Crustal Contamination of Kilauea Volcano Magmas Revealed by Oxygen Isotope Analyses of Glass and Olivine from Puu Oo Eruption Lavas

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Oceanic island basalts have a large range in $\delta^{18}O$ values (4·5–7·5‰) compared with the assumed primordial mantle values (5·5–6·0‰) and with mid-ocean ridge basalts (5·7 ± 0·2‰). Some Hawaiian tholeiitic basalts have low ^{18}O values (4·6–5·2‰), which have been interpreted to be either a primary source feature or caused by crustal contamination. This study was undertaken to evaluate the cause of low $\delta^{18}O$ values in Hawaiian tholeiitic basalts. We determined the $\delta^{18}O$ values of glassy matrix material and coexisting olivines from pristine basalts produced during the current, 14-year-old Puu Oo eruption of Kilauea Volcano. Our results show that the Puu Oo eruption lavas have significant ranges in matrix (0·7‰) and olivine $\delta^{18}O$ values (0·5‰) which do not correlate consistently with other geochemical parameters and that many of the lavas are out of oxygen isotopic equilibrium. These features probably reflect partial assimilation of and oxygen exchange with metamophosed Kilauea rocks during the magma's 19 km transit through the volcano's east rift zone. The parental magmas for Puu Oo lavas had a $\delta^{18}O$ value of at least 5·2‰ and perhaps as high as 5·6‰. Thus, Puu Oo lavas do not give a clear indication of the $\delta^{18}O$ value of Kilauea's mantle source but they do indicate that the oxygen in these otherwise pristine basalts has undergone significant modification by interaction with crustal rocks.

KEY WORDS: *Kilauea Volcano; Hawaii; oxygen isotopes; Puu Oo eruption; crustal contamination*

INTRODUCTION

A 1996 conference on 'shallow level processes in ocean island magmatism' drew attention to the controversy that is developing on the possible extent of crustal contamination for oceanic island basalts (Bohrson *et al.*, 1997). This controversy is important because most studies of oceanic island basalts have assumed that these lavas provide a direct indication of the geochemical and isotopic composition of mantle (e.g. Zindler & Hart, 1986). This assumption has been questioned in several recent studies (e.g. Eiler *et al.*, 1996*a*; Thirlwall *et al.*, 1997) and it has been suggested that even the most primitive basalts from some oceanic islands were contaminated by crustal materials (e.g. Hemond *et al.*, 1993). Resolution of this controversy will have fundamental implications for our understanding of the magmatic history of oceanic island basalts and for the composition of the mantle. Oxygen isotopes are a potentially powerful tool to help resolve this debate because $\delta^{18}O$ values of magma can be substantially modified by assimilation of rocks that have interacted with the hydrosphere (e.g. Taylor, 1974).

Many oceanic island basalts have $\delta^{18}O$† values somewhat below the assumed mantle range, based on studies of mantle xenoliths and lunar rocks (4·6–5·3‰ vs 5·5–6·0‰;

e.g. Taylor & Sheppard, 1986; Mattey *et al.*, 1994; Harmon & Hoefs, 1995) and mid-ocean ridge basalts (MORB; 5.7 ± 0.2‰; Ito *et al.*, 1987). Many of these oceanic island basalts are mafic (>6·5 wt % MgO) and display no obvious signs of crustal contamination (Garcia *et al.*, 1989*b*). Thus, it has been argued that the mantle is heterogeneous in $\delta^{18}O$ (Harmon & Hoefs, 1995), which would make recognition of crustal contamination more difficult. Correlations have been noted between low $\delta^{18}O$ values of olivine and whole-rock ratios of $^{206}Pb/^{204}Pb$ in Hawaiian basalts, which have been interpreted to reflect assimilation of hydrothermally altered oceanic crust (Eiler *et al.*, 1996*a*). The same correlation for clinopyroxene and whole rocks with low $\delta^{18}O$ values from the Canary Islands has been related to either recycling of ancient altered oceanic crust or crustal contamination (Thirlwall *et al.*, 1997). Therefore, the role of crustal contamination in oceanic island magma petrogenesis is equivocal based on these previous studies.

Hawaiian tholeiitic glasses have yielded a considerable range of $\delta^{18}O$ values (4·6–5·8‰; Kyser *et al.*, 1982; Garcia *et al.*, 1989*b*, 1993), which overlaps with the range for MORB. Some of the low $\delta^{18}O$ values are for submarine Hawaiian tholeiites that apparently assimilated hydrothermally altered crust because these rocks have elevated δD values (–33 to –52‰ vs mantle values of –60‰ to –96‰; Kyser & O'Neil, 1984), boron concentrations and $\delta^{11}B$ values (Chaussidon & Jambon, 1994). These lavas also have obvious petrographic signs of assimilation and complicated magmatic histories (Clague *et al.*, 1995). There are, however, submarine Hawaiian tholeiitic lavas with a range of $\delta^{18}O$ values (4·9–5·8‰) and mantle-like δD (–61 to –88‰; Kyser & O'Neil, 1984; Garcia *et al.*, 1989*b*). Thus, the large variation in $\delta^{18}O$ values for these Hawaiian tholeiitic glasses apparently supports the interpretation from other isotopic work on Hawaiian tholeiites (e.g. West *et al.*, 1987) that at least two isotopically distinct reservoirs are present in the source for Hawaiian magmas.

We embarked on this study to evaluate whether the oxygen isotope variation in fresh Hawaiian tholeiitic basalts was indeed caused by mantle source heterogeneity or crustal contamination. To simplify this effort, we focused our attention on the pristine basalts from the current Puu Oo eruption of Kilauea Volcano on the island of Hawaii. This eruption is the best studied, longest lived (14 years and continuing), most voluminous (~1·5 km³) and one of the most compositionally variable (5·7–10·1 wt % MgO) historical eruptions of Kilauea Volcano. Unlike most previous studies on oceanic island basalts, our approach was to determine $\delta^{18}O$ values of both glassy matrix material (95 to >99 vol. % of these rocks) and olivine (0·1–3 vol. %) for all the compositional variants from this eruption and to check for temporal variation. Olivine analyses are a critical component of this study

because olivine is the liquidus mineral in Hawaiian tholeiitic magmas (Wright, 1971) and it is thought to be resistant to oxygen exchange, even at magmatic temperatures (Cole & Ohmoto, 1986). Thus, the olivine analyses should provide a good record of the early oxygen isotope history of Puu Oo magmas.

Our results for Puu Oo lavas show a temporal variation in matrix $\delta^{18}O$ values (4·56–5·25‰) that correlates with changes in vent location and eruption style. A sharp increase in matrix $\delta^{18}O$ (~0·4‰) occurred following such a change but the $\delta^{18}O$ of the coexisting olivines decreased slightly. The small difference between $\delta^{18}O$ for olivines and host matrix [Δ(ol–m)] in many Puu Oo lavas (>–0·4‰) is indicative of disequilibrium. Thus, although the Puu Oo lavas are pristine and have no other apparent geochemical evidence of crustal assimilation, the $\delta^{18}O$ disequilibrium records the effects of crustal contamination and oxygen exchange, which occurred after the crystallization of some of the olivine crystals. Our results indicate that caution should be exercised in interpreting low $\delta^{18}O$ values for basalts (<5·0‰), especially without oxygen isotope data for coexisting minerals, and that time series studies are important for interpreting geochemical processes.

BRIEF HISTORY OF THE PUU OO ERUPTION

The Puu Oo eruption started in January 1983 (episode 1) and is continuing vigorously with typical eruption rates of $(0.3–0.5) \times 10^6 m^3/day$ (Kauahikaua *et al.*, 1996). Between 1983 and the end of 1996, the eruption produced ~1·5 km³ of lava (dense rock equivalent). The initial episode of the eruption formed a 'curtain of fire' along an 8-km-long, discontinuous fissure system which intermittently produced lava for 20 days (Wolfe *et al.*, 1987). During the next 3·5 years (episodes 2–47), eruptive activity was episodic with repose periods of 8–65 days during which magma accumulated and fractionated in a shallow reservoir under the Puu Oo vent (Fig. 1). These eruptive episodes were usually short (5–100 h) with lava fountains of variable height (tens of meters to 400 m high).

In July 1986, the site of eruptive activity shifted 3 km down rift to form the Kupaianaha vent (Fig. 1), which was nearly continuously active for 5·5 years (Garcia *et al.*, 1996). A 56 m high shield was formed at this site before the locus of eruptive activity switched back to the flanks of the Puu Oo cone in February 1992 (Kauahikaua *et al.*, 1996), where it has continued to erupt up to March 1998.

The Puu Oo eruption lavas display substantial geochemical variation reflecting the combined effects of crystal fractionation and magma mixing within the east
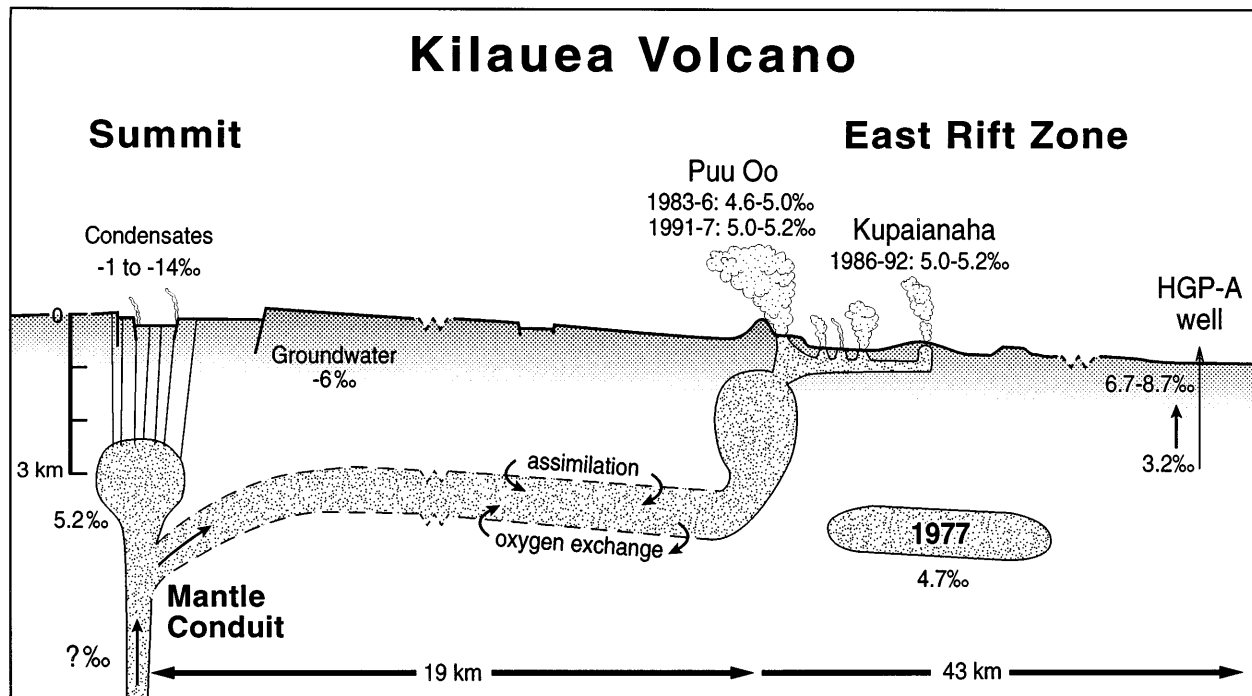
Fig. 1. Hypothetical cross-section of Kilauea's summit and east rift zone showing the inferred magma reservoir system for the Puu Oo eruption based on seismic and petrologic data (after Garcia *et al.*, 1996). The $\delta^{18}O$ values are shown for the matrix from Puu Oo eruption lavas (Table 1), HGP-A geothermal well cores (Smith & Thomas, 1990), the 1977 eruption magma (as represented by sample 1-39 erupted in 1983), and the matrix from six summit lavas erupted since 1924 (E. Ito, unpublished data, 1997). Groundwater and summit condensate $\delta^{18}O$ values (Hinkley *et al.*, 1995) are also given for comparison. The $\delta^{18}O$ value of Kilauea parental magma is unknown at this time. Oxygen isotope exchange with and assimilation of hydrothermally altered Kilauea lava is interpreted to have occurred during periods of slow magma migration through the rift, especially from 1983 to 1986. Distances from the summit are given for the Puu Oo vent and the HGP-A well locations; the two breaks in section along the rift zone should be noted.

rift zone of Kilauea, and progressive melting in the mantle source (Garcia *et al.*, 1992, 1996). The lavas from the first three episodes of the eruption are evolved (whole-rock MgO of 5·7–6·6 wt %) and contain phenocrysts and microphenocrysts of plagioclase and clinopyroxene, in addition to olivine (Garcia & Wolfe, 1988; Garcia *et al.*, 1989a). Later lavas are more mafic (7–10 wt % MgO) with few or no plagioclase or clinopyroxene crystals but sparse to common (0·1–3 vol. %), small (usually <1 mm) euhedral olivines. Some of the early eruptive episodes produced a wide range of lava compositions (e.g. 2 wt % variation in MgO) during brief intervals (<24 h for episodes 30 and 31) reflecting extreme crystal fractionation in a shallow magma reservoir (Garcia *et al.*, 1992). The parental magma for this eruption is estimated to have had ~10 wt % MgO based on olivine forsterite contents; this is also the MgO concentration of the most mafic Puu Oo lava (Garcia *et al.*, 1996).

SAMPLES

The 24 samples selected for O isotope analyses (Table 1) cover the first 14 years of the Puu Oo eruption (1983–

1997) and the eruption's entire compositional range (5·7–10·1 wt % MgO). Most of the samples from the first half of the eruption were collected from surface flows within 300 m of the vent (see Table 1). Later lavas were collected farther away from the vent because the lava was confined to inaccessible lava tubes near the vent. Samples from the early part of the eruption are from the sample collection of the US Geological Survey's Hawaiian Volcano Observatory; they are labeled according to the episode of eruption (first number) followed by a unique sample number. The other samples are from the University of Hawaii Puu Oo collection and are labeled according to the date of collection, which probably is within a day of its eruption.

All of the Puu Oo lavas analyzed in this study are weakly phyric, with only 0·1–3·0 vol. % olivine phenocrysts and microphenocrysts. Thus, the matrix $\delta^{18}O$ analyses are probably analytically indistinguishable from the whole-rock $\delta^{18}O$ values. Whole-rock major and trace element analyses for most of the samples examined in this study are published (Garcia *et al.*, 1989a, 1992, 1996). Nine additional samples are included in this study; whole-rock analyses for these samples are presented in Table 2. Four

Table 1: Sample information and geochemical results for lavas from the Puu Oo eruption

Sample number	Days[a]	Distance[b](m)	Matrix type	MgO[c] (wt %)	δ18O glass (n)[d]	δ18O[e] olivine	Δδ18O (olivine–matrix)	87Sr/86Sr	206Pb/204Pb	Rb/Y	K2O(10)[f]
1-49	1	0	glass	6.57	4.66 ± 0.02 (2)	—	—	—	—	0.340	—
1-39	12	10	mixed	5.70	4.76 ± 0.10 (4)	—	—	—	18.515	0.400	—
1-54	21	0	glass	6.12	4.56 ± 0.02 (2)	—	—	0.703564	18.472	0.385	—
5-139	182	10	glass	8.10	4.77 ± 0.03 (2)	4.89L	0.12	0.703592	—	0.313	0.487
30-358	761	0	glass	7.62	4.99 ± 0.04 (3)	4.65L	−0.34	—	—	—	0.414
30-362	762	15	mixed	9.43	4.76 ± 0.05 (2)	4.89L	0.13	0.703587	18.416	0.329	0.442
31-364	800	0	glass	7.73	4.91 ± 0.04 (2)	4.78L	−0.13	—	—	—	0.433
31-368	801	100	crystalline	9.47	4.89 ± 0.02 (2)	4.74 ± 0.05	−0.15	—	—	0.321	0.442
32-370	840	1000	crystalline	7.71	4.82 ± 0.10 (5)	4.79L	−0.01	—	—	0.309	0.448
46-545	1247	0	glass	7.59	4.94 ± 0.03 (9)	—	—	—	—	0.302	0.435
47-570	1271	1500	crystalline	7.66	4.77 ± 0.02 (2)	—	—	—	—	0.290	0.444
48-649	1350	300	mixed	7.80	5.17 ± 0.01 (2)	4.41 ± 0.03L	−0.76	0.703596	—	0.307	0.436
48-714	1534	0	crystalline	8.62	5.25 ± 0.02 (2)	4.56 ± 0.06L	−0.69	0.703594	18.412	0.314	0.435
26-Mar-89	2275	0	glass	9.00	5.11 ± 0.05 (2)	—	—	0.703586	18.385	0.315	0.424
7-Jan-90	2562	0	glass	8.53	5.03 ± 0.01 (2)	4.67L	−0.36	0.703591	18.397	0.292	0.412
12-May-91	3052	5500	glass	8.70	5.08 ± 0.04 (2)	4.78L	−0.30	—	18.400	0.289	0.407
F91-32	3132	0	glass	8.62	5.11 ± 0.04 (2)	4.75L	−0.36	—	—	—	0.406
6-Jun-92	3443	500	glass	8.94	5.04 ± 0.10 (2)	—	—	—	—	0.297	0.411
29-Dec-92	3649	1500	glass	8.80	4.99 ± 0.10 (4)	4.67L	−0.33	0.703601	18.397	0.283	0.410
13-Aug-93	3876	8000	glass	8.42	4.98 ± 0.07 (3)	—	—	—	—	0.262	0.402
25-Apr-94	4131	9000	mixed	7.71	5.01 ± 0.02 (3)	4.72C	−0.29	0.703605	18.407	0.257	0.403
27-Apr-95	4498	9500	mixed	8.40	5.25 ± 0.05 (4)	4.58L	−0.67	—	—	0.278	0.394
19-Jan-96	4765	9300	glass	10.14	5.19 ± 0.07 (3)	4.54 ± 0.03L	−0.64	—	—	—	0.395
10-Jan-97	5121	8200	glass	8.33	5.20 ± 0.05(2)	4.73L	−0.47	—	—	—	0.386

[a]Days since start of the eruption that sample was erupted. [b]Distance of flow from vent when collected. [c]Whole-rock MgO content. [d]Number of replicates; ± indicates total range of measured values. [e]Olivine analyses were done by laser (L) and conventional (C) methods. Sample 31-368 was run in both laboratories: 4.68 (C); 4.79 (L). Three olivine samples were analyzed in duplicate by laser. [f]K2O is normalized to a whole-rock 10 wt % MgO concentration by addition of equilibrium olivine in small steps. Trace element and isotope data from Garcia *et al.* (1996).

Table 2: XRF whole-rock analyses of some Puu Oo lavas

Sample	30-358	31-364	6-Jun-92	29-Dec-92	13-Aug-93	25-Apr-94	27-Apr-95	19-Jan-96	10-Jan-97
SiO_2	49·88	49·92	49·63	49·57	50·12	50·16	49·92	49·32	50·10
TiO_2	2·48	2·46	2·35	2·36	2·39	2·44	2·37	2·23	2·35
Al_2O_3	13·27	13·36	12·68	12·69	12·96	13·27	12·91	12·17	12·98
Fe_2O_3*	12·23	12·25	12·49	12·42	12·51	12·42	12·57	12·90	12·46
MnO	0·17	0·17	0·18	0·18	0·18	0·18	0·18	0·18	0·19
MgO	7·55	7·64	8·94	8·80	8·41	7·71	8·40	10·14	8·33
CaO	11·01	11·08	10·59	10·52	10·76	10·93	10·63	10·15	10·74
Na_2O	2·17	2·19	2·11	2·22	2·14	2·45	2·15	1·87	2·08
K_2O	0·44	0·45	0·42	0·42	0·42	0·43	0·41	0·39	0·40
P_2O_5	0·25	0·24	0·23	0·23	0·23	0·24	0·23	0·21	0·22
Sum	99·45	99·76	99·62	99·41	100·12	100·23	99·77	99·56	99·85

*Total iron.
Analysts: J. M. Rhodes, T. Hulsebosch, M. Garcia.
All values are in weight per cent.

of the 23 lava samples were erupted during the first year of the Puu Oo eruption. Samples 1-49 and 1-39 probably rose from separate pockets of rift-zone-stored magma (Garcia *et al.*, 1989a). Sample 1-54 is a hybrid formed from mixing these two pockets of magma and was erupted in the area where the Puu Oo cone later formed. Sample 5-139 formed from mixing the hybrid with the more mafic magma which intruded at the start of the eruption. Samples 1-39 and 5-139 contain both petrographic and geochemical evidence of magma mixing (Garcia *et al.*, 1992). Five of the samples (30-358, 30-362, 31-364, 31-368, and 32-370) are from the beginning, the end or just after episodes 30 and 31, which produced compositionally diverse lavas (e.g. 7·6–9·5 wt % MgO) with no signs of magma mixing. These samples were analyzed to evaluate processes within the shallow reservoir under the Puu Oo vent. Four samples are from the period just before (46-545 and 47-570) or after (48-649, 48-714) the vent location shifted 3 km down rift. Sample 46-545 is reticulite (basaltic foam) collected during a period of very high (400 + m) fountaining. Three additional samples (26-Mar-89, 7-Jan-90, and 12-May-91) were included in this study from the down-rift vent, which is thought to have been connected to the Puu Oo shallow magma reservoir by a shallow conduit (Fig. 1). To evaluate this hypothesis, a sample collected from the Puu Oo lava lake (F91-32), which remained active while lava flows were produced from the down-rift vent, was analyzed. The last six samples listed in Table 1 were erupted from the flank of the Puu Oo cone.

Glassy lavas from the Puu Oo eruption were crushed, sieved, washed and sonified in deionized water, and then hand picked with the aid of a binocular microscope. Samples with rare, small olivines were passed through the Frantz isodynamic magnetic separator to concentrate olivine before hand picking with the aid of a binocular microscope to avoid glass and chromite inclusions. The matrix material for the oxygen isotope analyses included glass, a mixture of glass and holocrystalline matrix material, or just holocrystalline material (see Table 1). Most of the glass is light brown in color and clear, although in a few cases it is black and cloudy. Olivines in the Puu Oo lavas are undeformed, euhedral, and normally zoned, except those from episode 1 which display resorption features (Garcia *et al.*, 1989a, 1992, 1996). Olivines from episode 1 were not analyzed because of their low abundance. Most of the olivine in Puu Oo lavas is microphenocrystic (0·1–0·5 mm across) but some lavas contain rarer larger crystals (0·6–1·5 mm). No olivine xenocrysts (i.e. deformed grains) have been observed in these lavas.

ANALYTICAL METHODS

Oxygen isotope ratios of matrix material were determined by conventional methods (Clayton & Mayeda, 1963) at the University of Minnesota using ClF_3 (Borthwick & Harmon, 1982). CO_2 gas from each extraction was analyzed on a Finnigan MAT delta E mass 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 1 for the total range of values and the number of replicates for each sample). For most samples, analytical reproducibility is 0·1‰ or better. A laboratory standard (Nain plagioclase) was analyzed for every four matrix samples. The overall reproducibility for Nain plagioclase

for the duration of this work was $\pm 0.18‰$ (1σ) for 106 analyses. A MORB glass from the East Pacific Rise, which had previously been analyzed at the Geophysical Laboratory (Ito *et al.*, 1987), was also analyzed at Minnesota to ascertain that the new data can be compared directly with the MORB data set. The results reported here are relative to VSMOW (Vienna standard mean ocean water), normalized against SLAP (standard light Antarctic precipitation, which is defined as –55‰ relative to VSMOW; Coplen, 1988).

Most of the olivine separates were analyzed by laser fluorination at the University of Wisconsin at Madison using methods described by Valley *et al.* (1995). Each olivine analysis represents tens of grains. Measured yields on olivine were $99 \pm 2\%$ on an average sample size of 1·5 mg, yielding 20 μmol of CO_2. Reproducibility of olivine analyses was monitored by analysis of fragments of a single grain of San Carlos olivine, which had a reproducibility of $\pm 0.07‰$ (1σ, $n = 35$) over the course of this study. Most of the Puu Oo lavas are very poor in olivine; sufficient material was available from three olivine separates for duplicate analyses, which yielded reproducibilities of 0·03, 0·03 and 0·06‰ (Table 1).

Three olivine separates were analyzed at the University of Chicago by T. K. Mayeda. The University of Chicago obtains a value of $5.72 \pm 0.16‰$ for UWG-2 (normalized to a constant value for NBS-28; Valley *et al.*, 1995). One of these three olivine separates (31-368) was analyzed at both the University of Chicago (UC) and the University of Wisconsin (UW), with the results being: UC: 4·68‰, UW: 4·79‰. One basaltic glass (30-362) was analyzed at both the University of Minnesota (UM) and by laser fluorination at the UW, with the results being: UM: $4.76 \pm 0.05‰$, UW: $4.91 \pm 0.08‰$. The intra-laboratory precision and inter-laboratory reproducibility for both standards and unknowns average better than $\pm 0.1‰$ (1σ), which we assume to be the typical uncertainty of the oxygen isotope data.

The whole-rock X-ray fluorescence (XRF) analyses (Table 2) were made in duplicate at the University of Hawaii and University of Massachusetts using methods described by Garcia *et al.* (1996).

RESULTS

The matrix material from the Puu Oo eruption ranges in $\delta^{18}O$ from 4·56 to 5·25‰ (Table 1). The early lavas (from 1983) have the lowest values (4·56–4·77‰) and those erupted just after the vent change in 1986 and during 1995–1997 have the highest (5·17–5·25‰). The largest change in $\delta^{18}O$ (0·4‰) occurred between episode 47 and the early portion of episode 48 (Fig. 2), a period when the vent moved 3 km down rift and eruptive style changed from episodic to continuous effusion. The matrix

$\delta^{18}O$ value for the Puu Oo basalts (except those erupted in 1983) are within the range of ratios previously reported for uncontaminated Hawaiian basalts (whole-rock and matrix $\delta^{18}O$ = 4·9–5·8‰ and δD = –61 to –84; Kyser *et al.*, 1982; Garcia *et al.*, 1989*b*) but are well below typical MORB values (5·7 $\pm$ 0·2‰; Ito *et al.*, 1987).

The olivines from the Puu Oo lavas display a smaller range in $\delta^{18}O$ (4·4–4·9‰; Table 1; Fig. 2), although most have ratios of 4·75 $\pm$ 0·15‰. This variation is somewhat greater than that reported by Eiler *et al.* (1996*a*, 1996*b*) for olivine phenocrysts from cores from each of two deep drill holes that span many tens of thousands of years: 15 samples from a ~750 m section of Mauna Kea range from 4·6 to 5·0‰ and 10 samples from a ~2 km section of Kilauea range from 4·9 to 5·2‰; Fig. 2). Both the Puu Oo and the drill core olivine analyses were determined by Eiler at the University of Wisconsin. Kyser *et al.* (1981) reported $\delta^{18}O$ values of 4·5–5·2‰ for olivines from a suite of submarine lavas from Kilauea's east rift zone. Thus, it is clear that Kilauea has produced a wide range of olivine $\delta^{18}O$ values, even during the short time interval of the Puu Oo eruption.

OLIVINE–MATRIX OXYGEN ISOTOPE FRACTIONATION

There is a strong negative correlation for olivine and matrix material $\delta^{18}O$ values from Puu Oo lavas (Table 1; Fig. 3). The difference between the values of $\delta^{18}O$ for olivine and matrix material [Δ(ol–m)] in these lavas varies from +0·13 to –0·76‰. Kyser *et al.* (1981) proposed a strong temperature dependence for the equilibrium fractionation of oxygen isotopes between olivine and melt. Their empirical estimates of magma temperatures (M_T) indicated that Δ(ol–m) is positive above ~1200°C [Δ(ol–m) = +1·2 at 1300°C] and negative below 1200°C [Δ(ol–m) = –1·1 at 1100°C]. Ito & Stern (1986) calculated an olivine–melt oxygen isotopic fractionation of –0·7‰ for basalts from empirical data and assumed no explicit temperature dependence. Chiba *et al.* (1989) experimentally examined the oxygen isotope fractionation for olivine–pyroxene pairs and found little or no temperature dependence between 1150 and 1220°C, the expected temperature range for olivine crystallization Puu Oo magmas. Thus, there is some uncertainty in the temperature dependence of the oxygen isotope equilibrium fractionation between olivine and melt.

Puu Oo lavas are potentially well suited for evaluating this issue because olivine crystals are in Fe/Mg equilibrium with their host lavas, with the exception of lavas erupted before episode 20 and the more mafic lavas from 1990 (Garcia *et al.*, 1992, 1996). Magmatic temperatures for these nearly aphyric rocks can be estimated using the Helz & Thornber (1987) MgO geothermometer, which
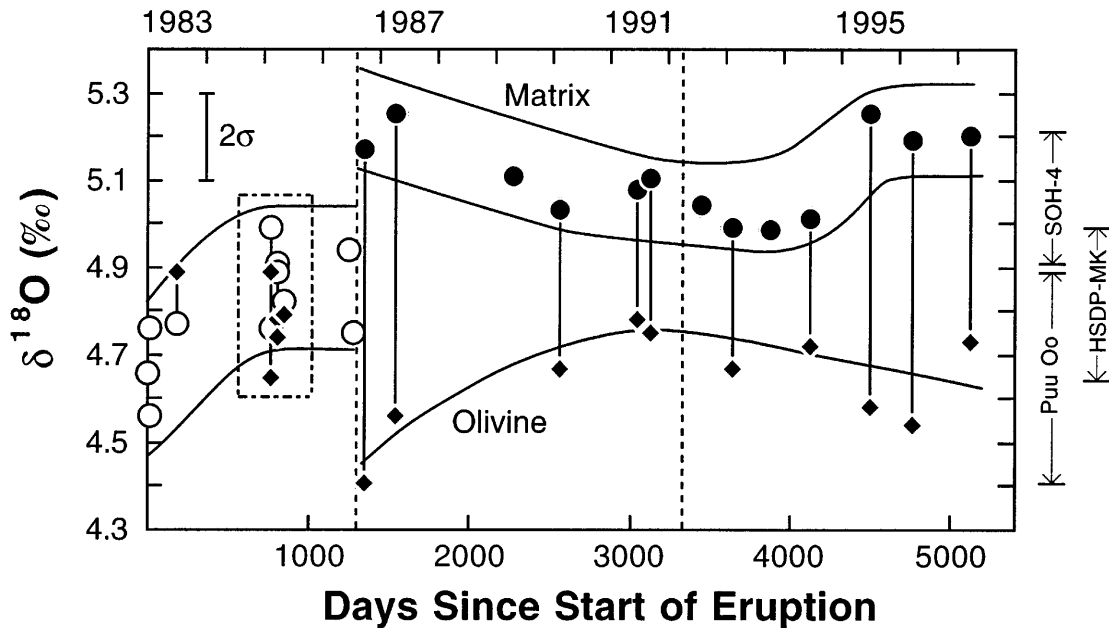
Fig. 2. Temporal variation of $\delta^{18}O$ values for matrix material ($\bigcirc$, lavas from episodes 1–47; $\bullet$, subsequent lavas) and olivine ($\blacklozenge$) from Puu Oo eruption lavas. The thin vertical lines connect matrix material and olivine analyses from the same rock. The parallel bold lines show the temporal variation in oxygen isotope variation for matrix material. Dashed vertical lines denote changes in vent location (from left to right; Puu Oo to Kupaianaha and back to Puu Oo). The ranges on the right side of the figure are for olivines from the Kilauea SOH-4 drill core lavas, the Mauna Kea HSDP drill core lavas (Eiler *et al.*, 1996*a*, 1996*b*), and Puu Oo eruption. The analytical errors for olivine and matrix material oxygen isotope analyses are essentially the same; the 2σ error bar is given in the upper left corner. The long–short dashed box covers samples from episodes 30 to 32, which are highlighted in Fig. 6, below.

has estimated errors of $\pm 10°C$. Although this geo-thermometer was calibrated for glass, the Puu Oo lavas used in this study contain 97 to >99 vol. % glassy matrix material, so their whole-rock MgO concentrations should be a good indication of the magmatic temperatures, especially during olivine crystallization.

There is no correlation between magma temperature (M_T) estimated from whole-rock MgO concentration and $\Delta(ol–m)$ values for Puu Oo lavas (Fig. 4; Table 1). Some of the more MgO-rich lavas (9·47 wt %; $M_T = 1204°C$) and the more evolved lavas (~7·75 wt % MgO; $M_T = 1168°C$) have moderate to low $\Delta(ol–m)$ values (0·13 to –0·15‰ and 0·12 to –0·33‰, respectively) but some lavas with intermediate MgO compositions ($M_T = 1171–1187°C$), have greater differences in (ol–m) values (–0·67 to –0·76‰), whereas others have lower values (0·12 to –0·36‰). Therefore, the variation in $\delta^{18}O$ values of Puu Oo lavas cannot be attributed to temperature.

DEGASSING EFFECTS ON OXYGEN ISOTOPES

Magma degassing is a potential mechanism for lowering the $\delta^{18}O$ values of lavas (e.g. Taylor, 1991). Puu Oo lavas

experienced variable amounts of degassing in the shallow Puu Oo reservoir before eruption (storage times varied from hours to tens of days), during eruption at the vent (fountain heights varied from tens of meters to 400 m high; Wolfe *et al.*, 1987) and, for some lavas, while they flowed ~10 km to the coast. The extreme case of degassing of Puu Oo magmas may have been during the high fountaining episodes of 1983–1986 when fountain heights of 300 m were observed, and basaltic foam (reticulite) was produced. The water contents of Puu Oo magmas are estimated to have been 0·4–0·5 wt %, based on studies of glass inclusions in olivines from episode 16 lavas (Wallace & Anderson, 1998). In contrast, glasses from two coastal flows from 1987 and 1989 were found to have extensively degassed. They contained ~0·02 wt % H_2O, <0·01 wt % S and no CO_2 (D. Muenow, unpublished data, 1997).

Among our Puu Oo sample suite, there is no systematic difference in $\delta^{18}O$ values for samples collected near the vent compared with those collected on the coastal plain (e.g. 7-May-90 vs 12-May-91) or between samples from the early, degassed stage of episodic eruptions compared with the later, gas-charged high fountaining stage of these episodes (e.g. samples 31-364 vs 31-368). Even the basaltic foam from episode 46 is not distinct in its $\delta^{18}O$ value
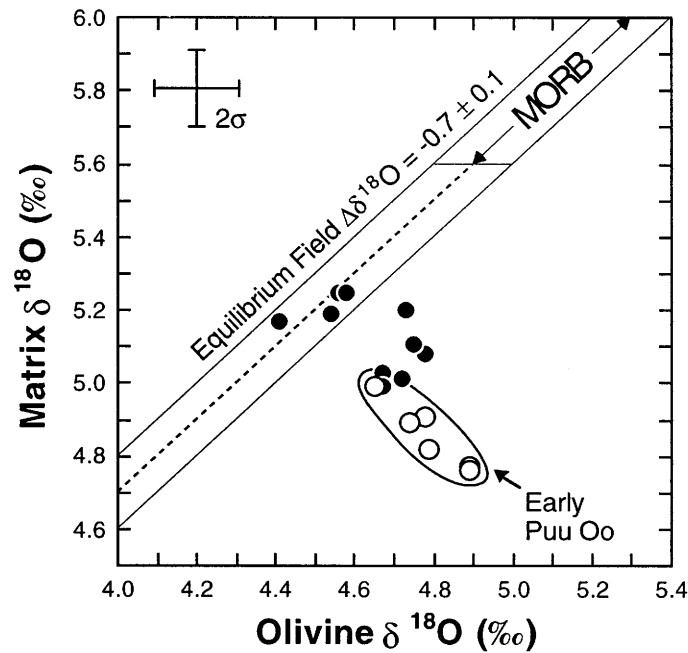
Fig. 3. Oxygen isotope ratios for matrix material and olivine from Puu Oo lavas. These data define a negative correlation which is at a right angle to the equilibrium field for olivine–melt fractionation, assuming a fractionation value of -0.7 ± 0.1‰ for olivine–melt (Ito & Stern, 1986). The range expected for MORB based on glass analyses of Ito *et al.* (1987) is shown for comparison. It should be noted that all of the lavas from the early, episodic phases of the Puu Oo eruption (circled field) plot well outside the equilibrium field. The 2σ error bars are given in the upper left corner of the figure. Symbols as in Fig. 2.

(Table 1). Thus, there appears to be no degassing effect on the $\delta^{18}O$ values of Puu Oo lavas.

## CORRELATION OF OXYGEN ISOTOPES WITH OTHER GEOCHEMICAL PARAMETERS?

A new study of oxygen isotopes in olivines from Hawaiian basalts showed a good correlation with radiogenic isotope ratios, especially $^{206}Pb/^{204}Pb$ (Eiler *et al.*, 1996*a*). Lavas from the Puu Oo eruption show a temporal variation in Pb isotope ratios, and in ratios of highly incompatible to moderately incompatible elements (Fig. 5). Most of the Pb isotope variation occurred during the first year of the eruption and there has been little or no change since 1985. The Pb isotopic variation for Puu Oo lavas is within the range observed for historical Kilauea lavas (Pietruszka & Garcia, 1998), which led Garcia *et al.* (1996) to conclude that the Pb isotope variation in the early Puu Oo lavas represents mixing of magmas from different mantle sources with similar Sr and Nd isotope ratios (Fig. 5). The trace element ratios in these lavas show a well-defined decrease in ratios of highly incompatible to moderately incompatible trace elements, which is due to a systematic decrease with time in the abundance of highly incompatible trace elements (e.g. Ba and La;

Garcia *et al.*, 1996). Ratios of highly incompatible elements remained constant (Fig. 5).

There is no correlation of olivine $\delta^{18}O$ values with any other geochemical parameter for Puu Oo lavas (Table 1). For example, during episode 31 there was a wide range in whole-rock MgO concentration but not in the olivine $\delta^{18}O$ values (Fig. 6a). A slightly smaller variation in olivine $\delta^{18}O$ (~ 0.35‰) was observed for four Mauna Kea drill core lavas, all of which have the same Pb isotope ratio (Eiler *et al.*, 1996*a*). Thus, although there is an overall correlation between Pb and O isotopes in Hawaiian lavas, some of the variation in olivine $\delta^{18}O$ values in Hawaiian tholeiites is not related to the cause of Pb isotope variation.

There are overall correlations of MgO concentrations, incompatible elements (such as Rb/Y and the MgO-normalized K_2O concentration) and Pb and Sr isotopes with matrix $\delta^{18}O$ values in Puu Oo lavas (Fig. 7; Table 1). This correlation, however, is controlled by the lavas from the first 2 years of the eruption (episodes 1–20; Fig. 5), which are thought to be products of variable mixing of two evolved magmas and one mafic magma (Garcia *et al.*, 1992). For example, the MgO correlation disappears if the episode 1 lavas are not included (Fig. 6b). Furthermore, there is no correlation of MgO with matrix $\delta^{18}O$ values for the lavas from episodes 30 and 31, which have large variations in MgO (Fig. 6a). For lavas erupted
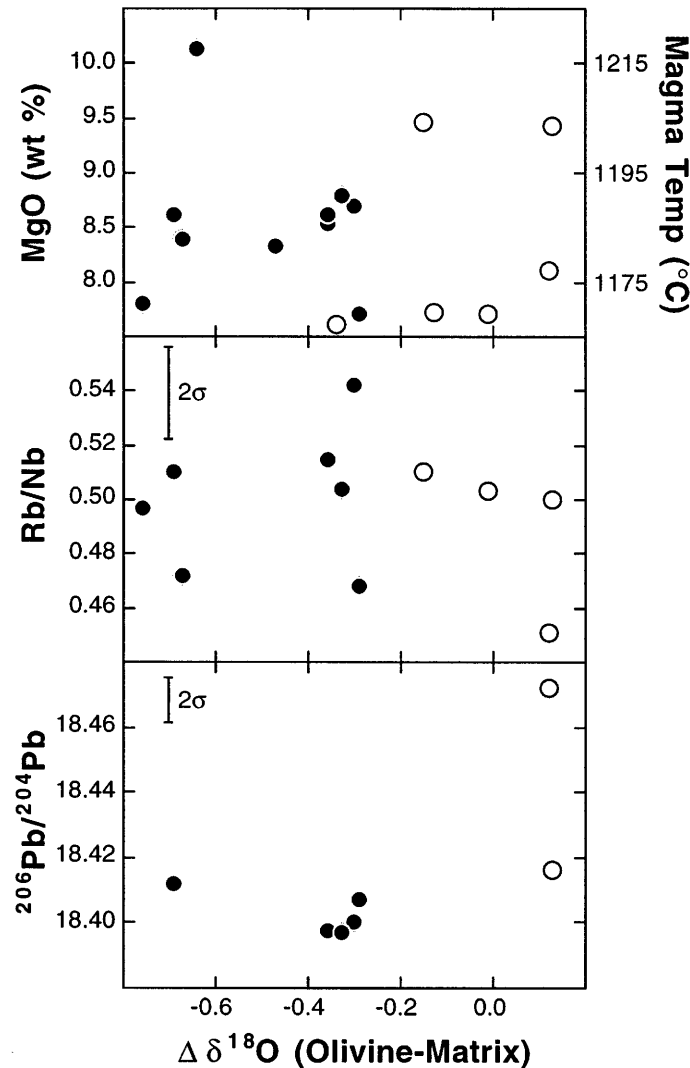
Fig. 4. Difference in values of $\Delta\delta^{18}O$(olivine–matrix) vs whole-rock MgO concentration [and magma temperature calculated using the Helz & Thornber (1987) MgO geothermometer], Rb/Nb ratio, and $^{206}Pb/^{204}Pb$ ratio for Puu Oo lavas. Samples with $\Delta\delta^{18}O$(olivine–matrix) values greater than −0·5‰ were in disequilibrium. The lack of correlation of these values with the other geochemical parameters should be noted. Symbols as in Fig. 2.

after the magma mixing period (episodes 1–20), the correlation between $\delta^{18}O$ and other geochemical parameters is poor or absent because there is a significant variation in matrix $\delta^{18}O$ with little or no variation in the other geochemical parameters (Fig. 7). Furthermore, the shift in matrix $\delta^{18}O$ with the 1986 change in vent location (Fig. 2) is not correlated with any change in Pb isotope ratios or in the ratios or abundances of trace elements (Fig. 5). Therefore, whatever caused the shift in matrix $\delta^{18}O$ as the vent location changed did not have any apparent effect on the Pb, Nd and Sr isotope or trace element ratios in these lavas. Thus, the overall correlation of Pb isotope ratios and other geochemical parameters with matrix $\delta^{18}O$ for the early Puu Oo lavas is probably

related to a combination of mantle and crustal processes.

Another potential process indicator is the Δ(ol–m) $\delta^{18}O$ values for Puu Oo lavas. The equilibrium value is assumed to be −0·7‰; values for Puu Oo lavas range from −0·7‰ to +0·1‰. This wide range of values does not correlate with any geochemical parameter for Puu Oo lavas (Fig. 4).

CAUSES OF OXYGEN ISOTOPE VARIATION IN PUU OO LAVAS

The variation in $\delta^{18}O$ for Puu Oo lavas is the result of source heterogeneity and/or crustal contamination.
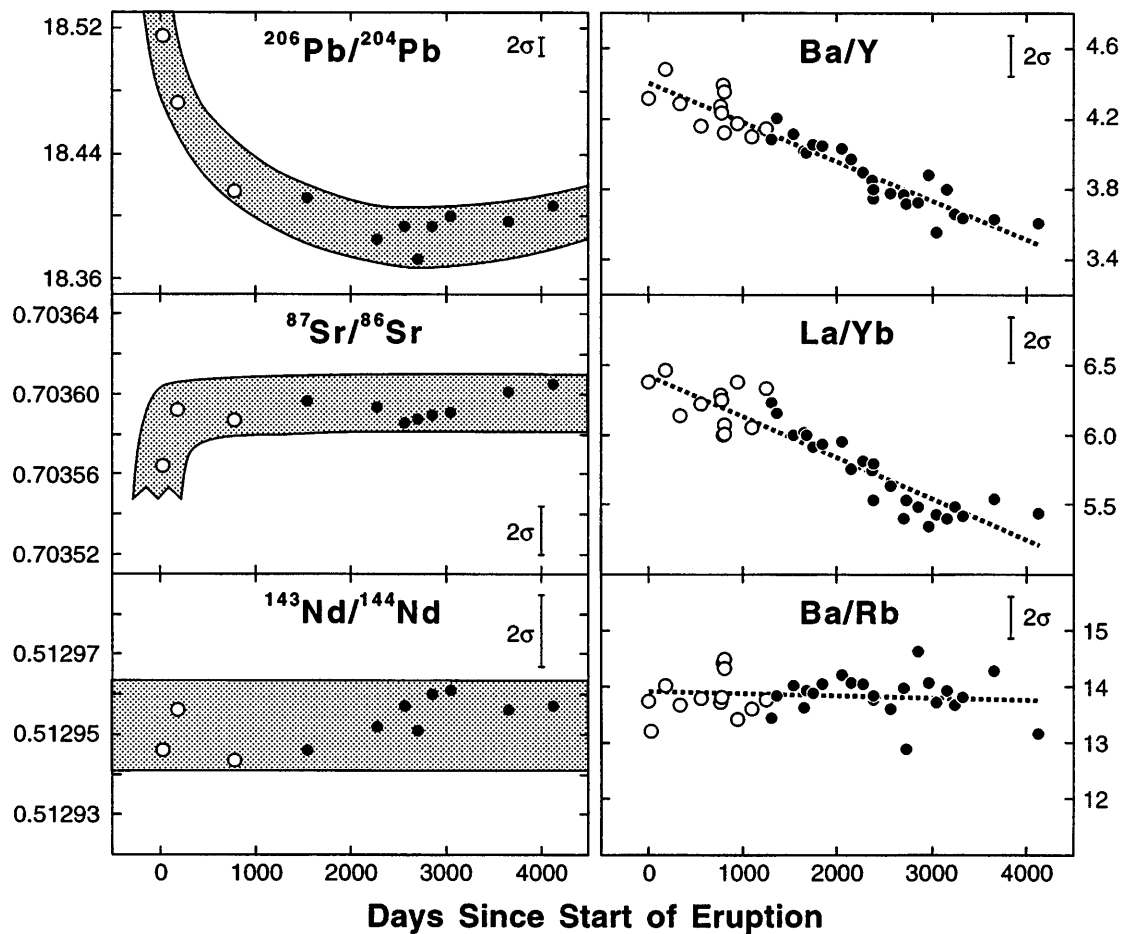
Fig. 5. Temporal variation for incompatible trace element and Pb, Sr and Nd isotope ratios for lavas from the Puu Oo eruption [data from Garcia *et al.* (1996)]. Most of the variation in Pb and Sr isotope ratios occurred during the first 2 years of the eruption when magma mixing was the dominant process controlling compositional variation. Ratios of Nd, Pb and Sr isotopes, and of highly incompatible elements (e.g. Ba/Rb) have remained constant from this period to the present, whereas ratios of highly incompatible to moderately incompatible elements have progressively decreased (e.g. La/Yb). Symbols as in Fig. 2. The 2σ errors bars are given for reference.

Although several previous studies have related the variation in $\delta^{18}O$ values for Hawaiian lavas to source heterogeneity (e.g. Garcia *et al.*, 1989*b*; Harmon & Hoefs, 1995), the good negative correlation of $\delta^{18}O$ for olivine and matrix material (Fig. 3) is strong evidence that the oxygen isotope variations in the Puu Oo lavas are related to a disequilibrium process such as crustal contamination because the trend of the olivine–matrix correlation is opposite to that predicted from equilibrium crystallization (Ito & Stern, 1986). Among Puu Oo lavas, those from the intermittent geyser-like eruptions of episodes 5–47 show the greatest signs of disequilibrium because of their small $\Delta(ol–m)$ values (0·13 to –0·34‰) and lower matrix $\delta^{18}O$ values (<5·0‰). If these olivines are comagmatic with their host matrix, an interpretation based on the euhedral, undeformed shape of the olivines and their Fe/Mg compositional equilibrium with the host matrix,

and assuming olivine is resistant to oxygen isotope exchange (Cole & Ohmoto, 1986), then the $\delta^{18}O$ value of the Puu Oo magma was probably lowered by interaction with hydrothermally altered crust after the growth of much of the olivine but before eruption.

It is unlikely that water can directly contaminate magmas before their eruption but it may extensively exchange with magma chamber wall rocks. These hydrothermally altered rocks might be stoped into the magma and partially assimilated, modifying the magma's primary $\delta^{18}O$ value (e.g. Taylor & Sheppard, 1986). Kilauea fluids range widely in their $\delta^{18}O$ values (Hinkley *et al.*, 1995; Conrad *et al.*, 1997); Hawaiian ocean water has a $\delta^{18}O$ of 0·4‰ and a rain water sample taken in July 1990 from the Puu Oo area has a $\delta^{18}O$ of –0·9‰. Rain from the higher elevations of the island, which supplies the groundwater along Kilauea's east rift zone
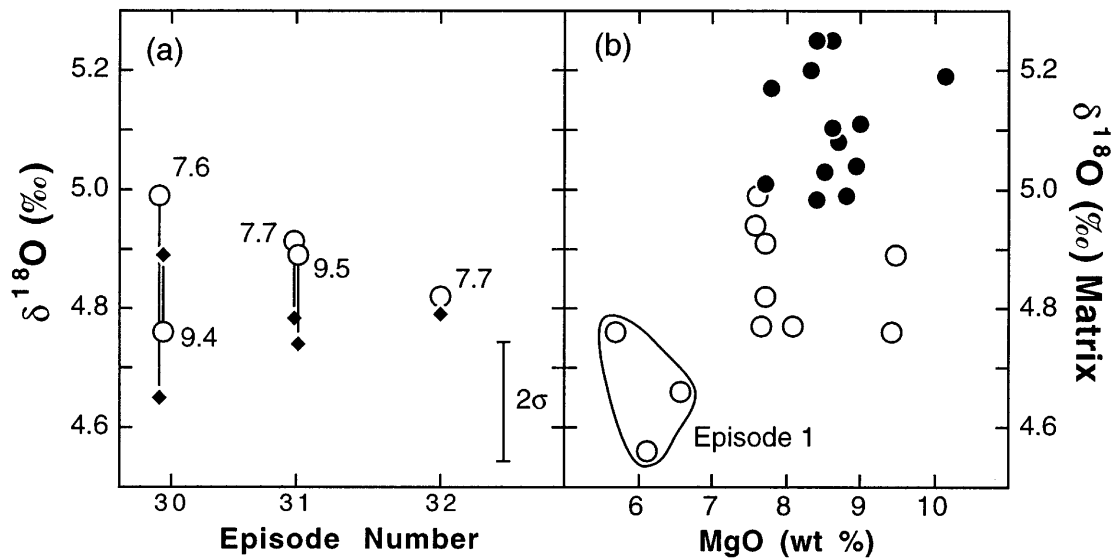
Fig. 6. (a) Variation in matrix and olivine $\delta^{18}O$ values for lavas from episodes 30–32. The first sample shown from episodes 30 and 31, and the sample from episode 32 are the lowest MgO lavas from these episodes (numbers on plot are in wt %); the second sample shown from episodes 30 and 31 is the higher MgO lava. There is no systematic variation of matrix or olivine $\delta^{18}O$ values with MgO concentration for these lavas. (b) Matrix $\delta^{18}O$ values vs whole-rock MgO for Puu Oo lavas. Although there is a crude positive correlation for Puu Oo lavas, it disappears if the rift-zone-stored lavas from episode 1 are excluded.

(Conrad *et al.*, 1997), has a $\delta^{18}O$ of –6‰. Fumarole condensates from the summit of Kilauea range from –0·6 to –14·4‰.

The effects of fluids on the $\delta^{18}O$ of Kilauea lavas have been evaluated for the weakly to moderately, hydrothermally altered cores from several ~2 km deep holes drilled into the magmatic core of Kilauea's east rift zone. Lavas from the HGP-A well, which produced hydrothermal energy, yielded whole-rock $\delta^{18}O$ values of 3·2–8·7‰, with those from the weakly altered part of the hole (650–1050 m depth) giving $\delta^{18}O$ values of 6·7–8·7‰ (Smith & Thomas, 1990). Lavas recovered from below 1050 m in the hole showed an irregular decrease in $\delta^{18}O$ down to 3·2‰ near the bottom of the hole (Smith & Thomas, 1990) where temperatures of ~350°C were measured (Conrad *et al.*, 1997). Lavas from three other deep drill holes showed similar variations but do not have $\delta^{18}O$ values as low as the HGP-A lavas (Conrad *et al.*, 1997).

Using the lowest rock $\delta^{18}O$ value from these geothermal drill holes (3·2‰) and assuming a parental magma $\delta^{18}O$ value of 5·2‰ (see later discussion on Puu Oo parental magma), we calculate that ~30% assimilation would be needed to produce the observed range in matrix material $\delta^{18}O$ ratios (4·56–5·25‰) for the entire Puu Oo eruption. This is a geologically unreasonable level of contamination. Intrusive rocks, metamorphosed to greenschist facies, from the basal complexes of Canary Island volcanoes have yielded $\delta^{18}O$ values as low as –1·4‰ (Javoy *et al.*, 1986). If Puu Oo magmas were contaminated with such

intrusive rocks, only 11–12% assimilation would be needed to explain the overall variation in Puu Oo matrix $\delta^{18}O$ values. A study of metamorphosed accidental blocks from Kilauea's summit 1924 phreatic explosions is under way to better assess the range of $\delta^{18}O$ values for summit magma chamber wall rocks. In the absence of a suitable contaminant, we propose that the Puu Oo lavas experienced both partial assimilation of and oxygen exchange with hydrothermally altered Kilauea lavas. The same conclusion was made to explain the low $\delta^{18}O$ values in some Icelandic basalts (e.g. Hattori & Muehlenbachs, 1982). Unlike those rocks, Puu Oo lavas do not appear to contain xenoliths of hydrothermally altered lavas. We cannot, however, preclude the possibility that some assimilation may have occurred. The Puu Oo magmas are extremely fluid and were stored in a shallow reservoir before eruption. These factors contribute to the overall low abundance of phenocrysts in Puu Oo lavas, even in those that are strongly fractionated, and may have effectively removed any xenoliths that might have been present in the Puu Oo magmas.

TIMING AND LOCATION OF PUU OO MAGMA CONTAMINATION

There are several possible sites where the $\delta^{18}O$ value of Puu Oo magma may have been lowered after being intruded from the volcano's summit. The most obvious site is the shallow magma reservoir under the Puu Oo
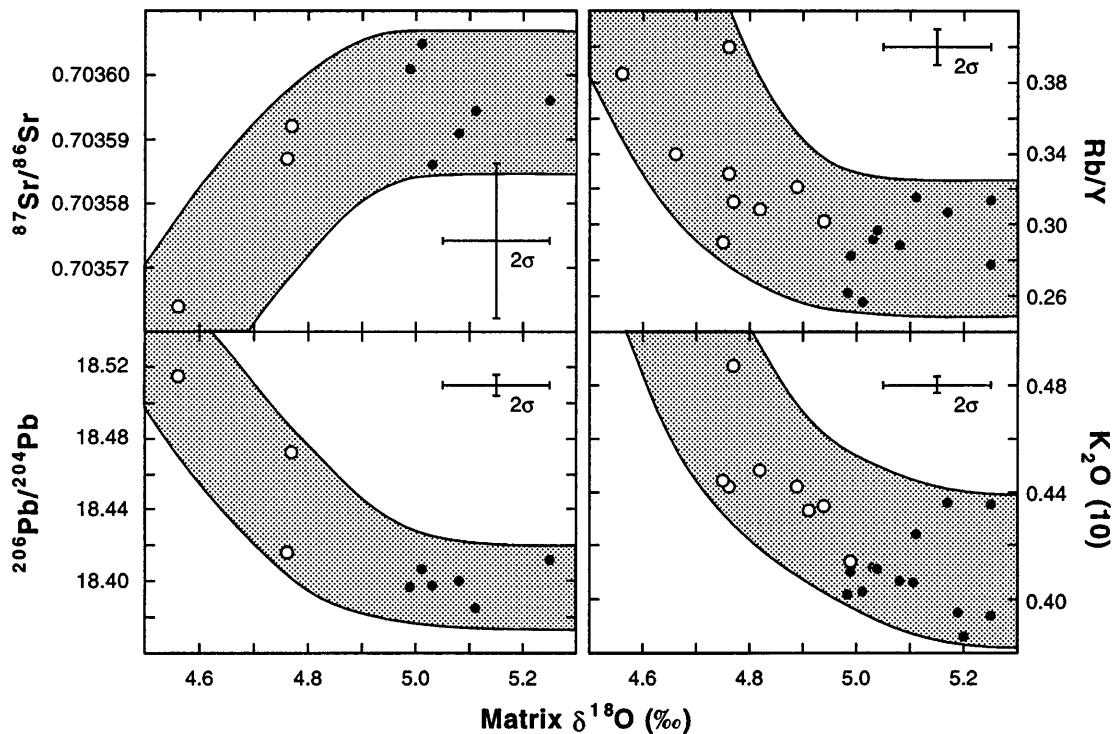
Fig. 7. Oxygen isotope ratios for matrix material vs whole-rock Pb and Sr isotope ratios, Rb/Y ratio, and $K_2O(10)$ for Puu Oo eruption lavas. $K_2O(10)$ is the abundance of K_2O in wt % normalized to 10 wt % MgO by addition of equilibrium olivine in small steps (Garcia *et al.*, 1996). The lavas from episodes 1–47 (◯) show good correlations, but these correlations are thought to be related to magma mixing. The later lavas show no correlations between matrix oxygen isotope ratios and the other geochemical parameters. The variations in trace elements at a given matrix oxygen isotope value are well outside analytical error but those for Pb and Sr isotopes are not. Thus, the variations in trace elements are probably unrelated to the matrix oxygen isotope variations. Garcia *et al.* (1996) related the trace element variations to progressive melting of a relatively homogeneous source. The 2σ errors bars are given for reference.

vent. To evaluate this hypothesis, we analyzed lavas from the beginning and the end of two episodes (30 and 31) that produced relatively large volumes of compositionally variable lava (MgO variations of ~2 wt %). These brief eruptive episodes (21 and 23 h) were interpreted to have completely drained the shallow Puu Oo reservoir (Hoffmann *et al.*, 1990). The most mafic lavas were erupted at the end of these episodes and are thought to be representative of the parental magma that was being supplied to this shallow reservoir (Garcia *et al.*, 1992).

The $\delta^{18}O$ values for matrix material from five samples erupted during or just after these episodes (samples 30-358 to 32-370 in Table 1) are uniform (4.77 ± 0.12‰) within analytical error ($1\sigma \pm 0.10$‰). The olivine $\delta^{18}O$ values from these lavas are also uniform within analytical error and identical to the matrix (4.81 ± 0.08‰, except sample 30-358; Fig. 2b), reflecting disequilibrium before eruption. If the local reservoir was drained during each of these episodes and the most mafic lavas are representative of the parental magmas, then the proposed oxygen isotope exchange and/or assimilation and the crystallization of most of the coarser olivine in these rocks

occurred before storage of the magma in the shallow Puu Oo reservoir.

Before reaching the Puu Oo reservoir, the magma traveled 19 km through Kilauea's east rift zone (Fig. 1). The transit time of Puu Oo magmas in the rift zone may have varied from as long as a year during the episodic eruptions of episodes 4–47 (1983–1986; Parfitt & Wilson, 1994) to about 20 days after the vent changed location and the eruption became nearly continuous in mid-1986 (Garcia *et al.*, 1996). Thus, there was a marked change in the residence time of magma in the rift which coincides with the largest shift in matrix material $\delta^{18}O$ (~0.4‰) and may be a valuable clue for understanding the oxygen exchange history of these lavas. Alternatively, this shift in $\delta^{18}O$ value might have been a consequence of the Kupaianaha and Puu Oo vents having been fed from independent magma reservoirs within the rift zone, as postulated by Kauahikaua *et al.* (1996).

Samples from both vents that were erupted in 1991 were used to test this hypothesis. Sample F91-32 from Puu Oo and sample 12-May-91 from Kupaianaha are nearly identical in major and trace element compositions,

and in their matrix and olivine $\delta^{18}O$ values (Garcia *et al.*, 1996; Table 1). Thus, the two vents were probably connected at shallow depths (Fig. 1), which would explain why the Puu Oo vent produced so much volcanic fume compared with the Kupaianaha vent (Garcia *et al.*, 1996). Therefore, we conclude that the 1986 shift in matrix $\delta^{18}O$ value probably reflects the marked change in residence time of the Puu Oo magma in the rift zone. The longer residence time during the early, episodic eruptions allowed more opportunity for oxygen isotope exchange during the transit of the magma along Kilauea's east rift zone to the shallow Puu Oo reservoir (Fig. 1).

The increase in the matrix $\delta^{18}O$ values during the vent location change in 1986 (Fig. 2) was not accompanied by any other geochemical changes (Fig. 5). Therefore, the contaminant and the early Puu Oo magma were probably of similar chemical composition, except for the former's lower $\delta^{18}O$. If the contaminant was a metamorphosed Kilauea lava with a $\delta^{18}O$ of 3·2‰ (the lowest $\delta^{18}O$ reported for a Kilauea lava; Smith & Thomas, 1990), then ~20% bulk oxygen isotope exchange and/or assimilation is needed to explain the difference in $\delta^{18}O$ values for lavas erupted during episode 47 and early 48 (if the lower value for metamorphosed Canary Islands intrusive rocks is used, the level of contamination is ~6%). We have no independent evidence for the extent of the proposed oxygen exchange. Studies of the hydrothermally altered lavas from Kilauea east rift zone drill holes have found that low K and Rb concentrations are the only distinct major or trace element signatures for these altered lavas (T. Hulsebosch, personal communication, 1996). Partial assimilation of these lavas would mask these features because these elements are concentrated in the melt during partial melting. This contaminant verification problem is compounded by the significant temporal geochemical variation of Kilauea lavas (e.g. Hofmann *et al.*, 1984; Pietruszka & Garcia, 1998), which makes it difficult to link Puu Oo lavas with any specific parent magma that was erupted from the summit reservoir and thus to evaluate the effects of this contamination.

Between 1987 and 1993, there was a gradual decrease of the matrix $\delta^{18}O$ values (5·2 to 5·0‰), which was accompanied by an increase in the olivine $\delta^{18}O$ (~4·4 to 4·8‰), resulting in a decrease in the $\Delta(ol-m)$ from –0·7 to –0·3‰ (Fig. 2). During this period, a major earthquake occurred near the eruption site in 1989, there were 12 eruptive pauses in 1990, and the Kupaianaha vent died in 1992 (Kauahikaua *et al.*, 1996). Although none of these events is individually recorded in the temporal $\delta^{18}O$ variation trend (Fig. 2), they undoubtedly contributed to the observed gradual decrease in magma eruption rate (Kauahikaua *et al.*, 1996), which resulted in a longer transit time for the magma in the rift zone and in more oxygen isotope exchange. This temporal trend in $\delta^{18}O$

reversed itself markedly in 1995, returning to a higher matrix $\delta^{18}O$ value (~5·2‰) and equilibrium values for $\Delta(ol-m)$ (e.g. –0·6 $\pm$ 0·1‰).

IMPLICATIONS FOR RECENT KILAUEA PARENTAL MAGMA $\delta^{18}O$ VALUES

Kyser *et al.* (1982), Garcia *et al.* (1989*b*, 1993) and Harmon & Hoefs (1995) have argued that one of the mantle source components for Hawaiian shield volcanoes has a lower $\delta^{18}O$ than the MORB mantle source. In contrast, Eiler *et al.* (1996*a*) proposed that low $\delta^{18}O$ olivines in Hawaiian lavas (like those from Kilauea) were caused by assimilation of hydrothermally altered Cretaceous oceanic crust. The Puu Oo data clearly indicate that some Hawaiian lavas have been crustally contaminated, perhaps by hydrothermally altered Hawaiian lavas. However, the matrix $\delta^{18}O$ value for the least contaminated Puu Oo lava, which has the highest $\delta^{18}O$ and an equilibrium olivine–matrix value, is only ~5·2‰. Weakly olivine-phyric lavas erupted at the summit of Kilauea since the 1924 explosions also have relatively low $\delta^{18}O$ ratios (5·15 $\pm$ 0·1‰ for six samples; E. Ito, unpublished data, 1997) compared with MORB glass (5·7 $\pm$ 0·2‰; Ito *et al.*, 1987). Thus, for the last 65 years, the least contaminated lavas erupted at Kilauea have matrix $\delta^{18}O$ values of ~5·2‰. These results would seem to indicate that the mantle source for Kilauea lavas has a lower $\delta^{18}O$ than the MORB source.

One complication for this interpretation is the presence of olivines with $\delta^{18}O$ values of 4·7–4·9‰ in some Puu Oo lavas. These results indicate that the parental magmas for these olivines had $\delta^{18}O$ values of 5·5 $\pm$ 0·1‰, if we assume an olivine–melt fractionation value of –0·7‰ (Ito & Stern, 1986). As Kilauea summit lavas apparently had $\delta^{18}O$ of ~5·2‰ for the last 65 years, these results indicate that these Puu Oo olivines and their host lavas may not have come from the summit reservoir. This explanation is consistent with the interpretation of Garcia *et al.* (1996) for the rapid change in trace element ratios for Puu Oo lavas compared with those of Kilauea summit lavas. If at least some Puu Oo parental magmas had $\delta^{18}O$ of 5·5 $\pm$ 0·1‰, then recent Kilauea summit lavas also may be contaminated and the source for all of these lavas may have been similar in $\delta^{18}O$ to MORB. This hypothesis is supported by 15 laser $\delta^{18}O$ analyses of other Kilauea olivines, which range from 4·9 to 5·2‰ (Eiler *et al.*, 1996*a*) and the negative correlation of Puu Oo olivine and matrix $\delta^{18}O$ values (Fig. 3). This remarkable correlation seems to indicate that olivines in some early Puu Oo lavas (after episode 1) were crystallized from unmodified magmas but that these magmas experienced the greatest

modification of $\delta^{18}O$ during their long transit from the summit reservoir to the surface. During the subsequent phase of continuous eruption activity, magmas had shorter transit times and lavas show less evidence of oxygen isotope disequilibrium between olivine and matrix, except between 1990 and 1992 when eruption rates decreased.

CONCLUSIONS

Puu Oo lavas record a significant variation in matrix and olivine $\delta^{18}O$, especially for a single eruption. The matrix of some of these lavas has apparently exchanged oxygen isotopes with and/or assimilated some contaminant after the growth of olivine crystals, judging from oxygen isotope disequilibrium between olivine and matrix material. The contaminant had no apparent effect on the ratios of highly incompatible elements, or Pb, Sr and Nd isotopes in these lavas. Thus, the low $\delta^{18}O$ contaminant is hydrothermally altered Kilauea lavas. The extent of contamination was greatest during the first few years of the eruption when the magma's transit time within Kilauea's east rift zone was greatest, perhaps up to 1 year. This contamination was greatly reduced or stopped during late 1986, when the eruption shifted to continuous effusion. No suitable contaminant has been identified at Kilauea (even from 2 km deep geothermal holes into Kilauea's east rift zone) to explain the $\sim0.7\permil$ variation in matrix $\delta^{18}O$ by reasonable amounts of assimilation (<20 vol. %). However, only 11–12% assimilation would be needed if the contaminant for Puu Oo magmas had a $\delta^{18}O$ value similar to that of metamorphosed intrusive rocks from Canary Island volcanoes ($-1.4\permil$). We conclude that Puu Oo magmas exchanged oxygen with and partially assimilated metamorphosed Kilauea rocks (Fig. 1) during periods of slow magma movement within the rift zone.

The matrix $\delta^{18}O$ of the least contaminated Puu Oo lavas is identical to that of lavas erupted at the summit of Kilauea for the last 65 years but is well below the assumed mantle value (5.1–5.2 vs 5.5–6.0‰; Taylor & Sheppard, 1986). Olivines from some Puu Oo lavas preserve the record of a parental magma with MORB-like $\delta^{18}O$ ($\sim5.6\permil$), if we assume a $\Delta(ol–m)$ of $-0.7\permil$. Thus, the results for Puu Oo lavas do not provide a clear indication of whether the mantle source for Kilauea tholeiites has a range of $\delta^{18}O$ values that overlap with those for the mantle source for MORB or whether Puu Oo lavas have MORB source-like $\delta^{18}O$ values and have sustained two periods of contamination (beneath the summit of the volcano and within its east rift zone). This issue is being evaluated by determining oxygen isotopes of olivines in historical Kilauea summit lavas and in possible contaminants.

The apparent absence of other independent geochemical or isotopic evidence for crustal contamination in the early Puu Oo lavas should be noted by those who study oceanic basalts. Our results indicate that oxygen isotope analyses, especially for mineral–matrix pairs, are essential to evaluate the possible role of crustal contamination in otherwise pristine lavas even when they are erupted through thin crustal sections. Another important component of this study was the availability of samples collected throughout the eruption; without it, interpretation of the results would have been problematic.

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