sample has rare higher forsterite olivines (88%; Garcia *et al.*, 2003). Glass MgO contents of the summit

samples range widely (from 9.3 wt% in the 1820 samples to 6.2 wt% in the September 1982 sample, 1982S-12; Table 3). Whole-rock MgO contents (labeled 'R' in Table 3 for samples without glass) range from 12.3 to 6.6 wt%. These values are considered reasonable indicators of matrix MgO content in the olivine-poor samples (<2.5 vol.%). Sample 1790-1, with 4.7 vol.% olivine, is the exception.

To evaluate possible crustal contaminants for Kīlauea magmas, new samples were collected from the accidental debris from the 1924 explosions (denoted by the prefix Z followed by a number and either 'b' for basalt or 'g' for gabbro) and from well cuttings collected every ~3 m from the Puna Geothermal Venture well KS-3 in the lower east rift zone of Kīlauea (labeled PGV followed by the depth of sample collection in meters). This well, which reached temperatures of 320°C (D. Thomas, personal communication, 2006), provides deep samples (up to 2237 m) from the interior of Kīlauea volcano. The cuttings are 2–4 mm across and most have a gray matrix with sparse to common olivine. Within each sample interval studied, the chips are petrographically similar.

The accidental blocks were derived from the shallow section (<300 m) overlying the summit magma reservoir (Jagger, 1924; Macdonald, 1944) and are thought to be possible contaminants for the summit reservoir, especially the 1924 collapse (Pietruszka & Garcia, 1999a). The blocks range in diameter from 25 to 150 cm, contain abundant olivine (~30 vol.%) and have a grayish green coating. Sample Z19b is distinctive for its black olivine, which has been interpreted to result from high-temperature metamorphism (>700°C; Haggerty & Baker, 1967). Olivines in sample Z19b range from forsterite 94 to 98, the highest ever reported for a Hawaiian rock. These high forsterite contents result from exsolution of magnetite within olivine. Jagger (1924) measured accidental block temperatures to 700°C, a minimum pre-eruption value. Mineral compositions (olivine, magnetite and orthopyroxene) within this block yielded temperatures of $970 \pm 170^\circ\text{C}$ using the Quilf95 program (D. Lindsley, personal communication, 1999). Sample Z6g has mildly oxidized olivine (metallic gray color), whereas olivines in sample Z2b are unoxidized. Thus, these blocks show a broad range of metamorphic histories from mild (Z2b) to intense baking (Z19b).

METHODS AND RESULTS

Whole-rock XRF

The new accidental block and well cutting samples were analyzed by X-ray fluorescence (XRF) at the University of Massachusetts for whole-rock major and trace (Nb, Rb, Zr, Sr, Y, V, Zn, Ni, Cr, Ba, La, and Ce) elements using methods described by Rhodes & Vollinger (2004). The analytical uncertainties for these analyses have been

Table 2: XRF major and trace element analyses of Kīlauea rocks

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ *	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total	LOI	K/P
<i>Cuttings</i>													
PGV-1353	50.89	2.920	13.68	12.54	0.19	6.35	10.40	2.34	0.383	0.303	100.00	2.14	1.26
PGV-1536	51.91	2.654	13.07	12.87	0.19	6.30	10.34	2.30	0.388	0.269	100.29	1.79	1.44
PGV-1780	49.16	2.804	13.37	12.54	0.18	8.22	10.63	2.09	0.357	0.281	99.63	2.61	1.27
PGV-2024	50.60	2.853	13.62	12.20	0.19	6.58	10.98	2.36	0.411	0.300	100.09	1.37	1.37
PGV-2237	50.45	2.723	12.37	12.70	0.18	8.96	9.01	2.27	0.443	0.306	99.41	1.60	1.45
<i>Blocks</i>													
Z2-B	47.55	1.780	9.16	12.31	0.18	19.50	7.13	1.58	0.555	0.290	100.04	0.20	1.91
Z6-G	46.34	1.126	7.84	13.98	0.20	21.61	7.13	1.04	0.175	0.110	99.55	0.02	1.59
Z19-B	46.70	1.733	9.28	12.64	0.19	18.87	7.83	1.63	0.360	0.170	99.40	0.22	2.12
	V	Cr	Ni	Zn	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Zr/Nb
<i>Cuttings</i>													
PGV-1353	298	116	57	116	4.6	336	30.0	189	17.2	126	12	36	11.0
PGV-1536	277	218	70	103	3.9	308	28.0	173	17.1	127	13	34	10.1
PGV-1780	276	338	177	117	3.5	394	25.9	171	17.8	138	12	34	9.6
PGV-2024	277	157	81	100	4.0	380	28.7	188	18.2	170	14	39	10.3
PGV-2237	274	308	273	64	8.5	337	30.0	197	19.2	130	15	41	10.3
<i>Blocks</i>													
Z2-B	198	1078	874	101	13.6	225	22.9	175	13.6	131	14	30	12.9
Z6-G	168	1056	928	109	3.4	203	11.6	61	5.2	65	4	12	11.7
Z19-B	194	1123	850	98	6.0	230	17.0	104	9.0	77	7	16	11.6
<i>Standard</i>													
BHVO-2	287	296	113	110	8.3	386	25.4	176	18.4	137	13	40	9.6

*Total Fe given as Fe₂O₃.

given by Rhodes & Vollinger (2004). Samples were washed in deionized water until the solution was clear. Clean chips were hand picked before crushing in a tungsten carbide mill for less than 2 min.

The KS-3 geothermal well cuttings have typical Hawaiian tholeiite major element compositions with MgO concentrations of 6.3–9.0 wt%. Their compositions resemble Kīlauea lavas in having relatively high TiO₂, moderate SiO₂, and Zr/Nb of 9.6–11 (Table 2). These samples have experienced at least moderate levels of alteration based on their loss on ignition (LOI) of 1.4–2.6 wt%, their somewhat low K₂O/P₂O₅ compared with magmatic values (<1.5 vs >1.5; Wright, 1971), and their low Rb contents (<5 ppm, except the deepest sample). There is no correlation of these alteration indicators with the depth at which the cuttings were collected (Table 2). Except for these indicators, the major and trace element compositions of the five chip samples are remarkably similar to those of typical Kīlauea lavas (e.g. Nb/Zr of 10–11; Rhodes *et al.*, 1989; Garcia *et al.*, 2000, 2003).

The accidental blocks are high-MgO tholeiites (18.9–21.6 wt%) with correspondingly high Cr and Ni concentrations (Table 2). The blocks have a wide range in K₂O, TiO₂ and incompatible trace elements (Table 2), magmatic K₂O/P₂O₅ (1.6–2.1) and low LOI values (<0.25 wt%). The blocks have Kīlauea-like Zr/Nb ratios (12–13; Rhodes *et al.*, 1989). They are petrographically and geochemically similar to the suite C picritic basalts from Kīlauea's caldera cliffs (see Casadevall & Dzurisin, 1987).

Matrix oxygen isotopes

Oxygen isotope analyses of matrix material were made by conventional methods (Clayton & Mayeda, 1963) at the University of Minnesota using ClF₃ (Borthwick & Harmon, 1982). CO₂ gas from each extraction carried out during 1993 and 1994 was analyzed on a Finnigan MAT delta E mass spectrometer. CO₂ gas extracted during 1997 and 1998 was analyzed with a Finnigan MAT 252 mass

Table 3: Oxygen isotope data for Kīlauea summit volcanics, accidental blocks and cuttings from east rift zone well

Sample	Year	Glass MgO	Matrix	±	<i>n</i>	Olivine	±	Matrix-olivine	²⁰⁶ Pb/ ²⁰⁴ Pb	⁸⁷ Sr/ ⁸⁶ Sr	Nb/Y
<i>Summit volcanics</i>											
1790-1	1670	10.6R	4.91	0.08	2	5.03	0.11	-0.12	18.508	0.70360	0.534
1790-6	1670	6.9	4.89	0.01	4	—	—	—	18.394	0.70356	0.554
1820-1	1820	9.3	5.18	0.03	2	5.02	0.02	0.16	18.400	0.70367	0.543
1820-2	1820	9.3	5.27	0.02	3	5.23	0.07	0.04	—	—	0.533
1832	1832	7.6R	5.52	0.06	3	5.18	—	0.34	18.429	0.70365	0.612
1866	1866	6.5R	5.62	0.08	2	—	—	—	18.559	0.70353	0.605
K1877	1877	7.0R	5.17	0.03	3	—	—	—	—	—	0.656
1885-4	1885	7.2R	5.43	0.04	2	5.04	0.03	0.39	18.540	0.70356	0.748
1894-2	1894	6.6R	5.55	0.02	2	4.91	0.00	0.64	18.552	0.70353	0.739
95-TAJ3	1912	6.8	5.30	0.02	3	—	—	—	18.599	0.70352	
H1026	1917	7.1	5.53	0.10	2	5.06	0.09	0.47	18.648	0.70348	
1921-4	1921	6.7	5.60	0.10	2	5.10	0.10	0.50	—	—	0.775
H1054	1929	6.7	5.35	0.07	5	—	—	—	18.572	0.70357	
1931 HM	1931	7.4R	5.43	0.09	2	—	—	—	18.555	0.70358	
1934	1934	7.3	5.36	0.01	2	—	—	—	—	—	
1954-1	1954	7.0R	5.11	0.01	2	5.19	—	-0.08	18.573	0.70361	0.886
K61-22	1961	7.1	5.18	0.03	3	—	—	—	18.540	0.70355	0.776
1971S	1971	6.5	5.10	0.03	3	4.70	0.02	0.40	18.509	0.70359	0.703
1982-A-20	1982	6.8	5.24	0.05	3	4.60	0.04	0.64	18.454	0.70358	0.631
1982S-12	1982	6.2	5.08	0.01	2	5.17	—	-0.09	—	—	0.625
1982S-3	1982	7.4	—	—		5.09	—	-0.01	—	—	
<i>1924 explosion blocks</i>											
Z2b basalt	1924	19.5R	5.46	0.04	3						
Z19b black basalt	1924	18.9R	5.54	0.15	4						
Z6g gabbro	1924	21.6R	5.46	0.04	3						
<i>Rift well cuttings depth (m)</i>											
PGV-1353	1353	6.35R	5.32	0.09	3						
PGV-1536	1536	6.30R	5.08	0.10	2						
PGV-1780	1780	8.22R	2.43	0.05	3						
PGV-2024	2024	6.58R	2.59	0.03	3						
PGV-2237	2237	8.96R	1.86	0.07	3						

Values with R are for whole-rock MgO values in wt% where glass not available; ± is one standard deviation; olivine standard deviations are based on duplicate measurements. If no standard deviation is given, only one split was run. Pb and Sr isotope data from Pietruszka & Garcia (1999a); Nb/Y data from Garcia *et al.* (2003).

spectrometer. Each sample was split into 2–5 aliquots depending on the total sample weight, and at least two aliquots were analyzed to check for analytical reproducibility (see Table 3 for the number of replicates for each). For all but one sample (accident block Z19b, with the black olivines), analytical reproducibility is 0.1% or better. For 1993 and 1994 extractions, one laboratory standard (Nain plagioclase) was analyzed for every four matrix samples. The overall reproducibility for Nain plagioclase for the duration of this work was ±0.20‰ (1σ) for 125 analyses. A mid-ocean ridge basalt (MORB) glass from East Pacific Rise (EPRD 10RB), which had previously

been analyzed at the Geophysical Laboratory (Ito *et al.*, 1987), was analyzed as a laboratory standard during 1997 and 1998. The overall reproducibility for EPRD 10RB for the two years was ±0.17‰ (1σ) for 56 analyses. The results reported here are relative to δ¹⁸O_{VSMOW}, normalized against SLAP (Standard Light Antarctic Precipitation, which is defined as -55‰ relative to VSMOW; Coplen, 1988).

The matrix δ¹⁸O values for the summit suite of samples vary from 4.90 to 5.62‰ (Table 2) with no systematic variation with the date of eruption (Fig. 2). PVG K3-3 cuttings show a wide variation δ₁₈O from 1.75 to 5.31‰, generally

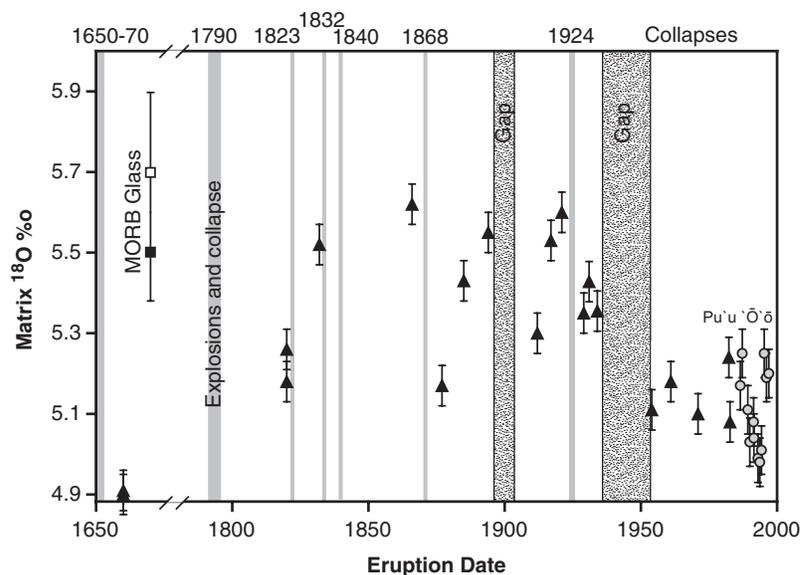


Fig. 2. Temporal variation in matrix oxygen isotope values for Kīlauea summit (▲) and Puʻu ʻŌʻō (○) lavas. Gray vertical bars show times of major collapses (dates are listed at top of figure); stippled zones show major gaps in eruptive activity (see Table 1 for details). There are marked decreases in matrix oxygen isotope values following summit collapses in 1868 and 1924, and following eruptive hiatuses in ~1897–1902 and 1934–1952. Puʻu ʻŌʻō data are shown only for the continuous phase of activity from 1986 to 1997 (data from Garcia *et al.*, 1998). MORB glass values: □, Ito *et al.* (1987); ■, Eiler (2001). MORB glass error bar represents combined range from these two studies. Other bars are the maximum standard variation based on 2–3 analyses of each sample (see Table 3 for specific samples).

decreasing with depth (Table 3). The three accidental blocks are remarkably similar in their O isotope values ($5.50 \pm 0.04\%$) given their wide range in degree of metamorphism.

Olivine oxygen isotopes

Olivines were separated from historical Kīlauea lavas and tephra by hand picking from coarsely crushed, but otherwise untreated, samples. Oxygen isotope compositions of *c.* 2 mg aliquots of these separates were determined by laser fluorination, using a 50W CO₂ laser and BrF₅ as reagent (Valley *et al.*, 1995). Product O₂ was converted to CO₂ by reaction with hot graphite; CO₂ was then analyzed for its isotopic composition by dual-inlet gas source mass spectrometry on a Thermo Finnegan 253 system at California Institute of Technology. Data are reported in units of per mil versus the VSMOW standard. Analyses were standardized by comparison with measurements of Gore Mountain garnet standard (Valley *et al.*, 1995) and a San Carlos olivine (Eiler *et al.*, 1995, 1996; Bindeman *et al.*, 2006). Both standards were analyzed between two and five times on each day of analysis, and data for unknowns analyzed on that day were corrected by the average difference between measured and accepted values for these standards. The external precision of repeat measurements of separate splits of unknown samples averaged $\pm 0.05\%$ (1σ). This is comparable with the typical external precision for replicate measurements of silicate standards for this

laboratory and technique (e.g. Eiler *et al.*, 1995, 1996; Bindeman *et al.*, 2006), suggesting that the olivine separates analyzed in this study are homogeneous in $\delta^{18}\text{O}$ at the scale of *c.* 2 mg aliquots. Garcia *et al.* (1998) evaluated the interlaboratory differences between Caltech and the University of Minnesota by comparing the results for a matrix glass from the Puʻu ʻŌʻō eruption. The sample was run in duplicate in both laboratories. The results were 4.68% by conventional methods vs 4.79% by laser, which are within the analytical error of the two methods.

Ten of 13 olivine separates yield average $\delta^{18}\text{O}$ values that group tightly around a value of $5.11 \pm 0.07\%$ (Fig. 3). Members of this population are indistinguishable from one another, within analytical precision, and equal in $\delta^{18}\text{O}$ to olivine in equilibrium with typical MORB (Eiler *et al.*, 2000; Cooper *et al.*, 2004). This average value is also similar to the $\delta^{18}\text{O}$ values of olivines from Mauna Loa, Lōʻihi, shield-building Haleakalā (i.e. Honomanu series), submarine Mauna Kea lavas, and olivines recovered from the Kīlauea SOH4 drill core (all of which have suite-average $\delta^{18}\text{O}$ values from 5.05 to 5.22; Eiler *et al.*, 1996; Wang *et al.*, 2003), and within the range typical of olivines from most ocean-island basalts and mantle peridotites ($\delta^{18}\text{O}$ values of 5.0–5.4‰; Eiler, 2001).

Three historical Kīlauea olivine samples are distinguishable from this tightly grouped set of 10 samples. Olivine from sample 1894-2 has a $\delta^{18}\text{O}$ of 4.91% , just below the range typical of mantle-derived olivines and similar to

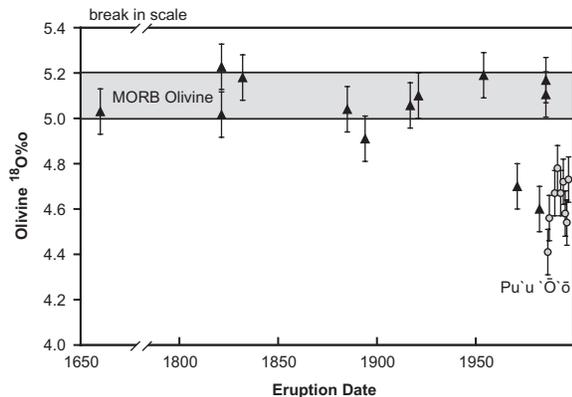


Fig. 3. Temporal evolution in olivine oxygen isotope values for Kīlauea summit (▲) and Pu'u'Ō'ō (○) lavas. Most of the summit olivines plot within the MORB olivine field (if the errors bars are included), with no temporal variation. The exceptions are the 1961 and 1971 samples and Pu'u'Ō'ō lavas (only data for the continuous phase of activity are shown; Garcia *et al.*, 1998). MORB olivine range is from Eiler (2001). Error bars are \pm maximum standard variation based on replicate analyses (see Table 3).

previously observed averages for the Kūla series of Haleakalā. Samples 1971S and 1982-A-20 have the lowest values for summit lavas, 4.70 and 4.60, respectively, overlapping the range of values for olivines from the continuous phase of Kīlauea's Pu'u'Ō'ō eruption (Fig. 3) and within the range typical of subaerial Mauna Kea lavas (Eiler *et al.*, 1996; Wang *et al.*, 2003). Relatively low $\delta^{18}\text{O}$ values in Hawaiian olivines have been previously interpreted to result from lithospheric contamination (Eiler *et al.*, 1996), a low- $\delta^{18}\text{O}$ plume component (Lassiter & Hauri, 1998) or contamination within the volcanic edifice (Garcia *et al.*, 1998; Wang *et al.*, 2003).

DISCUSSION

The wide range in matrix $\delta^{18}\text{O}$ values (4.9–5.6‰) during the \sim 310 year period for Kīlauea summit lavas is in striking contrast to the nearly constant matrix $\delta^{18}\text{O}$ values ($3.1 \pm 0.1\%$) for \sim 800 years at Iceland's Grimsvötn volcano, including the 15 km^3 Laki eruption (Bindeman *et al.*, 2006). The variation observed at Kīlauea is a magmatic signature rather than a secondary feature because all of the summit samples are fresh, rapidly quenched volcanic rocks (Garcia *et al.*, 2003). Could the Kīlauea variation be related to mantle source variations, as suggested for oceanic island basalts (e.g. Harmon & Hoefs, 1995)? The rapid variations in Kīlauea summit $\delta^{18}\text{O}$ values are difficult to reconcile with components in the Hawaiian mantle, especially given the lack of correlation of $\delta^{18}\text{O}$ values with incompatible trace element ratios (Nb/Y; Fig. 4) that are considered a good source indicator (Rhodes & Hart, 1995). Furthermore, $\delta^{18}\text{O}$ values of olivines from summit lavas are relatively constant from prehistoric times to 1982 ($5.1 \pm 0.1\%$; Fig. 3), whereas Sr,

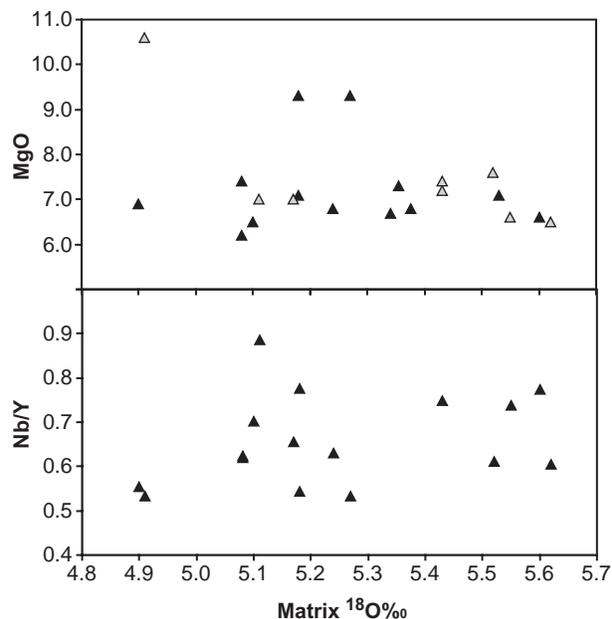


Fig. 4. Matrix oxygen isotope value vs MgO (▲, glass; △, rock) and whole-rock Nb/Y in historical Kīlauea summit lavas. The lack of correlations of these geochemical parameters indicates that fractionation (which is dominated by olivine in these rocks; Garcia *et al.*, 2003) and source (Nb/Y is strongly influenced by source in Hawaiian basalts; e.g. Pietruszka & Garcia, 1999a) have not played an important role in controlling the oxygen isotope values in Kīlauea summit lava. Error bars are smaller than the symbol size. Data from Table 3 and Garcia *et al.* (2003).

Pb and Nd isotope ratios varied considerably during this period (e.g. $^{206}\text{Pb}/^{204}\text{Pb}$ 18.39–18.66; Pietruszka & Garcia, 1999a). These results are also distinct from those for subaerial HSDP2 core olivine, which showed lower average values ($4.79 \pm 0.13\%$; Wang *et al.*, 2003). Variable amounts of peridotite partial melting or crystallization of olivine and minor spinel are likely to have opposite but minimal impacts on the matrix $\delta^{18}\text{O}$ value ($+0.1\%$ for 20% crystallization vs -0.1% for up to 30% partial melting; Eiler 2001; Wang *et al.*, 2003). Also, there is no correlation in the extent of fractionation (MgO content; Fig. 4) with matrix $\delta^{18}\text{O}$ value (e.g. at 7.0 MgO, $\delta^{18}\text{O}$ values span the entire range of values; Table 3). Below we examine the temporal variation and discuss the possible causes for the $\delta^{18}\text{O}$ variation in historical Kīlauea lavas.

Temporal variation in oxygen isotopes

Two features emerge when the data are viewed in the context of Kīlauea summit activities (Table 1): (1) matrix $\delta^{18}\text{O}$ values are lower following major summit collapses (100+ m; 1868 and 1924) or significant gaps in eruptive activity (>5 years; 1898 and 1934; Fig. 2); (2) they increase during periods of nearly continuous eruptive activity between these events (1877–1894 and 1912–1921), except for the period of short, infrequent eruptions from 1952 to 1982 (when very little lava was erupted; Dvorak &

Dzurisin, 1993) and during the continuing Pu'u'Ō'ō eruption (Fig. 2). The drop in matrix $\delta^{18}\text{O}$ values following summit collapses and during gaps in eruptive activity or reduced levels of effusion may represent times when the summit reservoir magma is contaminated. The second feature, increasing matrix $\delta^{18}\text{O}$ values, may indicate that contaminated magma was progressively diluted with new, uncontaminated magma. New magma was more or less continuously added to the summit reservoir during historical times (e.g. Finch, 1940; Macdonald *et al.*, 1983; Dvorak & Dzurisin, 1993). For the Pu'u'Ō'ō eruption, there was a 0.2–0.3‰ increase in matrix $\delta^{18}\text{O}$ values when the eruptive style switched from episodic to continuous effusion, although there was no change in other geochemical parameters (Garcia *et al.*, 1998). These fluctuations in Pu'u'Ō'ō matrix $\delta^{18}\text{O}$ values were interpreted to represent variable amounts of crustal contamination within Kīlauea's east rift zone, with less contamination during periods of higher effusion (Garcia *et al.*, 1998).

The olivine $\delta^{18}\text{O}$ values for summit historical lavas record a different history. The values are all relatively high, comparable with those for MORB olivine, and nearly constant except for the 1961 and 1971 lavas (Fig. 3). The Pu'u'Ō'ō lavas also have low olivine values. These results are in contrast to the wide variation in olivine isotope values for the Laki eruption (2.3–5.2‰), which were attributed to the incomplete equilibration of olivine from influxes of mantle-derived magma into a large chamber with $\delta^{18}\text{O}$ -depleted magma (Bindeman *et al.*, 2006). The Kīlauea summit olivines apparently grew in magmas with $\delta^{18}\text{O}$ values of 5.45–5.75‰, assuming equilibrium growth and an olivine–melt isotopic fractionation of 0.55‰ [average of 0.7‰ (Ito & Stern, 1986) and 0.4‰ (Wang *et al.*, 2003)]. The summit olivine data do not provide independent evidence for contamination except for the 1961 and 1971 summit and Pu'u'Ō'ō lavas (Fig. 3).

If the matrix and olivine $\delta^{18}\text{O}$ values are compared (Fig. 4), a record of disequilibrium in Kīlauea summit magmas is revealed. The extent of disequilibrium was greatest following the late 17th century major explosions and progressively decreased through the end of the 19th century when equilibrium values were achieved (Fig. 4). The 1924 major summit collapse and explosions, and the 1934–1954 eruptive hiatus marked another major matrix–olivine disequilibrium event, with the magnitude of the disequilibrium decreasing from 1954 to 1971 (Fig. 5). However, the April 1982 lava and many of the Pu'u'Ō'ō lavas (those erupted during periods of lower eruption rate) show disequilibrium values. No event was recorded that might explain contamination in the 1982 lavas. The presence of normal $\delta^{18}\text{O}$ values in olivine (5.0–5.2‰) from the September 1982 eruption (Fig. 3) suggests that these magmas were contaminated after the olivines grew, probably during eruption. All of the post-1950 lavas have

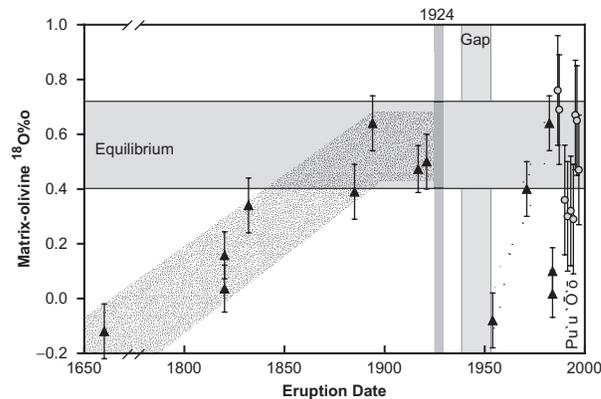


Fig. 5. Temporal evolution in the difference between matrix and olivine oxygen isotope values for Kīlauea summit (\blacktriangle) and Pu'u'Ō'ō (\circ) lavas. Only the 1924 collapse and 1934–1952 eruption pause are shown because they mark a major reversal in matrix–olivine ratios. Pu'u'Ō'ō data are shown only for the continuous phase of activity from 1986 to 1997 (data from Garcia *et al.*, 1998). Estimates for the equilibrium fractionation between matrix and olivine range from 0.7 to 0.4‰ (Ito & Stern, 1986; Wang *et al.*, 2003). The equilibrium field shown spans these two values and covers the higher values observed for summit lavas. The values below this field are thought to reflect contamination. Error bars are the combined olivine and matrix maximum variation based on replicate analyses (see Table 3).

low matrix $\delta^{18}\text{O}$ isotope values indicating that there was a major disruption in the magmatic plumbing system, which may have allowed for more magma contamination. As discussed above, the Pu'u'Ō'ō lavas with disequilibrium matrix–olivine values were erupted during periods of lower eruption rates. In summary, the two large summit events in the late 17th and early 20th centuries had a profound impact on the $\delta^{18}\text{O}$ values of Kīlauea magmas. If contamination caused the drop in O isotope values, where did it occur?

Implications of O, Sr and Pb isotope data for contamination source and location

There is a general correlation of $\delta^{18}\text{O}$ with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, to a lesser extent with $^{206}\text{Pb}/^{204}\text{Pb}$ (Fig. 6) but none with ϵNd . The Kīlauea summit samples with the lowest $\delta^{18}\text{O}$ values tend to have higher Sr and somewhat lower Pb isotope ratios, although there is a broad range at a given $\delta^{18}\text{O}$ value (Fig. 6). These results help to identify potential sources of the contamination that created the lower $\delta^{18}\text{O}$ values in historical Kīlauea summit lavas. Shallow-level, low-temperature processes should produce higher $\delta^{18}\text{O}$ values (Gregory & Taylor, 1981). For example, values up to 8.7‰ have been reported for rocks from the shallow levels of Kīlauea geothermal wells (Smith & Thomas, 1990). Deeper in these wells where temperatures are higher ($\sim 300^\circ\text{C}$), the $\delta^{18}\text{O}$ values are lower (3.2‰; Smith & Thomas, 1990). This trend is confirmed with our new data for well KS-3, which generally decrease with depth from

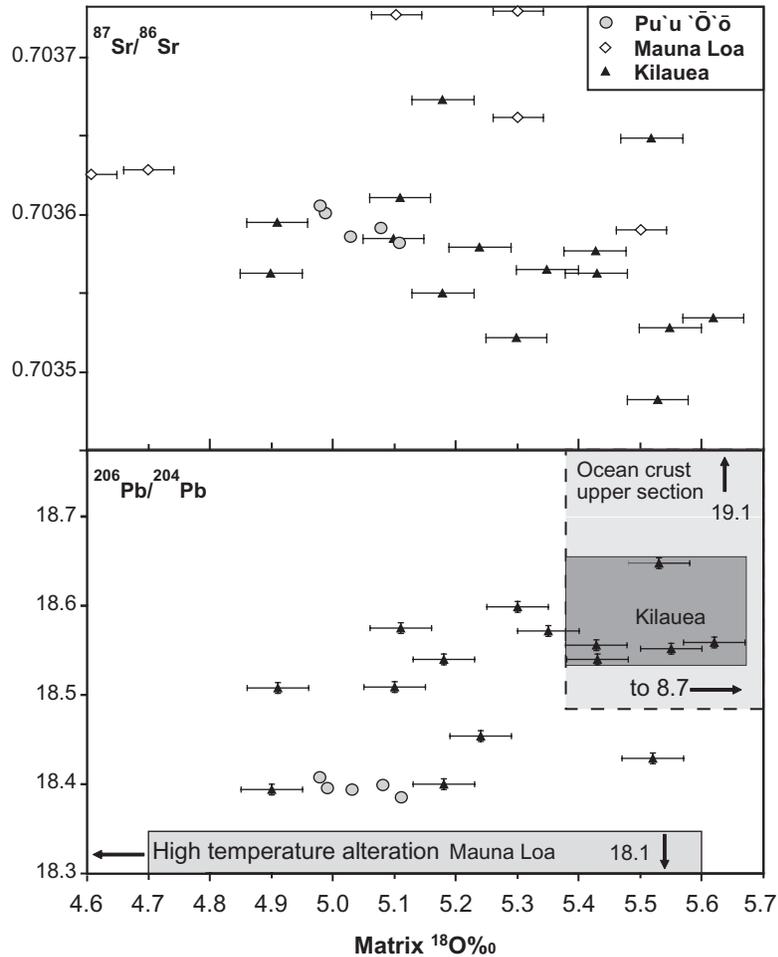


Fig. 6. O isotope matrix values vs whole-rock $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for Kīlauea summit (\blacktriangle), Pu'u'Ō'ō (\circ), and Mauna Loa submarine rift (\diamond) lavas. The isotopes show a broad correlation, which may result from contamination of Kīlauea magma by high-temperature altered Mauna Loa lavas. O isotope data for Mauna Loa from Garcia *et al.* (1989); oceanic crust upper section from King *et al.* (1993). Pb isotope data for Mauna Loa from Kurz *et al.* (1995) and Rhodes & Hart (1995); Kīlauea data from Pietruszka & Garcia (1999a); Pu'u'Ō'ō data from Garcia *et al.* (1998, 2000); oceanic crust data from King *et al.* (1993) and Fekiacova *et al.* (2007). Sr isotope data for Mauna Loa from Gurriet (1988). Kīlauea field based on samples with mantle-like O isotope values of 5.4–5.6‰, which are assumed to be uncontaminated.

5.32‰ at intermediate depths (1353 m) to 1.86‰ at 2237 m (Table 3), the lowest value reported for Hawaiian lavas. The Kīlauea high-temperature metamorphosed accidental blocks from the 1924 eruption, which were derived from depths <300 m (Jaggard, 1924), lack low $\delta^{18}\text{O}$ values (Table 3). Therefore, they are unsuitable contaminants for generating the lower $\delta^{18}\text{O}$ values observed in some summit lavas (Fig. 6).

The Pacific oceanic crust section, which was invoked by Gaffney *et al.* (2005) to explain low $\delta^{18}\text{O}$ values in West Maui lavas, has $^{206}\text{Pb}/^{204}\text{Pb}$ ratios too high (18.5–19.1; King *et al.*, 1993; Fekiacova *et al.*, 2007) to explain the range or correlation in Kīlauea matrix O and Pb isotope values (Fig. 6). The only other potential contaminant for Kīlauea magmas is Mauna Loa lavas (Fig. 7), which have lower $^{206}\text{Pb}/^{204}\text{Pb}$ and higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than Kīlauea

lavas (Fig. 6). Glasses from fresh Mauna Loa submarine lavas have a wide range in $\delta^{18}\text{O}$ values (4.7–5.5‰; Garcia *et al.*, 1989). The lavas with lower values would be suitable contaminants for Kīlauea magmas to generate the positive O–Sr and O–Pb isotope correlation (Fig. 6). An alternative contaminant would be moderately hydrothermally altered Mauna Loa lavas.

The relatively high $\delta^{18}\text{O}$ values for the summit olivines (Fig. 3), and the disequilibrium between olivine and matrix $\delta^{18}\text{O}$ values in some samples (Fig. 5), indicate that the contamination occurred late, probably just prior to or during eruption. The most likely location for this contamination would be in Kīlauea's shallow (3–6 km deep; Klein *et al.*, 1987) magma chamber, which is probably located within the flanks of Mauna Loa, or in the conduit during eruption (Fig. 7). The frequent, major collapses of the

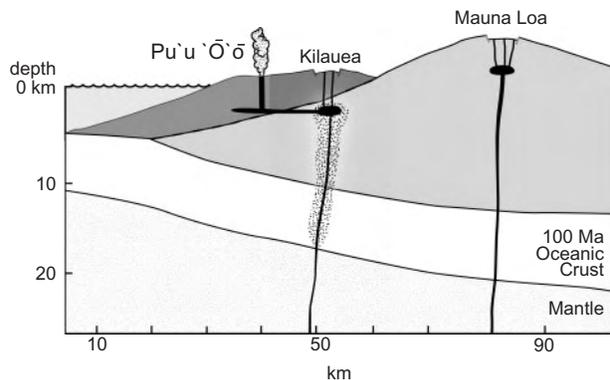


Fig. 7. Schematic cross-section of the southern part of the island of Hawai'i (see Fig. 1 for location) showing the basement stratigraphy and magmatic plumbing system for Kīlauea volcano based on regional geology and seismic cross-sections (Macdonald *et al.*, 1983; Hill & Zucca, 1987; Klein *et al.*, 1987; Garcia *et al.*, 2000). Stippled zone around Kīlauea conduit is a region of dunite and gabbroic cumulates. Age of oceanic crust adjusted from ODP Site 843, located 300 km west of the island of Hawai'i (Waggoner, 1993).

summit crater floor of 100+ m and the gaps in eruptive activity provide a suitable mechanism for disruption of the roof of the summit magma chamber and the assimilation of Mauna Loa or Kīlauea hydrothermally altered rocks into Kīlauea magma. The 1924 collapse resulted in significant changes in lava trace element chemistry, which were explained by 3–5% contamination from partially melted, seawater altered Kīlauea basalt (Pietruszka & Garcia, 1999a). However, the trends of the lava chemistry changes following this event are consistent with a Mauna Loa source (decreasing Pb and Nd and increasing Sr isotopes). The small drop in the $\delta^{18}\text{O}$ value during this period (0.22‰; Table 3) would require ~5% bulk contamination, if the lowest $\delta^{18}\text{O}$ value from the KS-3 well (1.86‰) is used. The results from these two assimilation models are consistent and suggest that the extent of the contamination was small but significant for the 1924 event. The larger drop in matrix $\delta^{18}\text{O}$ value following the 1868 collapse (0.45‰; Table 3) requires more extensive contamination (~12%) using the same assumptions. Unfortunately, no Pb, Sr or Nd isotope data are available for the 1877 sample to test this hypothesis. Additional testing of contamination scenarios using rock major or trace element data is complicated by the probability that the contaminants were only partially digested (e.g. 1924 eruption; Pietruszka & Garcia, 1999a). Mauna Loa rocks have lower incompatible elements than Kīlauea rocks, although during partial melting and assimilation, the incompatible element concentrations of the resulting melts will be increased relative to the host Kīlauea magma. An alternative process to bulk contamination for the summit rocks with more typical Kīlauea geochemistry (higher Pb and lower Sr isotope ratios; e.g. sample 1954-1)

is O isotope exchange with groundwater or altered lavas, which would leave no geochemical signature other than lowering the $\delta^{18}\text{O}$ value (e.g. Kīlauea groundwater and steam condensates have $\delta^{18}\text{O}$ values of –1 to –14‰; Hinkley *et al.*, 1995). Regardless of the contamination source, the rapid change in matrix $\delta^{18}\text{O}$ values suggests that Kīlauea's shallow magma reservoir is small, which is consistent with some geophysical estimates (e.g. Decker, 1987) and geochemical modeling (Pietruszka & Garcia, 1999b). The Kīlauea situation is in marked contrast to the consistency of matrix $\delta^{18}\text{O}$ values for Grimsvötn volcano over the last 800 years. The consistency of Grimsvötn's matrix $\delta^{18}\text{O}$ values was related to its large crustal magma chamber, which is supported by the 15 km³ flood basalt flow it produced in 1783 (Bindeman *et al.*, 2006). In contrast, Kīlauea's summit reservoir is thought to have been small (only 2–3 km³) over the last 200 years (Pietruszka & Garcia, 1999b). The crustal contamination of Kīlauea magmas is superimposed on a longer-term geochemical variation that reflects source heterogeneity (Pietruszka & Garcia, 1999a). The $\delta^{18}\text{O}$ composition of this source is discussed in the next section.

Kīlauea source oxygen isotope values

The origin of the diverse $\delta^{18}\text{O}$ values observed in mantle-derived basalts has been of considerable interest. Although a limited range of $\delta^{18}\text{O}$ values typifies MORB glasses (5.4–5.8‰), $\delta^{18}\text{O}$ values correlate with source geochemical parameters (Eiler 2001) suggesting a mantle origin for at least some of the observed $\delta^{18}\text{O}$ diversity in mantle-derived basalts (Harmon & Hoefs, 1995). However, concern has surrounded the origin of lower O isotopes (<5.4‰, below normal MORB values), which are observed in many ocean island basalts. Some studies relate lower values to crustal contamination (e.g. Garcia *et al.*, 1998; Thirlwall *et al.*, 1997), whereas others have suggested they are an inherent feature of the mantle (e.g. Garcia *et al.*, 1993; Harmon & Hoefs, 1995). For example, Wang *et al.* (2003) argued for a 'primary' mantle $\delta^{18}\text{O}$ value of 5.5‰ for HSDP2 Mauna Kea lavas, with lower values resulting from contamination (e.g. Wang *et al.*, 2003). The new results presented here for historical Kīlauea summit lavas support the contamination explanation for lower $\delta^{18}\text{O}$ values.

The consistency of the olivine $\delta^{18}\text{O}$ values in historical Kīlauea summit lavas (5.1 ± 0.1 ‰; Fig. 3), despite the significant range in Pb and Sr isotopes during this period (Table 3), is strong evidence in favor of the interpretation that there is a limited range in $\delta^{18}\text{O}$ values in the mantle source (5.45–5.75‰; the value depends on the magnitude of the equilibrium matrix–olivine fractionation), despite the heterogeneous source producing Kīlauea magmas (e.g. Pietruszka & Garcia, 1999a). This range is consistent with the prevailing value for MORB mantle (Ito *et al.*, 1987; Eiler 2001), suggesting that the $\delta^{18}\text{O}$ value of the

Hawaiian mantle plume feeding Kīlauea is typical of the upper mantle. However, it should be noted that diversity exists within the plume. In particular, olivines from some Kōōlāu volcano lavas have much higher $\delta^{18}\text{O}$ values (5.5–6.0 vs 5.0–5.2‰), which are inferred to result from melting eclogite blocks within the Hawaiian plume (Eiler *et al.*, 1996).

SUMMARY

A wide range in matrix $\delta^{18}\text{O}$ value (4.9–5.6‰) was determined for Kīlauea summit lavas spanning ~310 years of eruptive history. These results are in marked contrast to the essentially constant but much lower matrix $\delta^{18}\text{O}$ values ($3.1 \pm 0.1\%$) reported for the last 800 years of eruptive activity for the Icelandic hotspot volcano Grimsvötn. Kīlauea matrix values do not vary systematically with time, although lower values were found in rocks erupted following major summit collapses or eruptive hiatuses. The difference between the matrix $\delta^{18}\text{O}$ values for these volcanoes probably reflects the size of the magma reservoir system, with the Kīlauea system being much smaller. Olivine $\delta^{18}\text{O}$ values in most of the Kīlauea lavas are nearly constant ($5.1 \pm 0.1\%$), whereas those from Grimsvötn volcano show substantial variation (2.3–5.2‰). The disequilibrium between matrix and olivine $\delta^{18}\text{O}$ values in Kīlauea samples indicates that the lower matrix values were acquired by the magma after olivine grew, probably just before or during eruption. The sources of the contamination of Kīlauea historical lavas are probably the host rocks for the magma reservoir system. These include Mauna Loa and Kīlauea rocks, based on O, Pb and Sr isotope data, whereas oceanic crust contamination is not indicated. The extent of crustal contamination of Kīlauea historical magmas was probably minor (~5%) for the 1924 collapse, depending on the assumed contaminant. The contamination signature of Kīlauea magma is superimposed on a larger, longer-term cyclic geochemical variation that reflects source heterogeneity. Kīlauea's heterogeneous source, which is well represented by the analyzed summit lavas, probably has $\delta^{18}\text{O}$ values within the normal MORB mantle range (5.4–5.8‰), based on the new olivine $\delta^{18}\text{O}$ values.

ACKNOWLEDGEMENTS

This paper is dedicated to David Green on the occasion of his 70th birthday. David has been an inspiration to all who study basaltic magmas. Thanks go to the many friends who have assisted with this study, including Sorena Sorensen for lending critical samples from the Smithsonian collection; Nancy Baker, Rachel Konishi, Joann Romano, Kate Bridges, Kristina Garcia and Joe Horrell for help in the field; Chad Shishido and Kelly Kolysko for sample preparation; to Rhea Workman for assistance with the

laboratory work; and Reed McEwan and John Tacinnelli for matrix sample oxygen isotope analysis. Analytical work in the Caltech stable isotope laboratories was supported, in part, by NSF grant EAR-0337736 and a grant from the EAR Technician support program. Our thanks go to journal reviewers Amy Gaffney, J. M. Rhodes and Ilya Bindeman for their helpful comments. This paper is SOEST Contribution 7149, and was supported by NSF grants (EAR03-36874) to MG and (EAR-0345905) to JE.

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