Discerning crystal growth from diffusion profiles in zoned olivine by in situ Mg–Fe isotopic analyses

Corliss Kin I Sio, Nicolas Dauphas, Fang-Zhen Teng, Marc Chaussidon, Rosalind T. Helz, Mathieu Roskosz

Abstract

Mineral zoning is used in diffusion-based geospeedometry to determine magmatic timescales. Progress in this field has been hampered by the challenge to discern mineral zoning produced by diffusion from concentration gradients inherited from crystal growth. A zoned olivine phenocryst from Kilauea Iki lava lake (Hawaii) was selected for this study to evaluate the potential of Mg and Fe isotopes for distinguishing these two processes. Microdrilling of the phenocryst (~300 µm drill holes) followed by MC-ICPMS analysis of the powders revealed negatively coupled Mg and Fe isotopic fractionations (δ26Mg from +0.1‰ to −0.2‰ and δ56Fe from −1.2‰ to −0.2‰ from core to rim), which can only be explained by Mg–Fe exchange between melt and olivine. The data can be explained with ratios of diffusivities of Mg and Fe isotopes in olivine scaling as D2/D1 = (m1/m2)b with bMg/26 = 0.16 and bFe/56 = 0.27. LA-MC-ICPMS and MC-SIMS Fe isotopic measurements are developed and are demonstrated to yield accurate δ56Fe measurements within precisions of ~0.2‰ (1 SD) at spatial resolutions of ~50 µm. δ56Fe and δ26Mg stay constant with Fo# in the rim (late-stage overgrowth), whereas in the core (original phenocryst) δ56Fe steeply trends toward lighter compositions and δ26Mg trends toward heavier compositions with higher Fo#. A plot of δ56Fe vs. Fo# immediately distinguishes growth-controlled from diffusion-controlled zoning in these two regions. The results are consistent with the idea that large isotopic fractionation accompanies chemical diffusion in crystals, whereas fractional crystallization induces little or no isotopic fractionation. The cooling timescale inferred from the chemical-isotope zoning profiles is consistent with the documented cooling history of the lava lake. In the absence of geologic context, in situ stable isotopic measurements may now be used to interpret the nature of mineral zoning. Stable isotope measurements by LA-MC-ICPMS and MC-SIMS can be used as standard petrologic tools to identify samples for diffusion-based geospeedometry. © 2013 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Chemical diffusion profiles in zoned minerals may be used to infer the thermal history of geological systems. Zoned plagioclase, olivine, and pyroxene have been used for such diffusion-based geospeedometry in igneous rocks (e.g., Grove et al., 1984; Costa and Chakraborty, 2004; Saunders et al., 2012, see Costa et al., 2008 for a review).
A major challenge with these methods is that diffusion-driven zoning cannot always be discerned from crystal growth zoning. That is, fractional crystallization in a solid solution series can produce identical chemical profiles as diffusive transport. Costa and Dungan (2005) suggested using multi-element models on a single crystal to recognize diffusion-controlled zoning. The idea is that diffusion rates are different for the multiple elements in olivine. If diffusion calculations for all profiles converge to the same magmatic timescale, it is likely that the zonings are diffusion-controlled. However, the mineral-melt partition coefficients and diffusion coefficients of minor elements are uncertain (Chakraborty, 2010; Spandler and O’Neill, 2010). Furthermore, model parameters (crystal growth, surface boundary conditions, crystal geometry, $/O_2$–P–T path) are often unknown. These difficulties make such an approach non-diagnostic of diffusive processes in complex systems. An unambiguous way to identify diffusive transport is to look into evidence recorded by the diffusing species. Such evidence is present in the form of isotopic variations along diffusion profiles (Beck et al., 2006; Teng et al., 2006; Dauphas, 2007; Jeffcoate et al., 2007; Parkinson et al., 2009; Gallagher and Elliott, 2009; Dohmen et al., 2010; Chopra et al., 2012).

Dauphas et al. (2010) and Teng et al. (2011) introduced a new isotopic method to unambiguously identify diffusion-driven zoning in minerals. Chemical diffusion can induce large isotopic fractionations because light isotopes always diffuse faster than their heavier counterparts (Richter et al., 2009b and references therein). Dauphas et al. (2010) calculated that Mg–Fe interdiffusion in olivine should result in a negative correlation of Mg and Fe isotopic compositions. Teng et al. (2011) reported this negative correlation of Mg and Fe isotopic compositions in olivine fragments from Kilauea Iki lava lake (Hawaii), which directly implicated Mg–Fe interdiffusion in controlling the stable isotopic compositions of these elements in olivine. The large Fe isotope variations measured in olivines from various basalts from Germany and the Canary Islands may also be due to diffusion but no isotopic profile or Mg–Fe isotope correlation was provided to ascertain the cause of these variations (Weyer and Seitz, 2012).

Here we report spatially resolved, negatively coupled Mg and Fe isotopic profiles in a single olivine from Kilauea Iki lava lake. By comparing with results from microdrilling, we show that laser-ablation multi-collector inductively coupled plasma mass spectrometry (LA-ICPMS) and multi-collector secondary ion mass spectrometry (MC-SIMS) can provide accurate Fe isotope measurements in zoned olivines at higher spatial resolutions than what is achievable by microdrilling, suggesting that these instruments can be powerful tools for understanding the nature of zoning in minerals.

2. SAMPLES

The Kilauea Iki lava lake was formed in 1959 by flow of magma into a pre-existing crater. The crust stabilized within a few days after the eruption, allowing the lava lake to act as a self-roofed magma chamber. The lava lake was drilled repeatedly since 1960 to monitor magmatic differentiation through time (Helz, 1980, 1987a). The drill cores have been extensively studied (e.g., Murata and Richter, 1966; Helz et al., 1989; Helz, 2009). Data on the compositions and equilibration temperatures of the drill cores were used to constrain the thermal history of the lava lake (Helz, 1987b; Helz and Thornber, 1987; Helz et al., in press).

Olivine has been identified as the only phenocryst in the lava lake (Helz, 1987b). It has been recognized that some of these olivines re-equilibrated with the evolving melt through Mg–Fe exchange during slow cooling (Helz, 1987b; Teng et al., 2011). A virtue of these samples is that diffusion models for olivine phenocrysts can be tested against observation – the cooling timescale is the time between the 1959 eruption and quenching of the samples by core drilling.

The sample KI81-5-254.5 (drill year 1981, core #5, 254.5 ft or 77.6 m depth) was selected for this study as it shows extensive zoning in olivine crystals (Teng et al., 2011). The olivine rim compositions, $\sim$Fo68 ($\text{Fo}_{\#} = 100 \times$ atomic Mg/[Mg + Fe]), are much more Fe-rich than those found in all other drill cores (Fo80) at similar depths (Helz et al., in press). Another important observation with this core (KI81-5) is that it was drilled only 6.9 m away from another core (KI81-1) that penetrated to a similar depth 3 weeks before (Helz and Wright, 1983). Furthermore, thermal and seismic experiments took place continuously before KI81-5 (our sample) was retrieved (e.g., Hardee et al., 1981). These observations suggest that the distinctively high Fe rims in the olivines in KI81-5-254.5 may be overgrowths resulting from the rapid cooling induced by nearby activities. As a result, we began this study under the hypothesis that the olivine phenocrysts in KI81-5-254.5 experienced two stages of thermal evolution. First, the phenocryst cooled slowly for 21.4 years in a magma of evolving composition (drilling date for KI81-1 minus eruption date), which was followed by a short stage of accelerated cooling (3 weeks) that led to the formation of the overgrowths.

A section of KI81-5-254.5 was made to expose a 4.5 mm × 2.7 mm olivine phenocryst. This sample was mounted in epoxy and polished. The olivine is anhedral, with overgrowth texture at the rim enclosing glass and smaller augite crystals, which grew in situ in the lava lake (Fig. 1a). The matrix consists of plagioclase laths, augite, ilmenite, glass, and groundmass olivines (2.3 vol.%).

For the development of in situ Fe isotopic measurements, a suite of natural olivine crystals was collected to evaluate the influence of sample matrix on measurements obtained by LA-ICPMS and MC-SIMS (see Table 1 for details). These olivines cover the whole solid solution from fayalite (Fo0) to forsterite (Fo100). All standards were mounted in epoxy and studied under the SEM. Fo0 (Rockport fayalite) contains inclusions of magnetite, biotite, and grunerite (Rose et al., 2009). Eight small fragments were dissolved, analyzed independently, and were found to have identical iron isotopic compositions. Fo0 and Fo10 are small and inclusion-free olivines (~200 μm) embedded in rock fragments. These olivines were crushed and extreme care was utilized in handpicking clear olivine fragments for solu-
tion MC-ICPMS measurements. Fo_{54} and Fo_{64} came as sorted grains of ~100 μm in diameter. Those single grains are unzoned but small compositional differences can be detected from grain to grain. Fo_{76} to Fo_{95} are large and homogenous grains that can be easily handpicked under a microscope.

3. METHODS

LA-MC-ICPMS and MC-SIMS provide high spatial resolution for in situ isotopic measurements. However, these techniques are susceptible to matrix effects – the influence of isotopic analyses of an element due to the presence
### Table 1
Characterization of olivine matrix standards.

<table>
<thead>
<tr>
<th>Fo# (EMPA)</th>
<th>Condition</th>
<th>Locality</th>
<th>Source</th>
<th>Catalogue #</th>
<th>Fo# (sol)</th>
<th>δ⁵⁶Fe</th>
<th>δ⁵⁷Fe</th>
<th>δ²⁵Mg</th>
<th>δ²⁶Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fo₀</td>
<td>Impure grain</td>
<td>Rockport, Massachusetts, USA</td>
<td>Chicago Field Museum M7652</td>
<td>0.17 ± 0.06</td>
<td>0.269 ± 0.035</td>
<td>0.394 ± 0.047</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Fo₆</td>
<td>Rock</td>
<td>Soutpansberg, Transvaal, South Africa</td>
<td>Chicago Field Museum M18152</td>
<td>0.14 ± 0.038</td>
<td>0.806 ± 0.048</td>
<td>1.157 ± 0.085</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Fo₁₆</td>
<td>Impure grains</td>
<td>Skaergaard, East Greenland</td>
<td>University of Chicago YS/EG4145</td>
<td>15.71 ± 1.62</td>
<td>0.065 ± 0.037</td>
<td>0.106 ± 0.052</td>
<td>0.140 ± 0.034</td>
<td>0.280 ± 0.054</td>
<td></td>
</tr>
<tr>
<td>Fo₅₄</td>
<td>Sorted grains</td>
<td>Vampula, Susimaki, Finland</td>
<td>Smithsonian Institute 135839</td>
<td>54.09 ± 2.70</td>
<td>0.020 ± 0.036</td>
<td>0.031 ± 0.049</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Fo₆₄</td>
<td>Sorted grains</td>
<td>–</td>
<td>University of Chicago TS 8</td>
<td>64.34 ± 0.98</td>
<td>0.351 ± 0.037</td>
<td>0.527 ± 0.052</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Fo₇₆</td>
<td>Rock</td>
<td>Haleakula Observatory</td>
<td>University of Chicago HM18</td>
<td>75.75 ± 0.48</td>
<td>0.084 ± 0.037</td>
<td>0.136 ± 0.052</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Fo₇₉</td>
<td>Rock</td>
<td>Moohoek, Transvaal, South Africa</td>
<td>Chicago Field Museum M18156</td>
<td>78.62 ± 0.44</td>
<td>0.048 ± 0.041</td>
<td>0.062 ± 0.060</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Fo₈₅</td>
<td>Single grain</td>
<td>Mt. Vesuvius, Italy</td>
<td>Chicago Field Museum M16636</td>
<td>85.39 ± 0.22</td>
<td>0.021 ± 0.038</td>
<td>0.045 ± 0.060</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Fo₈₈</td>
<td>Single grain</td>
<td>San Carlos, Arizona, USA</td>
<td>Chicago Field Museum M7688</td>
<td>88.44 ± 0.14</td>
<td>0.034 ± 0.038</td>
<td>0.080 ± 0.060</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Fo₉₀</td>
<td>Single grain</td>
<td>San Carlos, Arizona, USA</td>
<td>Chicago Field Museum H1849</td>
<td>90.49 ± 0.14</td>
<td>0.015 ± 0.038</td>
<td>0.026 ± 0.060</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Fo₉₁</td>
<td>Single grain</td>
<td>Navajo Nation, New Mexico, USA</td>
<td>Chicago Field Museum H1853</td>
<td>91.34 ± 0.14</td>
<td>0.031 ± 0.050</td>
<td>0.051 ± 0.061</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Fo₉₂</td>
<td>Grains</td>
<td>W North Carolina, USA</td>
<td>Chicago Field Museum M17315</td>
<td>91.89 ± 0.22</td>
<td>0.008 ± 0.050</td>
<td>0.019 ± 0.061</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Fo₉₅</td>
<td>Rock</td>
<td>Mt. Vesuvius, Italy</td>
<td>Chicago Field Museum M16643</td>
<td>95.22 ± 0.22</td>
<td>0.093 ± 0.036</td>
<td>0.154 ± 0.049</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

Fo# = 100 × atomic Mg/(Mg + Fe), δFe = [(Fe/²⁵²⁵Fe)sample] / (Fe/²⁵²⁵FeIRMM014) − 1] × 1000.

δMg = [(Mg/²⁴²⁴Mg)sample] / (Mg/²⁴²⁴MgDS3) − 1] × 1000.

Fo# (EMPA) were measured at Université de Lille 1. They are compared with Fo# (sol) measured by solution MC-ICPMS to show that only clean olivine fragments were dissolved for Fe and Mg isotopic analyses.

Uncertainties are 95% confidence intervals for Fe and Mg isotopes (Dauphas et al., 2009).

* This SC used as the bracketing standard for LA-MC-ICPMS measurements.
of other elements (e.g., Norman et al., 2006; Knight et al., 2009; Janney et al., 2011). For this reason, the $^{56}$Fe values of microdrilled samples and olivine standards were measured by solution MC-ICPMS for calibration and accuracy assessment of in situ measurements by LA-MC-ICPMS and MC-SIMS.

3.1. Chemical characterizations

Prior to isotopic measurements, more than 500 point-analyses on the olivine phenocryst were done using a JEOL SEM at the University of Chicago to generate the
Fig. 3. Schematic mounts used for LA-MC-ICPMS and MC-SIMS measurements. (a) The Kilauea Iki lava lake olivine phenocryst is spatially bracketed by San Carlos olivine (SC, marked R for right, L for left, T for top, and B for bottom). Each profile was measured 4 times along 4 directions in the sample chambers by rotating the mount $4 \times 90^\circ$. The matrix standards (Fo76 to Fo95) in this mount were not used for LA-MC-ICPMS matrix correction because they are not spatially bracketed by SC. These matrix standards were only used for MC-SIMS measurements. (b) Schematic matrix standard mount for MC-SIMS analyses in which all crystals were mounted in a restricted central area of the mount. The numbers indicate the Fo# of the matrix standards. The MC-SIMS iron isotopic compositions for Fo# between 76 to 95 were measured in both mounts (a and b) and were found to have identical compositions. (c) Schematic matrix standards mount specifically made for the LA-MC-ICPMS measurements to minimize the sample chamber position effect. Each matrix standard is spatially bracketed in all directions by SC. The numbers indicate the Fo# of the matrix standards. (d) Example of data collection by LA-MC-ICPMS for a horizontal traverse across the Kilauea Iki olivine phenocryst. Each spot measurement is bracketed in space and time. For example, to correct for instrumental and sample position effects a traverse measured from left to right will be measured in a sequence LSC, sample, RSC, sample, LSC, and so on.
compositional map shown in Fig. 1b. All analyses done on cracks or that did not sum to olivine stoichiometry were discarded.

After the LA-MC-ICPMS and MC-SIMS sessions, the olivine phenocryst was analyzed by electron-probe in order to determine the chemical composition at each measurement spot and to correct for matrix-induced instrumental mass fractionation (IMF) on the Fe isotopic measurements. Mg, Si, Fe, and Ni concentrations were measured by a Cameca SX100 microprobe at the Université de Lille 1, France (15 kV, 15 nA). In this same session, the Fo# for all olivine standards were also measured. Each Fo# is the average of at least ten analyses over a large grain or many small grains.

Al, Ca, Cr, and Fe profiles from the core to the rim of the olivine phenocryst were made using a Cameca SX-50 electron-probe at the University of Chicago (20 kV, 150 nA, Fig. 2). Backgrounds were collected between each point analysis, and X-rays intensities were acquired for 30 s at each position. Points were manually selected so as to avoid cracks in the sample. In this session, all concentrations were determined by comparing measured counts to in-house standards using the technique of Bence and Albee (1968) with a-factors from Albee and Ray (1970).

3.2. Crystallographic orientation of olivine

Because Mg–Fe interdiffusion in olivine is strongly anisotropic (Buening and Buseck, 1973; Misener, 1974; Chakraborty, 1997), it is important to calculate the appropriate 2ΣMg–Fe to use along the traverses where chemical-isotopic profiles were taken (Costa et al., 2008). Two focused ion beam (FIB) sections were cut parallel to the surface of the olivine phenocryst, close to the 3rd and the 11th microdrill holes along the horizontal profile (marked as or-...
the San Carlos olivine standard (SC = Fo 90, spot size 70 μm), different spot diameters were used for the rim (40 μm) and the rest of the olivine phenocryst (55 μm). Data reduction was done using an in-house Fortran code to remove transient points at sample introduction and termination. A total of 15 cycles were used for each spot analysis.

To correct for isobaric interference on 54Fe, 54Cr was calculated from 53Cr intensity, assuming that they had the same instrumental bias as iron (57Fe/56Fe ratio). For detailed technique discussions, the reader is referred to the Supplementary materials.

Initial tests to measure iron isotopic compositions by LA-MC-ICPMS revealed that a position-dependent artifact was present, which could only be corrected by surrounding the sample with standards. As a result, the sample was remounted and re-polished, resulting in the erosion or disappearance of microdrill holes.

Each spot analyzed was bracketed in space and in time (see Fig. 3a and d). Analyses were done in straight lines with sample alternatively bracketed by SC on either side of the profiles. Tests done to evaluate this position effect suggested that linear interpolation of the 56Fe/54Fe ratios of SC at each position was the best way to correct for the position effect. A further strategy was adopted to remove any bias introduced by the location of the spot analysis in the sample chamber. Each profile was analyzed four times, each time rotating the mount about its center by 90° from its previous position in the sample chamber. For example, the first position measured widely spaced points across the horizontal and vertical profiles. Then, the mount was taken out, rotated by 90°, and reinserted into the sample chamber. New spots were chosen adjacent to the previous spots. The process was repeated 2 more times to arrive at 4 repeat analyses across the same traverse. This procedure yielded values relative to SC (δ56FeSC/LA) that still have to be corrected for matrix effect.

A special epoxy mount was made for the olivine matrix standards: each sample with a given Fo# was surrounded on four sides by SC (Fig. 3c). Measurements were made on the matrix standards by alternatively bracketing them five times in the left and right directions, followed by five times in the up and down directions. This method is effective in minimizing sample chamber position effects, because SC spatially bracketed by itself shows no resolvable fractionation (0.01 ± 0.8‰, 1 SD). This procedure yields matrix-induced shifts in δ56Fe, which can be used to correct for the instrumental mass fractionation (IMF),

\[
\Delta^\text{Fe}(\text{std Fo#})(\text{IMF, LA}) = \delta^\text{Fe}_{SC} - [\delta^\text{Fe}_{IRMM}^{\text{sol}} + \delta^\text{Fe}_{IRMM}^{\text{sol}}].
\]

The IMF curve shows a positive relationship with Fo#. SigmaPlot was used to generate a linear regression for the data points (Fig. 4a). The 68% confidence interval was used as the uncertainty for the IMF correction.
The IMF-corrected sample value relative to IRMM014 is therefore,

$$\delta^{56}\text{Fe}_{\text{IRMM}}(\text{LA}) = \delta^{56}\text{Fe}_{\text{SC}}(\text{LA}) - \Delta^{56}\text{Fe}(\text{smp Fo#})/(\text{IMF}, \text{LA}) + \delta^{56}\text{Fe}_{\text{IRMM}}(\text{sol}),$$

where the value of $\Delta^{56}\text{Fe}$ depends on the sample Fo#, calculated from the average of four EMPA analyses done around each crater after the LA-MC-ICPMS measurements. The errors on the Fo# are estimated to be 0.5 (2 SD).

For each of the four profiles made on the same traverse in four directions by sample rotation, Fe isotopic compositions are linearly interpolated between data points. Each final data point is reported as an average of one actual LA-MC-ICPMS analysis, and up to three interpolated points. The error bars are calculated by quadratically combining errors (“E,” all 1 SD); point-to-point reproducibility after correcting for the sample chamber position effect ($=E_{\text{amp}}$ $\approx 0.16\%$ on $^{56}\text{Fe}$ and $\approx 0.23\%$ on $^{57}\text{Fe}$, based on tests ran on a large SC grain), uncertainty in the IMF regression ($=E_{\text{IMF}}$ $\approx 0.04\%$ on $^{56}\text{Fe}$ and $\approx 0.06\%$ on $^{57}\text{Fe}$), and uncertainty in the solution MC-ICPMS measurement of SC olivine ($=E_{\text{SC}}$ $\approx 0.02\%$ on $^{56}\text{Fe}$ and $\approx 0.03\%$ on $^{57}\text{Fe}$). The overall uncertainty is:

$$E(\text{LA}) = \sqrt{(E_{\text{amp}}(\text{LA}))^2 + (E_{\text{IMF}}(\text{LA}))^2 + (E_{\text{SC}}(\text{LA}))^2}.$$  

### 3.6. MC-SIMS

Analyses were carried out using a multi-collector IMS 1280-HR ion probe at CRPG-CNRS, Nancy, France. The sample was sputtered with O$^-$ beam at a current of $\approx 60$ nA and 13 kV acceleration voltage. This beam produced craters of $\approx 30$ by 80 $\mu$m and several microns deep. Secondary ions were accelerated at 10 kV and analyzed at a mass resolving power (M/AM) of $\approx 4800$. Typical signal on $^{54}\text{Fe}$ for the olivine phenocry was $1-2 \times 10^6$ cps. Isotopes $^{54}\text{Fe}$, $^{56}\text{Fe}$, and $^{57}\text{Fe}$ were collected in Faraday cups while $^{52}\text{Cr}$ was collected on an electron multiplier. The interference of $^{52}\text{Cr}$ on $^{54}\text{Fe}$ was corrected by assuming that the instrumental fractionation for Cr was the same as that measured for Fe isotopes. After Cr-correction all data plot on a mass fractionation line for $^{57}\text{Fe}/^{54}\text{Fe}$ vs. $^{56}\text{Fe}/^{54}\text{Fe}$. For each analysis, a pre-sputtering time of 120 s was used. A single analysis consisted of 50 cycles with 5 s integration time.

In an effort to evaluate whether the measurements were affected by the sample location in the sample chamber, the same isotopic traverse was measured in 4 different directions as was done for the LA-MC-ICPMS measurements. This involved breaking the vacuum, physically rotating the mount about its center by 90º, and putting it back in vacuum for measurement in at different locations in the chamber.

All MC-SIMS iron isotopic compositions are calculated as follows:

$$\delta^{56}\text{Fe} = \left[\left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{unknown}} - 1\right] \times 10^3,$$

where in this case, $^{56}\text{Fe}_{\text{IRMM014}}$ is the certified IRMM014 ratio of $^{57}\text{Fe}/^{56}\text{Fe}$ (0.36257) and internally normalized ratio of $^{56}\text{Fe}/^{54}\text{Fe}$ (15.7044) based on MC-ICPMS measurements (Schoenberg and von Blanckenburg, 2005; this study; see Supplementary material). Measurements on the matrix standards from F076 to F095 were done on two separate mounts, with or without the Kilauea Iki olivine phenocryst (Fig. 3a and b, respectively). Matrix standards from F076 to F095 were measured 10 to 28 times each, with analyses spread across the two mounts. Iron isotopic measurements for each Fo# in the two mounts gave identical results within 1 SD uncertainty. The more Fe-rich matrix standards were measured 2 to 8 times for each standard with a given Fo#. These measurements were used to evaluate the effect of sample matrix on instrumental mass fractionation:

$$\Delta^{56}\text{Fe}(\text{std Fo#})/(\text{IMF, SIMS}) = \delta^{56}\text{Fe}_{\text{std Fo#}}(\text{SIMS}) - \delta^{56}\text{Fe}_{\text{IRMM}}(\text{smp Fo#})/(\text{IMF, SIMS}).$$

As with LA-MC-ICPMS, the IMF curve for MC-SIMS also defines a positive correlation. SigmaPlot was used to run a second order polynomial regression through the data points (Fig. 4b). A 68% confidence interval was calculated for the regression as an assessment of the uncertainty of IMF correction.

The IMF-corrected values for the olivine phenocry are reported relative to IRMM014:

$$\delta^{56}\text{Fe}_{\text{IRMM}}(\text{SIMS}) = \delta^{56}\text{Fe}_{\text{IRMM}}(\text{smp Fo#})/(\text{IMF, SIMS}).$$

In a manner similar to that used for LA-MC-ICPMS analyses, the value of $\Delta^{56}\text{Fe}$ depends on the Fo# of each sputtered spot, calculated from the average of four EMPA analyses done around each ion beam spot.

The reported values are calculated in a similar manner as was done for LA-MC-ICPMS: one actual measurement and up to 3 interpolated points were averaged. The overall uncertainty is also calculated the same way, where the point-to-point reproducibility ($=E_{\text{amp}}$ $\approx 0.25\%$ on $^{56}\text{Fe}$ and $0.32\%$ on $^{57}\text{Fe}$) is added quadratically to the uncertainty in IMF correction ($=E_{\text{IMF}}$ $\approx 0.11\%$ on $^{56}\text{Fe}$ and $\approx 0.23\%$ on $^{57}\text{Fe}$).

$$E(\text{SIMS}) = \sqrt{(E_{\text{amp}}(\text{SIMS}))^2 + (E_{\text{IMF}}(\text{SIMS}))^2}.$$  

### 4. RESULTS

#### 4.1. SEM and EMPA

SEM analyses done prior to in situ isotopic measurements revealed that the most Mg-rich composition lies on the right side of the phenocry (refer to the color image of Fig. 1b). The rim of the olivine has a range of compositions from Fo66 to Fo72.

The chemical analysis obtained after in situ isotopic measurements revealed the presence of two Mg-rich cores with normal zonings (Fo83 on the left side and Fo3.6 on the right side). The joint zoning could result from a peanut-shaped crystal or from synneusis (attachment of crystals). Approximately 95% by mass of Kilauea Iki oli-
Fig. 5. Microdrill solution MC-ICPMS data for (a) the horizontal and (b) the vertical profiles. The curves represent diffusion models using \( \beta_{\text{Fe}} = 0.27 \) and \( \beta_{\text{Mg}} = 0.16 \). (c) \( \delta^{56}\text{Fe} \) and \( \delta^{26}\text{Mg} \) are plotted against the Fo# of the solutions. (d) \( \delta^{56}\text{Fe} \) plotted against \( \delta^{26}\text{Mg} \); the slope is \( \sim 3.69 \pm 0.39 \), similar to that reported by Teng et al. (2011) for bulk olivine fragments from the same sample KI81-5-254.5 (plotted in open symbols). The Mg isotopes (orange squares) were measured at the University of Arkansas. The Fe isotopes (blue circles) and Fo# were measured at the University of Chicago. Some error bars are smaller than the sizes of the symbols.

Table 2
Fe and Mg isotopic compositions of powders microdrilled from the Kilauea Iki olivine phenocryst (KI81-5-254.5), obtained by solution MC-ICPMS.

<table>
<thead>
<tr>
<th>Spot #</th>
<th>Dist. (mm)</th>
<th>Fo#</th>
<th>( \delta^{56}\text{Fe} )</th>
<th>( \delta^{57}\text{Fe} )</th>
<th>( \delta^{25}\text{Mg} )</th>
<th>( \delta^{26}\text{Mg} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Horizontal profile</strong></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1</td>
<td>0.15</td>
<td>75.6</td>
<td>-0.300 ± 0.047</td>
<td>-0.424 ± 0.059</td>
<td>-0.040 ± 0.037</td>
<td>-0.132 ± 0.048</td>
</tr>
<tr>
<td>2</td>
<td>0.39</td>
<td>79.5</td>
<td>-0.316 ± 0.045</td>
<td>-0.466 ± 0.057</td>
<td>-0.135 ± 0.059</td>
<td>-0.183 ± 0.080</td>
</tr>
<tr>
<td>3</td>
<td>0.60</td>
<td>81.2</td>
<td>-0.269 ± 0.045</td>
<td>-0.383 ± 0.057</td>
<td>-0.139 ± 0.044</td>
<td>-0.205 ± 0.063</td>
</tr>
<tr>
<td>4</td>
<td>0.91</td>
<td>81.3</td>
<td>-0.323 ± 0.047</td>
<td>-0.479 ± 0.072</td>
<td>-0.103 ± 0.059</td>
<td>-0.206 ± 0.080</td>
</tr>
<tr>
<td>5</td>
<td>1.19</td>
<td>81.1</td>
<td>-0.321 ± 0.047</td>
<td>-0.466 ± 0.072</td>
<td>-0.124 ± 0.044</td>
<td>-0.226 ± 0.063</td>
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<tr>
<td>6</td>
<td>1.43</td>
<td>80.8</td>
<td>-0.339 ± 0.054</td>
<td>-0.435 ± 0.083</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>1.74</td>
<td>80.3</td>
<td>-0.486 ± 0.047</td>
<td>-0.698 ± 0.072</td>
<td>-0.090 ± 0.037</td>
<td>-0.166 ± 0.048</td>
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<tr>
<td>8</td>
<td>2.13</td>
<td>82.9</td>
<td>-0.773 ± 0.048</td>
<td>-1.166 ± 0.085</td>
<td>-0.042 ± 0.037</td>
<td>-0.074 ± 0.048</td>
</tr>
<tr>
<td>9</td>
<td>2.47</td>
<td>82.7</td>
<td>-1.096 ± 0.054</td>
<td>-1.637 ± 0.083</td>
<td>0.024 ± 0.035</td>
<td>0.048 ± 0.048</td>
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<td>10</td>
<td>3.00</td>
<td>85.0</td>
<td>-1.164 ± 0.054</td>
<td>-1.791 ± 0.083</td>
<td>0.056 ± 0.040</td>
<td>0.094 ± 0.063</td>
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<tr>
<td>11</td>
<td>3.33</td>
<td>82.9</td>
<td>-1.117 ± 0.050</td>
<td>-1.654 ± 0.077</td>
<td>-</td>
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</tr>
<tr>
<td>12</td>
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<td>-1.167 ± 0.060</td>
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<td>13</td>
<td>4.03</td>
<td>79.8</td>
<td>-0.422 ± 0.049</td>
<td>-0.629 ± 0.066</td>
<td>-0.098 ± 0.031</td>
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<tr>
<td>14</td>
<td>4.27</td>
<td>76.2</td>
<td>-0.184 ± 0.049</td>
<td>-0.269 ± 0.066</td>
<td>-0.117 ± 0.065</td>
<td>-0.151 ± 0.100</td>
</tr>
<tr>
<td><strong>Vertical profile</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.15</td>
<td>78.3</td>
<td>-0.241 ± 0.050</td>
<td>-0.361 ± 0.056</td>
<td>-0.102 ± 0.057</td>
<td>-0.224 ± 0.087</td>
</tr>
<tr>
<td>2</td>
<td>0.45</td>
<td>80.8</td>
<td>-0.290 ± 0.050</td>
<td>-0.445 ± 0.056</td>
<td>-0.099 ± 0.057</td>
<td>-0.211 ± 0.087</td>
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<tr>
<td>3</td>
<td>0.77</td>
<td>82.6</td>
<td>-0.619 ± 0.050</td>
<td>-0.942 ± 0.056</td>
<td>-0.051 ± 0.057</td>
<td>-0.123 ± 0.087</td>
</tr>
<tr>
<td>4</td>
<td>1.07</td>
<td>82.9</td>
<td>-1.088 ± 0.050</td>
<td>-1.573 ± 0.056</td>
<td>-0.010 ± 0.057</td>
<td>-0.009 ± 0.087</td>
</tr>
<tr>
<td>5</td>
<td>1.32</td>
<td>83.2</td>
<td>-1.108 ± 0.057</td>
<td>-1.678 ± 0.119</td>
<td>0.020 ± 0.043</td>
<td>0.043 ± 0.066</td>
</tr>
<tr>
<td>6</td>
<td>1.56</td>
<td>80.6</td>
<td>-0.948 ± 0.050</td>
<td>-1.422 ± 0.056</td>
<td>0.000 ± 0.037</td>
<td>-0.027 ± 0.049</td>
</tr>
<tr>
<td>7</td>
<td>1.93</td>
<td>77.1</td>
<td>-0.378 ± 0.050</td>
<td>-0.568 ± 0.056</td>
<td>-0.040 ± 0.043</td>
<td>-0.127 ± 0.066</td>
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<tr>
<td>8</td>
<td>2.20</td>
<td>70.7</td>
<td>-0.160 ± 0.050</td>
<td>-0.237 ± 0.056</td>
<td>-0.058 ± 0.057</td>
<td>-0.134 ± 0.066</td>
</tr>
</tbody>
</table>

Distances are given relative to the left or top edges of the olivine (marked “H0” and “V0”, Fig. 1c).

Fo# and delta notations are explained in Table 1.

Fo# were measured by solution MC-ICPMS. The same solutions were used for Fe and Mg isotopic analyses. Uncertainties are 95% confidence intervals for Fe and Mg isotopes.
vines from the 1959 eruption scoria studied by Schwindinger and Anderson (1989) are affected by synneusis and most attached crystals have similar crystallographic orientations. Synneusis was also observed in the lava lake samples (this study; see Supplementary material). Only the side that contains the vertical profile (right side) was used in the diffusion model.

Minor elements analyses reveal that CaO, Al$_2$O$_3$, Cr$_2$O$_3$, and NiO concentrations are zoned. Following the suggestion of Costa et al. (2008), we plotted the minor element concentrations against Fo# to test whether the minor elements would show changes in behavior reflecting different zoning regimes (diffusion-controlled vs. growth-controlled zoning). Fig. 2 shows that Cr$_2$O$_3$ and NiO wt% display simple positive correlations with Fo# across the entire range of Fo#, while Al$_2$O$_3$ wt% is flat from the core to Fo$_{80}$ and then decreases with Fo#. By contrast, CaO wt% is negatively correlated with Fo# from the core to Fo$_{80}$, and the correlation becomes positive from Fo$_{80}$ to the olivine rim. This change reflects the onset of augite and plagioclase crystallization, but does not provide any clue on the nature of the process that established the profile. The rim more Fe-rich than Fo$_{80}$ could have grown when augite and plagioclase were crystallizing. The presence of augite crystals embedded in the olivine rim indicates that this is a plausible hypothesis. Alternatively, the phenocryst was initially homogeneous in CaO wt%, but augite and plagioclase crystallization changed the boundary Ca concentration, which propagated into the crystal by diffusion.

4.2. Crystallographic orientation of olivine

The two FIB sections, taken close to the Mg-rich cores of the phenocryst, were found to have identical crystallo-
graphic orientation, which was confirmed using a petrographic microscope. The stereographic projections are shown in Fig. 1a.

4.3. FTIR

Characteristic FTIR spectra of three olivine single grains from K181-5-254.5 were compared to a reference olivine (“Kaapvaal” in Fig. S1), which has a comparable crystallographic orientation and is known to contain 19 ppm H₂O (Fig. S1; Ingrin and Grégoire, 2010). The absorbances were normalized to the sample thicknesses. Typical bands of hydroxyl in olivine are barely resolved in the Kilauea Iki olivine phenocrysts, indicating that the water content is less than 1 ppm. The total water content is estimated to be close to 0.3 ppm using the conventional calibration of Bell et al. (2003).

4.4. Microdrilling and solution MC-ICPMS

The δ²⁶Mg and δ⁵⁶Fe values of the microdrilled spots are negatively correlated; δ²⁶Mg ranges from +0.99‰ to −0.23‰, and δ⁵⁶Fe ranges from −1.23‰ to −0.16‰ from core to rim (Fig. 5; Table 2). The ranges of isotopic compositions are consistent with previously reported values for Kilauea Iki olivine fragments (see Fig. 5d; Teng et al., 2008, 2011). Teng et al. (2011) reported a negative correlation for δ²⁶Mg and δ⁵⁶Fe but for the first time, this relationship is spatially resolved through traverses across a single olivine crystal.

The Fo# measured for the drilled samples and the olivine matrix standards were close to the expected values. To evaluate the precision and accuracy of the Fo# determination by solution, four geostandards, UBN, BIR1a, W2a, and AVG were measured in the same session. The expected Fo# are 89.26, 62.85, 53.66, 34.52, and the measured numbers are 89.37, 63.21, 53.49, 34.38, respectively. These geostandard measurements give an overall uncertainty of ~0.5 (2 SD) for the Fo# of the microdrilled samples and olivine standards, which were also measured to check purity of handpicked grains.

4.5. LA-MC-ICPMS

The difference in Δ⁵⁶Fe(Fo#)<IMF, LA> between rim and core of the Kilauea Iki olivine phenocryst is only ~0.18‰.

Iron isotopic compositions range from +0.13‰ at the rim to ~1.10‰ at the core (Fig. 6c and f; Table 3). The error bars of ~0.16‰ on δ⁵⁶Fe (1 SD) are realistic given the
sample chamber position effect. To assess the error bars without this effect, a single SC grain was analyzed more than 60 times, and the 1 SD value was 0.05 \% on $\delta^{56}$Fe, and 0.07 \% on $\delta^{57}$Fe. These errors are similar to those reported by Graham et al. (2004), Kösler et al. (2005), Horn et al. (2006), and Steinhoefel et al. (2009), but smaller than that reported by Hirata and Ohno (2001) and Nishizawa et al. (2010).

4.6. MC-SIMS

The difference in $\Delta^{56}$Fe(Fo\#)<IMF, SIMS> between rim and core of the olivine is $\sim 1.3$ \%, which is about the range of iron isotopic fractionation measured in the olivine phenocryst.

The final Fe isotopic compositions range from $-1.28$ \% to $+0.32$ \% from core to rim (Fig. 7c and f; Table 4). The point-to-point reproducibility of $\sim 0.25$ \% on $\delta^{56}$Fe (1 SD) is similar to that reported by Whitehouse and Fedo (2007) but larger than that reported by Marin-Carbonne et al. (2011). Precision on $\delta^{57}$Fe ($\sim 0.32$ \%, 1 SD) has not been reported previously. The internal precision given by counting statistics was $\sim 0.02$ \% on $\delta^{56}$Fe and $\sim 0.04$ \% on $\delta^{57}$Fe (1 SD/$\sqrt{n}$ with $n = 50$) for the olivine phenocryst.

4.7. Isotopic profiles

The profiles measured by microdrilling, MC-SIMS, and LA-MC-ICPMS are all very similar. For the horizontal traverse (Fig. 8a), relatively flat profiles are seen on the left followed by U-shape profiles. For the vertical profile (Fig. 8b), only the U-shape can be seen. Although the three datasets independently show the same features, direct comparison is not straightforward because the profiles are not immediately adjacent to one another. Because Fo\# is a function of distance, Fe isotopic compositions can be plotted against Fo\#. Such a plot shows excellent agreement between the three techniques (Fig. 8c). The isotopic compositions in the Fe-rich region for LA-MC-ICPMS and MC-SIMS data are the least constrained because only one or two measurements could be made.

Different trends of $\delta^{56}$Fe and $\delta^{26}$Mg vs. Fo\# can be seen. At compositions more Mg-rich than Fo\#80, $\delta^{56}$Fe values are steeply sloping toward lighter compositions, and $\delta^{26}$Mg...
values are sloping toward heavier compositions (Figs. 5 and 8). At compositions more Fe-rich than Fo80, $\delta^{56}$Fe and $\delta^{56}$Mg stay constant (Figs. 5 and 8). The significance of these trends will be discussed below.

### 5. DISCUSSION

#### 5.1. Origin of isotope zoning profiles

Possible mechanisms to explain the Mg and Fe isotopic profiles are (1) Rayleigh distillation attending fractional crystallization with equilibrium isotopic fractionation at the interface between melt and crystal, (2) diffusion-limited growth for the olivine crystal, (3) Mg–Fe exchange of the olivine phenocryst, which is opposite to the expectation for a Rayleigh distillation driven by fractional crystallization from a finite melt volume (Teng et al., 2008). The rim should display the largest isotopic shift from the bulk, as it is where the last increment of crystal growth should have occurred from the most evolved melt. In the olivine analyzed, the rim has $\delta^{56}$Mg and $\delta^{56}$Fe values close to the bulk and is therefore little fractionated isotopically.

During rapid growth, transport of elements from and to the growing crystal surface can be limited by diffusion in the liquid medium, which can impart kinetic isotope fractionation (Dauphas and Rouxel, 2006; Watson and Müller, 2009; DePaolo, 2011). The degree of isotopic fractionation is directly proportional to the elemental partitioning ratio, $K$, between olivine and melts (Watson and Müller, 2009). The $K_{\text{FeO}}$ is $\sim$1.7, and the $K_{\text{MgO}}$ is $\sim$5.6 at 1130 °C (Roeder and Emslie, 1970). Given similar Mg and Fe diffusivities in a basaltic melt at 1130 °C ($D_{\text{Mg}} \sim 5 \times 10^{-12} \text{ m}^2/\text{s}$, Chen and Zhang, 2008; $D_{\text{Fe}} \sim 10^{-12} \text{ m}^2/\text{s}$, Lowry et al., 1982) and $f_{\text{Fe}} \sim 0.05$, $f_{\text{Fe}} \sim 0.03$ in silicate melts (Richter et al., 2009a), Mg and Fe isotopes should be fractionated in the same direction and fractionation in $\delta^{56}$Mg should be an order of magnitude higher than that of $\delta^{56}$Fe. The Kilauea Iki olivine phenocryst, however, shows negatively correlated Mg and Fe isotopic compositions and variation in $\delta^{56}$Mg is only about 1/3 of that in $\delta^{56}$Fe. As a result, the isotopic fractionation observed cannot be attributed to diffusion-limited growth.

Evidence points toward Mg–Fe interdiffusion as the explanation for the negatively coupled Mg and Fe isotopic fractionations (Dauphas et al., 2010; Teng et al., 2011).
Petrographic observation suggests that melt compositions had evolved to be less Mg-rich following the 1959 eruption (Helz and Thornber, 1987). In order to re-equilibrate, Mg has to diffuse out of and Fe has to diffuse into the olivine phenocryst. Because light isotopes diffuse faster than their heavy counterparts (e.g., Richter et al., 2009b), light Mg isotopes are enriched in the rim of the olivine. Conversely, light Fe isotopes are enriched in the center of the olivine. Thus, $\delta^{26}$Mg and $\delta^{56}$Fe are negatively coupled because they diffuse in opposite directions. Magnesium isotopes have a larger relative mass difference, so that isotopic fractionations are expected to be larger. However, this large fractionation is diluted by a larger background of isotopically unfractonated Mg.

A plot of $\delta^{56}$Fe and $\delta^{26}$Mg vs. $\text{Fo#}$ reveals that for spots more Fe-rich than $\text{Fo}_{80}$, the Fe and Mg isotopic compositions are constant, dramatically different from the trends observed for the higher $\text{Fo#}$ (Figs. 5 and 8). The flatness in $\delta^{56}$Fe and in $\delta^{26}$Mg suggests that the anomalously Fe-rich region (more Fe-rich than $\text{Fo}_{80}$) was unaffected by diffusion. This is consistent with our hypothesis discussed in Section 2 that olivine with $\text{Fo#} < 80$ is late-stage overgrowth. From $\text{Fo}_{80}$ to the core, the zoning is controlled by chemical diffusion.

The two-stage thermal history of KI81-5-254.5 exemplifies the virtue of using Mg and Fe isotopes to identify diffusive zoning in minerals. If zoning is due to fractional crystallization without re-equilibration through diffusion, no or little Mg and Fe isotopic fractionation should be detected. If zoning is diffusion-controlled, large and negatively correlated variations in Mg and Fe isotopes should be produced.

### 5.2. Diffusion model

Here, we model the chemical-isotopic profiles of the region affected by diffusion ($\text{Fo#} > 80$; Sections 2 and 5.1). The model is also limited to the right side of the phenocryst, which contains the vertical profile and the more Mg-rich core (Sections 2 and 4.1).

Spherical geometry for the olivine is assumed, and the partial differential equation used for composition dependent diffusion is:

$$\frac{\partial X_{\text{Mg}}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D \frac{\partial X_{\text{Mg}}}{\partial r} \right),$$

where $X_{\text{Mg}}$ is the mole fraction of Mg in olivine $[\text{Mg}/(\text{Mg} + \text{Fe})]$, $t$ is time, and $r$ is the radial distance from the center of the sphere. The diffusion coefficient, $D$, is a
function of temperature, pressure, oxygen fugacity, and Fe content of the olivine, parameterized by Dohmen and Chakraborty (2007). The PDE is solved using Mathematica and the embedded finite difference method. The mathematical code is provided in Electronic Annex.

Solution to the PDE requires two boundary conditions. One is given by the condition of the spherical geometry, with no flux at the center of the crystal:

$$\frac{\partial X_{Mg}}{\partial r} = 0, \quad r = 0.$$

The other boundary condition describes the Fo content at the rim of the olivine as a function of temperature in the lava lake, $X_{Mg}(T(t), r = a)$, where $T$ is temperature, $t$ is time, and $a$ is the radius of the olivine (see Section 5.2.2).

5.2.1. Temperature and initial conditions

Chemical diffusion occurred at the onset of the 1959 eruption that formed the Kilauea Iki lava lake. Prior to eruption, temperature in the magma chamber was close to 1230 °C, and olivine phenocrysts had a constant composition of Fo$_{90.5}$ (Helz et al., in press). Therefore, the initial conditions are:

$$T_0 = 1230 \degree C; \quad X_{Mg}(T_0, r = T_{Mg,0} = 0.865.$$

The erupted magma rapidly cooled to the initial temperature of the lava lake, 1190 °C (Helz, 2009; Helz et al., in press). The present study assumes that the temperature drop from 1230 to 1190 °C occurred during the eruption period of 36 days. Peck et al. (1977) and Helz et al. (in press) showed that the lava lakes of ‘Alae and Kilauea Iki cooled in the conductive cooling regime, which is described by an error function. The thermal evolution at the center of the lava lake is therefore (shown in Fig. 9):

$$T(t) = \begin{cases} T_0 - \frac{T_0 - T_i}{\Delta t} \times t & 0 \leq t \leq 36 \text{ days} \\ T_i \times \text{erf} \left( \frac{c}{36} \right) & 36 \text{ days} < t \end{cases}$$

where $T_0$ is the pre-eruption temperature, $T_i$ is the initial lava lake temperature, $t$ is time, $\Delta t$ is duration of the eruption (=36 days), and $c$ is a time constant.

5.2.2. Boundary condition at olivine rim

Helz and Thornber (1987) found empirically that the Mg content in the melt decreases linearly with temperature. The rim composition of olivine also evolves as a function of temperature (Helz, 1987b; Helz et al., in press):

$$X_{Mg}(T(t), a) = \frac{T_0 \times X_{Mg,0} - T_i \times X_{Mg,0}}{T_0 - T_i} + T(t) \times \frac{X_{Mg,0} - X_{Mg,0}}{T_0 - T_i}$$

where $X_{Mg,0}$ is the rim composition of the olivine at the time of quenching by core drilling, and $T_q$ is the temperature at quench.

Note that $X_{Mg,0}$ and $T_q$ were not obtained directly from the phenocryst of the present study. As discussed in Sections 2 and 5.1, this olivine went through a late-stage of rapid growth unique to K181-5 core samples, so the values of a more pristine drill core (K181-1) were used ($X_{Mg,0} = 0.80, T_q = 1130 \degree C; \quad Helz et al., in press).

5.2.3. Olivine growth accompanying chemical diffusion

The olivine phenocryst could have grown during its residence time in the lava lake. The size of this growth rim was assessed by studying a sample that did not experience late-stage overgrowth. Particularly, the sizes of groundmass olivines and the sizes of phenocryst rims that enclose augite crystals were measured in a thin section of KI79-1-189.0 (Fig. S2). By both methods, it was found that the phenocrysts grew less than 100 μm in radius, which is small.
compared to the radius of the phenocryst. Therefore, crystal growth can be neglected in the diffusion calculation.

5.2.4. Modeling isotopic fractionations

It is assumed that diffusivities scale as the masses of the isotopes involved. The empirical formula from Richter et al. (1999) is used:

\[ D_{i,1} = \left( \frac{m_{i,2}}{m_{i,1}} \right)^{\beta_i} \]

where 1 and 2 are isotopes of element i, which is Fe or Mg in this study. The \( \beta \)-exponents are estimated by fitting the isotopic profiles. It is worth noting that \( \beta \)-values depend strongly on the boundary conditions used in the modeling. Reasonable estimates may be obtained from natural samples only if their boundary conditions are well constrained. This highlights the virtue of laboratory experiments, from which determinations of \( \beta \)-values can help to constrain boundary conditions for natural systems.

A list of variables and the values used in the diffusion model can be found in Table 5.

5.3. Modeling results

For the observed cooling timescale of 21.4 years and at the crystallographic directions of the chemical-isotopic profiles, the parameterization of Dohmen and Chakraborty (2007) predicts a \( \Delta_{\text{Mg-Fe}} \) that is too low by a factor of ~4 relative to what is needed to explain the diffusion profiles. The measured water content by FTIR is only ~0.3 ppm, much less than the 10 ppm required for water to affect the rate of Mg-Fe interdiffusion in olivine (Hier-Majumder et al., 2005; Costa and Chakraborty, 2008). Dohmen and Chakraborty (2007) quoted half an order of magnitude uncertainty on predicted \( D_{\text{Mg-Fe}} \) values, so the inconsistency may only be apparent.

The \( \beta_{\text{Fe}} \) and \( \beta_{\text{Mg}} \) extracted from the diffusion model (Figs. 5 and 8) are insensitive to the \( D_{\text{Mg-Fe}} \) values (i.e., changing the radius of crystal and \( D_{\text{Mg-Fe}} \) simultaneously to reproduce the range of Fo48 does not change \( \beta \)-values required to reproduce the range of isotopic fractionations). However, the \( \beta \)-values are sensitive to the surface boundary conditions, which is driven by the thermal evolution of the lava lake.

The \( \beta \)-exponents required to reproduce the isotopic profiles are \( \beta_{\text{Mg}} \sim 0.16 \), and \( \beta_{\text{Fe}} \sim 0.27 \) (Figs. 5 and 8). Changing model parameters within acceptable ranges yields uncertainties of ~±0.05 in \( \beta_{\text{Mg}} \) and ~±0.04 in \( \beta_{\text{Fe}} \). The slope of \( \delta^{26}\text{Fe} \) vs. \( \delta^{28}\text{Mg} \) measured in the olivine phenocryst constrains the \( \beta_{\text{Fe}}/\beta_{\text{Mg}} \) ratio to be 1.8±0.3 (Fig. 5d; Dauphas et al. 2010). The estimated \( \beta_{\text{Mg}} \) is higher than those found in basalt-rhyolite melt couples (\( \beta_{\text{Mg}} \sim 0.05 \), Richter et al., 2009a), but similar to those found in anorthite-diopside melts (\( \beta_{\text{Mg}} \sim 0.1 \), Watkins et al., 2011), MgO liquids (\( \beta_{\text{Mg}} \sim 0.1 \), theoretical estimate, Tsuchiyama et al., 1994), and MgSiO3 liquids (\( \beta_{\text{Mg}} \sim 0.14 \), theoretical estimate, Goel et al., 2012). The estimated \( \beta_{\text{Fe}} \) is also higher than those found in basalt-rhyolite melt couples (\( \beta_{\text{Fe}} \sim 0.03 \), Richter et al., 2009a), but similar to those found in metallic alloys (\( \beta_{\text{Fe}} \sim 0.3 \); Mullen, 1961; Roskosz et al., 2006; Dauphas, 2007 and references therein). The similarity in \( \beta_{\text{Fe}} \) values between olivine and metals may suggest that crystalline materials have higher \( \beta \)-values than liquids. Further experimental work is needed to test this hypothesis and to ascertain the \( \beta \)-values estimated in this study.

5.4. Future applications to natural olivines

The Kilauea Iki olivine phenocryst is unique in the sense that core drilling and thorough petrologic studies provide many constraints for the diffusion model. In most other cases, modeling parameters would be more poorly constrained. Here we discuss how close one can approximate magmatic timescales using measurements constrained by a thin section and by knowing the original lava composition. In particular, we treat Kilauea Iki olivine as a case study by posing the question: what timescale would we have obtained if the olivine that we studied came from a random rock with little geologic context?

We applied the MELTS algorithm (Ghiorso and Sack, 1995) to estimate how boundary conditions evolve with falling temperature given a starting composition. The most magnesian glass composition in the eruption pumice in Table 25.4 of Helz (1987b) was taken as the original lava composition. From the MELTS algorithm, the calculated liquidus temperature is 1231 °C at NNO, corresponding to an equilibrium olivine composition of Fo85.5, which would be the assumed starting olivine composition. At 1145 °C, the olivine reaches Fo80 (rim of olivine phenocryst) marking quenching of the sample. An error function is used to model conductive cooling, which is a good assumption for igneous bodies, and proven to work well for the 1963 ‘Alae and the 1959 Kilauea Iki lava lakes (Section 5.2.1). Following this study, a factor of 4 in \( D_{\text{Mg-Fe}} \) is applied to the oriented olivine in both vertical and horizontal traverses.

The retrieved cooling timescales are 19.8 and 47.8 years for the vertical and horizontal traverses, respectively. The difference in the timescales results from the uncertainty in the geometry of the olivine. In some studies, linear cooling was assumed (e.g., Miyamoto et al., 1986); this cooling regime will generate timescales of 8.5 and 25.5 years for the vertical and horizontal profiles, respectively. Overall, the MELTS application is able to retrieve the cooling timescales of the lava lake, paying attention to the choice of \( fO_2 \), starting composition, and crystallographic orientation of the olivine.

6. CONCLUSION

It has been previously recognized that diffusive transport in olivine is accompanied by large Mg and Fe isotopic fractionations (Dauphas et al., 2010; Teng et al., 2011). For the first time, these isotopic fractionations are spatially resolved using in situ measurements. We calibrated LA-ICPMS and MC-SIMS using microdrilling followed by solution MC-ICPMS to show that accurate Fe isotopic measurements can be obtained. The ability to resolve diffusion-driven isotopic fractionations for the major elements in zoned olivine has significant implications
for the field of diffusion-based geospeedometry: diffusion-controlled zoning may now be unambiguously teased apart from growth-controlled zoning, as the former process is accompanied with large isotopic fractionations. Using the Fe and Mg isotopic measurements, we discerned a core olivine composition that was affected by diffusion and a rim overgrowth that also shows some zoning but was not affected by diffusion. Chemically, the overgrowth cannot be distinguished from the core, demonstrating the usefulness of isotopic measurements to recognize diffusion in zoned minerals.

As in situ stable isotopic measurements can be done routinely using matrix-matched standards, we propose that these techniques be used as standard petrologic tools for the study of zoned minerals in igneous and metamorphic rocks. It remains to be investigated whether other commonly zoned minerals such as garnet, pyroxenes, plagioclase, and oxides display similar diffusion-driven, intra-crystalline isotopic profiles.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2013.06.008.

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