The \(^{87}\text{Sr}/^{86}\text{Sr}\) and \(^{143}\text{Nd}/^{144}\text{Nd}\) disequilibrium between Polynesian hot spot lavas and the clinopyroxenes they host: Evidence complementing isotopic disequilibrium in melt inclusions

Matthew G. Jackson  
Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543–1525, USA  
Now at Carnegie Institution of Washington, Washington, D. C. 20015, USA (mjackson@ciw.edu)

Stanley R. Hart, Nobumichi Shimizu, and Jerzy S. Blusztajn  
Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543–1525, USA

[1] We report \(^{87}\text{Sr}/^{86}\text{Sr}\) and \(^{143}\text{Nd}/^{144}\text{Nd}\) data on clinopyroxenes recovered from 10 ocean island lavas from three different hot spots (Samoan, Society, and Cook-Austral island chains). The clinopyroxenes recovered from eight of the 10 lavas analyzed in this study exhibit \(^{87}\text{Sr}/^{86}\text{Sr}\) disequilibrium with respect to the host lava. The \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios in clinopyroxene separates are 95–3146 ppm (0.0095–0.31%) different from their respective host whole rocks. Clinopyroxenes in three lavas have \(^{143}\text{Nd}/^{144}\text{Nd}\) ratios that are 70–160 ppm (0.007–0.016%) different from the host lavas. The \(^{87}\text{Sr}/^{86}\text{Sr}\) and \(^{143}\text{Nd}/^{144}\text{Nd}\) disequilibrium in one lava (the oldest lava considered in this study, Mangaia sample MGA-B-47) can be attributed to post-eruptive radiogenic ingrowth, but the isotope disequilibrium in the other, younger lavas cannot be explained by this mechanism. In five of the lava samples, two populations of clinopyroxene were isolated (black and green, separated by color). In four out of five of these samples, the \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios of the two clinopyroxene populations are isotopically different from each other. In addition to \(^{87}\text{Sr}/^{86}\text{Sr}\) disequilibrium, the two clinopyroxene populations in one of the lavas (Tahaa sample TAA-B-26) have \(^{143}\text{Nd}/^{144}\text{Nd}\) ratios that are \textasciitilde 100 ppm different from each other. Given the resilience of clinopyroxene to seawater alteration and the likelihood that the Sr and Nd isotope composition of fresh clinopyroxene separates provides a faithful record of primary magmatic compositions, the clinopyroxene-clinopyroxene isotope disequilibrium in these four lavas provides strong evidence that a mechanism other than seawater alteration has generated the observed isotopic disequilibrium. This study confirms the isotopic diversity in ocean island lavas previously observed in olivine-hosted melt inclusions. For example, the Sr isotopic variability previously observed in olivine-hosted melt inclusions is mirrored by the isotopic diversity in clinopyroxenes isolated from many of the same Samoan lavas. The isotopic data from melt inclusions and clinopyroxenes are not consistent with shallow assimilation of sediment or with entrainment of xenocrystic clinopyroxene from the oceanic crust or upper mantle. Instead, the data are interpreted as reflecting isotopic heterogeneity in the mantle sources of the lavas. The isotopic diversity in clinopyroxenes and melt inclusions suggests that a single lava can host components derived from isotopically diverse source regions.

Components: 11,716 words, 6 figures, 3 tables.

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1. Introduction

Ocean island lavas erupted at hot spots are thought to be melts of upwelling regions of the mantle, and thus provide clues about the composition of the inaccessibly deep Earth. The observation of heterogeneous radiogenic isotopes (e.g., $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{176}\text{Hf}/^{177}\text{Hf}$, etc.) in ocean island lavas led to the conclusion that the mantle is heterogeneous [Gast et al., 1964; Hart, 1971; Zindler and Hart, 1986a; Hofmann, 1997]. Importantly, the scale lengths of mantle heterogeneities appear to be variable: Mantle heterogeneities have persisted at both large (hemispheric, or DUPAL-scale [Hart, 1984]) and small (submeter [Hofmann and Hart, 1978]) length scales.

The smallest length scales of heterogeneity in the mantle are likely to be smaller than the dimensions of the mantle melting region beneath a single volcano. If a melting column beneath a hot spot volcano has the geometry of a fractal tree (where small capillaries may sample more distal regions of the melting regime and join like river tributaries to form progressively larger branches en route to the surface [Hart, 1993]), more than one mantle source will likely contribute melt to any single lava erupted at the surface. However, information about the isotopic diversity of the mantle sources contributing to a single lava is lost because of aggregation of magmas during ascent.

Fortunately, small volumes of melt are trapped in growing magmatic phases at depth, and these melt inclusions sample “snapshots” of intermediate mixing steps before complete melt aggregation. In a ground-breaking study, Saal et al. [1998] observed that melt inclusions preserve isotopic diversity not seen in analyses of whole-rock basalts. They found that melt inclusions isolated from a single hand sample can exhibit up to 50% of the Pb isotopic variability observed in ocean island basalts (OIB). Subsequent Pb isotope studies in melt inclusions confirmed these results [Kobayashi et al., 2004; Yurimoto et al., 2004; Jochum et al., 2004; Saal et al., 2005; Maclennan, 2008], and Sr isotope measurements in melt inclusions also revealed significant isotopic heterogeneity within individual lavas [Jackson and Hart, 2006]. However, melt inclusions are extremely small, composing a tiny fraction of the mass of a bulk lava ($\ll 0.1\%$), and their importance in the genesis of lavas can be easily overlooked.

Owing to the potentially large fraction of an erupted lava that is composed of olivine, clinopyroxene and/or plagioclase, the discovery of isotopic disequilibrium between lavas and the magmatic phases they host is potentially very important to understanding their petrogenesis. Clinopyroxene and plagioclase in lavas erupted in continental (flood basalt), subduction zone and mid-ocean ridge settings have been found to exhibit Pb isotopic compositions different from the host lava [Bryce and DePaolo, 2004]. Using a laser ablation technique, Ramos et al. [2005] found significant isotopic disequilibrium between plagioclase and whole rock in the Colombia River floods basalts. However, lavas erupted in continental and subduction zone settings can suffer contamination by shallow-level assimilation, and it is difficult to deconvolve evidence for mantle source heterogeneity from shallow-level assimilation processes. By contrast, OIBs are thought to avoid significant shallow-level contamination during ascent, owing to the fact that they transit through a much thinner, more trace element depleted crust. Thus, the OIBs erupted at the surface can be used as windows into the compositional heterogeneity of the mantle.

Hanyu and Nakamura [2000] explored the isotopic composition of OIBs and the clinopyroxenes they host. They observed Sr isotopic disequilibrium in the clinopyroxenes relative to the whole rocks, and they attributed this to seawater contamination of the whole rock. They suggested that the $^{87}\text{Sr}/^{86}\text{Sr}$ of the host clinopyroxenes better represent the primary magmatic Sr isotopic composition of the original, erupted lava. Here we show that clinopyroxenes recovered from ocean island lavas...
can exhibit both Sr and Nd isotope disequilibrium. Additionally, we show that two different populations of clinopyroxene in a single lava can exhibit different $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$. If Hanyu and Nakamura’s [2000] hypothesis is right, that clinopyroxene hosted in OIB lavas better represent their primary magmatic isotopic compositions than the whole rocks, our data on clinopyroxene pairs suggest that more than one primary magmatic isotopic signature can contribute to a single erupted lava. We maintain that the isotopic disequilibrium observed between clinopyroxenes and whole rocks support the hypothesis (developed primarily through melt inclusions studies) that a lava does not sample an isotopically homogeneous mantle, but that the mantle sources contributing to a single OIB lava can be isotopically diverse.

## 2. Methods

Ten geochemically well-characterized whole-rock lavas from four hot spots (Samoa, Society, and Cook-Austral island chains) were selected for clinopyroxene analysis. The whole-rock isotopic, major and trace element data for these samples are reported elsewhere (see Table 1 for references). The whole-rock isotopic data for the lavas reported in Table 1 were obtained on leached powders only.

Each sample was crushed in a jaw crusher and fresh clinopyroxene grains were separated. In five of the hand samples, two populations of clinopyroxene, distinguished by color (black and green) were isolated for isotopic analysis. There was slight overlap between the two populations, as green clinopyroxene were often visibly zoned and hosted regions of darker clinopyroxene (and vice versa), so it was not possible to completely separate the green and black populations and still obtain sufficient material for isotopic analysis. Clinopyroxene grains with visible alteration were avoided. The freshest remaining clinopyroxene grains were leached following the protocol of Taras and Hart [1987]. The grains (30–100 mg of material per sample) were then washed in distilled water and powdered in an agate mortar. In many cases, over 100 clinopyroxene grains were required for analysis of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$.

Sr and Nd chemistry was performed with conventional ion chromatography using DOWEX 50 cation resin and HDEHP-treated Teflon for Nd separation (following Taras and Hart [1987]). Analyses of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ were made on the NEPTUNE multicollector ICP-MS (inductively coupled plasma mass spectrometer) at Woods Hole Oceanographic Institution (WHOI). The protocol and associated errors and standard normalizations are given by Hart and Blusztajn [2006]. In-run (internal) precision was 3–22 ppm ($\sigma$, standard error) for $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ measurements on most clinopyroxenes, and the in-run signal intensities on $^{86}\text{Sr}$ and $^{144}\text{Nd}$ were comparable to those obtained in typical runs of basaltic glass. However, two clinopyroxene measurements had somewhat lower signal intensities and therefore had lower internal precision; the $^{87}\text{Sr}/^{86}\text{Sr}$ run of ALIA-115-18 green cpx (2σ standard error is 29 ppm) and the $^{143}\text{Nd}/^{144}\text{Nd}$ run of ALIA-115-03 cpx (2σ standard error is 43 ppm).

Estimates for the external precision are based on long-term standard analyses of $^{87}\text{Sr}/^{86}\text{Sr}$ (SRM987 Sr standard) and $^{143}\text{Nd}/^{144}\text{Nd}$ (La Jolla Nd standard). After adjusting to 0.710240 (SRM987 Sr standard) and 0.511847 (La Jolla Nd standard), external precision is estimated to be 15–25 ppm (2σ) and 15–30 ppm (2σ), respectively, for $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ runs with normal signal intensities. However, the $^{87}\text{Sr}/^{86}\text{Sr}$ run of ALIA-115-18 green cpx and $^{143}\text{Nd}/^{144}\text{Nd}$ run of ALIA-115-03 cpx, the two runs with lower-than-average signal intensities, are expected to have somewhat worse external precision. Nonetheless, the diminished external precision of the $^{87}\text{Sr}/^{86}\text{Sr}$ measurement of ALIA-115-18 green cpx does not affect our ability to resolve the whole rock and clinopyroxene; at only 10 ppm different from the whole rock, the $^{143}\text{Nd}/^{144}\text{Nd}$ of ALIA-115-03 cpx is considered to be analytically indistinguishable from the whole rock.

Major element compositions of clinopyroxenes were determined at the electron microprobe facility at the Massachusetts Institute of Technology. During all measurements, a 10 nA beam current and a 15 kV voltage were used. The spot size of the beam was 1 µm and the CITZAF matrix correction was employed. Where two clinopyroxene populations (distinguished by color in visible light, black and green) were identified for isotopic measurement, major element analyses were made of both populations. Sufficient clinopyroxene material was not always available for isotopic analyses of both populations of clinopyroxene, and in such cases, green and black clinopyroxene were combined to obtain sufficient material for isotopic measurement (the two cases where different populations were combined are noted in Table 1). Thus, there are more major element data for green-black clinopyroxene pairs than there are isotope data (compare...
Table 1. Sr and Nd Isotope Analyses for Magmatic Clinopyroxene Mineral Separates and Their Host Whole-Rock Lavas

<table>
<thead>
<tr>
<th>Hot Spot/Island/Seamount</th>
<th>Sample ID</th>
<th>Ages</th>
<th>Signal Intensity Mass 88 (Volts)</th>
<th>Signal Intensity Mass 144 (Volts)</th>
<th>$\Delta^{87}$Sr/$^{86}$Sr (ppm)</th>
<th>$\Delta^{143}$Nd/$^{144}$Nd (ppm)</th>
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<tbody>
<tr>
<td>Cook-Austral Mangaia</td>
<td>MGA-B-47</td>
<td>16–20 Ma</td>
<td>12.1</td>
<td>2.0</td>
<td>0.702760 ± 8</td>
<td>0.512886 ± 6</td>
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<tr>
<td></td>
<td>MGA-B-47 green cpx</td>
<td></td>
<td>41.9</td>
<td>3.4</td>
<td>0.702760 ± 6</td>
<td>0.512878 ± 6</td>
</tr>
<tr>
<td>Society Tahaa</td>
<td>TAA-B-26</td>
<td>1.3–3.4 Ma</td>
<td>35.6</td>
<td>4.0</td>
<td>0.705368 ± 12</td>
<td>0.512649 ± 3</td>
</tr>
<tr>
<td></td>
<td>TAA-B-26 green cpx</td>
<td></td>
<td>35.8</td>
<td>10.0</td>
<td>0.705827 ± 5</td>
<td>0.512705 ± 4</td>
</tr>
<tr>
<td>Samoa Vailulu'u</td>
<td>AVON3-68-3</td>
<td>&lt;350 Ka</td>
<td>35.0</td>
<td>2.0</td>
<td>0.705370 ± 11</td>
<td>0.512747 ± 8</td>
</tr>
<tr>
<td></td>
<td>AVON3-68-3 green cpx</td>
<td></td>
<td>26.3</td>
<td>1.6</td>
<td>0.705485 ± 9</td>
<td>0.512720 ± 11</td>
</tr>
<tr>
<td></td>
<td>AVON3-68-3 black cpx</td>
<td></td>
<td>28.3</td>
<td>5.3</td>
<td>0.709171 ± 5</td>
<td>0.512584 ± 3</td>
</tr>
<tr>
<td>Samoa Malumalu</td>
<td>AVON3-71-2</td>
<td>&lt;8 Ka</td>
<td>21.7</td>
<td>1.8</td>
<td>0.707676 ± 9</td>
<td>0.512602 ± 8</td>
</tr>
<tr>
<td></td>
<td>AVON3-71-2 green cpx</td>
<td></td>
<td>38.6</td>
<td>5.3</td>
<td>0.708294 ± 3</td>
<td>0.512581 ± 4</td>
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<tr>
<td>Samoa Ofu</td>
<td>Ofu-04-06</td>
<td>&lt;1 Ma</td>
<td>34.5</td>
<td>6.7</td>
<td>0.704599 ± 7</td>
<td>0.512818 ± 3</td>
</tr>
<tr>
<td>Samoa Savai'i Dredge 115</td>
<td>ALIA-115-03</td>
<td>5.06 Ma</td>
<td>36.0</td>
<td>0.6</td>
<td>0.709171 ± 5</td>
<td>0.512588 ± 22</td>
</tr>
<tr>
<td></td>
<td>ALIA-115-03 black cpx</td>
<td></td>
<td>5.6</td>
<td>2.5</td>
<td>0.720380 ± 21</td>
<td>0.512285 ± 6</td>
</tr>
<tr>
<td></td>
<td>ALIA-115-03 black cpx</td>
<td></td>
<td>14.7</td>
<td>9.6</td>
<td>0.720323 ± 7</td>
<td>0.513030 ± 5</td>
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<tr>
<td>Samoa Savai'i Dredge 115</td>
<td>ALIA-115-21</td>
<td>4.8 Ma</td>
<td>29.4</td>
<td>12.0</td>
<td>0.721630 ± 7</td>
<td>0.512274 ± 2</td>
</tr>
<tr>
<td></td>
<td>ALIA-115-21 black cpx</td>
<td></td>
<td>43.0</td>
<td>2.0</td>
<td>0.711808</td>
<td>0.512426</td>
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</tbody>
</table>

*cx, clinopyroxene; wr, whole-rock lavas. Errors are standard error (2σ, absolute) in-run precision. Long-term external precision for Sr and Nd isotope analyses at WHOI is provided in the text. The expressions used to calculate clinopyroxene-whole-rock isotope disequilibrium, or $\Delta^{87}$Sr/$^{86}$Sr_(cpx-WR) and $\Delta^{143}$Nd/$^{144}$Nd_(cpx-WR), are defined in the text. Isotopic disequilibrium is expressed in parts per million, or ppm. Whole-rock data for the Mangaia and Tahaa lavas are given by Hauri and Hart [1993, 1997]. Whole-rock data for the Samoan AVON3 lavas are given by Workman et al. [2004]. Whole-rock data for the Samoan Ofu lava are given by Jackson et al. [2007b, 2008]. Whole-rock data for the Samoan ALIA lavas are given by Jackson et al. [2007a]. When the color of clinopyroxene is not specified (AVON3-68-3 cpx and ALIA-115-03 cpx), it is because we did not attempt to distinguish between the various populations from the same lava (i.e., both green and black clinopyroxenes were combined to obtain sufficient material for isotopic measurement). The ages of the lavas are from the following sources: The Society and Mangaia lava ages are from Hauri and Hart [1993]; the ages of the Ofu lava and sample ALIA-118-23 are estimated using the observed age progression for Samoan shield lavas reported by Koppers et al. [2008]; the Samoan lava AVON3-68-3 has not been dated directly, but all other lavas recovered from this young seamount have eruption ages of <350 ka [Sims et al., 2008]; maximum ages for Samoan lavas AVON3-71-2 and AVON3-78-1 were determined using uranium series disequilibrium [Sims et al., 2008]; and the ages of ALIA lavas 115-03, 115-18 and 115-21 are reported by Koppers et al. [2008]. The data reported in this table are not corrected for radiogenic ingrowth. All whole-rock isotope data were obtained on leached powders.
Tables 1 and 2). Additionally, BSE (backscattered electron) imaging revealed that many clinopyroxene grains were zoned, and where possible, both bright and dark regions, as observed in BSE images, were analyzed.

[12] Trace elements (Ti, Cr, Sr, Y and Zr) and rare earth elements (REE, La, Nd, Sm, Yb) were measured using the Cameca IMS-3f ion microprobe at the Northeast National Ion Microprobe Facility at WHOI. During trace element measurement, a primary beam (consisting of negatively charged oxygen ions) with a current of approximately 0.8 nA was focused to a spot size of ~10 μm. For trace element analyses, positively charged secondary ions were mass analyzed using a high-energy offset of ~90 eV and an energy band pass of ±15 eV (to suppress molecular interferences [see Shimizu et al., 1978]). Counting times were 5 s on 28Si and 20 s for the trace elements, including 47Ti, 52Cr, 88Sr, 89Y and 90Zr. For REE analyses, the beam current was approximately 1.5 nA, the spot size was focused to ~20 μm, and a −70 eV offset with a ±15 eV window was used. Counting times during REE analyses were 5 s for 28Si, and 30 s for REE, including 158La, 146Nd, 147Sm and 174Yb. For both trace element and REE analyses, four cycles of measurements were made and average intensities (normalized to Si) were calculated. Intensities were calibrated against KL2G basalt glass, and the resulting empirical relationship (working curve) was used to determine trace element concentrations. For REE analyses, overall uncertainties are better than 15%, and better than 5% for trace elements.

3. Data and Observations

[13] Unfortunately, clear systematic major and trace element variations do not exist between the two color groups (Tables 2 and 3). For example, while most of the green clinopyroxenes tend to have higher Mg #s than the black clinopyroxenes, a single green clinopyroxene (from sample MGA-B47) exhibits one of the lowest Mg #s among the clinopyroxenes analyzed in this study (Figure 1). The two clinopyroxene color groups also fail to exhibit systematic trace element differences (Figure 2).

[14] The lack of clear systematic major and trace element differences between the green and black clinopyroxene populations may be a result of complicated magmatic histories before eruption. For example, many of the clinopyroxene grains from both color groups exhibit zoning in BSE images. In general, the brighter regions in BSE images have higher Al₂O₃ and FeO, but lower SiO₂ and MgO, than the darker regions from the same clinopyroxene, where increasing brightness indicates increasing average molecular weight. While we have not made an attempt to document whether trace element concentrations complement the zoning observed in BSE images, we note that core and rim analyses in clinopyroxene grains from two samples (Ofu-04-06 and ALIA-115-03; see Table 3) exhibit different trace element concentrations. Complex zoning in clinopyroxenes in OIB lavas has been documented elsewhere [e.g., Hanyu and Nakamura, 2000; Shimizu and Le Roex, 1986]. In this study, the trace elements in the clinopyroxenes are, in several cases, clearly not in equilibrium with the host lava. For example, the Nd concentrations in three Samoan ALIA clinopyroxenes approach the whole-rock values.

[15] Isotopic data obtained on the clinopyroxenes confirms their complex magmatic histories, and complement the disequilibrium indicated by the trace element analyses. In Figure 3, the 87Sr/86Sr and 143Nd/144Nd ratios of the clinopyroxenes are plotted with the respective whole-rock analyses. Each panel in Figure 3 also presents the extent of known isotopic heterogeneity (determined from whole-rock analyses) for the particular seamount or island from which the whole-rock-clinopyroxene pairs were sampled. Generally, a single lava sample was taken from each island/seamount for clinopyroxene separation and analysis in this study. However, from two locations, Vailulu’u (AVON3-71-2 and AVON3-68-3) and Savai’i (ALIA-115-03, ALIA-115-18, ALIA-115-21), clinopyroxenes from more than one lava sample were analyzed for isotopes.

[16] Given the external precision for measurement of 87Sr/86Sr (15–25 ppm, 2σ) on whole rocks and clinopyroxenes, we consider an isotopic difference of >50 ppm (i.e., twice the upper limit of the external precision) to be the minimum required to analytically resolve isotopic disequilibrium between a lava and the clinopyroxene it hosts. In order to analytically resolve Nd isotopic disequilibrium, a correspondingly larger isotopic difference (>60 ppm) is required. Given these criteria, out of the 10 lavas examined in this study, clinopyroxenes separated from just two of the lava samples (Ofu-04-06 and AVON3-68-3) have both Sr and Nd isotopes that are analytically indistin-
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Zonation in BSEb</th>
<th>Region of Grain</th>
<th>SiO$_2$  (wt %)</th>
<th>TiO$_2$  (wt %)</th>
<th>Al$_2$O$_3$  (wt %)</th>
<th>Cr$_2$O$_3$  (wt %)</th>
<th>FeO  (wt %)</th>
<th>MgO  (wt %)</th>
<th>CaO  (wt %)</th>
<th>Na$_2$O  (wt %)</th>
<th>Total Cation</th>
<th>Cation Totals</th>
<th>Na$_2$O/TiO$_2$</th>
<th>Mg #</th>
<th>Cr #</th>
<th>wo</th>
<th>en</th>
<th>fs</th>
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</thead>
<tbody>
<tr>
<td>MGA-B47 green cpx</td>
<td>bright</td>
<td></td>
<td>45.71</td>
<td>3.14</td>
<td>8.25</td>
<td>0.04</td>
<td>6.94</td>
<td>0.15</td>
<td>11.86</td>
<td>22.76</td>
<td>0.45</td>
<td>99.30</td>
<td>4.021</td>
<td>0.14</td>
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<td>32</td>
<td>50.9</td>
<td>36.9</td>
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<tr>
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<td>dark</td>
<td></td>
<td>51.35</td>
<td>0.65</td>
<td>2.84</td>
<td>1.12</td>
<td>4.06</td>
<td>0.06</td>
<td>16.18</td>
<td>22.60</td>
<td>0.43</td>
<td>99.27</td>
<td>4.019</td>
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<td>87.7</td>
<td>20.92</td>
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</tr>
<tr>
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<td></td>
<td>50.11</td>
<td>1.28</td>
<td>4.08</td>
<td>0.70</td>
<td>5.33</td>
<td>0.10</td>
<td>14.82</td>
<td>22.32</td>
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<td>4.013</td>
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<td>83.2</td>
<td>10.36</td>
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<td>50.29</td>
<td>1.22</td>
<td>3.57</td>
<td>0.68</td>
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<td>0.12</td>
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<td>11.35</td>
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<td>darkd</td>
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<td>22.37</td>
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<tr>
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<td>darkd</td>
<td></td>
<td>51.73</td>
<td>1.00</td>
<td>3.10</td>
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<td>16.02</td>
<td>22.92</td>
<td>0.17</td>
<td>100.08</td>
<td>4.008</td>
<td>0.17</td>
<td>86.0</td>
<td>7.85</td>
<td>46.9</td>
<td>45.6</td>
</tr>
</tbody>
</table>

a In hand samples where two different clinopyroxene (cpx) grain populations could be distinguished by color, electron probe analyses were made on a representative green cpx and a representative dark cpx. Mg # = molar ratio of MgO/(MgO + FeO); Cr # = molar ratio of Cr$_2$O$_3$/Cr$_2$O$_3$ + Al$_2$O$_3$. Wollastonite (wo), enstatite (en) and ferrosilite (fs) components of the clinopyroxenes are also provided.

b Zonation in BSE (or “Backscattered Electron” image). In clinopyroxene grains that exhibit zonation in BSE, analyses were made of the bright and dark regions.

c Average of two analyses.

d Grain mostly dark in BSE image, but there is a thin region of brighter clinopyroxene on the grain edge that is too narrow to analyze.

Trace green clinopyroxenes are also found in sample ALIA-118-23. However, isotope data were not obtained on the green clinopyroxene from this lava. Major element data for this clinopyroxene population are thus not provided here, as this table provides major element data only for clinopyroxene populations used in obtaining Sr and Nd isotope data.
Table 3. Trace Element and Rare Earth Element Analyses on Clinopyroxene and Their Respective Host Whole Rocks

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ti (ppm)</th>
<th>Cr (ppm)</th>
<th>Sr (ppm)</th>
<th>Y (ppm)</th>
<th>Zr (ppm)</th>
<th>La (ppm)</th>
<th>Nd (ppm)</th>
<th>Sm (ppm)</th>
<th>Yb (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MGA-47 whole rock</td>
<td>10430</td>
<td>1499</td>
<td>281</td>
<td>16.0</td>
<td>112</td>
<td>18.8</td>
<td>19.4</td>
<td>4.5</td>
<td>1.2</td>
</tr>
<tr>
<td>MGA-47 green cpx</td>
<td>2257</td>
<td>2706</td>
<td>19</td>
<td>2.6</td>
<td>8</td>
<td>0.3</td>
<td>1.7</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>MGA-47 green cpx</td>
<td>8243</td>
<td>2152</td>
<td>37</td>
<td>9.6</td>
<td>50</td>
<td>1.8</td>
<td>6.8</td>
<td>2.3</td>
<td>0.9</td>
</tr>
<tr>
<td>MGA-47 black cpx</td>
<td>7160</td>
<td>2354</td>
<td>45</td>
<td>8.8</td>
<td>32</td>
<td>1.5</td>
<td>6.3</td>
<td>1.9</td>
<td>0.7</td>
</tr>
<tr>
<td>MGA-47 black cpx</td>
<td>6584</td>
<td>2348</td>
<td>40</td>
<td>8.1</td>
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<td>1.6</td>
<td>7.7</td>
<td>2.2</td>
<td>0.8</td>
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<td>19300</td>
<td>451</td>
<td>739</td>
<td>28.6</td>
<td>346</td>
<td>52.1</td>
<td>52.0</td>
<td>10.2</td>
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<td>TAA-B-26 green cpx</td>
<td>7019</td>
<td>3063</td>
<td>62</td>
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<td>43</td>
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<td>13.3</td>
<td>3.7</td>
<td>1.3</td>
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<td>3345</td>
<td>56</td>
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<td>10.9</td>
<td>3.4</td>
<td>1.1</td>
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<td>1101</td>
<td>83</td>
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<tr>
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<td>15270</td>
<td>822</td>
<td>387</td>
<td>22.5</td>
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<td>29.3</td>
<td>28.5</td>
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<td>0.6</td>
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<tr>
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<td>3023</td>
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<td>28</td>
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<td>4.1</td>
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<td>0.7</td>
</tr>
<tr>
<td>AVON3-71-2 whole rock</td>
<td>8650</td>
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<td>224</td>
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<td>98</td>
<td>17.1</td>
<td>16.5</td>
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<td>0.9</td>
</tr>
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<td>AVON3-71-2 green cpx</td>
<td>2324</td>
<td>2631</td>
<td>31</td>
<td>4.0</td>
<td>8</td>
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<td>2.4</td>
<td>0.8</td>
<td>0.4</td>
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<td>1079</td>
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<td>6.4</td>
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<td>1.7</td>
<td>0.6</td>
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<tr>
<td>AVON3-78-1 whole rock</td>
<td>11770</td>
<td>1289</td>
<td>333</td>
<td>19.6</td>
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<td>AVON3-78-1 green cpx</td>
<td>3021</td>
<td>3820</td>
<td>39</td>
<td>6.2</td>
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<td>1.7</td>
<td>6.2</td>
<td>2.2</td>
<td>0.6</td>
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<tr>
<td>AVON3-78-1 black cpx</td>
<td>5327</td>
<td>778</td>
<td>49</td>
<td>9.6</td>
<td>40</td>
<td>2.4</td>
<td>7.4</td>
<td>2.3</td>
<td>0.6</td>
</tr>
<tr>
<td>Ofu-04-06 whole rock</td>
<td>29670</td>
<td>533</td>
<td>599</td>
<td>30.3</td>
<td>293</td>
<td>37.9</td>
<td>44.1</td>
<td>10.8</td>
<td>1.7</td>
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<td>Ofu-04-06 black cpx</td>
<td>6266</td>
<td>1773</td>
<td>54</td>
<td>8.9</td>
<td>38</td>
<td>1.5</td>
<td>6.6</td>
<td>2.3</td>
<td>0.6</td>
</tr>
<tr>
<td>Ofu-04-06 black cpx</td>
<td>6100</td>
<td>1622</td>
<td>53</td>
<td>9.4</td>
<td>39</td>
<td>2.7</td>
<td>10.3</td>
<td>4.2</td>
<td>0.9</td>
</tr>
<tr>
<td>ALIA-115-3 whole rock</td>
<td>21440</td>
<td>370</td>
<td>617</td>
<td>27.3</td>
<td>305</td>
<td>53.2</td>
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<td>1.6</td>
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<tr>
<td>ALIA-115-3 green cpx</td>
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<td>47</td>
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<td>1.1</td>
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<td>ALIA-115-3 black cpx</td>
<td>5903</td>
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<td>24.1</td>
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<td>ALIA-115-18 black cpx</td>
<td>3928</td>
<td>794</td>
<td>48</td>
<td>28.8</td>
<td>50</td>
<td>12.0</td>
<td>43.4</td>
<td>10.5</td>
<td>2.5</td>
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<td>478</td>
<td>20.3</td>
<td>390</td>
<td>81.3</td>
<td>58.9</td>
<td>10.2</td>
<td>1.4</td>
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<tr>
<td>ALIA-115-21 black cpx</td>
<td>4515</td>
<td>1308</td>
<td>54</td>
<td>26.4</td>
<td>53</td>
<td>9.7</td>
<td>33.6</td>
<td>8.5</td>
<td>2.3</td>
</tr>
</tbody>
</table>

a. cpx, clinopyroxene. Trace element and rare earth element (REE) analyses by ion probe were not made on the same spots as the major element analyses by electron probe. Whole-rock major and trace element data are available from Jackson et al. [2008, 2007a, 2007b], Workman et al. [2004], and Hauri and Hart [1997]. Trace element and REE analyses were not made on clinopyroxene from sample ALIA-118-23.

b. The two analyses of MAG-B-47 green cpx were made on different locations of the same clinopyroxene grain.

c. The two analyses of MAG-B-47 black cpx were made on different locations of the same grain.

d. The two analyses of TAA-B-26 green cpx were made on two different grains.

e. The two analyses of Ofu-04-06 black cpx were made on the same grain, but the second (lower Ti) analysis was made on the grain’s rim.

f. The two analyses of ALIA-115-03 black cpx were made on the same grain: The analysis with higher Ti was made on the grain’s core, and the other analysis was made on the rim.

guishable from the respective whole rocks. All other clinopyroxene-whole-rock pairs exhibit $^{88}$Sr/$^{86}$Sr disequilibrium. A smaller number of the clinopyroxene-whole-rock pairs exhibit measurably different $^{143}$Nd/$^{144}$Nd. The smaller number of lavas with measurable $^{143}$Nd/$^{144}$Nd disequilibrium may relate to the fact that the external precision ($\pm 15$–30 ppm) for $^{143}$Nd/$^{144}$Nd measurement represents a large proportion of the total global OIB $^{87}$Sr/$^{86}$Sr variability. Measurement error plays a smaller role in obscuring differences in $^{87}$Sr/$^{86}$Sr between mantle reservoirs, or between reservoirs sampled by a lava and the clinopyroxene it hosts, than it does for $^{143}$Nd/$^{144}$Nd.

In 5 cases (samples TAA-B-26, MGA-B-47, AVON3-71-2, AVON3-78-1 and ALIA-115-18), $^{87}$Sr/$^{86}$Sr and $^{143}$Nd/$^{144}$Nd data from two different clinopyroxene populations (green and black grains) from each whole rock are presented. In 4 out of 5 cases, the green and black clinopyroxenes are not in $^{87}$Sr/$^{86}$Sr equilibrium with each other. Sample MGA-B-47 represents the only case where green
and black clinopyroxene grains have indistinguishable $^{87}\text{Sr}/^{86}\text{Sr}$. In the 4 lavas where the black and green clinopyroxene can be analytically resolved using Sr isotopes, the black clinopyroxenes have isotopic compositions more similar to the whole rock than the green clinopyroxenes.

In contrast to the $^{87}\text{Sr}/^{86}\text{Sr}$ data, 4 of the 5 green and black clinopyroxene pairs exhibit analytically indistinguishable $^{143}\text{Nd}/^{144}\text{Nd}$. Only in sample TAA-B-26 do the green and black clinopyroxene populations exhibit analytically different $^{143}\text{Nd}/^{144}\text{Nd}$. Nonetheless, this single example of clinopyroxene-clinopyroxene $^{143}\text{Nd}/^{144}\text{Nd}$ disequi-

Figure 1. $\text{Na}_2\text{O}/\text{TiO}_2$ is plotted against (top) Mg # and (bottom) CaO for the clinopyroxenes in this study. Also plotted are clinopyroxenes recovered from mantle xenoliths. The magmatic clinopyroxenes examined in this study (gray field, see Table 2 for major element data) are resolved from clinopyroxenes hosted in ultramafic (blue and yellow fields) and pyroxenitic (red field) xenoliths. In general, magmatic pyroxenes have lower $\text{Na}_2\text{O}/\text{TiO}_2$ than the xenolith clinopyroxenes, as the latter equilibrated at higher pressures. The Samoan ultramafic xenoliths are from Savai’i island, and the data are from Hauri and Hart [1994] and Hauri et al. [1993]. The Societies xenoliths are from Tahiti, and the data are from Tracy [1980]. The pyroxenite xenoliths are from Salt Lake Crater in Oahu, Hawaii, and the data are from Bizimis et al. [2005]. A single xenolith clinopyroxene overlaps with the field of magmatic clinopyroxene, and this clinopyroxene was interpreted by Tracy [1980] to have crystallized from a primary melt that formed a dike in a lherzolitic xenolith. This plot provides evidence that the major element data on the clinopyroxenes in this study are inconsistent with a mantle xenolith origin.
The (Sm/Yb)_N notation signifies that the measured Sm/Yb ratio has been normalized to Primitive Mantle [McDonough and Sun, 1995]. The symbols are the same as in Figure 1, except for abyssal peridotites (orange diamonds) and gabbro clinopyroxenes (purple triangles). The clinopyroxenes presented in this study (gray field, see Table 3 for data) do not overlap with clinopyroxenes from peridotite xenoliths from Samoa [Hauri et al., 1993; Hauri and Hart, 1994], pyroxenite xenoliths from Oahu, Hawaii [Bizimis et al., 2005], abyssal peridotites (abyssal peridotite data are from the compilation of Workman and Hart [2005]), or gabbro clinopyroxenes from ODP Hole 735B [Gao et al., 2007]. Trace elements measured in the clinopyroxenes in this study support the contention that they are not xenocrysts from the oceanic crust or upper mantle.

Figure 2. The (Sm/Yb)_N versus Sm compositions of clinopyroxenes in this study are plotted with clinopyroxenes from abyssal peridotites, Hawaiian pyroxenite xenoliths, and Samoan peridotite xenoliths. The (Sm/Yb)_N notation signifies that the measured Sm/Yb ratio has been normalized to Primitive Mantle [McDonough and Sun, 1995]. The symbols are the same as in Figure 1, except for abyssal peridotites (orange diamonds) and gabbro clinopyroxenes (purple triangles). The clinopyroxenes presented in this study (gray field, see Table 3 for data) do not overlap with clinopyroxenes from peridotite xenoliths from Samoa [Hauri et al., 1993; Hauri and Hart, 1994], pyroxenite xenoliths from Oahu, Hawaii [Bizimis et al., 2005], abyssal peridotites (abyssal peridotite data are from the compilation of Workman and Hart [2005]), or gabbro clinopyroxenes from ODP Hole 735B [Gao et al., 2007]. Trace elements measured in the clinopyroxenes in this study support the contention that they are not xenocrysts from the oceanic crust or upper mantle.

[19] Following Bryce and DePaolo [2004], whole-rock-clinopyroxene isotope disequilibrium is defined in the following manner, using the example of Sr isotopes:

$$\Delta^{87}\text{Sr}^{86}\text{Sr}_{(\text{cpx-}}^{\text{WR}} = \left(\frac{^{87}\text{Sr}^{86}\text{Sr}_{\text{cpx}}}{^{86}\text{Sr}} - \frac{^{87}\text{Sr}^{86}\text{Sr}_{\text{WR}}}{^{86}\text{Sr}}\right) / ^{86}\text{Sr}^{86}\text{Sr}_{\text{WR}} \times 10^6$$

where $^{87}\text{Sr}^{86}\text{Sr}_{\text{cpx}}$ and $^{87}\text{Sr}^{86}\text{Sr}_{\text{WR}}$ are the $^{87}\text{Sr}^{86}\text{Sr}$ measurements on a clinopyroxene (cpx) and the host whole rock (WR), respectively; Nd isotope disequilibrium is defined in a similar manner. In Figure 4, clinopyroxenes form a broad, negatively sloping array that passes through the origin. By definition, clinopyroxenes that are in isotopic equilibrium with the host whole rock will plot at the origin. Clinopyroxenes plotting in the second (or upper left) quadrant are more isotopically depleted (have lower $^{87}\text{Sr}^{86}\text{Sr}$ and higher $^{143}\text{Nd}^{144}\text{Nd}$) than the whole rock. Most clinopyroxenes plot in this quadrant. However, in several cases the clinopyroxenes are more enriched (have higher $^{87}\text{Sr}^{86}\text{Sr}$ and lower $^{144}\text{Nd}^{144}\text{Nd}$) than the whole rock and plot in the fourth (or lower right) quadrant. In two cases (ALIA-115-03 cpx and AVON3-71-2 green cpx) the clinopyroxene separates plot in the third (or lower left) quadrant, a region where clinopyroxenes exhibit more depleted (lower $^{87}\text{Sr}^{86}\text{Sr}$ and more enriched (lower) $^{143}\text{Nd}^{144}\text{Nd}$ values than the whole rock. There are no clinopyroxenes that plot in this first quadrant.

[20] Sr isotopes were previously measured in olivine-hosted melt inclusions recovered from four of the Samoan lavas [Jackson and Hart, 2006] examined in this study, and they provide information that complements the observed clinopyroxene-whole-rock isotopic disequilibrium (Figure 5). In several lavas, the $^{87}\text{Sr}^{86}\text{Sr}$ disequilibrium (or equilibrium) between clinopyroxenes and host whole rocks is reflected in the $^{87}\text{Sr}^{86}\text{Sr}$ heterogeneity previously reported in olivine-hosted melt inclusions. In samples AVON3-71-2 and AVON3-78-1, olivine-hosted melt inclusions tend to sample lower $^{87}\text{Sr}^{86}\text{Sr}$ than the respective whole rocks. Similarly, the green and black populations of clinopyroxene from these two lavas sample a less radiogenic $^{87}\text{Sr}^{86}\text{Sr}$ component than the respective whole rocks. By contrast, the Ofu-04-06 melt inclusions are analytically indistinguishable from the whole rock, on the basis of estimates of the external precision ($\pm 320$ ppm, $2\sigma$) for $^{87}\text{Sr}^{86}\text{Sr}$ measurements in melt inclusions. Like the melt inclusions, the clinopyroxenes recovered from sample Ofu-04-06 are also the same as the whole rock, within the quoted external precision.

[21] Samoan lava AVON3-68-3, the fourth lava with $^{87}\text{Sr}^{86}\text{Sr}$ measured on both olivine-hosted melt inclusions and clinopyroxenes, presents a more complicated case. Sr isotopes were measured on just three melt inclusions from this sample: Two of the melt inclusions sample a component with more radiogenic $^{87}\text{Sr}^{86}\text{Sr}$ than the whole rock, and the third melt inclusion samples a component less radiogenic than the whole rock. The $^{87}\text{Sr}^{86}\text{Sr}$ of the clinopyroxene from this lava is analytically indistinguishable from the host whole rock. Thus,
isotopic heterogeneity observed in olivine-hosted melt inclusions may not always be reflected in clinopyroxenes from the same lava. However, we note that the clinopyroxene grains in this sample were much smaller than the clinopyroxenes from the other lavas analyzed in this study, and the grains may have simply reached diffusive isotopic
equilibrium with the host lava (see section 4.2 below).

Additionally, olivine and clinopyroxene-hosted melt inclusions from Mangaia (MGA-B-47) and Tahaa (TAA-B-26), from the Cook-Austral and Society Islands, respectively, exhibit disequilibrium in Pb isotopes with respect to the host whole rocks [Saal et al., 1998]. The Pb isotopic disequilibrium observed in melt inclusions from TAA-B-26 is reflected in the $\frac{87}{86}$Sr/$\frac{143}{144}$Nd disequilibrium measured in black and green clinopyroxenes recovered from this lava. While MGA-B-47 also hosts olivine-hosted melt inclusions with heterogeneous Pb isotopes, the isotopic disequilibrium observed between the clinopyroxenes and whole-rock lava may not be a primary magmatic signature, but may instead reflect radiogenic ingrowth of $^{143}$Nd and $^{87}$Sr since the lava erupted at 16–20 Ma (see section 4.1.4 below).

4. Discussion

4.1. Origin of Clinopyroxene-Whole-Rock Isotopic Disequilibrium: Shallow-Level Contamination/Alteration, Radiogenic Ingrowth, or Entrainment of Xenocrystic Clinopyroxene?

Before considering a possible primary magmatic origin for the isotopic disequilibrium observed between whole-rock lavas and the clinopyroxenes they host, it is important to first consider other processes that may have contributed to the isotopic disequilibrium. For example, sea-
water contamination of the host rock relative to the host clinopyroxenes might generate isotopic dis-equilibrium. Similarly, assimilation of shallow marine sediment could generate isotopic dis-equilibrium between a contaminated magma and clinopyroxenes that crystallized before magma contamination. Additionally, entrainment of xenocrystic clinopyroxenes from the oceanic crust and/or the shallow mantle also must be considered. Finally, posteruptive radiogenic ingrowth of $^{87}\text{Sr}$ and $^{143}\text{Nd}$ can, given sufficient time, generate isotopic dis-equilibrium between clinopyroxenes and whole-rock lavas. Owing to the fact that two of the 10 lavas examined in the study host clinopyroxene that are in Sr and Nd isotopic equilibrium (Ofu-04-06 and AVON3-68-3), only the remaining eight lavas and their host clinopyroxenes are discussed in the following section.

### 4.1.1. Seawater Contamination

The matrix (or groundmass) that constitutes the bulk of the whole rocks is more susceptible to seawater contamination than the clinopyroxenes they host [Hanyu and Nakamura, 2000]. Therefore, clinopyroxene-whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$ dis-equilibrium caused by seawater contamination would tend to shift whole-rock isotopic compositions closer to seawater relative to the host clinopyroxenes. (In the past 20 million years, the period over which the lavas in this study were erupted, the $^{87}\text{Sr}/^{86}\text{Sr}$ of seawater has changed very little, and has increased from 0.7085 to 0.7092 [Hodell et al., 1991]). However, the most altered sample considered in this study, ALIA-118-23, hosts clinopyroxene $^{87}\text{Sr}/^{86}\text{Sr}$ (0.710337) more similar to seawater than the host rock (0.711808) (see description of this sample by Jackson et al. [2007a]). This is the opposite of the trend expected for isotopic dis-equilibrium generated by seawater alteration. Similarly, whole-rock sample ALIA-115-03 hosts clinopyr-

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**Figure 5.** A comparison of the $^{87}\text{Sr}/^{86}\text{Sr}$ measured in whole rocks, clinopyroxenes, and olivine-hosted melt inclusions in four Samoan lavas. The open white squares represent the Sr isotopic composition of the whole rock from which the clinopyroxene (black and green circles) and olivine-hosted melt inclusions (gray diamonds) were separated. Two populations of clinopyroxene (green and black in visible light) were separated from lava samples AVON3-71-2 and AVON3-78-1. Clinopyroxene data are from this study, and melt inclusion data are from Jackson and Hart [2006]. The error bars plotted on the melt inclusions are in-run precision ($2\sigma$). The in-run precision error bars for the clinopyroxene and whole-rock analyses are smaller than the data symbols. Error bars for (estimated) external precision ($\pm320$ ppm [$2\sigma$] for the melt inclusions, $\pm25$ ppm [$2\sigma$] for clinopyroxene and whole-rock measurements) are plotted to the right of each data symbol.
oxenes (0.709171) that are more similar to seawater that the host lava (0.711409), also the opposite trend expected for seawater alteration. It is clear that a process other than seawater alteration has generated the clinopyroxene-whole-rock isotopic disequilibrium in these two lavas.

[25] Unlike samples ALIA-118-23 and ALIA-115-03, five lavas with clinopyroxene-whole-rock isotopic disequilibrium (AVON3-78-1, AVON3-71-2, TAA-B-26, ALIA-115-18, ALIA-115-21) have whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are more similar to seawater than the clinopyroxenes they host. (While sample MGA-B-47 also possesses clinopyroxenes with this sense of disequilibrium, it is not included here, as much of the whole-rock-clinopyroxene Sr isotopic disequilibrium in this sample is likely due to post-eruptive radiogenic ingrowth; see section 4.1.4 below). However, this does not necessarily mean that the isotopic disequilibrium in these lavas is due to seawater contamination. Four of these lavas (AVON3-78-1, AVON3-71-2, TAA-B-26, ALIA-115-18) host two populations of clinopyroxenes (green and black) that are not in $^{87}\text{Sr}/^{86}\text{Sr}$ equilibrium with each other. Given the resilience of clinopyroxene to seawater alteration, and the likelihood that the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of fresh clinopyroxene separates provides a faithful record of primary magmatic compositions [Hanyu and Nakamura, 2000], the clinopyroxene-clinopyroxene isotopic disequilibrium in these four lavas provide strong evidence that a mechanism other than seawater alteration has generated the observed isotopic disequilibrium. Unfortunately, only one clinopyroxene population was observed in sample ALIA-115-21. Thus, we cannot rule out seawater as the sole mechanism driving the isotopic disequilibrium observed in this lava. In fact, we cannot rule out a component of seawater alteration in the four whole-rock lavas that exhibit clinopyroxene-clinopyroxene isotopic disequilibrium (AVON3-78-1, AVON3-71-2, TAA-B-26, ALIA-115-18). Nonetheless, the different $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between the green and black clinopyroxene populations in these four lavas indicates that there was isotopic disequilibrium inherent to the lavas at the time of eruption.

[26] Two of the lavas (TAA-B-26 and AVON3-78-1) exhibit $^{143}\text{Nd}/^{144}\text{Nd}$ disequilibrium between the whole rock and the clinopyroxenes they host. Owing to much higher Sr/Nd ratios in seawater compared to the lavas in this study, seawater contamination has a greater influence on the Sr isotopic composition of the whole rock than on its Nd isotopic composition. In general, Nd isotopes in lavas are considered to be relatively immune to seawater alteration, particularly in relatively fresh lavas like TAA-B-26 and AVON3-78-1. Clinopyroxenes are even less susceptible to alteration than the whole rock [Hanyu and Nakamura, 2000], and the $^{143}\text{Nd}/^{144}\text{Nd}$ disequilibrium between two populations of clinopyroxene in sample TAA-B-26 is not likely a result of seawater alteration. Thus, we interpret the different $^{143}\text{Nd}/^{144}\text{Nd}$ ratios between the whole rock and clinopyroxene in the two lavas (and between the two populations of clinopyroxene in sample TAA-B-26) to indicate that some process other than seawater alteration has contributed to the isotopic disequilibrium in these lavas.

4.1.2. Shallow Sediment Assimilation

[27] In $\Delta^{207}\text{Pb}/^{204}\text{Pb}$ versus $\Delta^{208}\text{Pb}/^{204}\text{Pb}$ isotope space [Hart, 1984], Jackson et al. [2007a, 2007b] showed that the fields of Samoan basalts and modern global marine sediments do not overlap, but instead exhibit diverging trends. Thus, Pb isotope data indicate that assimilation of modern marine sediment can be ruled out as a mechanism contributing to the isotopic diversity of Samoan lavas. Similarly, MGA-B-47 [Hauri and Hart, 1993] plots outside the region of modern marine sediment. However, TAA-B-26 [Hauri and Hart, 1993] does plot in the region of modern marine sediment, but this does not necessarily mean that this sample has been contaminated with shallow marine sediment: The Os isotopes in this sample are unradiogenic [Hauri and Hart, 1993] and inconsistent with shallow sediment assimilation.

4.1.3. Xenocrystic Clinopyroxene From the Oceanic Crust and Upper Mantle

[28] The upper mantle can also be ruled out as a source for the nonequilibrium clinopyroxene. Migmatic clinopyroxenes, like the ones examined in this study, tend to have low Na$_2$O/TiO$_2$, as they formed at low pressures (Figure 1). By comparison, clinopyroxenes from ultramafic xenoliths from the Societies [Tracy, 1980] and Samoan [Hauri and Hart, 1994; Hauri et al., 1993] hot spots have much higher Na$_2$O/TiO$_2$ than found in migmatic clinopyroxenes. Mantle pyroxenites, like those recovered from Salt Lake Crater in Oahu, Hawaii [e.g., Bizimis et al., 2005], also have higher Na$_2$O/TiO$_2$ than the clinopyroxenes examined in this study. Thus, the major element data on the clinopyroxenes in this study (Table 2) are inconsistent with a mantle xenolith origin.
Trace element data obtained on the clinopyroxenes in this study (Table 3) are also inconsistent with a mantle xenolith origin. Figure 2 reveals that mantle pyroxenites from Salt Lake Crater have (Sm/Yb)N ratios higher than found in the magmatic clinopyroxenes in this study. Clinopyroxenes from ultramafic Samoan xenoliths [Hauri and Hart, 1994; Hauri et al., 1993] and abyssal peridotites (from the compilation of Workman and Hart [2005]) also show no compositional overlap with magmatic clinopyroxene.

Trace element data also indicate that the clinopyroxenes examined in this study are not xenocrysts entrained from the oceanic crust during magma ascent. Clinopyroxenes from gabbros in ODP Hole 735B [Gao et al., 2007] are used to evaluate the compositions of clinopyroxenes in the oceanic crust. Figure 2 shows that the gabbro clinopyroxenes have lower (Sm/Yb)N values than the OIB clinopyroxenes.

### 4.1.4. Posteruptive Radiogenic Ingrowth

All lavas examined in this study are alkaline, and have high Rb/Sr ratios. Owing to extremely low clinopyroxene-melt partition coefficients for Rb relative to Sr [Hart and Brooks, 1974], magmatic clinopyroxenes have very low Rb/Sr ratios. Therefore, with time, basalts will ingrow more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ than the clinopyroxenes they host. Of the lavas that exhibit $^{87}\text{Sr}/^{86}\text{Sr}$ disequilibrium between whole rock and clinopyroxene, two of the lavas (AVON3-78-1 and AVON3-71-2) are sufficiently young (<1 Ma [Sim et al., 2008]) that posteruptive radiogenic ingrowth cannot be responsible for the observed $^{87}\text{Sr}/^{86}\text{Sr}$ disequilibrium. Two older (∼5 Ma) lavas, ALIA-115-18 and ALIA-115-21, have more radiogenic clinopyroxene $^{87}\text{Sr}/^{86}\text{Sr}$ than the clinopyroxenes population it hosts, an observation that cannot be explained by radiogenic ingrowth. While samples TAA-B-26, ALIA-118-23 and ALIA-115-03 (with ages between 1.3 and 7 Ma) all exhibit higher whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$ than the host clinopyroxenes, this decay of $^{87}\text{Rb}$ cannot be responsible for the isotopic disequilibrium: The $^{87}\text{Sr}/^{86}\text{Sr}$ disequilibria in these three lavas are one to two orders of magnitude larger than that which can be generated by $^{87}\text{Rb}$ decay since eruption. However, at up to 20 millions years of age, MGA-B-47 is the oldest lava considered in this study, and radiogenic ingrowth is likely responsible for up to half of the clinopyroxene-whole-rock Sr isotopic disequilibrium observed in this sample. The present-day isotopic disequilibrium between whole rock and clinopyroxene in MGA-B-47 is ∼95 ppm, but correction for radiogenic ingrowth to the initial magmatic value diminishes the magnitude of the isotopic disequilibrium to below that which can be analytically resolvable (<50 ppm). Thus, we consider the clinopyroxenes in sample MGA-B-47 to have been analytically indistinguishable in $^{87}\text{Sr}/^{86}\text{Sr}$ from the whole rock at the time of eruption.

Only three of the 10 lavas examined in this study have clear clinopyroxene-whole-rock $^{143}\text{Nd}/^{144}\text{Nd}$ disequilibrium: AVON3-78-1, TAA-B-26 and MGA-B-47. AVON3-78-1 lava is too young (<8 ka) to require an age correction, and we conclude that the $^{143}\text{Nd}/^{144}\text{Nd}$ disequilibrium was inherent to the erupted lava. By comparison, TAA-B-26 is much older (1.3–3.4 Ma), but the 160 ppm isotopic difference between the whole rock and black clinopyroxene population in this sample cannot be explained by radiogenic ingrowth alone. Using the Sm/Nd measured in the black clinopyroxene (0.29, see Table 1) and the Sm/Nd ratio from the whole rock (0.196), radiogenic ingrowth of $^{143}\text{Nd}$ due to decay of $^{147}\text{Sm}$ has changed the clinopyroxene and whole-rock $^{143}\text{Nd}/^{144}\text{Nd}$ ratios by <10 ppm. We conclude that most of the isotopic disequilibrium between TAA-B-26 and the black clinopyroxene population it hosts was a feature of the lava at the time of eruption. By contrast, a large portion of the clinopyroxene-whole-rock isotopic disequilibrium in sample MGA-B-47 clearly owes to radiogenic ingrowth. Using the measured Sm/Nd (0.232) and $^{143}\text{Nd}/^{144}\text{Nd}$ from the whole-rock lavas [Hauri and Hart, 1993, 1997], and employing the maximum measured Sm/Nd of the green (∼0.39) and black (∼0.31) clinopyroxenes (Table 3) and their measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (Table 1), we calculate that the difference in $^{143}\text{Nd}/^{144}\text{Nd}$ between the two clinopyroxene populations and the whole rock was <60 ppm at the time of eruption. Thus, within the limits of the quoted external precision, the clinopyroxene and whole-rock $^{143}\text{Nd}/^{144}\text{Nd}$ in sample MGA-B-47 were analytically indistinguishable at the time of eruption.

### 4.2. How to Generate and Preserve Isotopic Heterogeneity in Magmatic Clinopyroxene

For most of the lavas considered in this study, the clinopyroxene-whole-rock isotopic disequilibrium cannot be explained by posteruptive radiogenic ingrowth, seawater alteration, sediment assimilation, or incorporation of xenolith clinopyroxene. Here we consider a primary magmatic origin for the isotope disequilibrium in these lavas.
We argue that, like melt inclusions, clinopyroxene can serve as capsules preserving the Sr and Nd isotopic compositions of the magmas from which they crystallized. However, the integrity of this preservation will depend on the diffusive exchange rates for different elements between clinopyroxene and melt, and melt inclusions in olivine and melt. Thus, if a melt parental to a clinopyroxene mixes with a melt with different $^{87}\text{Sr}/^{86}\text{Sr}$, the original clinopyroxene will preserve the Sr isotopic composition of its parental melt if the diffusive equilibration time for Sr in clinopyroxene is longer than the time scale between magma mixing and eruption. The diffusion coefficients for a number of elements of interest in diopside (Sr, Nd, Pb, Ca, O, He) are available in the literature, and a comparison of the diffusive equilibration times (at 1200°C) for these elements are shown in Figure 6.

[34] Times for 95% equilibration span a large range, from 30,000 years for Pb, to $10^3$ years for Sr, to 3 Ma for Nd and Ca. Several elements are fairly closely coupled: Sr ~ O, and Ca ~ Nd. We must be mindful however, that at least for Pb, there is a factor of ~ 10 difference in diffusion between diopside and more natural Fe-bearing clinopyroxenes [Cherniak, 2001]. Equivalent data does not exist for the other elements in Fe-bearing clinopyroxene. Given that the Mg # of the clinopyroxene studied here ranges from ~74 to 89 (Table 2), the actual and relative equilibration curves shown in Figure 6 should be taken as illustrative rather than absolute. The diffusion model presented in Figure 6 suggests that Nd will be equilibrated to only a minor extent (30%) when Sr is largely equilibrated (>95%). Also, any major element zonation represented by Ca should be allied tied to the $^{143}\text{Nd}/^{144}\text{Nd}$ composition, whereas the $^{87}\text{Sr}/^{86}\text{Sr}$ composition may be decoupled from Ca and $^{143}\text{Nd}/^{144}\text{Nd}$. In principle, by analyzing clinopyroxenes for all of these isotopes, one might construct a temporal history for melt sources and mixing events. Obviously, there are advantages of doing this with in situ techniques, so as to recover temporal data of higher resolution. While we have only dealt with diffusive equilibration here (assuming no grain growth), the magmatic clinopyroxenes are likely to be undergoing simultaneous growth (or resorption), so differentiating between diffusion and grain growth will ultimately be important.

[35] Relating the information contained in clinopyroxene “capsules” with that encoded in melt inclusions in olivine requires data for diffusion of these elements in olivine. To date, only Ca diffusion in olivine has been measured [Jurewicz and Watson, 1988; Gaetani et al., 2002; Coogan et al., 2005], and it is faster than Ca in clinopyroxene by three orders of magnitude, and faster than Pb (Figure 6) by a factor of 10. This suggests that Sr and Pb in melt inclusions in olivine may be more equilibrated with the host melt than Sr or Pb in clinopyroxene; in any event it appears that $^{143}\text{Nd}/^{144}\text{Nd}$ in clinopyroxene will stand the best
chance of retaining the least mixed melt composition from the early stages of melt production.

[36] On the basis of the slow diffusion rates for Nd (and Ca) in clinopyroxene, and typical magma “residence” times of <10$^5$ years (based on magma chamber cooling models [e.g., Jaeger, 1968; Zindler and Hart, 1986b]), it seems unlikely that any diffusive reequilibration of Nd or Ca will occur in clinopyroxene, so that $^{143}$Nd/$^{144}$Nd, and Ca zoning, in clinopyroxenes will essentially record times of clinopyroxene growth. By comparison, Sr and Pb diffuse much faster than Nd in clinopyroxene. Thus, without the injection of isotopically distinct melts into a magma body, the Sr and Pb isotope ratios in clinopyroxene will suffer diffusive reequilibration with the host melt over the time scales typical of magma residence times. Therefore, the observation of Sr isotope disequilibrium in clinopyroxenes indicates that the compositions of magma plumbing systems change rapidly, and that the time between mixing (of isotopically distinct magmas) and eruption can be very short.

4.3. Clinopyroxene-Whole-Rock Isotopic Disequilibrium: Implications for Mineral-Melt Thermobarometry

[37] The assumption of initial equilibrium, both isotopic and chemical, is important to for understanding the history of a lava. However, if the minerals and host melts are not in isotopic equilibrium, it may be difficult to assume that they were in chemical equilibrium. For example, the clinopyroxene-melt thermobarometer of Putirka et al. [1996] makes use of mineral-melt exchange equilibria, and is sensitive to Al activities in the clinopyroxene and melt. However, at magmatic temperatures (~1200°C), Al [Sautter et al., 1996b] diffuses more slowly in clinopyroxene than Sr [Sneeringer et al., 1984] (note that the Al curve is the same as the Ca curve in Figure 6, as the diffusivities of Al and Ca in clinopyroxene are indistinguishable at 1200°C). Thus, if Sr isotopes in clinopyroxene are not in isotopic equilibrium with the host lava, then Al is unlikely to be in equilibrium, and it will not be possible to estimate the temperatures and pressures of clinopyroxene formation in such a lava. In order to effectively use similar mineral-melt thermobarometers, establishing isotopic equilibrium (or lack thereof) can help to strengthen (or weaken) the assumption of chemical equilibrium. For example, eight of the 10 lavas in this study fail to exhibit clinopyroxene-whole-rock $^{87}$Sr/$^{86}$Sr equilibrium, and would be poor candidates for a thermobarometry study.

4.4. Clinopyroxene-Whole-Rock Heterogeneity: Implications for Melt Extraction From a Heterogeneous Mantle

[38] Melt inclusions hosted in Samoan olivines may provide clues about the origin of the isotopic disequilibrium between Samoan lavas and the clinopyroxenes they host. In lavas where the melt inclusion $^{87}$Sr/$^{86}$Sr ratios have been examined, most preserve $^{87}$Sr/$^{86}$Sr compositions that are different from their respective host whole rocks [Jackson and Hart, 2006]. Heterogeneous $^{87}$Sr/$^{86}$Sr ratios recorded in olivine-hosted melt inclusions from individual Samoa basalts suggest that mixing of magmas from isotopically distinct sources is not uncommon in Samoa. Likewise, heterogeneous Pb isotopes recorded in melt inclusions from Hawaii, Iceland, Pitcairn, Mangaia and Tahaa lavas suggest that similar magma mixing processes operate in the magma plumbing systems of other hot spots [Saal et al., 1998, 2005; Jochum et al., 2004; Kobayashi et al., 2004; Maclennan, 2008].

[39] The mechanism generating the isotopic disequilibrium in the melt inclusions, mixing of magmas with different isotopic characteristics, is likely responsible for generating the different isotopic compositions in the clinopyroxenes. In this scenario, a population of clinopyroxenes preserves the isotopic composition of one of the various, isotopically distinct parental magmas contributing to the final mixture recorded in the whole-rock analyses. The question is how the several, isotopically distinct parental magmas contributing to a single lava acquired heterogeneous isotopic compositions in the first place.

[40] On the basis of Sr and Nd measurements of abyssal peridotites and orogenic lherzolites, the mantle is isotopically heterogeneous at the subkilometer scale [e.g., Reisberg and Zindler, 1986; Zindler and Hart, 1986a; Salters and Dick, 2002; Cipriani et al., 2004; Warren, 2007], a scale that is smaller than the dimensions of a melting column. This observation supports the work of Hofmann and Hart [1978], who suggested that diffusive processes would allow Sr and Nd heterogeneities to persist in the solid mantle at short length scales (1–10 m) over time scales of 10$^5$ years. However, owing to enhanced diffusion through a partial melt, isotopic heterogeneities in the mantle are more rapidly homogenized during partial melting [Kogiso et al., 2004]. Nonetheless, isotopic data
from abyssal peridotites indicate that isotopic heterogeneities in the mantle persist at the subkilometer scale following partial melting [Warren, 2007].

[41] The geometry of melting regimes beneath volcanoes may be conducive to sampling such heterogeneities, so that melts from more than one mantle source contribute to an erupted lava. The melting regime beneath a volcano has been suggested to have the geometric form of a fractal tree, where a multitude of branches sample the most distal regions of a melting column and these tributary branches converge (and mix melts) with other channels at progressively shallower depths [Hart, 1993]. If the various capillaries and branches at the most distal portions of such a “fractal tree” melting column sample a melting mantle that has short-length-scale isotopic heterogeneities (<1 km), different branches of a melting column will channel melts with different isotopic compositions. Isotopically heterogeneous melts will be mixed thoroughly when melt tributaries converge, or when magmas are injected into magma chambers, and the result is that much information about isotopic differences between the different parental magmas that contribute to a single erupted lava will be lost. Fortunately, clinopyroxene and olivine (which host melt inclusions) crystallize before final magma mixing and eruption of lavas, preserving information about the various melts that existed before mixing. Crystallizing olivines trap melts (melt inclusions) that record the isotopic compositions of the earliest parental melts before complete melt aggregation. Similarly, crystallizing clinopyroxenes appear to record some of the isotopic diversity hosted in the early parental melts that would have otherwise been lost during mixing of melts.

[42] The observation of clinopyroxene-whole-rock isotopic disequilibrium, along with numerous other observations of isotopic disequilibrium in melt inclusions, suggest that melts produced by a locally heterogeneous mantle source migrate and mix in a fractal-tree-like system. However, mixing is incomplete when the melts are delivered to a crustal magma chamber where final mixing takes place before eruption. This owes to the fact that clinopyroxene crystallization and melt inclusion entrapment occur prior to the homogenization of melts, thereby preserving some of the chemical and isotopic diversity of earlier melt compositions. In this way, melt inclusions and clinopyroxenes provide an important window to gain insights into the range of mantle heterogeneities sampled by a single lava, and ultimately the degree of heterogeneity in the mantle source sampled by hot spot volcanoes.

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