Controlled Cooling-Rate Experiments on Olivine-Hosted Melt Inclusions: Chemical Diffusion and Quantification of Eruptive Cooling Rates on Hawaii and Mars

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Abstract
Controlled cooling-rate experiments were conducted on olivine-hosted melt inclusions to characterize the development of compositional zoning observed in natural inclusions. All of the experimentally cooled inclusions are zoned due to olivine crystallization on the inclusion wall and diffusive exchange between the boundary layer adjacent to the growing olivine and the inclusion centers. Experimentally cooled inclusions are characterized by lower MgO and FeO and higher SiO₂, Al₂O₃, and Na₂O (and other incompatible oxides) near the inclusion wall relative to the inclusion center. The compositions at the centers of inclusions are susceptible to modification by diffusion, particularly for small inclusions and those subjected to low cooling rates. Uphill diffusion is evident in every oxide and is recognized by local extrema along a diffusion profile. CaO exhibits the most extreme manifestation of uphill diffusion, and a model attributes the diffusion behavior in CaO to solution nonideality in the boundary layer liquid. MgO profiles from experimentally cooled inclusions were fit with a diffusion model by varying the cooling rate. The cooling rates that resulted in the best fit models were always within a factor of 2 and typically within ±10% of the experimental cooling rates, which ranged from 70 to 50,000 °C/hr. The model was applied to MgO profiles across natural glassy olivine-hosted melt inclusions from Hawaii and the shergottite Yamato 980459. Cooling rates from zoned melt inclusions in Yamato 980459 range from 85 to 1,047 °C/hr (mean = 383±43 °C/hr, 1σ, n=8) and support the hypothesis that the sample erupted at or near the Martian surface.

Plain Language Summary
Melt inclusions, which are small amounts of magma that become trapped within a growing crystal, are widely used by geologists as snapshots of the chemical evolution of magmas as they cool and crystallize. We performed a set of experiments that simulated the cooling of magmas by subjecting olivine crystals containing melt inclusions to a range of cooling rates. We then exposed the melt inclusions and measured the chemical zonation that developed during cooling. The experiments demonstrate that on the relatively short timescales of eruptions, the compositions of melt inclusions can be drastically changed. The diffusion equation, which was modified in a numerical code to describe a melt inclusion, was used to model the experimental zonation data. The cooling rates that resulted in the best fit model matched the known experimental rates to within a factor of 2, which is very accurate given that the experimental rates ranged from 70 to 50,000 °C/hr. The model was used to calculate the cooling rates of natural inclusions with unknown cooling histories from Hawaii and a meteorite from Mars. The results for the Martian meteorite support the hypothesis that the sample represents a magma that cooled rapidly, likely as a lava flow on the Martian surface.

1. Introduction
Efforts to analyze the compositions of glass inclusions in natural crystals at high spatial resolution have demonstrated that concentration gradients are preserved near the interface between the glass and its host (e.g., Anderson, 1974; Goodrich et al., 2001; Danyushevsky, Sokolov, & Falloon, 2002; Mercier, 2009; Colin et al., 2012; Newcombe et al., 2014; Manzini et al., 2017; Drignon et al., 2019). These concentration gradients are interpreted as having been generated by diffusive relaxation of a compositional boundary layer in the liquid that forms as the host mineral crystallizes on the inclusion wall during cooling (Albarede & Bottinga, 1972; Danyushevsky et al., 2000; Newcombe et al., 2014; Watson, 1982; Zhang, 1989). As the host phase crystallizes from the melt inclusion, the adjacent liquid becomes progressively depleted in components that are compatible in the host phase (e.g., MgO and FeO in olivine) and enriched in incompatible components.
components that are excluded from the growing crystal. Compositional zoning develops from continuous diffusive exchange between the evolving liquid at the boundary with the host phase and the liquid in the center of the melt inclusion. Zonation is preserved in glass inclusions that are cooled sufficiently rapidly such that the concentration gradients generated during cooling do not have time to homogenize by diffusion.

Newcombe et al. (2014) developed a model for the evolution of one-dimensional diffusion profiles in olivine-saturated spherical melt inclusions during cooling. By varying the cooling history, the authors fit this model to MgO concentration profiles measured in natural inclusions. Best fit cooling histories assume constant cooling rates for inclusions from the Siqueros Fracture Zone (subaqueous mid-ocean ridge basalt: cooling rates of 400–4,200 °C/hr) and from the Galapagos Islands plume (subaerial: 4,400–12,700 °C/hr, and subaqueous: 155 and 4,400 °C/hr) overlap with the range of eruptive cooling rates for terrestrial lavas calculated by independent methods such as enthalpy relaxation speedometry in basaltic glasses (e.g., Nichols et al., 2009; Wilding et al., 2000) and H2O speciation kinetics in rhyolitic glasses (Xu & Zhang, 2002).

In this paper, we report the results of a series of 1-atm controlled cooling experiments conducted on olivine-hosted melt inclusions to explore the cooling rate-dependent evolution of compositional zoning and to test the accuracy of determining cooling rates by inverting observed concentration gradients in MgO. The experiments support the interpretation that the zonation observed in melt inclusions is generated during syneruptive cooling of the host magma by the competing effects of the crystallization of olivine on the inclusion wall and diffusive exchange between melt at this boundary and in the interior of the melt inclusion. Subject to various assumptions (section 4), the model olivine-inclusion system can be used to retrieve cooling rates that accurately recover the measured cooling rates of the experiments conducted over ~3 orders of magnitude to within a factor of 2 or better (typically within ±10% relative). We conclude that because melt inclusions are common, microprobe analyses are routine, and diffusion in the liquid is rapid relative to that in solids, compositional zonation at melt-crystal boundaries has potential as a tool for quantifying the late-stage thermal histories of rapidly cooled geologic samples.

2. Methods

2.1. Sample Selection

Olivine-rich sand was collected by M. B. Baker from Papakolea Beach (Pu‘u Mahana), ~3 miles northeast of South Point, Hawaii (18°56′N, 155°38′W). The sands are remnants of 28 kyr wave-eroded olivine basalt flows and ash beds (Rubin et al., 1987), interpreted to be either a littoral cone (Stearns & Macdonald, 1947) or a primary ash vent (Walker, 1992) on the southern flank of Mauna Loa. Olivine grains 1–3 mm in largest dimension containing roughly spherical, glassy melt inclusions were separated from beach detritus under an optical microscope. Glassy inclusions were typically 100–150 μm in largest dimension and up to 250 μm across. Olivines that contained at least one roughly spherical inclusion ≥75 μm across were selected as starting materials for use in experiments. In transmitted light, glassy inclusions were orange-brown and translucent (Figure 1) but occasionally were clouded by clusters of olivine and pyroxene crystals. When such crystalline phases exceeded approximately several volume percent, an inclusion was rejected as a potential sample. Similarly, olivine crystals that had obvious alteration features (e.g., surface oxidation, etch pits, and pervasive cracks) were discarded. The glassy inclusions chosen for the experiments all contained an exsolved vapor bubble and minor (less than a few volume percent) Cr-Al-rich spinel, recognized as opaque octahedra usually attached to the inclusion wall or vapor bubble. Small, roughly spherical sulfide blebs (<5-μm diameter) were observed in a few natural inclusions, usually at the inclusion wall.

In total, 55 olivine grains containing one or more suitable melt inclusions were used in experiments and subsequently recovered and quantitatively analyzed. Optical microphotographs of a typical inclusion taken through the host olivine suspended in isopropanol before and after an experiment are shown in Figure 1. An additional 10 inclusion-bearing olivines were not reheated (hereafter referred to as natural as opposed to experimental); these were studied to characterize the zoning profiles in naturally occurring olivine and glass compositions for comparison with experimentally treated samples. Experimental inclusions are labeled according to the scheme H#X#, where the first number corresponds to the experiment (e.g., H2X) and the second to a particular olivine grain (e.g., H2X1 and H2X2). If more than one inclusion was analyzed in a single olivine grain, then they are distinguished by adding “_#” to the label (e.g., inclusions H5X4_1 and
H5X4_2). Homogenized inclusions are indicated by the letters XC in the sample name, e.g., H10XC1. Natural inclusions from Papakolea Beach are labeled HIGS#.

In addition to the 10 natural melt inclusions from Papakolea Beach, one melt inclusion in each of four olivines from sand in the Kilauea Iki crater was also studied (labeled KIO#), as were eight melt inclusions in five olivines from a polished thin section of the Yamato 980459 (Y980459) shergottite meteorite (labeled Y98MI#), on loan from the Japanese National Institute for Polar Research. The Kilauea Iki melt inclusions are petrographically similar from the Papakolea samples, and the melt inclusions from Y984059 are described in more detail in section 6.2.

2.2. Experimental Procedures

Homogenization and cooling experiments were run in a 1-atm Deltech vertical gas-mixing furnace. Two or three MgO buckets (drilled to a depth of ~3.5 mm), each containing 3–6 olivine grains, were suspended in the furnace hotspot from an MgO rod with 0.127-mm Pt hanging wire, adjacent to a Type-S thermocouple. This thermocouple was calibrated at the melting point of gold. In most experiments, the buckets were gradually lowered into the hotspot and held isothermally at 1,225 °C for 24 hr in order to homogenize the melt inclusions and to equilibrate the inclusions with the $\Delta F_{\text{O}_2}$ of the furnace gas (Bucholz et al., 2013; Gaetani et al., 2012). One set of experiments, H10X, was homogenized at 1,260 °C for 24 hr. Temperature was monitored and recorded manually throughout the isothermal heating period and then recorded digitally during cooling using a temperature logger (Omega UTC-USB, one measurement per second) connected to the Type-S thermocouple. For all experiments, after 24 hr of homogenization, one of the olivine-bearing buckets was drop-quenched into water by fusing the Pt hanging wire.

Immediately after quenching the first bucket, cooling was initiated and the remaining buckets were subjected to a controlled thermal history. For cooling rates of 70–1,570 °C/hr (six experiments), linear cooling to a set point of 800 °C was programmed using a Eurotherm controller attached to a Type B thermocouple near the furnace elements. For most experiments, the cooling olivine-bearing buckets were drop-quenched in water when the thermocouple adjacent to the sample read 1,000 °C. To monitor time- and temperature-dependent changes in the experiments during cooling, two sets of experiments (H2X at 1,570 °C/hr and H11X at 466 °C/hr) were quenched at multiple temperatures between 1,225 and 1,000 °C (H2X) or 900°C (H11X). Due to a limit on how fast the furnace can reject heat, cooling rates ≥1,600 °C/hr were achieved in two sets of experiments (H4X and H9X) by manually displacing downward the rod on...
Experimental Conditions

<table>
<thead>
<tr>
<th>Name</th>
<th>Homogenization temperature (°C)</th>
<th>Quench temp °C (n)</th>
<th>Stage 1 cooling rate (°C/hr)</th>
<th>Stage 2 cooling rate (°C/hr)</th>
<th>Cooling method</th>
<th>emf</th>
<th>log₁₀(O₂) (bars)</th>
<th>ΔFMQ</th>
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<tr>
<td>H2X</td>
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<td>1,160 (2), 1,070 (2), 1,000 (5)</td>
<td>1,570</td>
<td>-</td>
<td>T.C. Controlled</td>
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<td>-9.18</td>
<td>-1.16</td>
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<tr>
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<td>1,000 (5)</td>
<td>49,640</td>
<td>-</td>
<td>Displacement</td>
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<td>-9.18</td>
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<td>1,225</td>
<td>1,225 (2), 1,000 (4)</td>
<td>715</td>
<td>-</td>
<td>T.C. Controlled</td>
<td>-682</td>
<td>-9.18</td>
<td>-1.16</td>
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<tr>
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<td>1,225 (2), 1,000 (3)</td>
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<td>-</td>
<td>T.C. Controlled</td>
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<td>-9.15</td>
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<td>-</td>
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<td>93</td>
<td>859</td>
<td>T.C. Controlled</td>
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<td>466</td>
<td>-</td>
<td>T.C. Controlled</td>
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<td>-9.18</td>
<td>-1.16</td>
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* a = number of olivine recovered and polished to expose melt inclusions.
  b = See section 2.2 for details.
  c = Measured with Y-stabilized Zr oxygen sensor in furnace. 

which the olivine-bearing buckets were suspended, such that the samples moved out of the furnace hotspot into a cooler part of the furnace in less than 2 s. In order to monitor temperature during cooling using this displacement method, a Type S thermocouple was placed inside an empty MgO bucket and attached to the same rod that carried the olivine container so they moved out of the hotspot in tandem (see Figure S1 in the supporting information for a schematic diagram of the experimental setup). For the two experiments cooled using this displacement method, the temperature at the displaced position was 415 °C (H4X) and 930 °C (H9X). The cooling olivine-bearing buckets in the displacement experiments were quenched in water when the digital thermocouple output read 1,000 °C. Finally, the experiment held at 1,260 °C for 24 hr, H10X, did not cool on a single linear t-T path as did all the others, but rather was broken into two cooling segments: 1,260 to 1,134 °C at 93 °C/hr and 1,134 to 1,000 °C at 859 °C/hr. Table 1 details the experimental run conditions for all of the experiments. Thermocouple data from the experiments are shown in Figure 2 and described in more detail in section 3.1.

Oxygen fugacity was controlled using an H₂CO₂ gas mixture that was calibrated with a Y-stabilized Zr oxygen sensor. For all runs, the gas mixture was fixed (14% H₂ and 86% CO₂, by volume) such that the JO₂ at the temperature of the hotspot during the 24-hr homogenization step at 1,225 °C was ΔFMQ = -1.15 ± 0.07 (log₁₀ relative to fayalite-magnetite-quartz (FMQ) buffer (FMQ); Frost, 1991). Note that experiment H10X, which was homogenized at 1,260 °C, was run under the slightly more reducing conditions of ΔFMQ = -1.34 (Table 1). The uncertainty in the measured JO₂ is ~0.05 log units based on bracketing the Fe→FeO reaction in the furnace and monitoring emf fluctuations of the oxygen sensor during the isothermal homogenization step. During cooling from 1,225 °C, the mixing ratio of the gas was unchanged, resulting in a progressive decrease in the furnace JO₂ to ΔFMQ = -1.8 at 1,000 °C based on monitoring of the oxygen sensor; this is slightly more reducing than the expected change in JO₂ to ΔFMQ = -1.6 if the H₂CO₂ gas maintained equilibrium down to 1,000 °C (Beckett & Mendybaev, 1997). The JO₂ for the experiments was chosen to be within the range of calculated JO₂ values based on wet chemically determined Fe⁴⁺/Fe⁵⁺ of glasses from Mauna Loa lava flows (ΔFMQ = -2.5 to +1, with 10 of 15 samples within 0.5 log units of ΔFMQ = -1; Rhodes & Vollinger, 2005).

After the completion of the experiments, Dr. Mary Peterson measured one doubly polished experimental inclusion homogenized at 1,225 °C and quenched in water and two unheated Papakolea inclusions using Fe X-ray absorption near-edge structure spectroscopy (XANES) at the Advanced Photon Source, Argonne National Laboratory. One additional experimental inclusion and two unheated Papakolea inclusions were measured in a second XANES session by Dr. Maryjo Brounce (see the supporting information of Brounce et al., 2017, for details of XANES methods and data reduction). The four unheated Papakolea inclusions, each with two analyses at the inclusion center, yielded Fe⁴⁺/Fe_total ranging from 0.16–0.17 (inclusion HIGS21) to 0.20 (inclusion HIGS14; Table S1 in the supporting information). This ratio of ferric to total iron in the Papakolea glass compositions corresponds to ΔFMQ = +0.2 to +0.6 (Kress & Carmichael, 1991), which is considerably more oxidizing than the JO₂ of the gas mixture used in the heating/cooling experiments. The two experimentally homogenized inclusions (H7XC1 and H11XC1) were each measured twice with XANES and yielded Fe⁴⁺/Fe_total of 0.06–0.07 and 0.07, respectively, which corresponds to a range of
ΔFMQ = −1.7 to −2.3 at 1,225 °C based on Kress and Carmichael (1991). The Fe³⁺/Fe₅₀ ratio of the homogenized melt inclusions decreased significantly during the 24-hr homogenization step, suggesting that the inclusions were in communication with the gas mixture outside their olivine hosts during the homogenization step of the experiments. However, at 0.06–0.07, their measured Fe³⁺/Fe₅₀ ratios are lower than the values of ~0.10 that would be expected based on the Kress and Carmichael model if the melt inclusion had equilibrated with the gas mixture in the furnace. This difference may be an artifact related to the accuracy of the measurement at low Fe³⁺ contents, or perhaps due to the fact that Kress and Carmichael (and other available parameterizations of fO₂ vs. Fe³⁺/Fe₂⁺) were calibrated with sulfur-free liquids. Preliminary XANES data on homogenization experiments at higher fO₂ indicate that the measured Fe³⁺ is systematically lower than that predicted by Kress and Carmichael (1991), but when plotted as \( \log_{10}(\text{Fe}^{3+}/\text{Fe}^{2+}) \) vs. \( \log_{10}(\text{fO}_2) \), the data have the predicted slope of 0.2. In any case, the decrease in Fe³⁺/Fe₅₀ during the experiments from values of 0.16–0.19 based on the XANES analyses of unheated Papakolea glass inclusions to the lower values in the experimentally homogenized inclusions (Fe³⁺/Fe₅₀ = 0.06–0.07) is consistent with the fO₂ of the experimentally heated inclusions having changed by interaction with the furnace atmosphere across the olivine host during the 24-hr homogenization period (Bucholz et al., 2013; Gaetani et al., 2012). It is unlikely that during the controlled
cooling phase of the experiments, the changing $fO_2$ of the furnace was transmitted through the olivine to the melt inclusions due to the relatively short durations of cooling (Figure 2) and the exponential decrease in diffusivities with decreasing temperature (Bucholz et al., 2013). To determine H$_2$O contents, one doubly polished experimentally homogenized inclusion (H7XC1) and four doubly polished natural inclusion samples were measured using Fourier transform infrared spectroscopy (Figure S2 and Table 1). Based on the intensity of the absorbance at 3,550 cm$^{-1}$, a molar absorptivity of 63.8 L · mol$^{-1}$ · cm$^{-1}$ (Mercier et al., 2010), and an approximate glass density of 2.7 g cm$^{-3}$, the natural glassy olivine-hosted melt inclusions from Papakolea contain 0.10–0.27 wt % H$_2$O ($n$ = 4; 2σ = 0.02–0.04 wt %), within the range of published values for unheated Mauna Loa olivine-hosted melt inclusions (Hauri, 2002; Sobolev et al., 2000; Wallace et al., 2015). The single experimentally homogenized inclusion H7XC1 we measured has a water content of 383–388 ppm, suggesting that the inclusion lost most of its water during the isothermal homogenization step. This value is higher than but on the same order as the calculated solubility of ~250 ppm H$_2$O in anorthite-diopside liquid at the $p$H$_2$O ($\approx$0.12 bars) of the furnace atmosphere at the experimental conditions (Newcombe et al., 2017).

2.3. Sample Analysis

For electron microprobe analysis, the olivine grains were mounted in epoxy and ground down using alumina papers to expose the largest melt inclusion (if there were multiple inclusions) near its center. When the target melt inclusion center was maximally exposed, several other inclusions were often partially exposed at the polished surface. Bright phases in the inclusions include both sulfides (panels b–d) and Cr-Al spinel (panels b and f). Contraction cracks are visible in all of the panels, and sometimes penetrate into the glass inclusion. The natural inclusions (not pictured here) look essentially the same as the experimental samples (e.g., see Figure 1a), except for the higher crack density in the experimental olivine in the latter. The thick translucent lines show the locations of high spatial resolution microprobe traverses (point beam analyses separated by 1.5- to 2-μm increments), which are shown in Figures 7, 8, and 12 from the same samples in the same 2×3 grid order. Crack-filling bright residue (e.g., panel e) is metal contamination from polishing.
exposed, including in a few cases an additional relatively large melt inclusion as much as several tens of microns across. The sample surface was then polished with increasingly fine diamond powder from 2- to 0.25-μm grit, cleaned with ethanol, and carbon coated.

Concentration profiles of major and minor oxides were measured in both natural and experimentally treated melt inclusions along transects extending from the enclosing host olivine on one side of an inclusion, across its center, and then back out into the olivine on the opposite side using Caltech’s JEOL JXA-8200 electron microprobe. Transects were selected to avoid vapor bubbles, spinel, and sulfide exposed on the polished surface, although in some cases the transects passed close to them. The electron beam was focused to <1 μm, and analyses were spaced 1.5–2 μm apart with a 10-nA beam current and 15-keV accelerating voltage. Backscattered electron images were acquired of all the inclusions that we studied; a subset of the images of experimentally heated and cooled inclusions is shown in Figure 3, including for each inclusion the locations of the microprobe traverses shown in Figures 7, 8, and 12.

Quantitative wavelength-dispersive analyses were done by measuring standards (listed in Table 2), periodically analyzing secondary glass standards, and correcting data using a modified ZAF procedure (Armstrong, 1988). Secondary glass standards (U.S. Geological Survey BHVO-2g and BIR-1g) were analyzed 3 times before and after each microprobe traverse to account for instrumental drift; however, this information was not used for data correction. To assess accuracy, the analyses of the secondary glass standards from fifteen analytical sessions were averaged to determine the percent deviations from preferred reference values compiled in the GeoReM database (Jochum et al., 2006): +2.87% for SiO2, −5.95% for TiO2, −1.65% for Al2O3, ±2.19% for FeO, −0.28% for MgO, −0.63% for CaO, −5.66% for Na2O, −14.46% for K2O, ±5.78% for MnO, and +12.65% for P2O5. As a measure of intrasession accuracy, 30 replicate analyses of BIR-1g in a single session gave standard deviations relative to the mean of 0.28% for SiO2, 3.8% for TiO2, 0.98% for Al2O3, 0.98% for FeO, 1.02% for MgO, 0.47% for CaO, 2.78% for Na2O, 39.68% for K2O, 9.65% for MnO, and 54.96% for P2O5.

3. Results

3.1. Natural Olivine and Glass Inclusions (Unheated)

Compositions were measured for 10 unheated olivines from Papakolea, Hawaii, and their melt inclusions in order to establish the compositional range of olivines and melt inclusions in the starting materials. These samples provide a baseline for comparison with experimentally treated olivines and inclusions, which could not be exposed and measured prior to the experiments. For an individual grain, the olivine composition was defined by averaging 10 analyses from the end of a microprobe traverse that was >150 μm away from a melt inclusion and at least 50 μm from the crystal edge. These analyses are referred to as the “far-field” olivine, which typically define compositional plateaus in the olivines (unless the host olivine was zoned) and are
not strongly influenced by the presence of a melt inclusion (see section 3.5 for details on zoning in olivine around the inclusions). The average of the mean forsterite contents (Fo = 100 × MgO/(MgO+FeO)) of the measured far-field olivine analyses is Fo87.8 (±1.9) (n = 10 olivine, where the number in the parentheses is 2σ of the distribution of means). When compared with previously published compositions for Mauna Loa olivine, the Papakolea compositions overlap with the previous analyses (Figure S3) and are concentrated near the forsteritic end of the range. We note here that the average far-field olivine composition of the experimentally treated population (Fo87.9 (±1.7) [n = 55]; yellow squares in Figure S3) is indistinguishable from the unheated olivine. Table 2 lists the average far-field olivine composition of the 65 analyzed olivines from Papakolea, which includes the 10 natural and 55 experimental samples.

All of the natural glass inclusions are zoned. Near the inclusion wall, MgO and FeO are low and SiO2, Al2O3, Na2O, and K2O are high relative to the inclusion center (Figures 4a and 4b). CaO was observed to be either high (Figure 4a) or low (Figure 4b) adjacent to the inclusion wall, a phenomenon that has been attributed to uphill diffusion in the liquid (Newcombe et al., 2014) and is discussed in detail in section 5. In five of the natural inclusions, there is a broad compositional plateau across the inclusion center and a narrow zone affected by diffusion near the inclusion wall (see sample HIGS9; Figure 4a), whereas in the remaining five, some or all of the oxide profiles are zoned across the entire inclusion (for example, MgO in sample HIGS6; Figure 4b). A bulk composition was calculated for each inclusion by approximating the inclusion as a sphere and numerically integrating each oxide profile across the inclusion. Corresponding average glass compositions (n = 10) span the following ranges: SiO2 = 52–55 wt %, TiO2 = 1.8–2.3 wt %, Al2O3 = 12–15 wt %, FeO* = 5.8–9.4 wt %, MgO = 6.2–7.2 wt %, Na2O = 1.9–2.4 wt %, K2O = 0.2–0.4 wt %, MnO = 0.11–0.16 wt %, and P2O5 = 0.1–0.3 wt %. The compositional zonation in the natural unheated glassy melt inclusions is discussed in more detail in section 6.

### 3.2. Temperature-Time Paths of Cooling Experiments

Temperature was recorded during cooling using a digital logger attached to the Type-S thermocouple placed next to the olivine in the furnace hotspot (Figure 2). We chose to fit the temperature-time curves with lines (including each of the two roughly linear cooling segments in experiment H10X), and with the exception of experiment H9X (Figure 2c), the linear approximations fit the data with r² > 0.9935. As described in section 2.2, experiments H4X and H9X were manually displaced from the hotspot in order to achieve high cooling rates. Because these two samples were displaced into a colder spot in the furnace, the measured thermal histories follow asymptotic temperature-time paths (Figure 2b), compared to the approximately linear cooling paths in the more slowly cooled experiments in which cooling was imposed by the Type-B control thermocouple (Figure 2a). For experiment H4X, the total duration of cooling was only 16 s and sufficiently rapid such that the cooling path from 1,225 to 1,000 °C corresponded to the steep initial limb of the asymptotic cooling curve, which is nearly linear (Figure 2c; r² = 0.9935, giving a linear rate of 49,644 °C/hr). In experiment H9X, the temperature-time curve between 1,225 and 1,000 °C has more curvature, and a parabolic fit (r² = 0.9986) is a better approximation than linear (r² = 0.9642), and the best fit polynomial curve intersects t = 0 at 1,242 °C, which is well above the actual homogenization temperature of 1,225 °C. For the purposes of the paper, for experiment H9X, we use the best fit linear rate of 20,190 °C/hr (Figure 2c).

The best fit linear cooling rates for each experiment are listed in Figure 2 and in Table 2.

### 3.3. Textural Description of Experimental Samples

Olivine grains recovered from the experiments were first examined in transmitted light using an optical microscope. Cracks were pervasive in many experimentally quenched olivine grains, making individual inclusions difficult to see and photograph in transmitted light. Based on examination of the quenched samples in reflected light and in back-scattered electron imaging, cracks sometimes penetrated partially into the inclusions (e.g., Figures 3a, 3d, and 3e) suggesting that they were glassy prior to crack propagation, consistent with the fact that no melt was observed to have penetrated cracks in the olivine. These cracks probably formed due to contraction by thermal shock during the rapid drop-quench from high temperatures into room temperature water.

Optical images of samples taken before and after experimental homogenization do not show any significant change in inclusion volume or in its location within the olivine grain (Figure 1). A vapor bubble was present in all natural inclusions prior to the experiments, as well as in the inclusions quenched after the
homogenization for 24 hr at 1,225 or 1,260 °C. The vapor bubbles did not change position or size significantly during the experiments, although rarely a second vapor bubble formed and the original bubble shrank (e.g., Figure 1). Spinel crystals present inside the inclusions prior to experiments were not observed to change size or location during the experiment.

Opaque spherules are present in the experimentally heated inclusions and were determined by wavelength-dispersive analyses to be sulfides of composition Fe$_{28.54}$Cu$_{1.4}$Ni$_{7.32}$S$_{21.36}$ ($n = 6$). Such sulfide blebs are found in at least one inclusion in 80% of the experimental olivines and are often spatially associated with the inclusion wall and vapor bubble (Figure 3c). Comparison of images of the inclusions before and after the experiments demonstrates that most (but not all) of these blebs formed during reheating. The formation of immiscible sulfide liquids is consistent with the reduced experimental conditions ($\Delta$FMQ ≈ −1), which

Figure 4. (left column, a and b) Microprobe traverses across selected natural unheated inclusions and (right column, c and d) experimentally homogenized and cooled inclusions from Papakolea, Hawaii. The shaded rectangles in c and d show the 2σ range about the mean value measured for each oxide across all inclusions experimentally homogenized at 1,225 °C and quenched in water (Table 2; the values exclude liquid near the inclusion wall influenced by quench crystallization; see section 3.4.1 and Figure 5). The vertical grey bars indicate the boundary between glass (interior to the lines) and olivine (exterior to the lines). The x axis is radial distance in microns relative to the center of the glass inclusion.
stabilizes Fe$^{2+}$ and S$^{2-}$ in the liquid relative to the more oxidized starting materials ($\Delta$FMQ = +0.2 – +0.6) leading to sulfide oversaturation and precipitation of an FeS phase (Fincham & Richardson, 1954; Nash et al., 2019; O’Neill & Mavrogenes, 2002). Three out of 12 unheated Papakolea olivines have one or two visible sulfide blebs in melt inclusions; the natural inclusions had fewer and larger sulfides than most of the experiments, and they do not seem to be associated with the vapor bubble. Some olivines contain multiple melt inclusions, some of which have sulfides and others that do not (e.g., H9X2_1 and H9X2_2 in Figure 3b); in these cases, the sulfide-bearing inclusions have higher total S (e.g., 705–830 ppm in H9X2_1) compared to the sulfide-free inclusions (e.g., 541–670 ppm in H9X2_2; Note that S was measured 3 times at the center of each inclusion with a 5-μm beam under the same conditions as described in section 2.3). The radii of 268 sulfides in experimental inclusions were measured in backscattered electron images, and they have a mean radius of 1 μm and a maximum of 4.6 μm.

3.4. Compositional Zonation in Experimental Inclusions
3.4.1. Homogenized and Quenched Inclusions (Not Subjected to Controlled Cooling)
In the liquid at 1,225 °C, the time scale for homogenization of the slowest diffusing species (e.g., Al$_2$O$_3$; 3.4.1. Homogenized and Quenched Inclusions (Not Subjected to Controlled Cooling)

To assess whether local equilibrium between the olivine and melt was achieved during the 24-hour heating step, the glass compositions are homogeneous within the analytical uncertainty of the electron microprobe measurements. In some inclusions, particularly those homogenized and quenched from 1,260 °C (Figures 5c and 5d), microprobe analyses within 3 μm of the inclusion wall were affected by growth of olivine during the quench from high temperature and show the incipient development of a diffusion profile. Also shown in Figure 5 are the averages of the homogeneous glass compositions in all of the analyzed melt held at either 1,225 or 1,260 °C for 24 hr; the colored bands for each element represent ±2σ of these averages over all analyzed homogenized inclusions for each element (Table 2; the few points nearest the olivine that were affected by quench crystallization were discarded when determining these averages). The offsets of the colored bands relative to the data points for the individual profiles shown illustrate the variability of the homogenized glass compositions.

To assess whether local equilibrium between the olivine and melt was achieved during the 24-hour homogenization step, the $K_{D,Fe^2+Mg} = (Fe^{2+}/Mg)_{olivine}/(Fe^{2+}/Mg)_{liquid}$ was calculated for homogenized inclusions. Fe$^{2+}$ in the melt was calculated from the electron microprobe-measured total iron content using either the XANES-measured mean ratio of Fe$^{3+}$/Fe$^{Total}$ of 0.07 or assuming Fe$^{3+}$/Fe$^{Total}$ = 0.10, which is the prediction based on Kress and Carmichael (1991) for a basalt in equilibrium with the furnace gas at ΔFMQ = −1.15 at both 1,225 or 1,260 °C. Taking the plateau FeO*/MgO of the homogenized inclusions and the olivine measured adjacent to the inclusion wall gives $K_{D,Fe-Mg} = 0.298–0.337$ or 0.308–0.350 (n = 10 inclusion-olivine pairs), respectively, for the two assumptions for Fe$^{3+}$/Fe$^{Total}$ in the melt. These olivine-liquid $K_{D,Fe-Mg}$ values fall between estimates for natural melts from Kilauea, where Fe$^{3+}$/Fe$^{Total}$ was measured with XANES (0.280±0.06(2σ); Helz et al., 2016) and experimentally determined values for Hawaiian liquids (0.345±0.018(2σ); Matzen et al., 2011), consistent with local Fe/Mg equilibrium having been achieved olivine on the inclusion wall and the coexisting liquid during the homogenization step.

3.4.2. Homogenized and Cooled Inclusions
After the 24-hour homogenization step, one bucket of olivines was quenched, and the remaining olivine-bearing buckets were cooled at 70 to 50,000 °C/hr and then drop-quenched into water. Overall, the shapes and magnitudes of compositional gradients recorded in oxide concentration profiles from the experiments (right column in Figure 4) closely resemble those in natural samples from the Papakolea flows (left column in Figure 4) and from the Galapagos Islands and Siqueros Fracture Zone (Newcombe et al., 2014). For example, in the most rapidly cooled inclusions (such as H4X3, cooled at ~50,000 °C/hr; Figure 4c), a boundary layer formed in the melt that is depleted in MgO and FeO (compatible oxides in olivine that are extracted from the melt during crystallization on the inclusion wall) and enriched in SiO$_2$, Al$_2$O$_3$, and CaO (relatively incompatible oxides that are excluded from the crystallizing olivine). The width of the boundary layer differs from oxide to oxide, reflecting their diffusivities in the melt (Newcombe et al., 2014), and the boundary layers
terminate at compositional plateaus established during the homogenization step. In natural sample HIGS9 (Figure 4b), a similar boundary layer is observed that is narrow relative to the inclusion radius, suggesting that it also experienced relatively rapid cooling. For experimental inclusions cooled at lower rates, the boundary layers are wider than for more rapidly cooled samples (compare Figures 4c and 4d). For example, in experimentally cooled inclusion H5X1_1 (Figure 4c; 715 °C/hr), the boundary layer generated by olivine crystallization on the inclusion wall reached the inclusion center, leading to lower FeO and MgO and higher...
SiO$_2$ and Al$_2$O$_3$ contents across the entire inclusion relative to the initially homogeneous composition, and to an absence of a plateau in the inclusion center. In some natural inclusions such as HIGS6 (Figure 4b), the profile shapes suggest a similarly prolonged cooling history that led to the formation of wider zones relative to that in HIGS9 (Figure 4a). Note that for both the rapidly and slowly cooled samples, the concentration profiles of the oxides that have higher concentrations in olivine than in the liquid (e.g., FeO and MgO) are concave down, whereas for most oxides with lower concentrations in olivine than in the liquid (e.g., SiO$_2$, Al$_2$O$_3$, TiO$_2$, Na$_2$O, and K$_2$O; see section S3 in the supporting information), the profiles are concave up. However, although CaO is incompatible in olivine and its concentration profile is concave up in the rapidly cooled experimental inclusions (Figure 4, top row), in the slowly cooled samples, CaO is depleted near the olivine wall and in the inclusion center is enriched relative to the initial homogenized melt composition (i.e., it has a concave down profile similar to FeO and MgO despite the average CaO increasing in the liquid during cooling; Figures 4b and 4d). This anomalous CaO behavior, which was previously described in natural samples by Newcombe et al. (2014), is also observed in the natural Papakolea and Kilauea Iki inclusions and will be discussed in more detail in sections 5 and 6.

Experiment H11X was cooled at 466 °C/hr after homogenization at 1,225 °C and quenched at successively lower temperatures between 1,200 and 900 °C. A temperature series of MgO concentration profiles across melt inclusions from these experiments demonstrate the systematic development and evolution of compositional zoning during cooling (Figure 6). Because MgO in the liquid reflects the progressive extraction of olivine and is used as the basis for modeling in section 4, for emphasis and clarity, it is the only oxide shown in Figure 6 (and Figure 7), but section S3 includes similar plots as Figures 6 and 7 for the other oxides. Initially homogeneous at 1,225 °C (Figure 6a), by 1,200 °C (Figure 6b), sufficient olivine crystallization and diffusion had occurred over the 216 s since cooling began for the MgO-depleted boundary layer adjacent to the olivine to have reached the inclusion center such that the central MgO contents were lowered relative to the initial value of 9.01±0.26(2 σ) wt % established during the homogenization step. With continued cooling, the MgO content of the liquid analyzed at the olivine-melt interface continually decreased as olivine was progressively extracted by crystallization on the inclusion wall, and the evolving boundary melt continued to exchange via diffusion with the inclusion interior. At lower temperatures (Figures 6d–6f), while MgO continued to decrease in the interface liquid with progressive olivine crystallization, diffusive exchange with the interior of the inclusion slowed because of decreasing temperature, resulting in steepening of the concentration profiles near the inclusion wall, and leaving the inclusion centers relatively unchanged. FeO is similarly concave down and progressively depleted in the interface liquid, whereas the relatively incompatible elements (e.g., SiO$_2$ and Al$_2$O$_3$, but notably not CaO) show the opposite behavior, with interface melt concentrations increased relative to the starting liquid compositions and concave up diffusion profiles (e.g., Figure 4 and see section S3). As emphasized by Newcombe et al. (2014), compositional zoning across melt inclusions reflects the competition between the changing composition of the melt at the inclusion wall as olivine crystallizes and diffusive exchange between this interface melt and the interior of the inclusion. The diffusion profile widths and shapes depend for each oxide on inclusion size, cooling rate, and on its diffusivity (including its composition and temperature dependence). For example, although all of the inclusions in experiment H5X were homogenized at 1,225 °C, cooled at 715 °C/hr, and quenched at 1,000 °C, the compositions at the inclusion centers are systematically related to the inclusion size (Figure S4): central MgO contents from these inclusions are lower in smaller inclusions than in larger ones subjected to the same cooling history, whereas the central Al$_2$O$_3$ contents are enriched in smaller inclusions. This is consistent with the shorter distances necessary in small inclusions for diffusion to exchange between their walls and centers. Note, however, that even though Al$_2$O$_3$ is building up adjacent to olivine crystallizing on the inclusion walls during cooling, the effect of inclusion size is less dramatic on Al$_2$O$_3$ than for MgO because there has been less exchange between the inclusion wall and center for the relatively slowly diffusing Al$_2$O$_3$. This size-dependent behavior is important to consider when comparing inclusions across experiments, and it has implications for the interpretation of analyses of the centers of inclusions within a population of natural samples since central compositions are more likely to be diffusively modified for smaller inclusions and for samples subjected to lower cooling rates (Newcombe et al., 2014).

Concentration profiles from experimental inclusions of similar size (~50- to 80-μm radius) that were cooled at different rates (70 to ~50,000 °C/hr) over the same 1,225–1,000 °C temperature interval illustrate the cooling rate-dependent aspects of the development of compositional zoning in melt inclusions (Figure 7). In the
most rapidly cooled experiments, the diffusion profile terminates at an MgO content that is unchanged from that established during the homogenization step (Figures 7a and 7b). The width of the diffusively modified boundary layer grows with decreasing cooling rate until it reaches the center of the inclusion, after which the composition of the inclusion center no longer represents the homogeneous melt that initially occupied the whole inclusion (Figures 7c–7f). This progressive behavior is qualitatively similar to that of the temperature-dependent evolution of profiles cooled at a single cooling rate but quenched at progressively lower temperatures (Figure 6). If low cooling rate samples were quenched at high enough temperature, they too would preserve the homogenized compositional plateau near the inclusion center because there would have been insufficient time for the boundary layer to have diffusively reached the inclusion center in the system cools sufficiently rapidly to low temperatures.

Several of the experimentally generated concentration gradients have features that suggest the importance of uphill diffusion, analogous to those described in natural melt inclusions by Newcombe et al. (2014). Uphill diffusion refers to when a solution component appears to diffuse against its own concentration gradient due to interactions with other melt components and can be manifested by nonmonotonic and asymmetric diffusion profiles (Liang, 2010). Diffusion profiles with local maxima and minima are evident in some experimental profiles of every oxide, including MgO (Figures 6d and 6e), but are most prominent in profiles of CaO (Figure 8), FeO, SiO₂, Al₂O₃, TiO₂, and K₂O (section S3). The local extrema in concentration profiles are transient features (Liang, 2010) and are thus generally less pronounced in the lowest cooling rate...
experiments. CaO, which arguably exhibits the most extreme uphill diffusion behavior, exemplifies this transience clearly; for the experiments cooled at >1,000 °C/hr (Figure 8, top row), the profiles show clear local extrema, whereas at lower cooling rates, the profiles have a nearly monotonic concave down shapes (Figure 8, bottom row). As noted earlier, the shape of CaO profiles from slowly cooled samples is anomalous considering its incompatibility in olivine, and, as we describe in section 5, we ascribe it to a particularly extreme manifestation of multicomponent effects. For MgO, Newcombe et al. (2014) demonstrated that a simple model assuming a composition-independent effective binary diffusion coefficient (Chen & Zhang, 2008) could reproduce most of the variability measured in MgO profiles across natural inclusions. In the controlled cooling experiments there is subtle evidence that MgO may also be affected by uphill diffusion, including nearly horizontal compositional plateaus at MgO contents below the initial homogenized value (Figure 6e) and subtle but resolvable local maxima symmetric about the inclusion center (Figure 6d). The key point is that factors that produce uphill diffusion, such as diffusive coupling and solution nonideality (e.g., Liang et al., 1997), play a role in olivine-hosted basaltic liquids and would need to be addressed when attempting to construct a complete model of diffusion in the liquid. In section 4, following Newcombe et al. (2014), we choose to focus on MgO in our modeling, but we also extend their approach to include the dependence of the diffusivity of MgO on the evolving major element composition of the melt.

3.5. Zoning in Olivine

Olivine growth drives chemical zonation in the inclusion liquid, so zoning in olivine adjacent to the glass that crystallized during cooling provides complementary information that can be used to close the mass balance and test conclusions based on observations of the glass. In natural samples, the olivine adjacent to melt inclusions is typically characterized by Fe enrichments and Mg depletions toward the inclusion interface,

![Figure 7. MgO profiles across olivine-hosted glass inclusions from different experiments, all of which were held at 1,225 °C for 24 hr but cooled at different rates varying from (a) ~50,000 °C/hr to (f) 70 °C/hr. The cooling rate for each panel is shown in bold text. All of the experiments were quenched at a temperature of 1,000 °C along their respective cooling paths (Figure 2).

The horizontal red lines correspond to the mean MgO contents (9 wt %) of glasses homogenized at 1,225 °C (Table 2) and indicate the approximate MgO profile prior to the initiation of cooling. The vertical grey bars indicate the boundary between glass and olivine.](figure7.png)
attributed to postentrapment olivine growth on the inclusion wall and diffusive exchange with olivine in the far-field (Gaetani & Watson, 2000; Danyushevsky, McNeill, & Sobolev, 2002). The Fe/Mg zonation of olivine around natural inclusions from Papakolea is characterized by two to three zones (Figure 9a): in some olivine, there is a steeply zoned, narrow band of low Fo content olivine typically extending a few microns (up to ~7 μm in the Papakolea samples) into the olivine from the inclusion wall; this is adjacent to a broader zone with gradients of ~1–2 Fo% that extend an additional ~30–115 μm into the host olivine; beyond this, the far-field region is a compositional plateau or reflects grain-scale zoning formed during growth of the olivine phenocryst from the magma. In some samples there is an apparent break in slope between the broad zone and the steeply zoned olivine, consistent with the latter having formed by crystallization of olivine on the inclusion wall due to a perturbation of the olivine’s environment (e.g., abrupt cooling on eruption). The broad zones are interpreted as relaxed gradients from a prior episode of crystallization on the inclusion wall and/or from open-system diffusive exchange with an evolving melt external to the olivine (e.g., Danyushevsky et al., 2000; Gaetani & Watson, 2000). In half of the Papakolea samples, the break in slope between the broadly and steeply zoned olivine is not obvious, which results in two clearly recognizable zones (the broad zone and the far-field olivine), and either reflects the lack of any steep zone adjacent to the inclusion wall or that this zone is too narrow to be clearly identified by the electron microprobe.

The olivine zones defined for the natural inclusions in the previous paragraph are also observed in the experimentally heated and cooled inclusion-bearing olivines. Figure 9b illustrates these zones in the slowly cooled experimental sample H8X2_1 (70 °C/hr), which shows a steep narrow zone (~4.5 μm wide with an increase from Fo84.4 to Fo88.3 with increasing distance from the inclusion) adjacent to the inclusion wall interpreted to be due to growth during experimental cooling; this narrow zone is surrounded by a broad zone (~110 μm wide with an increase from Fo88.4 to Fo93.0); the broad zone terminates at a compositional plateau.
at ~Fo89 that extends into the crystal interior. The experiments were homogenized at 1,225 °C, at which temperature some Fe-rich olivine initially on the inclusion wall likely dissolved back into the inclusion, and Fe and Mg exchanged between the liquid and near-surface olivine until they were in local equilibrium. Once cooling was initiated, it led to regrowth of a steep narrow zone adjacent to the olivine-glass boundary; a broad zone extending further from this boundary into the host olivine; and a plateau in forsterite contents in the far-field. Far-field olivine reported in the text corresponds to microprobe analyses taken >150 μm from the inclusion wall.

4. Modeling
4.1. Model Description

In order to model the evolution of concentration profiles across olivine-hosted melt inclusions during cooling, the diffusion model of Newcombe et al. (2014) was adopted and modified. Described in detail in the original study, the numerical code calculates a one-dimensional forward model for diffusion of MgO across a spherical melt inclusion subjected to a cooling path, which we assume to be linear (i.e., a constant cooling rate). The model assumes local equilibrium between olivine and the liquid at the inclusion wall (referred to hereafter as the “interface liquid”) and imposes a temperature-dependent relationship between MgO in the interface liquid and Fo90.6 olivine; for this relationship, Newcombe et al. (2014) used the results of the olivine dissolution experiments of Chen and Zhang (2008). At each temperature decrement along the
linear cooling path, MgO is specified in the interface liquid as a boundary condition and the corresponding gradient in MgO is allowed to relax diffusively.

Given a microprobe profile of MgO concentration across a glassy spherical melt inclusion and assuming an initially homogeneous liquid at an initial temperature, the cooling rate parameter can be varied to minimize the difference between the measured profile and the forward model. Newcombe et al. (2014) used this approach to quantify the cooling rates of olivine-hosted melt inclusions from the Siqueros Volcano Zone and the Galapagos Islands but could not assess the accuracy to which the best fit thermal histories match those experienced by the samples in nature, since the rates were not known independently. In our experimentally cooled inclusions, the cooling rate, homogenization and quench temperatures, and initial melt composition are all known. The inverse model can then be run on the experimental inclusion MgO profiles to determine the cooling rate that results in the best fit between the model and data, which when compared to the measured experimental rates can be used to evaluate quantitatively the accuracy of the model.

The experiments can also be used to test, and if necessary modify, assumptions in the diffusion modeling because the temperature-time history of the samples as well as the initial composition of the melt inclusion prior to cooling are known (Figure 2 and Table 2). For example, the average composition of inclusions homogenized at 1,225 °C has MgO = 9.01±0.26 (2σ) wt %; however, for these MgO contents, the olivine-liquid thermometer of Chen and Zhang (2008) predicts a much lower temperature of 1157±8 °C. As a result, in the modeling presented here, we use the 1-bar alphaMELTS model (hereafter referred to as MELTS; Ghiorso & Sack, 1995; Smith & Asimow, 2005) to define the MgO vs. temperature boundary condition rather than the Chen and Zhang (2008) olivine-liquid thermometer used by Newcombe et al. (2014). Specifying the average composition of inclusions homogenized at 1,225 °C (Table 2) and approximating the experimental fO2 as ∆FMQ ≈ −1, MELTS predicts the olivine-saturated liquidus to be 1,229±2(2σ) °C.
with a liquidus olivine composition of Fo87.3±0.9(2σ) within error of the average composition of olivine analyzed at the olivine-glass interface in experimentally homogenized samples (Fo88.2±1.8(2σ)). Starting with this initial condition, which closely approximates the experimental conditions after homogenization and prior to cooling, MELTS was programmed to batch crystallize only olivine, and the MgO content of the output liquid composition as a function of temperature at a constant pressure of 1 bar was used as the temperature-dependent boundary condition at the olivine-melt interface (using fractional rather than batch crystallization would make negligible difference; see the next paragraph and Figure 10a). We note that pressures of Mauna Loa melt inclusions are estimated to be ~0.5–1 kbar (Wallace et al., 2015), but because the pressures are not known for the experimental melt inclusions and the effect on olivine-liquid equilibria is relatively small (e.g., pMELTS predicts the 1-kbar liquidus to be 6 °C higher than at 1 bar), we adopt the 1-bar calculation.

For two sets of experiments H2X (1,570 °C/hr) and H11X (466 °C/hr), which were quenched at several temperatures, the correspondence between model batch and fractional crystallization calculations and analyses of glasses near the inclusion wall are both good (Figure 10a), particularly at quench temperatures greater than 1,000 °C where both sets of experiments agree with either model by less than 0.4 wt % MgO (see Figure S6 for oxides other than MgO). For experiments cooled at rates ≤1,000 °C/hr and quenched at 1,000 °C, the average measured MgO content of the interface glass is 3.47±0.7(2σ) wt %, which is only slightly higher than that predicted by the MELTS fractional (3.24 wt %) or batch (3.41 wt %) calculations at 1,000 °C (Figure 10b). For experiments cooled at higher rates (H2X, H9X, and H4X), the MgO in the interface melt of inclusions quenched at 1,000 °C, based on analyses of glass as close as possible to the olivine (~1.5 μm) is systematically higher than the MELTS predictions for both fractional and batch crystallization and increasingly divergent at higher cooling rates (Figure 10b). This discrepancy can be mostly accounted for by extremely steep gradients near the interface in rapidly cooled experiments resulting in an inability of the microprobe to resolve this narrow zone (Figure 10b), although a failure to achieve local equilibrium is also possible.

In a crystallizing melt inclusion, the interface liquid will never actually follow a batch nor fractional crystallization path since it is continually influenced by diffusive exchange with the inclusion interior. However, the MELTS calculations provide an improved approximation of olivine-melt equilibria at the interface relative to the constant Fo90.6 assumption of Chen & Zhang, 2008; e.g., compare the data and MELTS models with the red dashed curve in Figure 10a). For the purpose of modeling the experimental melt inclusions, the boundary condition of the temperature dependence of the MgO content of the interface liquid was approximated by a second-order polynomial fit to the MgO contents of liquids on a MELTS-calculated batch crystallization liquid line of descent (at an FO2 fixed at ΔFMQ ≈ −1) starting with the average composition of our 1,225 ºC homogenization experiments (Table 2). The batch crystallization calculation was preferred over the fractional crystallization calculation due to better correspondence to the experimental data at lower temperatures (Figure 10a). The fit was for the 1,229–850 ºC temperature range (the upper temperature limit is the MELTS-calculated liquidus of the liquid composition):

$$C_{MgO}^{liq}(\Delta FMQ-1) = 4.471 \times 10^{-5} \times T^2 - 0.09971 \times T + 57.89$$

where $C_{MgO}^{liq}$ is the concentration in weight percent of MgO in liquid coexisting with olivine and $T$ is temperature in kelvin. This fit to the boundary condition is shown as the blue curve in Figure 10a.

The other modification made to the Newcombe et al. (2014) model was to the parameterization of $D_{MgO}$, the diffusivity of MgO in the liquid. Chen and Zhang (2008) parameterized $D_{MgO}$ as an effective binary diffusion coefficient (EBDC), which approximates diffusion in a multicomponent system as pseudobinary exchange between the component of interest and a second fictive component that is a combination of all of the other components in the solution (e.g., Chakraborty, 1993; Cooper, 1968; Liang, 2010; Watson & Baker, 1991). While the effective binary approach is useful in that it foregoes the need for a full diffusion matrix (e.g., Guo & Zhang, 2016, 2018), the EBDC is in general a function of composition (Cooper, 1968; Zhang, 1993) and can vary based on the geometry of the diffusion couple (Liang, 2010). Accordingly, the EBDC generally will vary across a diffusion profile, will be time-dependent unless the system has achieved steady state, and will in steady state depend on the geometry of the system (Cooper, 1968; Liang, 2010). Our experiments stress these limitations of the EBDC in that they are dynamic cooling rate experiments, substantial...
compositional gradients continually evolve in the melt boundary layer, and the inclusion radii are finite and for the smaller inclusions on the same order as the characteristic length scale for diffusion. This combination of factors likely contributes to variations in \( D_{MgO} \) with time and position within the inclusion during cooling, which may thus not be fully accounted for by a single temperature-dependent EBDC.

The grey dots in Figure 11a shows the measured MgO concentration profile of a representative experiment (inclusion H2X5), and the green curve is the result of a forward model with no free parameters (cooling at 1,570 °C/hr from 1,225 to 1,000 °C/hr) that uses equation (1) as the boundary condition for the interface liquid MgO and the temperature-dependent \( D_{MgO} \) from Chen and Zhang (2008). The black curve is a forward model (no free parameters) using equation (1) as the boundary condition for the interface liquid MgO and the composition-dependent \( D_{MgO} \) in equation (2). The blue curve is an inverse model that varied one parameter (linear cooling rate) to minimize the residuals between the model and data. All models were run from \( T_{\text{max}} = 1,229 \) °C to \( T_{\text{min}} = 1,025 \) °C/hr. The shaded circles are experimental microprobe data from inclusion H2X5. The solid lines are forward models (no free parameters) for (b) SiO\(_2\), (c) Al\(_2\)O\(_3\), (d) FeO, and (e) MgO (in mol %), corresponding to the best fit cooling rate (1,393 °C/hr). The horizontal black line indicates the initial mol% of the modeled oxide at 1,229 °C. The red curves show models corresponding to the first iteration of the model calculation (using MELTS as the temperature-dependent boundary condition, \( C_{MgO\text{liq}} \)), whereas the black curves show the second iteration which was used as the input to equation (2) (using mass balance with MgO to set \( C_{MgO\text{liq}} \); see sections 4.2 and S2). For MgO in (e), the red line was calculated with \( D_{MgO} \) from Chen and Zhang (2009; cpx dissolution into basalt), whereas the black line was calculated using \( D_{MgO} \) in equation (2).

Figure 11. (a) The shaded circles are MgO data (wt %) from experimental melt inclusion H2X5 (cooled at 1,570 °C/hr). The solid lines are different MgO diffusion models described in section 4.1. The horizontal black line indicates the initial modeled MgO content in the liquid at 1,229 °C prior to cooling (~9 wt %). The green curve is a forward model (no free parameters) using equation (1) as the boundary condition for the interface liquid MgO and the \( D_{MgO} \) from Chen and Zhang (2008). The black curve is a forward model (no free parameters) using equation (1) as the boundary condition for the interface liquid MgO and the composition-dependent \( D_{MgO} \) in equation (2). The blue curve is an inverse model that varied one parameter (linear cooling rate) to minimize the residuals between the model and data (best fit cooling rate is 1,393 °C/hr). All models were run from \( T_{\text{max}} = 1,229 \) °C to \( T_{\text{min}} = 1,025 \) °C/hr. (b–e) The shaded circles are experimental microprobe data from inclusion H2X5. The solid lines are forward models (no free parameters) for (b) SiO\(_2\), (c) Al\(_2\)O\(_3\), (d) FeO, and (e) MgO (in mol %), corresponding to the best fit cooling rate (1,393 °C/hr). The horizontal black line indicates the initial mol% of the modeled oxide at 1,229 °C. The red curves show models corresponding to the first iteration of the model calculation (using MELTS as the temperature-dependent boundary condition, \( C_{MgO\text{liq}} \)), whereas the black lines show the second iteration which was used as the input to equation (2) (using mass balance with MgO to set \( C_{MgO\text{liq}} \); see sections 4.2 and S2). For MgO in (e), the red line was calculated with \( D_{MgO} \) from Chen and Zhang (2009; cpx dissolution into basalt), whereas the black line was calculated using \( D_{MgO} \) in equation (2).
compositions (including self-, tracer-, and effective-binary-diffusion coefficients) to solve for the coefficients in equation (2) that best fit MgO diffusivities across temperature and composition space. Equation (2) reproduces these various diffusivities from available experiments of basaltic to rhyolitic compositions with a maximum deviation of 0.4 log units between calculated and measured values of \( D_{\text{MgO}} \) (Zhang, 2010). While the functional form for the effects of chemical composition on \( D_{\text{MgO}} \) used by Zhang (2010) in equation (2) is arbitrary, it provides a quantitative basis for taking into account the compositional dependence of MgO diffusion in a multicomponent melt that is strongly zoned.

In equation (2), silica content has the dominant effect on \( D_{\text{MgO}} \) due to its high cation mole fraction in basaltic liquids and the relatively large coefficient in the preexponential term in the Arrhenius equation. For example, in sample H2X5, cooled at 1,570 °C/hr and quenched at 1,000 °C, the concentration of SiO\(_2\) increases from 52.4 wt % in the inclusion interior to 56.6 wt % near the olivine-melt interface, and based on equation (2), the diffusion coefficient of MgO is expected to decrease by 0.65 log units (at 1,000 °C near the inclusion edge) solely due to this increase in silica. Accounting for additional changes due to the combined gradients in MgO, FeO, and Al\(_2\)O\(_3\) between the inclusion center and edge only reduces \( D_{\text{MgO}} \) by an additional 0.06 log units for H2X5. For more details related to the implementation of the composition-dependent \( D_{\text{MgO}} \), see section S2.1.

4.2. Application of the Modified Model

Using the MELTS boundary condition for \( C_{\text{MgO}}^{\text{liq}} \) (equation 1) and the composition-dependent \( D_{\text{MgO}} \) parameterization (equation 2) described in the previous section, forward models of the MgO profile vs. time for any cooling path can be calculated. For the case of the linear cooling paths of our experiments, the model was implemented given an initial temperature (\( T_{\text{max}} \)), final temperature (\( T_{\text{min}} \)), and cooling rate (\( q \)). At time \( t = 0 \), the liquid is homogeneous and \( T = T_{\text{max}} \) which is set by substituting the initial MgO concentration in the liquid into equation (1). For each subsequent time step, \( T \) is decreased based on the specified cooling rate and the boundary condition \( C_{\text{MgO}}^{\text{liq}} \) at the olivine-melt interface is set by substituting the new \( T \) into equation (1). At every time step, the resulting MgO profile is allowed to diffusively relax, using as an initial guess the temperature-dependent \( D_{\text{MgO}} \) from Chen and Zhang (2008). For a given \( T_{\text{max}} \) and cooling rate, this procedure is repeated until reaching the minimum temperature \( T_{\text{min}} \), which is defined by substituting the minimum value of MgO in the glass at the melt-olivine interface into equation (1) (as in Newcombe et al., 2014).

In order to implement the composition-dependent \( D_{\text{MgO}} \) in equation (2), the SiO\(_2\), Al\(_2\)O\(_3\), and FeO profiles must also be forward modeled in tandem with MgO. The approach used to model SiO\(_2\), Al\(_2\)O\(_3\), and FeO is described in detail in section S2, and example calculations for inclusion H2X5 are shown in Figures 11b–11d. To summarize, diffusion of these oxides is calculated using temperature-dependent and composition-independent diffusivities, and the fluxes at the boundary between the olivine and interface liquid are calculated by satisfying mass balance with the MgO lost to the growth of olivine, the composition of which is defined at each time step by MELTS. These calculations produce concentration profiles of SiO\(_2\), Al\(_2\)O\(_3\), and FeO, (and an initial guess of the MgO profile) at each time step. Using these profiles and applying equation (2), the concentration dependence of \( D_{\text{MgO}} \) was calculated at each position and time for a given cooling path and inclusion size. The MgO profile, initially calculated with a composition-independent \( D_{\text{MgO}} \), is then recalculated at each time step from \( T_{\text{max}} \) to \( T_{\text{min}} \) by numerically solving the diffusion equation where \( D_{\text{MgO}} \) (equation 2) varies with position and time.

Given \( T_{\text{max}} \) and the \( T_{\text{min}} \) calculated for a particular inclusion, the cooling rate was allowed to vary such that the difference between the model MgO profile at \( T_{\text{min}} \) and the experimental MgO data were minimized. Figure 12 shows examples of the model fits to MgO profiles from experimentally homogenized and cooled melt inclusions. The inverted model MgO concentration profiles fit the data with an average sum of square residuals between the model and data equal to 0.055 (Table 3). For H4X and H9X, the most rapidly cooled experiments, the residuals are artificially low because the most of the data points in the profile correspond to the MgO plateau and so the difference between the data and the model, with the initial MgO set by the central plateau, is small (e.g., Figures 12a and 12b). Qualitatively, the subtle misfits between the model and experimental profiles are systematic; MgO is sometimes overestimated by the model in the inclusion centers (typically by 0.1–0.2 wt % MgO), and the best fit model profiles are often slightly too steep close to
the inclusion walls (e.g., the difference between the blue lines and data in Figures 12c and 12e). Newcombe et al. (2014) observed the same discrepancies in their fitting of natural profiles and attributed it to a two-stage cooling history, but this cannot explain our experimental data since these samples experienced only a single stage of linear cooling. Where the systematic offset between model and data near the inclusion center is most obvious, the experimental MgO profiles are flattened near the center relative to the shape of the model profile (Figures 11a and 12c and 12e), in a similar region where MgO profiles have subtle local extrema.

Figure 12. Application of the inverse model for MgO diffusion described in section 4 to experimentally cooled olivine-hosted melt inclusions. The gray circles correspond to microprobe MgO data from inclusions quenched at 1,000 °C. Each panel shows the MgO profile across experimental glass inclusions cooled at a different rate. The red horizontal line corresponds to the initial MgO of the model calculation, corresponding to $T = T_{\text{max}}$ via equation (1) (section 4.2). The blue curves correspond to the best fit result of the inverse model, where cooling rate was the only adjustable parameter, and the corresponding cooling rates are listed below each profile along with the linear best fits to the experimental thermocouple data in Figure 2.

Table 3

<table>
<thead>
<tr>
<th>Name</th>
<th>Experimental cooling rate (°C/hr)</th>
<th>Number of experimental inclusions</th>
<th>Average calculated cooling rate (°C/hr)</th>
<th>Percent deviation from experimental rate</th>
<th>Standard deviation calculated cooling rate (1σ)b</th>
<th>Relative standard deviation (1σ/q)</th>
<th>Sum of squared residuals (SSR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H8X</td>
<td>70</td>
<td>5</td>
<td>104</td>
<td>+48.46%</td>
<td>28</td>
<td>0.27</td>
<td>0.008</td>
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<tr>
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<td>93</td>
<td>3</td>
<td>97</td>
<td>+4.50%</td>
<td>30</td>
<td>0.31</td>
<td>0.011</td>
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<tr>
<td>H7X</td>
<td>190</td>
<td>3</td>
<td>239</td>
<td>+25.70%</td>
<td>100</td>
<td>0.42</td>
<td>0.017</td>
</tr>
<tr>
<td>H11X</td>
<td>466</td>
<td>11</td>
<td>428</td>
<td>−8.23%</td>
<td>105</td>
<td>0.24</td>
<td>0.054</td>
</tr>
<tr>
<td>H5X</td>
<td>715</td>
<td>7</td>
<td>731</td>
<td>−2.17%</td>
<td>161</td>
<td>0.22</td>
<td>0.098</td>
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<tr>
<td>H2X</td>
<td>1,570</td>
<td>9</td>
<td>1,488</td>
<td>−5.19%</td>
<td>355</td>
<td>0.24</td>
<td>0.086</td>
</tr>
<tr>
<td>H9X</td>
<td>20,190</td>
<td>6</td>
<td>21,536</td>
<td>−6.67%</td>
<td>3,762</td>
<td>0.17</td>
<td>0.021</td>
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<tr>
<td>H4X</td>
<td>49,644</td>
<td>5</td>
<td>31,792</td>
<td>−35.96%</td>
<td>9,024</td>
<td>0.28</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Abbreviation: SSR: sum of square residuals.

a $100 \times (\text{average calculated rate} - \text{experimental rate})/\text{experimental rate}$.  
bStandard deviation of the mean calculated cooling rate for each inclusion, where the mean cooling rate was calculated by perturbing the MgO profile with Gaussian noise 10x, refitting each profile, and taking the average cooling rate from the fits to these synthetic profiles.  
cMean of the sum of the square of residuals between the modeled MgO profile and the best fit MgO profile.  
dStage 1 (1,260 to 1,134 °C) at 93 °C/hr of the two-stage experiment.
indicative of uphill diffusion (e.g., Figures 6d and 6e and 12e). These flattened MgO profiles (e.g., H2X5; Figure 12c) can look similar to the profiles produced in rapidly cooled samples (e.g., H4X4; Figure 12a) that also have MgO plateaus near inclusion centers. In the latter case the plateau is a relic of the original homogeneous MgO content, whereas in cases such as H2X5, the plateau is at an MgO content that has clearly been lowered by diffusion during the experiment relative to the original homogenized concentration of ~9 wt %. For example, as the humps in MgO (Figures 6d and 12e) migrate toward the inclusion center as a sample cools, they can merge to form a transient, approximate plateau, which evolves into a monotonic concave down profile that moves downward in MgO with further crystallization on the inclusion wall and diffusion of MgO from the inclusion center (e.g., Figures 12e and 12f). This may lead to confusion in inferring the initial MgO (and the related parameter, \( T_{\max} \)) in some natural samples (as pointed out in Newcombe et al., 2014). These diffusion-influenced plateaus could be due to multicomponent effects on \( D_{\text{MgO}} \) that are not captured in the parameterization of equation (2). The composition-dependent \( D_{\text{MgO}} \) in equation (2) provides a more realistic description of the diffusivity than one that is only temperature dependent, but a more sophisticated treatment of multicomponent diffusion that allows for cross terms and uphill diffusion in MgO would likely be necessary to improve the model fits to the data.

4.3. Assessing the Accuracy of Cooling Rates Extracted From Zoning Profiles of Olivine-Hosted Melt Inclusions

Modeling the development of zoning across olivine-hosted melt inclusions is a potentially useful quantitative tool for determining late-stage cooling histories of rapidly cooled igneous rocks (Newcombe et al., 2014). Because the experimental samples were subjected to known cooling histories, inverting their MgO profiles allows us to evaluate the accuracy of this approach to determine cooling rates. Figure 13a shows the ranges (gray squares are individual inclusions) and averages (blue circles) of cooling rates calculated for melt inclusions from each experiment compared to the measured cooling rate (i.e., linear fits to the thermocouple data in Figure 2). With the exception of two inclusions (H4X2 and H11X4C), the cooling rates calculated by inverting MgO profiles are within a factor of 2 of the experimental cooling rates (Table 3, Figure 13b, and Table S2), which span 3 orders of magnitude. The percent deviation of the average cooling rate calculated for inclusions from a given experiment from the experimental rate is between ~36% in H4X (49,644 °C/hr) and +48% in H8X (70 °C/hr), with four of seven experiments having mean percent deviations within ±10% relative to the known rate (Table 3). These data include experiments H1X (1,570 °C/hr) and H11X (466 °C/hr), which have inclusions that were quenched at temperatures other than 1,000 °C during cooling; for H11X there is no correlation between quench temperature and calculated cooling rate; however, for H2X the four inclusions quenched at temperatures higher than 1,000 °C had systematically higher calculated cooling rates (1,600–2,200 °C/hr) than the five quenched at 1,000 °C (980–1,400 °C/hr). The resolution of the model is calculated by dividing the standard deviation of the distribution of cooling rates calculated for a given experiment by the corresponding mean cooling rate, giving relative standard deviations which vary from 0.17 in H9X (20,190 °C/hr) to 0.42 in H7X (190 °C/hr; Table 3). In the context of determining cooling rates of natural samples, which span many orders of magnitude (see Newcombe et al., 2014 and section 6.1), the correspondence between the model and experimental rates demonstrates the usefulness of using diffusion across melt inclusions as a geospeedometer.

The two-stage experiment (H10X) was modeled by varying three parameters (two cooling rates for each linear stage and the temperature at which the second stage began), and while the model misfit is less than in the single-stage experiments (due to the introduction of two additional fitting parameters), the accuracy is reduced; the calculated cooling rates are within a factor of 2.5 of the measured rates, and the changover temperature is underestimated by 24–50 °C (see section S2.2 and Figure S7).

The experimental profiles can also be fit with the unmodified model provided in Newcombe et al. (2014), and the single-stage cooling rates recovered from their model are as accurate as those calculated with the updated model (typically ±10% relative and within a factor of 2). The accurate cooling rates calculated with the unmodified model are despite the fact that the modeled \( T_{\max} \) underestimates the homogenization temperature by ~70 °C (section 4.1). When substituting the MELTS boundary condition (equation 1) in the forward model, we recover the correct \( T_{\max} \) for the experiments, however continuing to use the composition-independent \( D_{\text{MgO}} \) in the model predicts MgO gradients across inclusions that are much
shallower than those in the experimental profile indicating that the composition-independent $D_{\text{MgO}}$ is too high at a given temperature to describe the data (green curve in Figure 11a). This result suggests that by using the simultaneously determined $D_{\text{MgO}}$ and MgO in the liquid versus temperature functions from the single study of Chen and Zhang (2008), inaccuracies in each of these functions compensated for each other, such that the Newcombe et al. (2014) model provides an accurate overall description of diffusion in the system despite the temperature offset of the MgO in liquid thermometer.

The agreement between the known and best fit cooling rates for the experimentally treated inclusions shows that for determining the cooling rate experienced during the last stages of the cooling history of an olivine-hosted melt inclusion, either the model presented here or that used by Newcombe et al. (2014) is accurate to within a few tens of percent. However, recovery of $T_{\text{max}}$, the temperature interval over which cooling occurred, and the cooling rate of our experiments require a modified treatment of the problem that incorporates both the changing melt and olivine compositions at the inclusion wall during cooling and a composition-dependent $D_{\text{MgO}}$ that can take into account the fact that the inclusions become strongly zoned during cooling, particularly in SiO$_2$. The updated model presented here achieves this and is capable of accurately retrieving the experimentally imposed cooling paths that span 3 orders of magnitude in cooling rate. We also note that for experiments where the narrow zone of olivine grown during cooling could be measured (sections 3.5 and S2.3), the model predicts olivine growth shell thicknesses that are within error of those measured by high-resolution EDS linescans (Figure S5). Although the function for interface liquid MgO vs. temperature is calculated for a particular composition and the $D_{\text{MgO}}$ represents a fit for dry basaltic to rhyolitic liquids, the approach we have taken can be applied more broadly provided that these functions are updated for the compositions of the melt (including and perhaps especially the water content of the melt, which increases the diffusivities of MgO and other oxides [Watson, 1981; Zhang, 2010] and lowers the olivine liquidus temperature).

5. CaO and Multicomponent Diffusion

5.1. Observations of CaO in the Experiments

During olivine crystallization, concentration profiles of incompatible elements are expected to be highest at the inclusion wall and to have a concave up shape due to being excluded from the growing olivine and progressively enriched in the adjacent liquid relative to the inclusion center. This is observed for Al$_2$O$_3$, SiO$_2$, Na$_2$O, and K$_2$O (Figures 4b and 4d and section S3). For rapidly quenched melt inclusions, CaO is enriched as expected in the liquid boundary layer (Figures 8a and 8b). However, despite its relatively low partition coefficient ($D_{\text{CaO}}^\text{ol/liquid} = 0.02$–0.1; Jurewicz & Watson, 1988; Libourel, 1999), in some natural inclusions studied by us and by Newcombe et al. (2014) and in our experiments at cooling rates $\leq 1,570$ °C/hr, CaO concentrations are lower at the olivine-melt boundary than in the inclusion center (Figures 9c–9f). This leads to CaO profiles in the melt that are qualitatively more similar to the zonation in olivine-compatible oxides such as MgO and FeO than to Al$_2$O$_3$ or Na$_2$O.

Although the CaO concentration adjacent to the olivine crystallization front is low relative to the inclusion center, the average CaO contents in the experimental inclusions progressively increase with decreasing cooling rate, as is required to satisfy mass balance for an incompatible oxide. Based on analyses of olivine and melt as close as possible to the inclusion wall, we cannot distinguish ($p<0.005$) the measured $D_{\text{CaO}}^{\text{ol/melt}}$ (where the ol/melt superscript refers to the partition coefficient as opposed to the diffusion coefficient) for our homogenization experiments at 1,225 °C ($D_{\text{CaO}} = 0.013$–0.080, with a mean of 0.026±0.034(2σ), $n = 10$ olivine/glass pairs) from those in the cooling rate experiments (range $D_{\text{CaO}}^{\text{ol/melt}} = 0.009–0.037$, with a mean of 0.018±0.008(2σ), $n = 94$ pairs). Note that the olivine CaO (mean = 0.30±0.09 wt % CaO at interface) for this calculation was uniformly lowered by 600 ppm to account for secondary fluorescence effects (Figure S8) based on the average distance of a clean olivine analysis from the glass boundary (3 μm). While it is possible that a narrow <3-μm band of Ca-rich olivine exists that could satisfy the elevated $D_{\text{CaO}}$ necessary to account for low CaO in the liquid boundary layer, this high partition coefficient would be inconsistent with the observed accumulation of CaO in the integrated inclusion with progressive cooling and crystallization, and previous experimental data on phenocryst-matrix pairs (Jurewicz & Watson, 1988; Libourel, 1999). Furthermore, in high-resolution EDS scans of olivines within 10 μm of the boundary with glass, no anomalously high Ca counts were observed. It is unlikely that changing olivine chemistry is driving the change...
manifestation in CaO profiles across melt inclusions is consistent with experimental studies that demonstrate strong diffusive coupling between Ca-bearing melt species and other components, particularly SiO₂ (Liang et al., 1996), FeO, Al₂O₃, and Na₂O (Guo & Zhang, 2018), resulting in large magnitude cross terms in calculated diffusion matrices. Further examination of the extreme CaO behavior in olivine-hosted melt inclusions—first described in Newcombe et al. (2014)—is now possible, however, due to its reproducibility and the systematic development of the CaO profile shape observed in our cooling experiments.

In natural samples from a variety of settings—including the Siqueros Fracture Zone and the Galapagos (Newcombe et al., 2014), Mauna Loa (see section 6.1), and Martian meteorites (see section 6.2)—CaO profiles in olivine-hosted melt inclusions have shapes ranging from concave up with a maximum at the inclusion wall to concave down with a minimum at the wall. In addition, profiles with low CaO contents in melts near the olivine interface relative to the inclusion center display varying amounts of relaxation and inward movement of the local maxima at intermediate distances from the inclusion edge. Qualitatively, the CaO profile shape can be used to deduce a relative order in the cooling rates of melt inclusions of similar size: profiles with the highest CaO concentration near the inclusion edge indicate rapid cooling, profiles with the highest CaO contents at the inclusion center imply slow prolonged cooling, and profiles with maxima at intermediate distances from the inclusion wall indicate transients only preserved at intermediate cooling rates. Note, however, that when subjected to the same cooling history, inclusions of smaller size will invert to fully concave down more quickly than larger inclusions, and this must be accounted for when comparing or modeling profiles.

An important point here is that the CaO profile shape can aid in interpreting cooling histories observed in other oxides: For example, as mentioned in section 3.4.2, some MgO profiles from experiments at lower cooling rates have nearly flat concentration profiles near the inclusion center (Figures 6e and 7c and 7e) but at MgO values significantly lower than the initially homogenized concentration prior to cooling and olivine growth on the wall, and they clearly do not indicate directly the MgO content of the initially homogeneous molten inclusion. Although we know in our experiments that the profile was initially homogeneous at a higher concentration than that defined by the flat central MgO content, in natural inclusions for which the initial MgO content of the inclusion prior to cooling is not known independently, this could be mistaken for a compositional plateau unaffected by diffusion due to rapid cooling. If so, the inferred cooling history would erroneously start at a lower temperature and therefore with an initially constant but low MgO content across the entire inclusion, as described by Newcombe et al. (2014). Examination of the CaO profile from the same inclusion can be used to indicate roughly whether cooling was so rapid that plateaus in MgO reflect the value at $T_{\text{max}}$, or alternatively that the MgO profile evolved during cooling to produce a central plateau at MgO contents lower than those prevailing at $T_{\text{max}}$ (e.g., by multicomponent diffusion), in which case the actual value of $T_{\text{max}}$ and the initial MgO must be reconstructed (section 6).

### 5.2. A Simplified Model of CaO Diffusion in Olivine-Hosted Melt Inclusions

In this section, we develop a simplified model that can explain semiquantitatively the anomalous behavior of CaO in our experiments and in natural inclusions. The diffusion matrix [D] can be decomposed into two other square matrices, one that describes activity-composition relationships ([G]) and a “kinetic matrix” ([L]) whose elements are phenomenological coefficients that satisfy Onsager’s reciprocal relations (Onsager,
1945; verified in the CaO-Al₂O₃-SiO₂ (CAS) system by Spera & Trial, 1993, and Liang et al., 1997). There are more constraints on activity-composition relationships (elements of \([G]\)) in basalts than measurements of \([L]\) and so we have developed a simplified model to provide insight into the observed behavior of CaO in natural and experimentally cooled melt inclusions that assumes \([L]\) to be diagonal for oxide components; that is, gradients in chemical potential or activity for each oxide can be described by one term (e.g., \(L_{CaO}\)), and thus, diffusion profiles of chemical potential or activity (but not necessarily of concentration) are monotonic with respect to the distance variable. The consequence is that any off-diagonal terms in \([D]\) are assumed to be due to off-diagonal terms in \([G]\); that is, to nonideality in the thermodynamic mixing relationships. The assumption of a diagonal \([L]\) is probably not generally valid for silicate melts, as has been shown for CAS liquids (Spera & Trial, 1993; Liang et al., 1997). This can be tested on the experimental inclusion profiles by converting the oxide profiles into chemical potential profiles using MELTS (see Figure S9 for details); the resulting profiles which have local extrema in concentration are also not monotonic in chemical potential, indicating that for these inclusions, in terms of the MELTS component space and thermodynamic model, \([L]\) is not diagonal. While acknowledging the limitations of our approximation of a diagonal \([L]\), we demonstrate in this section that such a model is capable of qualitatively describing and therefore providing insights into the cooling-rate dependent behavior of CaO concentration profiles in cooled, olivine-hosted melt inclusions.

Imagine a single increment of olivine crystallization followed by isothermal relaxation of the elevated CaO content in the olivine-depleted melt at the interface. If the melt was an ideal solution, diffusion of CaO would occur from the high-CaO melt at the interface to the interior of the inclusion, and the qualitatively simple,
expected concave upward profile of $X_{CaO}$ would develop (as it does for $Al_2O_3$ and $SiO_2$ in Figures 11b and 11c). However, gradients in other oxides from the interface toward the center of the inclusion are also produced by crystallization of olivine at the interface, and these (especially the alkalis; e.g. in MELTS; Libourel, 1999) contribute to an increase in the $CaO$ activity coefficient ($\gamma_{CaO} = a_{CaO}/X_{CaO}$) in the melt at the interface relative to the inclusion interior. If the diffusion of $CaO$ is much faster than those of the components contributing to this increase in $\gamma_{CaO}$, diffusion of $CaO$ from the interface toward the inclusion center would tend to equalize the chemical potential of $CaO$ (and its activity, $a_{CaO}$), while the concentrations of other, slower diffusing components would remain largely unchanged. Given the increase in $\gamma_{CaO}$ toward the interface due to the effects of other melt components, equalizing $a_{CaO}$ across the inclusion in this extreme example (i.e., where the other components are essentially immobile except to provide a counterflow) must lead to a decrease in $X_{CaO}$ from the center of the inclusion toward its edge and, in order to satisfy mass balance, to an increase in $X_{CaO}$ in the center of the inclusion relative to its initial concentration (as observed in Figure 8). The situations in our experiments and in nature are more complex since olivine crystallization is continuous during cooling and the temperature is not constant, but provided that the effect of composition on $\gamma_{CaO}$ is large enough, the same behavior for $CaO$ can be anticipated as we have described here for a single increment of olivine growth and isothermal relaxation of the $CaO$ concentration profile.

To model $CaO$, we adopt an activity-based approach for diffusion where the flux of the $CaO$ component in the liquid is proportional to its activity gradient (Zhang, 1993). In the context of this model, the batch olivine crystallization calculation based on MELTS used in section 4 predicts that the activity of $CaO$ in the residual liquid monotonically increases with decreasing temperature and progressive olivine crystallization and that crystallization of olivine at the inclusion wall would thus produce a concave-up activity profile decreasing from the edge to the center of the inclusion at all cooling rates (Figure 14c). Analogous to the boundary condition defined for MgO in equation (1), a polynomial fit to the MELTS calculation was used to define $a_{CaO,liq}$, the $CaO$ activity in the interface liquid in equilibrium with olivine as a function of temperature (Figure 14b). An intrinsic diffusion coefficient (Zhang, 1993) was adopted from $^{44}$Ca self-diffusion in a haplobasaltic melt (LaTourrette et al., 1996), and along with the $a_{CaO,liq}$ boundary condition, was used to forward model the $a_{CaO}$ profile evolution, analogous to the procedure described in section 4. The approximation of using self-diffusion coefficient to model activity gradients is valid given that we chose to model an effectively binary system, in which the intrinsic diffusivity and self-diffusivity are equivalent (see Zhang, 1993, for details). This model produces concave up, monotonic profiles of $a_{CaO}$ across the melt inclusion at each cooling rate (Figure 14c) and reflects the expected shape of the activity (or chemical potential) profile as a function of cooling rate if the [L] matrix was diagonal.

For simplicity, the compositional dependence of $\gamma_{CaO}$ was modeled assuming that $X_{Na_2O}$ is a monitor (if not the driver) of changes in the activity coefficient across the zoned inclusion. This assertion is supported by peridotite melting experiments, where $\gamma_{CaO}$ has been shown to be elevated in alkali-rich low-degree melts from fertile compositions compared to alkali-poor depleted compositions at the same melt fraction (Wasylenki et al., 2003). Additionally, the $D_{CaO-Na_2O}$ cross terms in the diffusion matrices of Guo and Zhang (2016, 2018) are the largest magnitude coupling term between $CaO$ and another oxide, indicating strongly coupled diffusion. $Na_2O$ is itself strongly coupled to the slowly diffusing $SiO_2$ (Liang, 2010; Watson, 1982) and $Al_2O_3$ (Guo & Zhang, 2018), the result being that steep gradients in $X_{Na_2O}$ persist (i.e., do not diffuse away rapidly, section S3) in the diffusive boundary layer. A function relating $\gamma_{CaO}$ to $X_{Na_2O}$ in the liquid (Figure 14b) was defined by taking the liquid composition from melt inclusions experimentally homogenized at 1,225 °C (Table 2), diluting or enriching it with $Na_2O$, and monitoring the corresponding changes in $\gamma_{CaO}$ at constant temperature using MELTS, ignoring changes in other melt components, which were proportionally changed at each dilution so the sum of mole fractions equaled one. The development of $X_{Na_2O}$ profiles across a melt inclusion was modeled (Figure 14a) assuming that $Na_2O$ is incompatible in olivine (analogous to modeling $Al_2O_3$; see section S2) and has a diffusion coefficient $D_{Na} = D_{Si}$ (adopted from Chen & Zhang, 2008). Using the relationship between $X_{Na_2O}$ and $\gamma_{CaO}$ shown in Figure 14b, $\gamma_{CaO}$ can be calculated at each position and time.

The $X_{CaO}$ profile is then obtained at each time step by dividing the modeled $a_{CaO}$ profile by the corresponding $\gamma_{CaO}$ profile, calculated from the $Na_2O$ model. Results of this forward model are shown in Figure 14d for linear cooling from 1,225 to 1,000 °C for a range of cooling rates comparable to those achieved.
Figure 14. All of the forward models shown on panels a and c–e were run over the temperature interval 1,225 to 1,000 °C.
(a) Forward models of Na$_2$O profiles (black curves) across a 75-μm radius melt inclusion cooled from 1,225 to 1,000 °C at rates of 50,000, 20,000, 5,000, 1,000, 500, and 100 °C/hr. The red horizontal line is the initial Na$_2$O of the liquid. The interface Na$_2$O was calculated by mass balance with olivine growth calculated with the MgO diffusion model (section 4) and is built up in the liquid near the inclusion wall because the Na$_2$O gradients are slow to relax. (b) Mole fraction Na$_2$O ($X_{Na_2O}$) vs. the CaO activity coefficient ($\gamma_{CaO}$) in the liquid according to MELTS. Described in section 5.1, the melt composition given in Table 2 was diluted by varying the mole fraction of Na$_2$O and then monitoring the corresponding changes in the activity coefficient of CaO in the liquid. The black curve is a second-order polynomial fit to the output of this exercise. (c) Forward models of the CaO activity in the liquid ($a_{CaO}$), calculated as described in section 5.1. The horizontal red line corresponds to the MELTS calculated activity of $a_{CaO}$ at 1,225 °C in a liquid whose composition is given in Table 2. The boundary condition of $a_{CaO}$ in the interface liquid is given by the MELTS calculation of batch olivine crystallization with the starting composition given in Table 2. (d) Forward models of the CaO mole percent in the liquid ($X_{CaO}$), calculated by dividing the $a_{CaO}$ profile at each temperature step by the corresponding $\gamma_{CaO}$, which was calculated by substituting the Na$_2$O profiles into the equation shown in panel b. The horizontal red line is the initial $X_{CaO}$ in the models. (e) Forward models for three inclusions of different sizes (50, 75, and 100 μm) all cooled at 1,000 °C/hr from 1,225 to 1,000 °C, which show how the transient maxima in the CaO profiles relax more quickly for smaller inclusions than for larger inclusions subjected to the same cooling path.
experimentally. Despite the oversimplification of using a single cross term to describe the activitycomposition relations, this forward model captures the distinctive features of the CaO profile evolution as a function of cooling rate: an elevated $X_{CaO}$ close to the interface relative to the center at the highest cooling rate, the inward movement and broadening of local maxima near the inclusion walls at intermediate rates, the ultimate complete inversion of the model profiles to concave down shapes at lower cooling rates where CaO is low at the olivine-liquid boundary relative to the inclusion interior, and the progressive increase in the average CaO in modeled melt inclusion as required by its incompatibility in the olivine crystallizing on the wall. The low $X_{CaO}$ near the inclusion wall for all profiles results from the buildup of Na$_2$O in the interface region during progressive olivine crystallization. The model also reproduces the expected effect of inclusion size on the shape of the CaO profile for a given cooling path (1,225–1,000 °C), where the transient humps relax more quickly in smaller inclusions for which diffusive exchange between the inclusion edge and center is more rapid (Figure 14e). We note, however, that in this model, due to the assumption that changes in $\gamma_{CaO}$ are solely due to $X_{Na_2O}$, CaO does not strictly obey mass balance; however, the magnitude of the deviation from mass balance is small. For example, at rates of 500–50,000 °C the integrated modeled CaO contents for a 75-μm radius inclusion (Figure 14d) deviate by less than 0.15 wt % from the expected bulk CaO assuming mass balance and $D_{CaO,ol/melt} = 0.02$, and at 100 °C/hr the modeled inclusion is 0.42 wt % deficient in CaO, corresponding to a 4% relative deficit from mass balance. While a more sophisticated approach may be necessary to accurately model CaO diffusion, the simplified model presented here reproduces the overall effect observed in melt inclusions.

Figure 15. Horizontal red lines indicate the initial CaO, MgO, and Na$_2$O contents of the liquid in weight %. The colored circles are microprobe data from selected experimental melt inclusions, blue: CaO; gray: MgO; green: Na$_2$O. The corresponding colored lines are forward models calculated with the CaO model described in section 5 over a temperature interval of 1,225–900 °C and specifying the measured experimental cooling rate. (a) H9X1_1: 20,190 °C/hr; (b) H2X5: 1570 °C/hr; (c) H5X1_1: 715 °C/hr; and (d) H7X1: 190 °C/hr.
Figure 15 compares microprobe data from four experiments to the corresponding forward model calculations for CaO, MgO, and Na2O, run with no free parameters by specifying $T_{max} = 1,225$ °C, $T_{min} = 1,000$ °C, and cooling rate. The shapes of the CaO profiles—-as well as those of Na2O and MgO—reproduce well those measured in the experimental inclusions, with elevated CaO near the interface is the more rapidly cooled experiments (Figure 15a and 15b) and low CaO at the interface relative to the inclusion center in the slowly cooled experiments (Figures 15c and 15d). The model is offset in absolute concentration from the measured experimental profiles, almost certainly reflecting the oversimplification that all changes in $\gamma_{CaO}$ are due to Na2O and inherent variability in the initial Na2O concentration of experimental inclusions (Table 2 and Figure 5b). Nevertheless, this simple model demonstrates that under certain plausible assumptions, it is possible to describe the main features of the CaO profile evolution as a manifestation of increased $\gamma_{CaO}$ in the boundary layer melt, which is enriched in those oxides that are slow to diffuse and which have a substantial influence on the solution properties of Ca-bearing liquid components. The model also shows that except for the most rapidly quenched samples and for the largest melt inclusions, the CaO contents measured at the center of the inclusion will be high relative to the initial concentration prior to crystallization during cooling, and thus in order to obtain the correct concentration of CaO in a glassy melt inclusion either the inclusion needs to be homogenized at the correct temperature or the CaO profile can be integrated across the inclusion (i.e., a single analysis from the inclusion center is likely to be an unreliable measure in all but the most rapidly cooled inclusions).

6. Natural Samples: Hawaii and Shergottite Y980459

6.1. Hawaii

Cooling rates were determined for glassy melt inclusions from Papakolea Beach olivine by fitting their measured MgO concentration profiles using the model described in section 4. For modeling natural inclusions, it is necessary to calculate either the composition or temperature ($T_{max}$) of the homogeneous inclusion liquid prior to cooling, which serves to define the model initial condition. There are several possible approaches to estimating this composition (see section S2 in Newcombe et al., 2014), and as described in section 5, the shape of the CaO profile can help distinguish whether plateaus in MgO are due to rapid cooling or to multi-component effects. Half of the natural inclusions we have studied show evidence for protracted cooling, either with CaO profiles that are highest in the inclusion center and lowest at the olivine-glass interface or with CaO maxima at positions between the inclusion center and the olivine interface; for such inclusions, the central MgO contents have likely been modified by diffusive exchange with the evolving interface melt (e.g., compare the MgO and CaO profiles in Figures 7 and 8 panels c- f and HIGS2 and HIGS14 in Figures 16c and 16d). In these cases, the initial temperature or MgO contents must be estimated using an alternative to taking the measured central MgO content as representative of the initial MgO content.

Five of the 10 natural Papakolea inclusions studied have CaO profiles that indicate they experienced rapid cooling and have compositional plateaus in MgO that can be used to directly set the model initial conditions (e.g., HIGS9 and HIGS4; Figures 16a and 16b). Because the unheated Papakolea samples are considerably more oxidized than in the experiments (see XANES results in section 2.2), a new boundary condition was calculated using a fit to the MELTS-calculated liquid line of descent for olivine crystallization at FMQ+0.3,

$$C_{MgO}^{liq} (\Delta FMQ + 0.3) = 3.352 \times 10^{-5} \times T^2 - 0.06828 \times T + 36.18$$

(3)

where $T$ is in K and $C_{MgO}^{liq}$ is weight percent MgO in the liquid. Equation (3) has the same form as equation (1) but takes into account that forsteritic olivine is stabilized at higher $fO_2$ (Nitsan, 1974) and is shown for comparison as the dashed light blue line in Figure 10a. Applying equation (3) using the corresponding central plateau MgO contents in the rapidly cooled samples (which ranges from 6.2 to 7.2 wt % in the different inclusions) gives temperatures of 1,123–1,160 °C (compared to using equation (1), giving 1,137–1,174 °C). For each inclusion with an MgO plateau interpreted as representing the initial MgO content of a homogeneous inclusion prior to cooling and crystallization, this calculation was used to set the initial temperature, $T_{max}$ after which the inversion model was run as described in section 4 for the experiments but with equation (3) substituting as the boundary condition for the temperature dependence of $C_{MgO}^{liq}$. Cooling rates that correspond to the best fit profiles for the five rapidly cooled inclusions (subset shown in Figures 16a and 16b,
all results in Table S2) have a range of 7,500–11,800 °C/hr. In addition to the errors inherent to the inverse model, there are additional uncertainties related to the precision of the MgO microprobe data. These errors are particularly important for rapidly cooled inclusions with narrow boundary layers because the model fits are sensitive to the few data points near the inclusion wall that have MgO contents less than the central plateau (section S2). Following the bootstrap approach employed by Newcombe et al. (2014) (Efron & Tibshirani, 1985), the errors were calculated by perturbing the MgO profiles with Gaussian noise sampling the uncertainty of the MgO microprobe data (1σ = 0.075 wt %), and then refitting each synthetic profile and calculating the distribution of best fit cooling rates. For the rapidly cooled inclusions, the errors in the calculated cooling rate correspond to 6–14% relative, and for the slowly cooled inclusions with no central plateau described below these errors are typically <1%. The inversions were also run assuming equation (1) as the boundary condition, which resulted in best fit cooling rates that differed by −20% (HIGS11) to +36% (HIGS4) from the rates calculated using equation (2).

In order to determine $T_{\text{max}}$ for those inclusions with center compositions that have been modified by diffusion during cooling, Newcombe et al. (2014) adopted the approach of taking the highest MgO value recorded for a given inclusion population and applying the MgO vs. $T$ thermometer of Chen and Zhang (2008). For the Papakolea samples, the highest MgO (7.2 wt %) comes from the compositional plateau of HIGS11, and applying equation (3) corresponds to a $T_{\text{max}}$ of 1,160 °C. An alternative to this assumption would be to reconstruct the initial composition of the liquid by adding liquidus olivine in increments to the integrated bulk composition of the inclusion until reaching a target liquidus olivine composition, as is commonly done to determine the composition and conditions of melt inclusion entrapment. Due to ambiguity in accurately knowing what olivine composition along its zoning profile was in equilibrium with the inclusion liquid at $T_{\text{max}}$ (see section

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**Figure 16.** Application of the inverse model for MgO diffusion described in sections 4 and 6 to natural Hawaiian olivine-hosted melt inclusions. (a–d) Papakolea, Hawaii. (e and f) Kilauea Iki, Hawaii. The blue curves show the best fit model to the data, and the corresponding cooling rate (°C/hr) is listed in each panel. The red horizontal line is the calculated initial MgO in the liquid prior to cooling at $T_{\text{max}}$. In addition to the MgO profile shown in dark gray filled circles, the corresponding CaO profiles are shown in blue circles to demonstrate the cooling-rate dependent shapes described in section 5 and used to evaluate relative cooling rates as discussed in section 6.
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In addition to the Papakolea samples, melt inclusions in four olivines collected in the Kilauea Iki crater were measured. The scoraceous olivine gravels are interpreted to be from a fire fountaining stage of the 1959 eruptions (Richter et al., 1970). All four inclusions have elevated CaO contents at the inclusion edge and compositional plateaus in the inclusion centers for MgO (Figures 16e and 16f) and all other oxides, indicating rapid cooling and permitting a straightforward calculation of $T_{\text{max}}$. The Fe$^{3+}$/Fe$^{\text{Total}}$ from measured in Kilauea Iki melt inclusions by Helz et al. (2016; ranging from 0.16 to 0.18, mean = 0.17, n = 5 inclusions) overlap with the Papakolea inclusions (Fe$^{3+}$/Fe$^{\text{Total}}$ = 0.16–0.22, n = 4 inclusions). Expressed relative to FMQ at 1,225 °C and 1 bar (Kress & Carmichael, 1991; equation 7), the data sets are statistically indistinguishable in terms of the oxygen fugacity recorded in their glasses ($\Delta$FMQ = 0.29±0.19 and + 0.45±0.18 [1σ], respectively). Accordingly, equation (3) (calculated at $\Delta$FMQ = + 0.3) was used to evaluate the $T_{\text{dependent}}$ boundary condition of MgO in the evolving interface liquid for the model calculation, as for the Papakolea inclusions. The MgO contents at the plateaus of these inclusions range from 7.2 to 7.7 wt %, giving modeled $T_{\text{max}}$ of 1,161–1,181 °C via equation (3). The best fit cooling rates for these four Kilauea samples range from 5,100 to 8,800 °C/hr (Figure 17 and Table S2). Errors associated with the uncertainty in the MgO microprobe analyses correspond to a 4–7% relative difference in the calculated cooling rate (1σ).

The Papakolea samples form two distinct groups, those with low cooling rates (51–854 °C/hr) and rapidly cooled samples (6,520–11,810 °C/hr); the Kilauea Iki samples (5,100–8,800 °C/hr) correspond well to the more rapidly cooled Papakolea samples. Taken together, these Hawaiian inclusions span a similar range of cooling rates as those obtained by Newcombe et al. (2014) for subaqueous and subaerial basalts (Figure 17a). Assuming a simple model of one-dimensional heat diffusion (Carslaw & Jaeger, 1959) into an infinite basaltic melt (thermal diffusivity $\kappa$ = 0.35 mm$^2$/s; Patrick et al., 2004), and that the inclusions cooled over the interval from $T_{\text{max}}$ to $T_{\text{min}}$, these cooling rates are consistent with olivine phenocrysts located 0.3–0.5 cm from a 0 °C boundary for the rapidly cooled group and ~2–8 cm for the more slowly cooled group. The difference between the more rapidly and more slowly cooled Papakolea inclusions—which do not differ significantly in their major element compositions—could be related to cooling at different depths in either subaerial or submarine basalt flows, but the implication that all formed within ~10 cm of a flow surface seems highly restrictive, unless glassy inclusions can only form under these conditions. On the other hand, the correspondence of the cooling rate ranges of the more rapidly cooled Papakolea samples, subaerial spatter from the Santiago volcano, and the Kilauea Iki samples (which are known to have formed during fire fountaining events) may reflect that they all experienced similar histories as ballistic molten basaltic fragments. This would be consistent with the conclusion of Walker (1992) that most of the Papakolea olivine beach sands were derived from erosion of overlying pyroclastic ash beds. In this case, the group of Papakolea inclusions that yield significantly lower cooling rates could represent a different emplacement mechanism, perhaps derived from the massive basalt flows that overlie the ash beds (Walker, 1992), or formed in larger droplets of molten basalt that cooled more slowly during fallout and/or continued cooling in the pyroclastic pile after deposition (e.g., Thomas & Sparks, 1992; Capaccioni & Cuccoli, 2005).

Another possibility is that water in the inclusion liquids affects MgO diffusion and that the apparent variability in cooling rate is due to different $H_2O$ contents. Using a $D_{MgO}$ determined from dry diffusion data to calculate a cooling rate from an MgO profile formed in a wet liquid would lead to erroneously low cooling rates, implying that the group of inclusions with low cooling rates should have significantly higher $H_2O$ contents. However, although the natural inclusion from Papakolea with the lowest calculated cooling rate (HIGS14, 51 °C/hr; Figure 16d) has $H_2O = 0.20±0.02$ wt % (2σ), which is higher than the $H_2O$ contents measured in a rapidly cooled inclusion (HIGS11, 7,900 °C/hr with $H_2O = 0.10±0.04$ wt % (2σ)), the low water contents in both and the relatively small difference between the two $H_2O$ contents are unlikely to account for the three order of magnitude difference in calculated cooling rate. Kilauea Iki melt inclusions have
H₂O contents from 0.25 to 0.95 wt % (Anderson & Brown, 1993; Sides et al., 2014; Tuohy et al., 2016), and yet the inclusions have uniformly high cooling rates. More samples would need to be analyzed to understand whether the bimodality in cooling rates determined for the Papakolea melt inclusions is robust or an undersampling a continuum; however, it is unlikely that the variability in cooling rates is due to different H₂O contents.

Figure 17. Histograms of cooling rates calculated for volcanic samples. (a) Cooling rates determined by MgO diffusion in olivine-hosted melt inclusions. The colored bars show the range of cooling rates calculated from MgO diffusion speedometry in natural melt inclusions from this study; Papakolea (red bars) and Kilauea Iki (green bar). The three gray bars below show cooling rates calculated by MgO diffusion speedometry in melt inclusions from the Galapagos and Siqueros Fracture Zone (Newcombe et al., 2014). The filled circles correspond to cooling rates from individual inclusions. (b) Cooling rates of Hawaiian glasses determined by enthalpy relaxation. The gray bars show ranges of cooling rates from Pu‘u ‘O‘o (Greshake et al., 2004), HSDP hyaloclastites and pillow rims (Nichols et al., 2009), and from Loihi Seamount (Potuzak et al., 2008). Note that the cooling rates calculated for the fine grain sieve from Loihi Seamount plot off of the chart (10⁸ °C/hr) and are indicated by an arrow. (c) Cooling rates calculated using a variety of techniques for shergottite Yamato 980459. The yellow bar and filled circles show cooling rates calculated from this study using MgO diffusion in glassy melt inclusions. The gray circles on the row below the yellow bar show estimated cooling rates for Stages 1–3 of Martian meteorite Yamato 980459 from the dynamic cooling experiments of First and Hammer (2016), and the gray rectangle shows the range of estimates for Stage 3 from Greshake et al. (2004) based on the morphology of olivine dendrites.
Most of the literature on quantifying cooling rates of natural volcanic glasses comes from enthalpy relaxation geospeedometry, where glasses are subjected to heating and cooling cycles through the glass transition in a differential scanning calorimeter that monitors heat capacity (Wilding et al., 1995). This technique has been applied to natural glasses, including several studies of Hawaiian glasses that report a wide range in cooling rates measured at the glass transition (Figure 17). These include degassed hyaloclastites and undegassed pillow rims from the Hawaii Science Drilling Project (HSDP) Core 2, giving rates of 360–260,000 °C/hr and 720–167,000 °C/hr, respectively (Nichols et al., 2009); glassy crusts of pahoehoe flows from Pu’u ‘O’o with cooling rates of 480–8,400 °C/hr (Gottsmann et al., 2004); and cooling rates recorded in sieved glass shards (300,000–600,000 °C/hr for the 0.8- to 1.2-mm fraction, and 10^5 °C/hr for 30- to 80-μm fraction) from explosive submarine eruptions at Loihi Seamount (Potuzak et al., 2008). The upper half of the distribution of cooling rates calculated based on zoning in melt inclusions overlap with the cooling rates based on the enthalpy relaxation approach applied to glassy pahoehoe crusts (Gottsman et al., 2004; compare Figures 17a and 17b) and the lower half of the distribution of HSDP glasses (for which the pillow rims are likely most comparable to the submarine mid-ocean ridge basalt and OIB samples investigated by Newcombe et al., 2014). However, the melt inclusion results do not approach to the highest rates (up to ~10^5–10^6 °C/hr) measured by enthalpy relaxation on the HSDP hyaloclastites and pillow rims or to the ~10^6–10^7 °C/hr measured by enthalpy relaxation on the Loihi glass shards. However, applying our model to inclusions experimentally drop-quenched directly from the 1,260 °C hotspot in experiment H10X into room temperature water (i.e., inverting the narrow MgO diffusion profiles caused by quench growth of olivine in the homogenized samples; black rectangles labeled “generated by quench growth” in Figure 5) yield cooling rates ranging from 44,000–120,000 °C/hr, suggesting that our approach may be capable of resolving rates at least this high in natural inclusions (although for such drop-quenched inclusions, there are sparse MgO analyses in the narrow boundary layer in the interface liquid and so the inversion for cooling rate is more sensitive to the uncertainty in MgO analyses (1σ = 0.075), giving associated errors of 16,000–100,000 °C/hr). In any case, the uncertainties on our derived cooling rates are far too small to explain the absence of natural samples extending to the extraordinarily high cooling rates determined for some submarine glasses based on enthalpy relaxation. Perhaps the difference reflects the higher temperature range probed by our approach relative to the enthalpy relaxation measurements, which measures cooling rates at the glass transition. And although asymptotic cooling would be expected to lead to lower cooling rates for the lower temperatures probed by the enthalpy relaxation technique, it is also possible that more complex thermal histories are involved in the low temperature thermal histories, especially for the Loihi glass shards produced by explosive submarine eruptions. Application of the techniques developed here and in Newcombe et al. (2014) to melt inclusions in olivines with adhered matrix glass to which the enthalpy relaxation technique could be applied would provide useful information on whether the two techniques are comparable when applied to samples that experienced identical cooling histories, and if not, what this might signify.

6.2. Mars

Melt inclusions occur in the olivines of Martian meteorites (i.e., olivine-bearing shergottites, nakhlites, and chassignites), but they are rarely entirely glassy (as opposed to partially crystalline) and even more rarely do they have SiO₂ contents <60 wt %, comparable to the basaltic glassy inclusions from Hawaii that we have studied (Ikeda, 2005). Moreover, the glassy inclusions in Martian meteorites are typically <10 μm in radius, and they are often in the same host grains as larger, partially crystallized inclusions. Because the number of microprobe points across such small glassy inclusions is limited, they typically preclude applying the inversion model described in section 4. The lack of large glassy inclusions in Martian minerals, and the prevalence of multiphase crystalline magmatic inclusions, has been interpreted to reflect prolonged episodes of slow cooling in most of the inclusion-bearing samples (Ikeda, 2005).

An exception is the olivine-phryic shergottite Yamato 980459 (Y980459), which has been extensively studied due to its vitrophyric groundmass texture indicative of rapid cooling, and a whole-rock composition that has been interpreted as a relatively primitive melt of the Martian mantle (First & Hammer, 2016; Greshake et al., 2004; Musselwhite et al., 2006; Usui et al., 2008). Thin sections of Y980459 have relatively large (up to ~100 μm longest dimension) glassy magmatic inclusions contained in olivine (Greshake et al., 2004; Ikeda, 2004; Ikeda, 2005). A multistage magmatic thermal history of Y980459 has been proposed to explain (1) large olivine phenocrysts formed during slow cooling from a liquidus temperature of 1,440 °C at rates <1 °C/hr (First
& Hammer, 2016); (2) the crystal size distributions of pyroxene phenocrysts, interpreted as requiring cooling rates <10 °C/hr (First & Hammer, 2016; Lentz & McSween, 2005); and (3) the vitrophyric groundmass texture, interpreted as evidence of a late stage of rapid cooling with rate estimates ranging from ~150 °C/hr (First & Hammer, 2016) up to 1,450–1,890 °C/hr (Greshake et al., 2004; Figure 17). Although the melt inclusions were likely trapped during the growth of phenocrysts early in the cooling history of the magma, the proposed cooling rates from stages 1 and 2 are too low to preserve measurable diffusion profiles in melt inclusion based on our results. For example, a forward model of an inclusion cooling from 1,150 to 1,050 °C predicts that the MgO gradient will be less than the 2σ uncertainty in the microprobe measurements (<0.15 wt %) for inclusions <50 μm in radius. The initial slow cooling stages were likely at temperatures of 1,440 °C down to ~1,115 °C (First & Hammer, 2016) where diffusion would have been even more efficient at homogenization of inclusions than in the example given in the previous sentence. Accordingly, the inverse model developed in section 4 is only applicable to cooling stage 3, the final cooling interval, which produced the vitrophyric matrix. We applied our model to determine cooling rates on glassy, olivine-hosted melt inclusions in Y980459, assuming that these inclusions were initially homogeneous at a reconstructed Tmax that postdates the growth of the olivine and pyroxene phenocrysts formed during cooling stages 1 and 2.

The sample analyzed was a polished thin section of Y980459. As opposed to the Hawaiian samples, which were individually selected and then polished to expose melt inclusions at their maximum dimension, the meteorite thin section was analyzed as received and so the original dimensions of exposed inclusions are unknown, as well as the orientation of the thin section cut through their initial shapes. When applying the inverse model to progressively off-center cuts through a model spherical melt inclusion, which sample more of the boundary layer (Newcombe et al., 2014), best fit cooling rates calculated by running the inversion model on the synthetic off-center MgO profiles always skew to lower rates (Figure S10). For an

Figure 18. Glassy inclusions in Martian meteorite Yamato 980459. (a and b) Backscattered electron images showing the locations of a subset of the glassy inclusions analyzed; note that Y98M17-10 was enclosed in the same olivine host. The white lines indicate the locations of microprobe traverses. (c) The gray circles show microprobe MgO data measured across the glass inclusions from Y980459. The blue curves are the best fit model calculated based on the cooling rates listed in the lower right corner.
inclusion exposed along an unknown cut, the individual cooling rate is thus considered a minimum estimate (while still subject to the other uncertainties inherent to the model).

Eight glassy inclusions were analyzed with the electron microprobe using the same conditions as described in section 2.3 (Figure 18). The inclusions chosen for analysis were roughly circular, with longest dimensions of 12–40 μm (median = 18 μm); their small sizes limited the number of microprobe points that could be acquired in a traverse, but enough high-quality points (9 to 19) were collected in some inclusions to produce an interpretable profile. As in the terrestrial samples, some inclusions contained an Fe-rich spinel phase that was avoided in the analyses. Relative to most other Martian melt inclusions (e.g., Ikeda, 2005), these are relatively low SiO2 glasses with a minimum of 56.3 wt % (center of inclusion Y98M16), and 6 of 10 inclusions with minimum SiO2 contents <60 wt % (the minimum SiO2 ranged from 56.3 to 64.3 wt %). Compared to other Martian samples (e.g., Ikeda, 2005), the inclusions also have relatively high MgO contents (up to ~3 wt % along zoned profiles), permitting the application of the MgO profile geospeedometer as described in section 4. The $D_{\text{MgO}}$ in equation (2) was fit over a range of SiO2 values from 43 to 70 wt % (Zhang, 2010), so it can be applied to model a composition-dependent $D_{\text{MgO}}$ in liquids spanning the range of the studied inclusion compositions. All of the Martian inclusions are zoned, and the shapes of oxide concentration profiles are qualitatively similar to those in terrestrial and experimental samples: MgO, CaO, and FeO are concave down, whereas SiO2, Al2O3, and Na2O are concave up (Figure 18 for MgO and section S3 for all oxides). However, the glass compositions differ systematically from the Hawaiian inclusions we have studied: MgO contents are lower in the Martian glasses (1.9–2.8 wt %) compared to the Hawaiian glasses (3.6–7.2 wt %), and SiO2 (56.3–66.0 wt %) and P2O5 (0.7–1.5 wt %) contents are generally higher than in the Hawaiian samples (52.7–58.5 wt % SiO2 and up to 0.7 wt % P2O5). Total Fe expressed as FeO* overlap, ranging from 5.7 to 9.5 wt % in Y980459 and 6.2–9.8 wt % in the Papakolea glasses. The far-field host olivines in Y980459 range from Fo72.0 to Fo76.7 (compared to the average Hawaiian olivine at ~Fo87) and are progressively enriched in FeO closer to the inclusion wall, with a minimum of Fo62.8 to Fo59.5 at the inclusion boundaries. Within 1–4 μm of the inclusion wall, there is a narrow zone of steep Fe enrichment in the olivine, which is adjacent to a broader zone of more magnesian olivine enclosing melt inclusions that extends ~5–15 μm from the inclusion wall grading into the far-field olivine compositions, similar to the zoning observed in the terrestrial olivine (Figure 9 and section S3.3 for zoning profiles around the Y980459 melt inclusions). The broad zone is consistent with a period of prolonged cooling, crystallization, and Fe-Mg interdiffusion in the olivine, likely related to cooling stages 1 and 2.

The inclusions are small relative to the Hawaiian olivines, and on the basis of their concave down CaO profiles (section S3.3), the diffusive boundary layer has reached the centers of all of the Martian inclusions; that is, the glass compositions in the inclusion centers have been modified by exchange with the interface melt, and so the initial compositions and $T_{\text{max}}$ of the inclusions need to be reconstructed. This is unsurprising given the small radii of the inclusions measured. An average composition for each inclusion was calculated by spherically integrating the zoned compositional profile, and then iteratively adding olivine back to the inclusion until it was in equilibrium with the olivine at the boundary between the narrow fayalitic zone (1.5–4 μm thick) adjacent to the inclusion wall and the onset of the broad zone. Corresponding target forsterite contents ranged from Fo73.2 to Fo75.8. The FO2 for the olivine addition calculation was set to the iron-wüstite buffer, consistent with vanadium partitioning oxybarometry between glass and olivine in Y980459 (Shearer et al., 2006). This calculation yielded a range of $T_{\text{max}}$ from 1,148 to 1,244 °C with a mean of 1,179 °C, which was chosen as the preferred $T_{\text{max}}$ for the cooling rate calculation. Following this procedure for eight inclusions gave reconstructed initial inclusion compositions of MgO of 5.1–8.5 wt %, SiO2 = 51.5–61.8 wt %, Al2O3 = 8.4–11.6 wt %, and FeO = 8.2–16.2 wt %. These reconstructed melt compositions correspond to addition of 30–45% olivine by volume back into the inclusions to achieve equilibrium with the enclosing olivine, consistent with the 30–40% by volume addition estimated for reconstructions of Y984059 melt inclusion compositions from Peters et al. (2015) using Petrolog3 (Danyushevsky & Plechov, 2011). Reconstruction of small glassy melt inclusions in Tissint by Sonzogni and Treiman (2015) similarly required 25–51% olivine addition by mass to the glasses in order to achieve equilibrium with the host olivine (Fo58–Fo72). This calculated amount of olivine extraction necessary to reconstruct compositions of shergottite melt inclusions is also consistent with the measured thickness of the narrow Fe-rich olivine zone adjacent to the inclusion walls (i.e., 4 μm of inward olivine growth on the wall of a spherical 20 μm radius inclusion represents a 49% change in volume).
For inclusions with centers that have been modified by diffusion during cooling, the cooling rates calculated using the model from section 4 are relatively insensitive to the choice of $T_{\text{max}}$ (section S2), and no choice of $T_{\text{max}}$ leads to a statistically significant improvement in the fitting of the microprobe data: For example, varying $T_{\text{max}}$ from 1,102 to 1,251 °C ($2\sigma$ of range of reconstructed $T_{\text{max}}$) results in relative changes in the calculated cooling rate of 5% for inclusion Y98MI1 and <1% for all other inclusions. Accordingly, $T_{\text{max}} = 1,179$ °C was chosen as the initial condition for all the inclusions, corresponding to an average initial MgO of 6.82 wt % in the reconstructed liquids. The initial SiO$_2$, Al$_2$O$_3$, and FeO were adjusted for each inclusion based on olivine addition. For the temperature-dependent boundary condition of MgO in the interface liquid, a MELTS batch olivine crystallization was used, starting from the average reconstructed liquid composition of the Y980459 inclusions. Forward modeling of these SiO$_2$, Al$_2$O$_3$, and FeO was done with the approach described in section 4.

Substituting the MELTS parameterization of the C$_{\text{MgO}}$ calculated at an JO$_2$ at the iron-wüstite buffer, the model as described in section 4 was run for the inclusions from Y980459. Because the MgO contents of the zoned inclusions are low and the gradients are relatively shallow (~1.5–3 wt % MgO with gradients of 0.5–1 wt % from the center to the edge of the inclusion; Figure 18c), the error associated with uncertainty in the MgO microprobe analysis has a more substantial effect on the calculated cooling rates (~10% relative, 1σ) compared to the Hawaiian examples (<1% relative for low cooling rates). The errors reported for these inclusions correspond to perturbing the profiles with 1σ MgO noise (0.075 wt %) and inverting 10 iterations of these synthetic datasets and exclude errors associated with the choice of $T_{\text{max}}$ or associated with an off-center cut. Cooling rates for individual inclusions vary from $85 \pm 11$ °C/hr (Y98MI2) to $1,047 \pm 109$ °C/hr (Y98MI9), and the largest inclusion measured, Y98MI1 (42 μm longest dimension), has a calculated cooling rate of $331 \pm 21$ °C/hr. The distribution of the average cooling rates (10 iterations perturbed with 1σ noise) calculated for each inclusion is $383 \pm 43$ °C/hr ($n = 8$). The different cooling rates are not correlated with size nor location in the thin section; that is, Y98MI9 has the highest cooling rate of the samples measured but is enclosed in the same olivine grain as Y98MI7, Y98MI8, and Y98MI10, which have rates from 223 to 389 °C/hr (Figure 18b). Boundary motion is not accounted for in the model, and by excluding its effect, we tend to overestimate the cooling rate by incorrectly using a smaller initial inclusion radius than was originally present at $T_{\text{max}}$, an effect which becomes increasingly important for smaller inclusions. For example, rescaling the MgO profile from a 20-μm radius inclusion (Y98MI1) to 16-μm radius and fitting each profile separately gives cooling rates of $555 \pm 40(1\sigma)$ °C/hr and $328 \pm 20(1\sigma)$ °C/hr, respectively.

Cooling rates calculated from MgO diffusion in melt inclusions correspond to stage 3 of the proposed cooling history of Y980459, which produced the vitrophyric texture in the rock. The distribution of rates recovered from the eight inclusions (ranging from 85 to 1,047 °C/hr) overlaps with the 150 °C/hr estimate based on crystal size distributions from the cooling experiments of First and Hammer (2016) and is within a factor of 2 of the estimates of 1,450 to 1,890 °C/hr from Greshake et al. (2004); Figure 17c). The very low H$_2$O contents measured in two melt inclusions from Y980459 (146–251 ppm and 458–841 ppm; Usui et al., 2012) indicate that the range in cooling rates is likely not due to the effect of variable H$_2$O on diffusion in the inclusion liquids. The cooling rates calculated with the MgO diffusion model are subject to uncertainties in reconstructing $T_{\text{max}}$ in the MELTS approximation of the olivine liquidus surface at Martian conditions (Balta & McSween, 2013, and that the small inclusions (<40 μm in longest dimension) permit only short profiles, which may be influenced by boundary motion. Despite these uncertainties, which are reflected in the range of cooling rates calculated from the eight inclusions, the inverse model produces profiles that fit the MgO profiles in glassy inclusions from Y980459 as well as in the terrestrial examples described in section 6.1. The quenched diffusion profiles in melt inclusions provide an independent quantitative estimate that further supports the hypothesis that Y980459 experienced rapid cooling through the glass transition, likely at or near the Martian surface (Balta & McSween, 2013; First & Hammer, 2016; Greshake et al., 2004).

7. Conclusions

1. A series of 1-atm experiments on olivine-hosted melt inclusions were homogenized for 24 hr at 1,225 and cooled at controlled rates of 70–50,000 °C/hr. Additionally, one set of experiments was homogenized at 1,260 °C with a cooling history of two linear segments. These experiments document the cooling rate and temperature-dependent evolution of compositional zoning across glassy melt inclusions that develop
during cooling due to progressive crystallization of olivine on the inclusion wall. All of the experimentally cooled inclusions are compositionally zoned, characterized by lower MgO and FeO and higher SiO₂, Al₂O₃, and Na₂O (and other incompatible oxides) near the inclusion wall relative to the inclusion center. The observed zoning evolves with time due to competition between continuous formation of a boundary layer in the melt adjacent to the inclusion wall and diffusive exchange between this boundary layer and the interior of the inclusion. The inclusion centers eventually become modified by diffusive exchange with the boundary layer liquid, resulting in central compositions that differ from that established during the homogenization step. Modification of central compositions by diffusion is more effective at lower cooling rates and for smaller inclusions. The experiments are consistent with and allow quantification of the hypothesis that the ubiquitous zoning in natural melt inclusions forms during syneruptive cooling of basaltic lavas (Newcombe et al., 2014).

2. A model for MgO diffusion (Newcombe et al., 2014) was modified to accommodate a boundary condition that uses MELTS to calculate the interface liquid composition at each temperature during the cooling history, and a composition- and temperature-dependent diffusivity of MgO (Zhang, 2010) that takes into account that the diffusivity of MgO decreases with the increases in SiO₂ and Al₂O₃ concentrations in the boundary layer that develops with progressive crystallization of olivine on the inclusion wall. By varying the cooling rate, the model was fit to MgO profiles measured along transects of experimental glass inclusions. When comparing the cooling rates that resulted in the best fit between model and data, the model accurately recovers the experimental rates: for intermediate cooling rate experiments (at 93, 466, 715, 1570, and 20,190 °C/hr) the best fit model cooling rates for inclusions from a given experiment deviate by less than ±10% from the known rate; for the lowest (70 °C/hr) and highest (49,644 °C/hr) experimental rates the best fit model cooling rates deviate from the known cooling rate by up to a factor of 2. These results indicate that such a model can be used to quantify eruptive cooling rates, which span several orders of magnitude in nature based on application of this model to natural inclusions from Hawaii.

3. The effects of multicomponent diffusion were observed in every liquid component measured in the experimental melt inclusions, including uphill diffusion producing local extrema along diffusion profiles (for instance in CaO) and flattening of the central portions of MgO profiles. CaO exhibits the most extreme manifestation of multicomponent diffusion effects: In particular, CaO is incompatible in olivine and is expected to be continually enriched in the liquid at the olivine crystallization front, and though this is observed in rapidly cooled samples, in more slowly cooled samples, CaO is low at the inclusion interface relative to the center. This leads to CaO profiles that qualitatively appear more similar to the profiles of compatible components such as MgO and FeO rather than to other incompatible components such as Al₂O₃. The CaO behavior was semiquantitatively modeled by assuming that the CaO component in the liquid diffuses down its own activity gradient but that increases in the CaO activity coefficient are driven by increases in Na₂O in the boundary layer near the inclusion wall. This model reproduces the cooling-rate dependent evolution of the CaO profile shape and is consistent with the extreme CaO diffusion behavior being due to the progressive buildup of steep gradients in elements such as Na, Al, and Si in the liquid adjacent to the olivine crystallization front that lead to strongly non-ideal behavior of the CaO component. The CaO profile shape can be used as a qualitative indicator of cooling rate: a profile with elevated CaO at the inclusion wall relative to the center is indicative of rapid cooling, whereas low CaO at the inclusion wall and a concave down profile is characteristic of prolonged cooling.

4. The MgO diffusion model was applied to natural glassy olivine-hosted melt inclusions from Papakolea, Hawaii (the olivine beach sands that were used as the starting materials for the experiments); from Kilauea Iki, Hawaii; and from the Martian meteorite Yamato 980459. The natural Papakolea inclusions yielded two inclusion populations, rapidly cooled (7,500–11,800 °C/hr, n = 5) and slowly cooled (51–854 °C/hr, n = 5), which is consistent with the beach sands being derived from both olivine-bearing ash beds and basalt flows (Walker, 1992). The cooling rates calculated using olivine-hosted melt inclusions from the fire-fountaining stage of Kilauea Iki uniformly gave rapid cooling rates of 5,100–8,800 °C/hr, which are consistent with rapid quenching of tephras in air. Cooling rates from zoned melt inclusions in Yamato 980459 range from 85 to 1,047 °C/hr with a mean and 1σ of the average cooling rate calculated for each inclusion of 383±43 °C/hr (n = 8). These rates overlap with estimates for cooling associated with stage 3 of the inferred thermal history of Y980450 (First & Hammer, 2016; Greshake et al., 2004) and support the hypothesis that the sample erupted at or near the Martian surface and was rapidly cooled through the glass transition.
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