Melt depletion and subsequent metasomatism in the shallow mantle beneath Koolau volcano, Oahu (Hawaii)

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[1] Xenoliths from Pali (Oahu, Hawaii) include samples of the mantle lithosphere underlying Koolau shield volcano. Most such xenoliths are spinel peridotites, the remainder being plagioclase-spinel peridotites, and garnet-free pyroxenites. Clinopyroxene separates from Pali peridotite xenoliths have relatively depleted $^{87}Sr/^{86}Sr$ (0.70309–0.70346) and $^{143}Nd/^{144}Nd$ (0.512967–0.513206). The mantle lithosphere beneath the Koolau volcano has a range of present-day ε_{Nd} = 6.9–11. On a $^{143}Nd/^{144}Nd$ versus $^{147}Sm/^{144}Nd$ diagram, they define a 61 ± 20 Ma errorchron, within error of the estimated age of ~80–85 Ma of the Pacific lithosphere at Oahu, and an intercept of ε_{Nd} = 6.8. We interpret the Pali spinel peridotites as samples of the Pacific lithosphere residual to melt extraction of the Pacific crust. These rocks were not metasomatized by melts having isotopic composition similar to the shield-building Koolau volcano, but they could have been metasomatized by melts related to the Honolulu Volcanic Series. Plagioclase mineral separates from two peridotites are in $^{87}Sr/^{86}Sr$ isotopic disequilibrium with coexisting clinopyroxenes. The plagioclases are light rare earth element depleted and have "enriched" $^{87}Sr/^{86}Sr$ ratios (0.70436 and 0.70443). The $\delta^{18}O$ of olivine (5.09–5.12‰) and clinopyroxene (5.32–5.33‰) from spinel peridotites are typical for oceanic upper mantle rocks. In contrast, $\delta^{18}O$ of olivine, pyroxene, and plagioclase in plagioclase-bearing peridotites are enriched by ~0.5‰ relative to the spinel peridotites (e.g., $\delta^{18}O$ ratios of olivines from plagioclase peridotites are 5.4–5.5‰). It is here interpreted that the plagioclases represent phases that formed by reaction with or precipitation from a melt that intruded the Pacific lithospheric mantle. The Pacific lithospheric isotopic composition is reflected in the clinopyroxene separates. The high $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ of the plagioclase resemble Koolau lavas and suggest that the melt passing through the lithosphere was plume-related. The elevated $\delta^{18}O$ of the plagioclase indicates that the melt from which it fractionated had a component of recycled crustal material not acquired from local crustal contamination. It is also estimated here that the duration of the porous melt flow of the Koolau-like melt though the mantle lithosphere was short-lived, ~10^2–10^4 years.

1. Introduction

[2] The Hawaiian Islands sit atop a broad bathymetric swell correlated with free-air gravity anomalies and a residual geoid high [*Watts et al.*, 1985]. These features arise from a plume of hot material ascending through the asthenosphere, which is presumed to be the source of the large volumes of basaltic magmas associated with the Hawaiian chain. The chemical and isotopic characteristics of Hawaiian lavas appear to require variable source contributions from the plume, the local mantle asthenosphere, and Pacific lithosphere [e.g., *Frey and Roden*, 1987; *Hauri*, 1996; *Lassiter and Hauri*, 1998]. Sorting out the isotopic compositions of end-members involved in plume magmatism has the ultimate goal of deciphering the composition of the Earth's deep mantle (e.g., tracing the postulated existence of ancient subducted slabs) and the mechanisms of interaction between the deep and shallow mantle at hot spot locations [e.g., *Hauri*, 1996; *Dixon and Clague*, 2001]. Unfortunately, despite the availability of a large isotopic data set for Hawaii, the compositions, origin, and relative proportions of some of the "components" mixed in the surface Hawaiian lavas have yet to be resolved. These debates in part arise from the fact that surface lavas are pooled and mixed melts [*Zindler and Hart*, 1986] and/or result from progressive melting of a heterogeneous source mixture [*Phipps Morgan*, 1999], which make identification of individual end-members difficult. The tholeiitic lavas of the Koolau caldera (Oahu) have the highest $^{87}Sr/^{86}Sr$ and lowest $^{143}Nd/^{144}Nd$ and $^{206}Pb/^{204}Pb$ of any Hawaiian lavas. The origin of these extreme isotopic signatures in the source of the Koolau lavas (and the Lanai and Kahoolawe shields that show similar isotopic characteristics) is of great importance to understanding Hawaiian magmatism because Koolau lavas define an extreme end-member to mixing trajectories with other Hawaiian shield volcanoes [e.g., *White and Hofmann*, 1982; *Chen and Frey*, 1983; *Zindler and Hart*, 1986; *West et al.*, 1987]. The source of the extreme isotopic compositions in Koolau lavas was originally thought to be a primitive mantle component [e.g., *DePaolo and Wasserburg*, 1976], on the basis of the near bulk-earth Sr, and Nd isotopic compositions. It has since been pointed out that Koolau lavas likely come from sources containing crustal oxygen [*Eiler et al.*, 1996]. Hafnium [*Blichert-Toft et al.*, 1999] and osmium [*Lassiter and Hauri*, 1998] isotopic compositions also indicate the presence of a recycled component. The lithologic composition of the Koolau end-member source is also debated; it has been suggested that the "enriched" isotopic signatures are related to recycled oceanic crust and are eclogitic or pyroxenitic domains [*Hauri*, 1996; *Lassiter and Hauri*, 1998; *Lassiter et al.*, 2000]. In contrast, some suggested that the recycled component appears not to be associated with a significant change in the lithologic composition of the source of the Hawaiian basalts but is well mixed within the peridotitic lithology [*Stracke et al.*, 1999].

[3] An alternative to deciphering the nature of the source end-members in basalts or melt inclusions is to study mantle xenoliths. Here we present results of a study of the isotopic compositions of mantle xenoliths sampled in volcanic rocks from Pali, a Honolulu Volcanic Series vent located in the Koo-

lau caldera area. The results are used to put constraints on (1) the isotopic composition of the upper mantle in the Oahu region, (2) the origin of the recycled component at Koolau in the source of Koolau lavas, and (3) timescales of plume-lithosphere interaction in the sub-Oahu shallow mantle.

2. Previous Xenolith Work and Sample Description

[4] Several localities of mafic and ultramafic xenoliths are known on the Hawaiian Islands, many of them on the island of Oahu, Hawaii [*White*, 1966; *Jackson and Wright*, 1970; *Sen*, 1987]. The island of Oahu consists of two major shield volcanoes, the older (age, 2.9–3.9 Ma) Waiane and the younger (age, 1.8–2.7 Ma) Koolau [*Doell and Dalrymple*, 1973]. The shield volcanic activity was followed by volumetrically minor alkalic volcanism, in a stage known as posterosional or rejuvenated [*Clague and Frey*, 1982; *Clague and Dalrymple*, 1988]. Almost all Oahu xenoliths occur in the posterosional Honolulu volcanics (age, < 1 Ma [*Jackson and Wright*, 1970]) that erupted in the Koolau shield. A geographic distribution pattern of xenolith suites was observed [*Sen and Presnall*, 1986]: Dunites are abundant in lavas from posterosional vents within the Koolau caldera, and lherzolites are typically found along the caldera edge, whereas garnet pyroxenite and garnet peridotite xenoliths [*Jackson and Wright*, 1970] occur only in the apron of the exposed part of the shield volcano. These differences may be related to the depth at which the ascending Honolulu Volcanic Series magmas [*Sen*, 1987] sampled the underlying crust and mantle. All localities summarized in the review paper of *Sen* [1987] also contain xenoliths of gabbro, clinopyroxenite, and wehrlite, presumed to be fragments of the underlying Cretaceous Pacific crust and mantle, and/or cumulates from Hawaiian magmas in crustal magma chambers. Isotopic ratios of Sr, Nd, and Pb were previously measured only on xenoliths from the Salt Lake Crater locality [*Vance et al.*, 1989; *Okano and Tatsumoto*, 1996]. Most Sr and Nd isotopic data for Salt Lake xenoliths plot outside the field of Pacific mid-ocean ridge basalt (MORB) but overlap the field of alkaline Honolulu volcanics. The iso-

topic compositions of the xenoliths are distinct from those of the Koolau caldera tholeiitic lavas. There are two exceptions: Two spinel peridotite xenoliths were reported to have Koolau-like Sr, Nd, and Pb isotopic ratios, suggesting that future, more detailed studies of such xenoliths might reveal a more complicated isotopic pattern for the sub-Oahu mantle [*Vance et al.*, 1989; *Okano and Tatsumoto*, 1996].

[5] In this study we focus on xenoliths from the Pali vent (Figure 1), which is located on the rim of the Koolau caldera [*Sen*, 1988]. Pali peridotite xenoliths include abundant spinel peridotites and less common plagioclase and spinel-bearing peridotites. Spinel peridotites, the most common petrographic type of xenoliths found at Pali, are composed of olivine (Fo_{86-92}) orthopyroxene, chrome-diopside, and spinel. Grain size of all phases varies considerably from small (0.05 mm diameter) to coarse (2–3 mm diameter). The textures are most commonly allotriomorphic granular (Figure 2a). Plagioclase lherzolites are rare in Oahu and were found mainly at the Pali locale. These rocks exhibit strong foliation in hand specimen and a porphyroclastic texture under the microscope (Figure 2b). Orthopyroxene and olivine occur as large (up to 1 mm diameter) porphyroclasts. Small olivine and clinopyroxene crystals (0.2 mm diameter) also occur as neoblasts. Plagioclase crystals are of equant habit. The modal abundance of plagioclase in the studied xenoliths (∼5–7%) is higher than typically found in abyssal peridotites. The ratio of modal plagioclase to clinopyroxene is ∼2, indicating that if this is a residual lithospheric assemblage, then the plagioclase formed after partial melting at the Pacific mid-ocean ridge [e.g., *Baker and Beckett*, 1999]. Spinel of variable compositions occur as small grains disseminated through the groundmass. On the basis of mineral compositions, the plagioclase lherzolites are similar to the spinel lherzolites [*Yang et al.*, 1998]. Equilibration pressures of ∼7 kbar were determined on plagioclase-bearing peridotites [*Sen*, 1988; *Yang et al.*, 1998]. The temperatures of equilibration of all peridotites range between 1000°C and 1150°C [*Sen*, 1988].

[6] Two prior ion microprobe studies of clinopyroxenes in peridotite xenoliths from Pali [*Sen et al.*, 1993; *Yang et al.*, 1998] showed systematic deple-
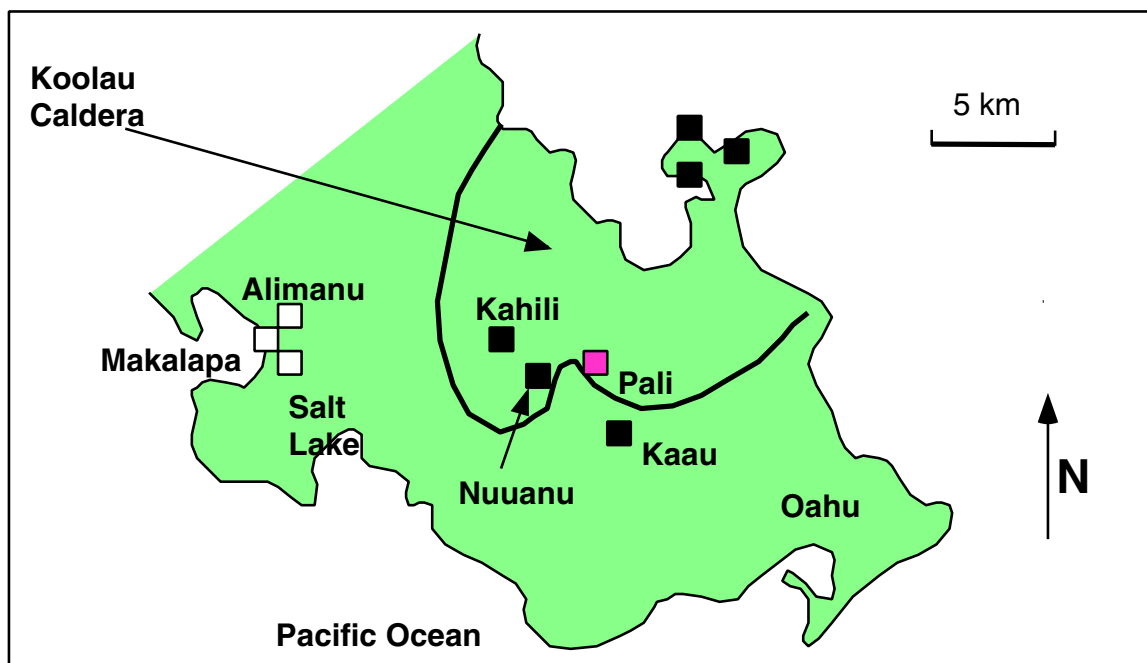
Figure 1. Map showing the location of principal xenolith-bearing vents of the Honolulu Volcanic Series on the southeastern side of Oahu, Hawaii [from *Sen*, 1987]. All vents contain peridotitic assemblages (mantle assemblages as well as magma chamber or crustal cumulates). The open squares also contain garnet pyroxenite xenoliths, whereas the

tions in light rare earth elements (LREEs) in some of the spinel peridotites, indicating that they may be fragments of the MORB-depleted lithospheric mantle. Shallower, plagioclase-bearing peridotites were found to be more LREE-depleted than spinel peridotites, in agreement with MORB melting models calling upon higher degrees of partial melting at shallow levels beneath mid-ocean ridges [e.g., *Klein and Langmuir*, 1987; *Yang et al.*, 1998]. Most pyroxenes studied by *Sen et al.* [1993] and *Yang et al.* [1998] showed evidence of cryptic metasomatism, which resulted in LREE enrichment of the clinopyroxene rims and an overall "U-shape" of the rim REE patterns. This cryptic event was proposed by these authors to relate to the pervasive porous melt transport of plume magmas through the shallow lithosphere, possibly the alkalic melts of the Honolulu Volcanic Series [e.g., *Sen et al.*, 1993; *Salters and Zindler*, 1995].

3. Analytical Techniques

[7] We measured the isotopic ratios of ^{87}Sr/^{86}Sr, ^{143}Nd/^{144}Nd, and the concentrations of Rb, Sr, Sm,

and Nd in seven peridotite samples (five spinel peridotites and two plagioclase-spinel peridotites) and two pyroxenite samples from Pali (Table 1). Rock samples were crushed to about one third of their grain size. Clinopyroxene and (when present) plagioclase were separated by picking under a binocular microscope. The mineral separates were mildly acid-leached in warm 1 *M* HCl for 30 min. Between 100 and 400 mg of sample powders were weighed, put in Teflon beakers, and dissolved in mixtures of hot concentrated HF-HNO$_3$ or, alternatively, mixtures of cold concentrated HF-HClO$_4$. The dissolved samples were spiked with Rb, Sr, and mixed Sm-Nd spikes after dissolution. Rb, Sr, and the bulk of the REEs were separated in cation columns containing AG50W-X4 resin, using 1 *N* to 2.5 *N* HCl. Separation of Sm and Nd was achieved in anion column containing LN Spec resin, using 0.1 *N* to 2.5 *N* HCl. Rb was loaded onto single Re filaments using silica gel and H$_3$PO$_4$. Sr was loaded onto single Ta filaments. Sm and Nd were loaded onto triple Re filaments.

[8] Mass spectrometric analyses (except oxygen isotopic ratios) were carried out on two VG Sector
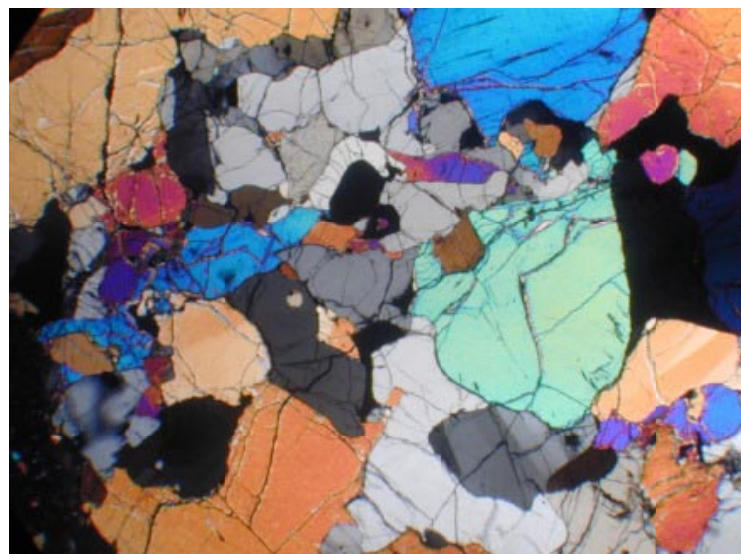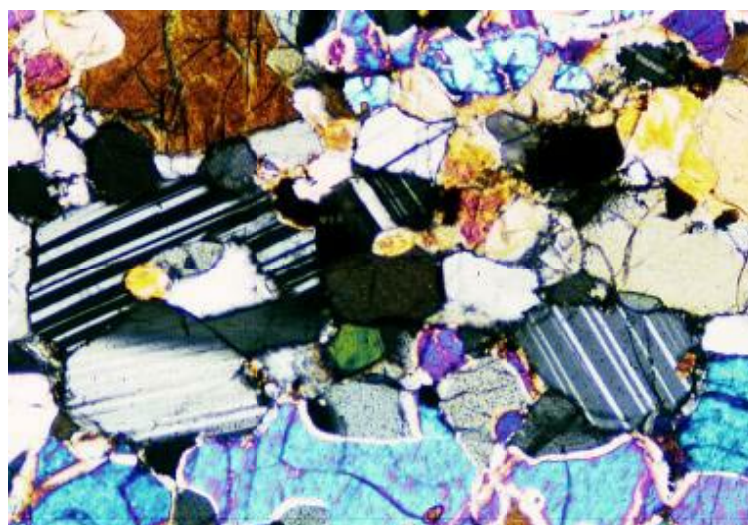
Figure 2. (a) Photomicrograph of spinel peridotite 99PA3 (polarized light). The xenolith is granoblastic and coarse. (b) Photomicrograph of plagioclase-bearing peridotite 99PA200 (polarized light). The rock is fine grained, allotriomorphic, and sheared. Note the presence of twinned plagioclase crystals forming a band parallel to the rock

multicollector instruments (Sr on a VG54 and Rb, Sm, and Nd on a VG354) fitted with adjustable 10^{11} Ω Faraday collectors and Daly photomultipliers [*Patchett and Ruiz*, 1987]. Concentrations of Rb, Sr, Sm, and Nd were determined by isotope dilution, with isotopic compositions of Sr and Nd determined on the same spiked runs. An off-line manipulation program was used for isotope dilution calculations. Typical runs consisted of 100 isotopic ratios. The mean result of four analyses of the standard NRbAAA performed during the course of this study is $^{85}Rb/^{87}Rb = 2.61199 \pm 20$. Ten analyses of standard Sr987 yielded mean ratios of: $^{87}Sr/^{86}Sr = 0.710285 \pm 7$ and $^{84}Sr/^{86}Sr = 0.056316$

Table 1. Trace Element and Sr and Nd Isotopic Composition of Pali Xenoliths[a]

Sample	Rock	Mineral	Sm	Nd	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	ε_{Nd}	Rb	Sr	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$
99PA202	Pxt	Cpx	0.40	1.50	0.164	0.512989	7.08	0.026	137.55	0.00054	0.703374
99PA19	Pxt	Cpx	0.20	0.72	0.173	0.512921	5.75	0.032	126.15	0.00073	0.703450
99PA27	SpP	Cpx	1.79	5.02	0.216	0.512967	6.18	0.009	14.35	0.00181	0.703296
99PA25	SpP	Cpx	1.38	1.06	0.786	0.513184	10.65	0.022	18.64	0.00341	0.703457
99PA3	SpP	Cpx	1.68	2.12	0.481	0.513111	8.97	0.009	24.16	0.00118	0.703091
99PA38	SpP	Cpx	1.23	1.75	0.425	0.513089	8.58	0.015	19.18	0.00226	0.703365
99PA201	SpP	Cpx	0.55	0.78	0.426	0.513091	8.60	0.012	15.34	0.00226	0.703275
99PA200	PlgP	Cpx	0.52	0.42	0.749	0.513201	10.75	0.009	0.42	0.06300	0.703152
99PA200	PlgP	Plg	0.01	0.03	0.202	–	–	0.009	11.23	0.00231	0.704435
99PA107	PlgP	Cpx	0.59	0.52	0.691	0.513206	10.96	0.008	0.52	0.04696	0.703094
99PA107	PlgP	Plg	0.02	0.03	0.403	–	–	0.011	8.88	0.00357	0.704357

[a] Rock abbreviations are as follows: PlgP, plagioclase-bearing peridotites; Pxt, pyroxenites; SpP, spinel-bearing peridotite. Mineral abbreviations are as follows: Plg, plagioclase separates; Cpx, clinopyroxene separates. The isotopic analyses are present-day ratios. The ε_{Nd} is calculated at present-day (zero age). The Sr isotopic ratios of standards and samples were normalized to $^{86}Sr/^{88}Sr = 0.1194$, whereas the Nd isotopic ratios were normalized to $^{146}Nd/^{144}Nd = 0.7219$. Sr and Nd standards are identical to values previously measured on the same batches of standards. The estimated analytical $\pm 2\sigma$ uncertainties for samples analyzed in this study are $^{87}Sr/^{86}Sr = 0.002\%$ and $^{143}Nd/^{144}Nd = 0.002-0.003\%$.

± 12. The mean results of five analyses of the standard nSmβ performed during the course of this study are $^{148}Sm/^{147}Sm = 0.74880 \pm 21$, and $^{148}Sm/^{152}Sm = 0.42110 \pm 6$. Fifteen measurements of the La Jolla Nd standard were performed during the course of this study, yielding the following isotopic ratios: $^{142}Nd/^{144}Nd = 1.14184 \pm 2$, $^{143}Nd/^{144}Nd = 0.511853 \pm 2$, $^{145}Nd/^{144}Nd = 0.348390 \pm 2$, and $^{150}Nd/^{144}Nd = 0.23638 \pm 2$. The Sr isotopic ratios of standards and samples were normalized to $^{86}Sr/^{88}Sr = 0.1194$, whereas the Nd isotopic ratios were normalized to $^{146}Nd/^{144}Nd = 0.7219$. The estimated analytical $\pm 2\sigma$ uncertainties for samples analyzed in this study are $^{87}Rb/^{86}Sr = 0.55\%$, $^{87}Sr/^{86}Sr = 0.0014\%$, $^{147}Sm/^{144}Nd = 0.8\%$, and $^{143}Nd/^{144}Nd = 0.002\%$.

[9] We report no $^{143}Nd/^{144}Nd$ measurements of the plagioclase separates from 99PA107 and 99PA200. Concentrations of Sm and Nd in plagioclases (measured by isotope dilution using a Daly photomultiplier) combined with the low modal abundance of plagioclase and small sample size yielded too little Nd after column chemistry ($\sim 0.5 - 1$ ng) for a reliable measurement of $^{143}Nd/^{144}Nd$.

[10] We measured the $\delta^{18}O$ of select olivine, pyroxene, and plagioclase mineral separates (Table 2). Mineral separates of olivine, pyroxene and/or plagioclase were prepared by hand picking from coarsely crushed rock chips. Separated grains were typically 200–500 μm in size. Minerals containing visible inclusions of glass or other minerals are common in the studied samples and were avoided when recognized. Mineral separates were cleaned of adhered dust by abrasion with filtered, compressed air and analyzed by laser fluorination at the California Institute of Technology using a 50 W CO_2 laser, BrF_5 reagent, and an apparatus for gas purification and conversion of O_2 to CO_2 based on designs by *Sharp* [1990] and *Valley et al.* [1995]. Oxygen yields were 96 ± 3%, based on the typical major element abundances of minerals of these rocks. Measurements of $\delta^{18}O$ were made on separate days. The mean $\delta^{18}O$ values for standards were nearly identical on most analysis days (5.18 ± 0.03, for daily averages for SCO-1) and within 0.1 of their nominal values based on previous analyses [*Eiler et al.*, 1995].

4. Results

[11] Clinopyroxene separates from all sampled analyzed in this study have $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratios similar to those previously measured for other xenoliths from Salt Lake Crater [*Vance et al.*, 1989; *Okano and Tatsumoto*, 1996], and the Honolulu Series volcanic rocks [*Roden et al.*, 1984; *Stille et al.*, 1983]. The $^{143}Nd/^{144}Nd$ ratios of clinopyroxenes are within the range of values typical of Pacific MORB mantle, whereas the $^{87}Sr/^{86}Sr$ ratios of clinopyroxenes are higher than typical MORB values (Figure 3). Sm/Nd ratios of clinopyroxenes range from 0.7 to 1.3 in peridotites and 0.27 to 0.3 in pyroxenites. These values are similar to ion microprobe determined Sm/Nd ratios of 0.5–1.4 on clinopyroxenes from Pali and Kaau peridotites [*Yang et al.*, 1998]. In contrast, isotope dilution analyses of clinopyroxenes from spinel peridotites from Salt Lake Crater yielded Sm/Nd of 0.17–0.37 [*Vance et al.*, 1989; *Okano and Tatsumoto*, 1996], significantly lower than those measured at Pali and Kaau and seemingly inconsistent with a simple residual MORB origin. We conclude that if Salt Lake Crater peridotite xenoliths are samples of the Pacific lithosphere, they were likely metasomatized subsequent to the formation of the lithosphere [*Sen et al.*, 1993].

Table 2. Oxygen Isotopic Compositions of Hawaiian Xenoliths[a]

Sample	Mineral	$\delta^{18}O$
Spinel Peridotites		
PA3	Ol	5.09
PA3	Cpx	5.32
PA38	Ol	5.12
PA38	Cpx	5.33
Plagioclase-Spinel Peridotites		
PA107	Ol	5.54
PA107	Cpx	5.81
PA107	Plg	6.21
PA200	Ol	5.48
PA200	Cpx	5.75
PA200	Plg	6.35

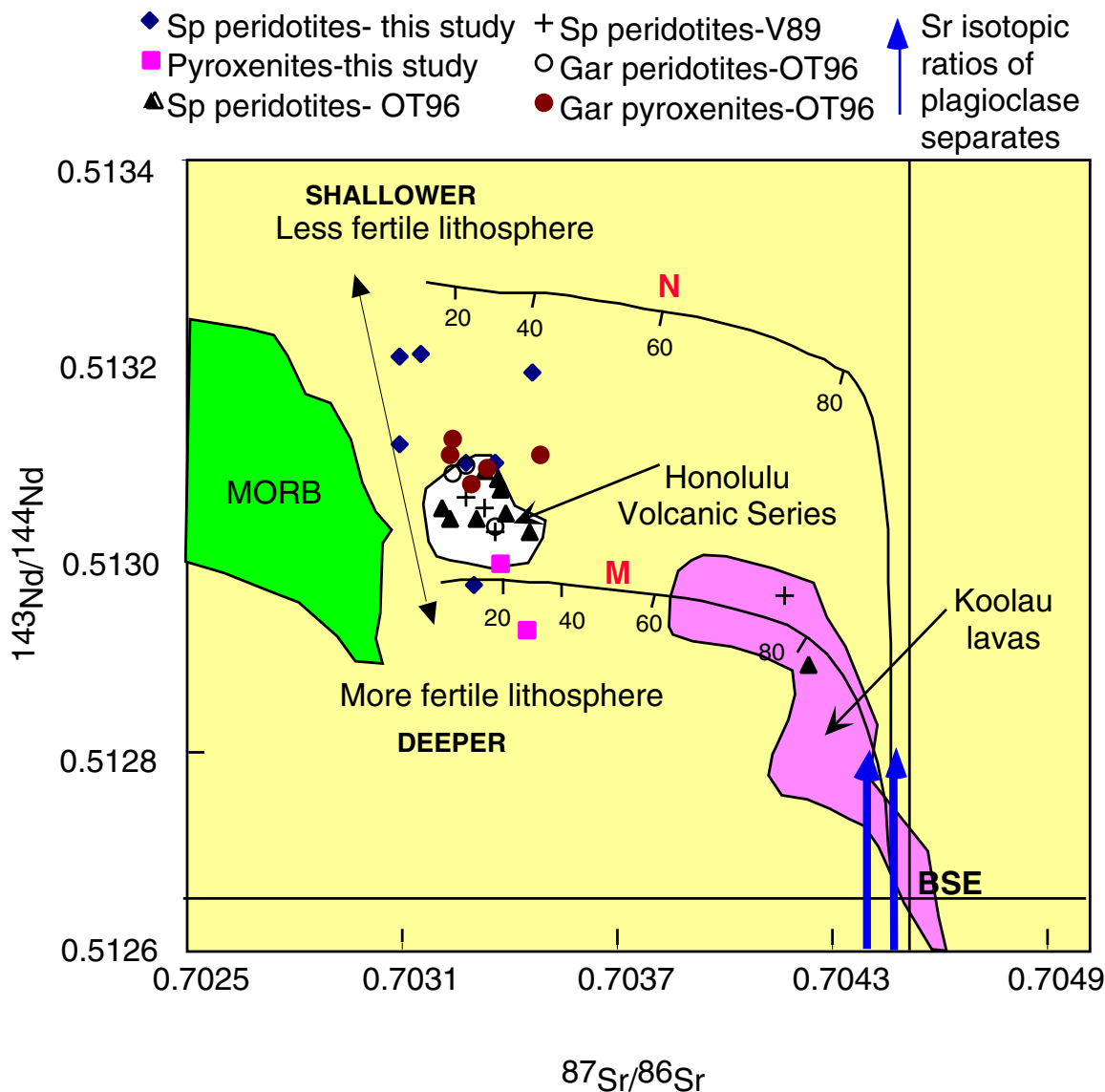[a] Abbreviations are as follows: Plg, plagioclase; Cpx, clinopyroxene, Ol, olivine.

Figure 3. Summary of Sr-Nd isotopic data on Oahu xenoliths. OT96, *Okano and Tatsumoto* [1996]; V89, *Vance et al.* [1989]. The fields of Pacific MORB, Honolulu Volcanic Series lavas, and Koolau lavas (a compilation of sources all cited by *Phipps Morgan* [1999] and *Roden et al.* [1994] are also shown. The thick blue arrows indicate the Sr isotopic composition of the two analyzed plagioclase-bearing peridotites. BSE, bulk silicate Earth. "M" and "N" (see text) are binary mixing hyperbolae between fertile and respectively depleted MORB peridotite and a component with BSE $^{143}Nd/^{144}Nd$ ratios ($^{143}Nd/^{144}Nd = 0.512638$) and $^{87}Sr/^{86}Sr$ and Sr/Nd of the plagioclase from peridotite

[12] On a $^{143}Nd/^{144}Nd$ versus $^{147}Sm/^{144}Nd$ diagram (Figure 4), the Pali peridotite clinopyroxenes define a positive correlation. A regression line though these data has a slope corresponding to an age of 62 ± 20 Ma and an intercept value of $^{143}Nd/^{144}Nd = 0.51292$ ($\varepsilon_{Nd} = 6.8$). Clinopyroxenes from the two pyroxenites have lower Sm/Nd (0.27–0.29) and $^{143}Nd/^{144}Nd$ (0.51292–0.51299),

and about 10 times higher Sr concentrations (126–137 ppm) than clinopyroxenes from peridotites. There are no correlations between the REE patterns in Pali peridotite clinopyroxenes (e.g., Sm/Nd or $^{147}Sm/^{144}Nd$ ratios) and the magnitude of their $^{87}Sr/^{86}Sr$ enrichment relative to typical MORBs (Figure 5). Plagioclase separates from our samples have significantly higher $^{87}Sr/^{86}Sr$ (0.70435–
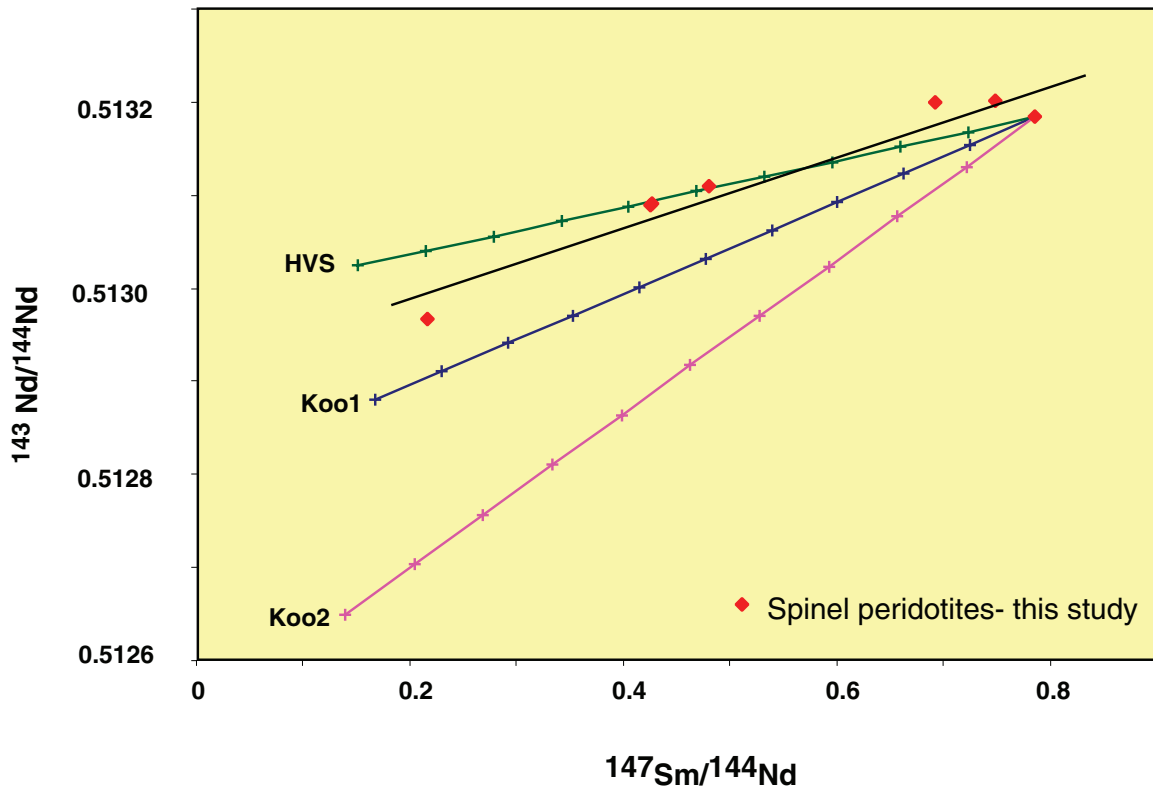
Figure 4. $^{143}Nd/^{144}Nd$ versus $^{147}Sm/^{144}Nd$ diagram for clinopyroxene separates from Pali spinel peridotites. Note the large range of $^{147}Sm/^{144}Nd$ and thus the depleted character of these rocks. If the fit is taken to have age significance, it suggests a depletion age of 62 ± 21 Ma, a mean square weighted deviate of 8.1, and an intercept of $\varepsilon_{Nd} = 6.8$. Alternatively, the correlation can be the result of multicomponent mixing. Mixing of depleted MORB (with the composition of the highest $^{147}Sm/^{144}Nd$ xenolith) with plume-related melts would, however, depart from the measured linear path, because the surface Koolau lavas in the region range in isotopic composition between end-member Koo1 and Koo2, shown in the image. In contrast, mixing with Honolulu Volcanic Series lavas (with an average shown as HVS in the image) is permissible. Tick marks represent 10% mixing increments on the binary mixing lines shown.

0.70443) than coexisting clinopyroxenes; that is, the samples are not in internal isotopic equilibrium. Plagioclase separates are also notably poor in Sr (9–11 ppm), Nd (0.03 ppm) and Sm (0.01–0.02 ppm). The concentrations of Sm and Nd also suggest that the plagioclase separates are LREE depleted.

[13] Oxygen isotopic ratios of minerals from two spinel lherzolites (Figure 6) are typical for upper mantle values (olivine $\delta^{18}O = 5.1‰$, clinopyroxene $\delta^{18}O = 5.3‰$). In contrast, the two plagioclase peridotites are enriched in ^{18}O relative to normal Hawaiian mantle values [*Eiler et al.*, 1996] by ~0.5‰ (olivine $\delta^{18}O = 5.5‰$, clinopyroxene $\delta^{18}O = 5.8‰$, plagioclase $\delta^{18}O = 6.3‰$). The data provide evidence that ^{18}O enrichments characteristic of Koolau shield lavas [*Eiler et al.*,

1996] (Figure 6) also occur in the mantle beneath Oahu. Such anomalous $\delta^{18}O$ values are very unusual in mantle rocks; we are aware of only two examples of similar ^{18}O enrichments in peridotites from the oceanic lithosphere [*Eiler et al.*, 1998].

[14] The temperature of equilibration among coexisting phases can be estimated based on the $\delta^{18}O$ of the plagioclase, olivine, and pyroxene (Figure 7). On the basis of experimental data of *Chiba et al.* [1989], our measurements are consistent with oxygen isotopic equilibrium among olivine, clinopyroxene, and plagioclase, at temperatures between 1100° and 1200°C, consistent with previous estimates based on cation thermometry [*Sen*, 1988]. It is noteworthy that in this respect, oxygen isotope
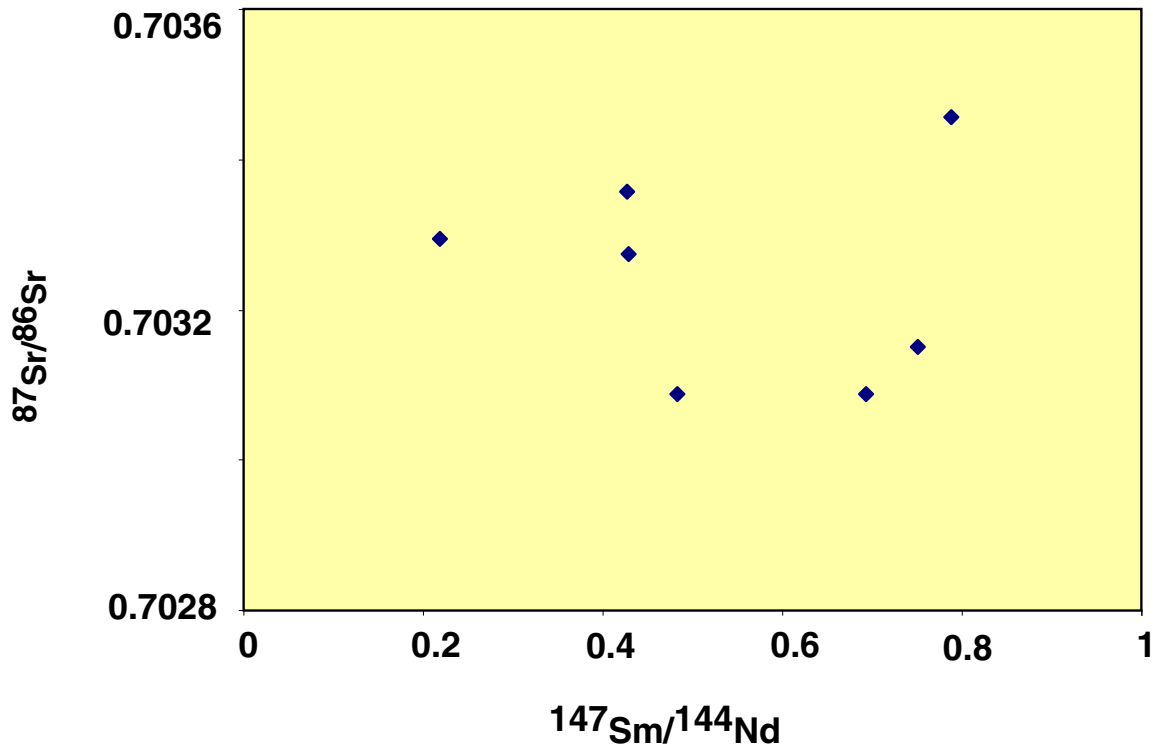
Figure 5. ^{87}Sr/^{86}Sr versus ^{147}Sm/^{144}Nd in peridotites shown in Figure 4. There is no apparent correlation between

systematics of these rocks contrasts with the dis-equilibrium recorded by Sr isotope systematics.

5. Discussion

[15] The data presented in section 4 constrain the nature of the oceanic lithosphere beneath Hawaii, the origin of the exotic isotopic compositions of the Koolau shield lavas, and the timescales of plume-lithosphere interaction in the shallow mantle beneath Oahu. These implications are discussed in the following sections.

5.1. Pacific MORB Mantle Origin of the Xenoliths

[16] The high Sm/Nd and ^{143}Nd/^{144}Nd ratios of Pali spinel peridotites are consistent with the peridotites being fragments of the oceanic lithosphere under-lying Hawaii, as first suggested on the basis of the ion probe study of *Yang et al.* [1998]. This inter-pretation is further supported by the positive corre-

lation between ^{143}Nd/^{144}Nd and ^{147}Sm/^{144}Nd, suggesting a young age of depletion. The errorchron fitting our peridotite data corresponds to an age of 62 ± 20 Ma. The age of the local MORB lithosphere at Oahu is not precisely constrained. However, the lithosphere age is well established to be ~110 Ma at Ocean Drilling Program site 843, ~200 km south-west of Oahu [*Waggoner*, 1993] and south of the left lateral Molokai fracture zone. Oahu is located on the northern side of the Molokai transform fault. On the basis of the location of site 843 and the shift in magnetic anomalies across the Molokai fault [*Atwater and Severinghaus*, 1989], the age of the Oahu lithosphere should be ~80–85 Ma.

[17] The scatter in the Nd isotopic data (Figure 4) and the error in estimating a true depletion age might be due to Nd-isotope heterogeneities at the time of Cretaceous MORB-related melting (i.e., not all samples had the same initial ^{143}Nd/^{144}Nd). If only the peridotites are considered, the intercept on the isochron is ^{143}Nd/^{144}Nd = 0.51292 (ε_{Nd} = 6.8), within but at the low end of the range of Nd isotopic
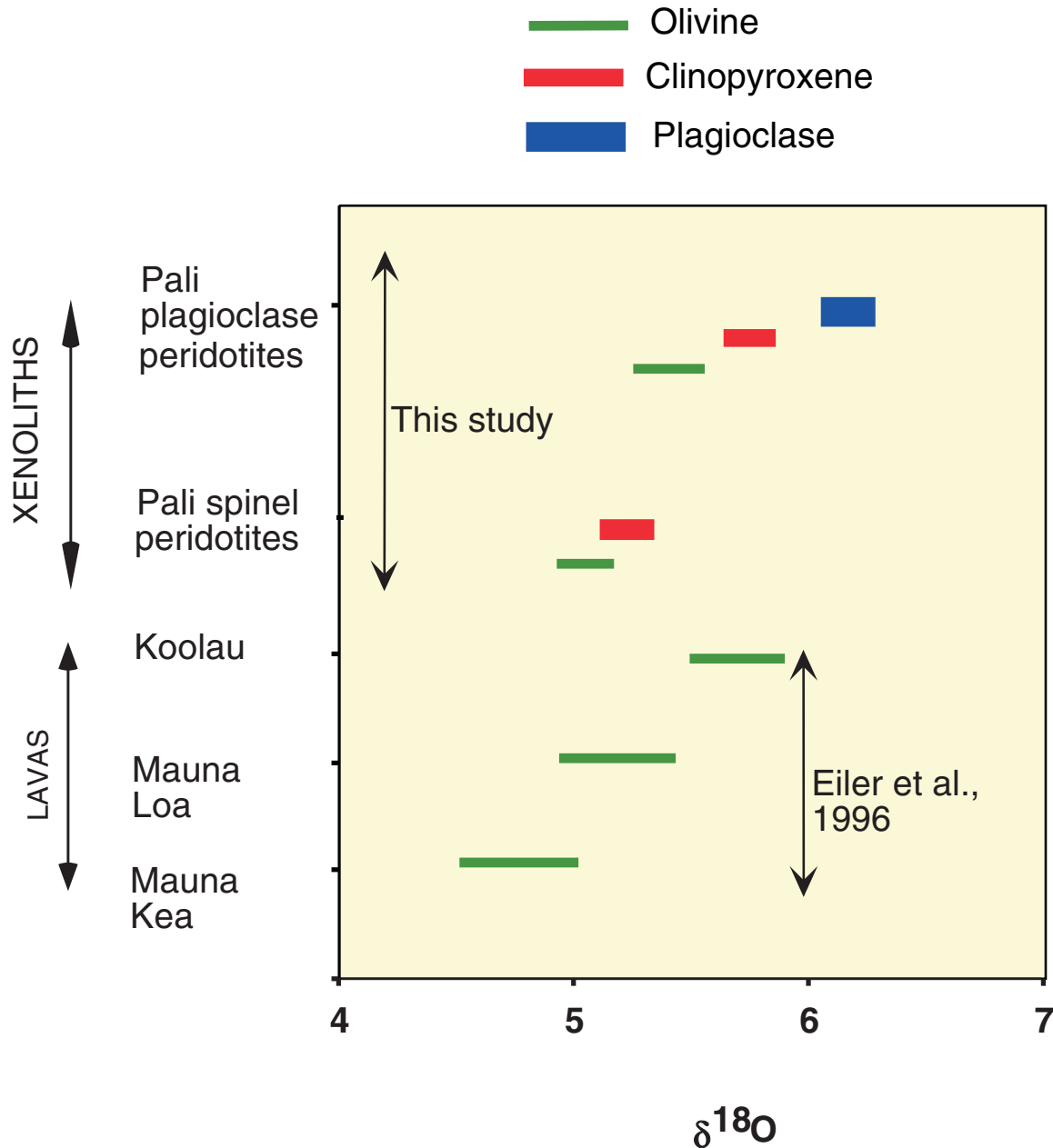
Figure 6. Mineral oxygen isotopic compositions of Hawaiian lavas and xenoliths.

ratios exhibited by Pacific MORB (Figure 4). The spinel pyroxenites from Pali analyzed in this study have present-day ε_{Nd} values of 5.5–6.8, only slightly off the errorchron defined by spinel peridotites. The pyroxenites have trace element characteristics of magmas intruded into the Pacific lithospheric mantle column [*Frey*, 1980]. The data are thus consistent with the pyroxenites being cumulates or veins precipitated from MORB melts

beneath the Cretaceous spreading center, although a younger age for pyroxenites cannot be ruled out. Clinopyroxenes in Salt Lake Crater peridotites [*Okano and Tatsumoto*, 1996] are less depleted (Sm/Nd < 0.4) relative to Pali spinel peridotites. This difference could be either because the Salt Lake xenoliths are overall sampled from deeper in the lithosphere where there has been less MORB melting, or because metasomatizing melts subse-
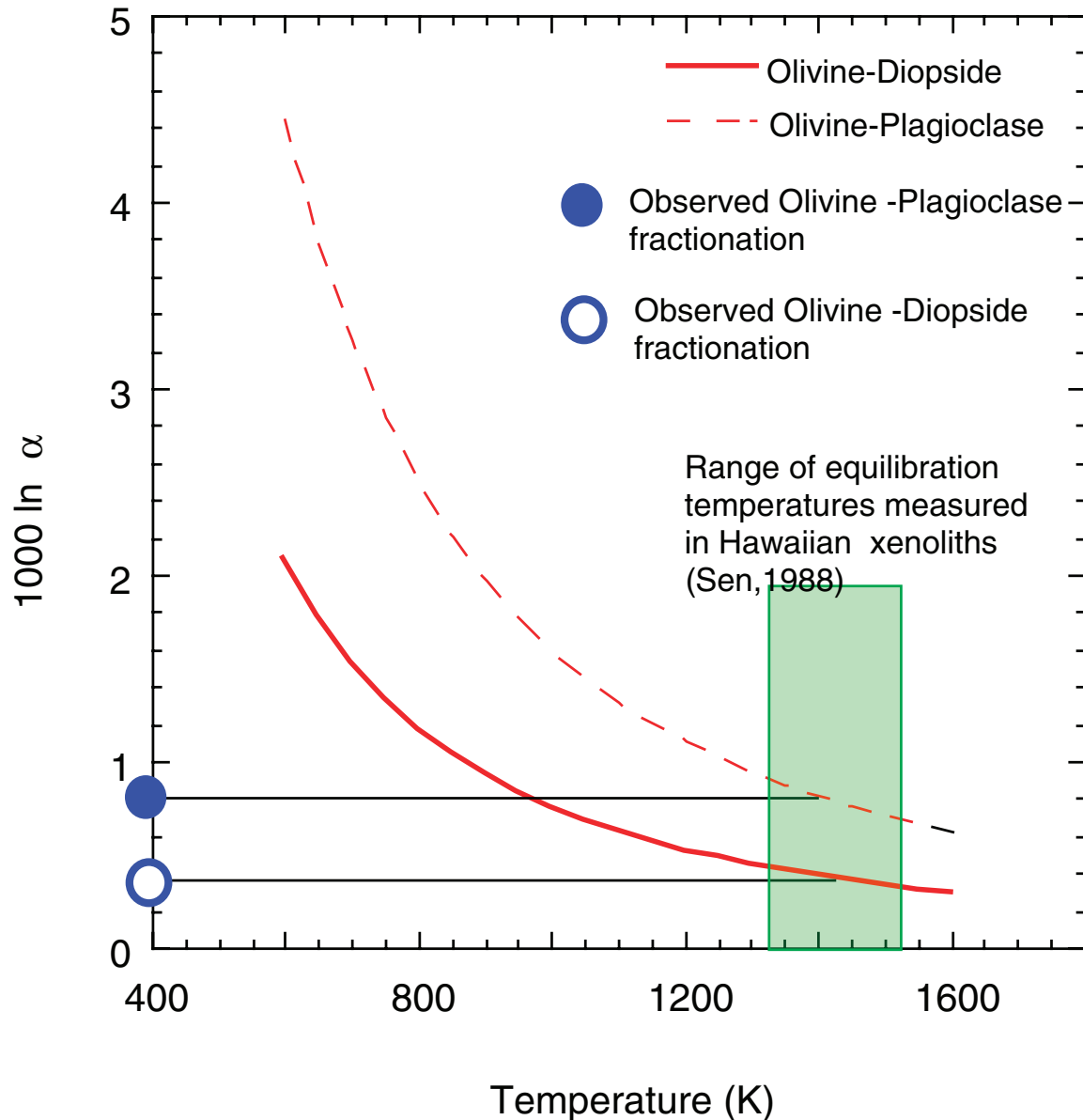
Figure 7. Predicted oxygen isotopic fractionation for olivine-diopside and olivine-plagioclase pairs and observed fractionation in Pali xenoliths. The results indicate that the equilibration of the xenoliths with respect to oxygen isotopes took place at high temperatures, in the mantle. The range of equilibration temperatures measured on Pali peridotite by conventional thermometry using major cation exchange [*Sen*, 1988] is also shown.

quently enriched the MORB-depleted lithosphere. The first hypothesis is consistent with the greater equilibration pressures measured in a variety of Salt Lake xenoliths, including garnet pyroxenites and garnet peridotites, when compared to Pali xenoliths [*Sen*, 1988]. An alternative interpretation of the positive correlation between $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ in Pali spinel peridotites (Figure 4) is

that rather than having age significance, it defines a mixing array between a depleted residual mantle end-member and more enriched metasomatizing melts or fluids. There is abundant evidence from trace element and isotopic studies of Hawaiian xenoliths that metasomatism has affected the Hawaiian lithosphere [e.g., *Roden et al.*, 1994; *Salters and Zindler*, 1995; *Vance et al.*, 1989; *Sen*

et al., 1993; *Yang et al.*, 1998]. In the case of individual clinopyroxene grains, their cores tend to preserve the trace element and isotopic characteristics of the original crystal, whereas the rims have compositions modified by a passing melt. This melt was most likely related to the Hawaiian plume magmatism [*Sen et al.*, 1993; *Yang et al.*, 1998], either similar Koolau or Honolulu Volcanic Series melts. *Yang et al.* [1998] showed that the Sm/Nd ratios of Pali clinopyroxene rims are not significantly different from cores (with the exception of their sample 77PAII-9), in contrast to the large within-grain range of elemental concentrations exhibited by La and Ce, qualitatively arguing against a strong metasomatic effect on these clinopyroxenes.

[18] If the isotopic composition of the metasomatic component resembles the Koolau magmas, the mixing trajectory could not take the path exhibited by our data in ^{143}Nd/^{144}Nd and ^{147}Sm/^{144}Nd space (Figure 4). However, the data in Figure 4 can be the result of mixing between a depleted peridotite and a metasomatizing melt that resemble the average of the Honolulu Volcanic Series lavas [*Roden et al.*, 1994]. About 50% by mass of the Honolulu Volcanic Series melt is required to decrease the ^{147}Sm/^{144}Nd ratio from 0.78 to 0.4. Such an extreme metasomatic effect should be evident in our Sr data; that is, more metasomatized clinopyroxenes should have higher Sr (ppm) and higher ^{87}Sr/^{86}Sr. Figure 5 shows that is not the case for the clinopyroxenes plotted in Figure 4. Without ruling out the hypothesis of metasomatism by Honolulu Volcanic Series lavas, we conclude that it is unlikely that the large range of ^{147}Sm/^{144}Nd in the analyzed spinel peridotites was produced by Honolulu Volcanic Series metasomatism.

[19] In conclusion, the range of Nd isotopic ratios exhibited by Pali spinel peridotites is consistent with the peridotites being residues of Cretaceous partial melting at the Pacific ridge. The lower the present-day ε_{Nd} for a given lithospheric sample, the deeper in the mantle lithosphere, the more fertile it would be. We cannot rule out the possibility of subsequent metasomatism by Honolulu Volcanic Series-like melts, but we propose that if present, metasomatism had a secondary effect compared to melt depletion at

the late Cretaceous mid-ocean ridge. In contrast, metasomatism by Koolau-like melts can be ruled out for the spinel peridotites analyzed here.

5.2. Origin of Plagioclase and Relevance to Koolau Lavas

[20] The plagioclase in the analyzed peridotites is in strong ^{87}Sr/^{86}Sr disequilibrium with coexisting clinopyroxenes. The ^{87}Sr/^{86}Sr values measured on plagioclase (0.7043–0.7044) are distinctively higher than all clinopyroxenes from Pali. ^{87}Sr/^{86}Sr ratios similar to those measured on plagioclase separates were previously measured in two spinel peridotites from Salt Lake Crater by *Vance et al.* [1989] (one sample out of a total of four analyzed peridotites) and *Okano and Tatsumoto* [1996] (one sample out of five analyzed peridotites), suggesting that such ^{87}Sr/^{86}Sr signatures might be widespread in the sub-Oahu lithosphere.

[21] The two plagioclase-bearing xenoliths described here have high δ^{18}O olivines (~5.5‰) compared to normal oceanic mantle olivines in Hawaii and elsewhere (~5.0‰ [*Eiler et al.*, 1996], Figure 6). One explanation of ^{18}O enrichments in mantle rocks is that they sample a component that once resided at or near the surface of the Earth were fluid/rock interactions produces large shifts in δ^{18}O. The emplacement of the plagioclase took place in the mantle, as attested by the high temperature equilibration recorded by oxygen exchange between olivine, clinopyroxene, and plagioclase in these two rocks and the presence of ductile fabric in plagioclase peridotites. This conclusion appears to contradict evidence from Sr isotopes that plagioclase and clinopyroxene are not in isotopic equilibrium. We suggest that this discrepancy is due to differences in rates of exchange of oxygen and strontium between minerals and metasomatic fluid or melt; this hypothesis is developed in the following section. First, however, we consider the likely origin of a metasomatic agent capable of producing high ^{87}Sr/^{86}Sr plagioclase and ^{18}O-enriched major phases in the sub-Oahu lithospheric mantle.

[22] The Sr isotope ratios are similar to those of the Koolau lavas. Therefore it is reasonable to consider

that the plagioclase precipitated from a melt related to the Koolau shield lavas rising through the lithospheric mantle. Future isotopic (e.g., Nd, Pb) studies should further test this inference. If, however, this conclusion is correct, it suggests that the Koolau magmas contained a component of ancient recycled crust.

[23] Metasomatism of depleted peridotite by basaltic melt raises its fertility (i.e., ability to generate partial melt). In particular, the addition of plagioclase to lithospheric mantle due to reaction with melts related to Koolau lavas could lead to later melting of that mantle, producing surface melts with isotopic ratios along trends labeled "M" and "N" in Figure 3. Most Hawaiian lavas fall along such trends [see summary by *Phipps Morgan*, 1999]. Furthermore, if interaction between lithospheric mantle and a Koolau-like melt characterized by high Sr/Nd were common throughout Hawaii, it could also generate the relatively high $^{87}Sr/^{86}Sr$ at any given $^{143}Nd/^{144}Nd$, a characteristic observed in all Hawaiian lavas and xenoliths. It should be noted, however, that the trends defined by Hawaiian lavas in $^{87}Sr/^{86}Sr-^{143}Nd/^{144}Nd$ diagrams are less hyperbolic than the "M" and "N" model trends, and that the Pb isotopic ratios of the Koolau lavas would not satisfy this explanation.

[24] Some features of the plagioclases remain puzzling, especially the low trace element abundances of REE and Sr, and the LREE depletion. The low trace elemental abundance, in conjunction with the high Sr/Nd ratio, precludes the possibility that the plagioclase is a direct cumulate of the surface Koolau lavas. That is simply because all liquids in equilibrium with such a fractionating phase would be too low in both Sr (<0.5 ppm) and Nd (<0.1 ppm) for any reasonable Sr/Nd ratio in the source (<500) compared to the Koolau lavas (Sr = 300–500 ppm; Nd = 10–20 ppm [e.g., *Roden et al.*, 1984]). The relative LREE depletion is an additional problem since the Koolau lavas are LREE enriched [*Frey et al.*, 1994; *Roden et al.*, 1984]. A possible type of magma that could have produced via fractionation of the trace element patterns observed in plagioclase is the "ultradepleted" type (UDM [e.g., *Sobolev and Shimizu*, 1993]). However, the UDM are considered late-

stage mid-ocean ridge features and thus are not expected to have $^{87}Sr/^{86}Sr$ enriched relative to MORB, especially in an essentially Rb-free phase like plagioclase.

[25] An alternative explanation for the high $^{87}Sr/^{86}Sr$ values in the plagioclase peridotites is that these shallow mantle samples, unlike the deeper xenoliths, have been subjected to seawater alteration. The difference in $^{87}Sr/^{86}Sr$ between plagioclase and clinopyroxene could possibly reflect the significantly slower diffusion of Sr in pyroxene relative to the plagioclase [*Sneeringer et al.*, 1984; *Coghlan*, 1990]. Without complementary Nd isotope data for plagioclase, this possibility cannot be ruled out using radiogenic isotopic evidence only. However, the $\delta^{18}O$ of hydrothermally altered deeper parts of the oceanic lithosphere is predicted to be lower than typical unaltered equivalents (average $\delta^{18}O = 5.5‰$ [*McCulloch et al.*, 1980], in contrast to the results from the Pali xenoliths.

[26] The ultimate origin of the plagioclase in these peridotites is thus very much open to question. Even if they originally formed by precipitation or melt-rock interaction, unresolved subsequent processes must have depleted them in incompatible elements. However, we interpret the plagioclase as a component that was intruded into the shallow mantle lithosphere, is probably plume-related, and contains a recycled component (i.e., a component that has been previously at or near the Earth's surface).

5.3. Timing of Formation of the Plagioclase

[27] We infer that high $\delta^{18}O$ plagioclase grew as a result of metasomatism in the lithospheric mantle by a melt or fluid related to the Hawaiian plume. We can estimate the timescales of metasomatism using the observed difference in Sr and O isotopic systematics, the xenoliths grain size as characteristic diffusion distance $(Dt^{0.5})$ for various elements [e.g., *Hofmann and Hart*, 1978]. The grain radii for the Oahu xenoliths are 0.5–1 mm, and the relevant diffusion data [*Sneeringer et al.*, 1984] was calculated at 1100 °C, the average equilibration temperatures recorded by major cation exchange in these xenoliths.

[28] Incompatible elements such as Sr and Nd attain local equilibrium in the presence of a partial melt within ~10,000–20,000 years in the studied xenoliths. The lack of equilibrium of radiogenic isotopes of Sr between clinopyroxene and plagioclase in these assemblages requires that the melting event that introduced the enriched plagioclase was shorter than a few tens of thousands of years. Olivine should equilibrate with respect to $\delta^{18}O$ in the presence of a melt over a timescale of hundreds of years (on the basis of diffusion data of *Reddy et al.* [1980]). The lack of Sr equilibration in xenoliths puts an upper bound on the duration of interaction between the enriched component and the depleted framework to less than about a few tens of thousands of years. Since major phases have equilibrated for oxygen, we estimate that the minimum timescale for melt percolation should have been of the order of hundreds of years.

[29] The estimated timescale of metasomatism of lithospheric mantle beneath Oahu is 2 orders of magnitude less than the timescale of the growth of Koolau volcano itself. We interpret that metasomatism took place within a small fraction of the main (shield) stage of magmatic activity at Koolau. Large-volume melts forming the Koolau caldera must have passed through the shallow oceanic lithosphere via larger conduits (dikes) and not by porous flow if sub-Koolau mantle columns (such as the one sampled at Pali) were to largely retain the MORB signature.

6. Conclusions

[30] A Sr, Nd, and O isotopic study of clinopyroxene and plagioclase separates from peridotite xenoliths from Pali (Oahu), combined with previously published trace element abundance data for related rocks [*Yang et al.*, 1998] reveals the following:

1. The Pacific lithospheric mantle is preserved beneath the Koolau volcano and has a range of ε_{Nd} = 6.9 to 11. Garnet-free pyroxenites in the suite are interpreted to have precipitated from Cretaceous basaltic melts.

2. Two peridotites contain plagioclase having $^{87}Sr/^{86}Sr$ strongly different from coexisting, LREE-depleted pyroxenes. In contrast, the plagioclase crystals are in high-temperature $\delta^{18}O$ equilibrium with olivines and pyroxenes. The high $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ of the plagioclase resemble characteristics of the Koolau shield lavas and suggest that the melt passing through the lithosphere was plume-related. The elevated $\delta^{18}O$ of the plagioclase indicates that the melt from which it fractionated contained a fraction of recycled crustal material not acquired by local crustal contamination. We estimate that the duration of metasomatism by the Koolau-like melt was $\sim10^2$–10^4 years.

Acknowledgments

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