Cracking the olivine zoning code: Distinguishing between crystal growth and diffusion

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ABSTRACT

Olivine composition and zoning patterns are widely used to reconstruct the evolution of mafic magmas from source to surface and to extract time scales of magmatic processes. Deciphering the olivine zoning code is challenging because the contributions of growth and diffusion may overlap. A detailed multielement (Fe, Mg, P, Al, and Ni) examination of zoning in an exceptional olivine with skeletal morphology allows unequivocal discrimination between these two processes using simple but powerful geometrical arguments. Olivine crystals initially grow rapidly and diagonally from corner locations, whereas diffusion effectively tracks mutually perpendicular crystal lattice orientations. Generating the zoning patterns for our case-study olivine required at least 4–5 months of diffusive reequilibration of Fe-Mg, further demonstrating that crystal morphologies produced by rapid growth can survive at magmatic temperatures for extended periods. No significant major element zoning is preserved after rapid growth, lending further credibility to time scales retrieved via diffusion modeling. Extending multielement approaches to decoding olivine zoning patterns can help determine whether the kinetic relationship between growth- and diffusion-induced zoning recognized herein is widely applicable. Such studies will improve our understanding of time scales of magma storage, solidification, mixing, and/or transit toward the surface.

INTRODUCTION

Olivine is a valuable petrological capsule for most mafic volcanic rocks. Its chemistry is routinely used to infer source lithology, as well as the evolution of the host magma from storage to ascent and eruption (e.g., Sobolev et al., 2007). Compositional zoning in olivine can also be used to retrieve time scales of magma residence, mixing, or transit via diffusion models (Costa and Dungan, 2005; Costa et al., 2008). On one hand, inferring source lithology and magma solidification histories requires that the chemical record of a studied olivine population be largely dominated by crystallization (e.g., Pearce, 1987). On the other hand, extracting time scales using compositional zoning in olivine usually relies on assuming a uniform or step-wise initial concentration, inferred to result from rapid crystal growth relative to diffusion (Costa et al., 2008). Both of these assumptions are controversial because (1) evidence for diffusion-related zoning is found in olivine populations typically used to infer source lithologies (e.g., Oeser et al., 2015), and (2) olivine growth is inferred to strongly modify the surrounding melt in Fe-Mg via fractional crystallization, thus resulting in initially zoned crystals (e.g., Pearce, 1987). The respective roles of growth and diffusion in determining zoning patterns in natural crystals can thus be ambiguous, and robust knowledge of the kinetics involved in both processes is necessary to resolve this issue.

Rates of chemical diffusion for common elements in olivine (e.g., Fe-Mg, Ni, Ca, and Mn) are well constrained (Chakraborty, 2010). For forsterite contents [Fo = 100 × Mg/(Mg + Fe)] between 60% and 90%, the diffusivity of Fe-Mg along the c crystallographic axis varies between 0.1 m^2/s and 1×10^{-15} m^2/s [Dohmen et al., 2007; assuming oxygen fugacity, f_{O_2}, near the quartz-magnetite-fayalite buffer (QFM), pressure, P = 0.1 MPa, and temperature, T = 1200 °C]. Diffusivities along the a and b axes are six times slower, yielding shorter concentration gradients compared to the c direction, which can be used to recognize diffusion-induced zoning in natural crystals (e.g., Costa et al., 2008).

Constraints on the rates of olivine growth are scarce. Experimentally derived growth rates depend largely on the degree of undercooling driving crystallization. Measured values range between 10^{-7} and 10^{-6} m/s for olivines formed at high undercooling ($\Delta T > 60$ °C) that exhibit skeletal and dendritic morphologies (referred to here as the rapid growth regime), and 10^{-10} m/s for crystals formed at lower undercooling ($\Delta T < 35$ °C) with polyhedral morphologies (slow growth regime) (Jambon et al., 1992). A careful examination of zoning patterns of slow-diffusing elements in olivine (P, Al) questioned the conventional view that phenocrysts grow concentrically around a central polyhedral seed (Welsch et al., 2014). Instead, P and Al zoning patterns reveal a crystallization history marked by rapid, diffusion-limited growth of a series of interconnected branches forming a skeletal framework, which eventually fills in to yield well-faceted polyhedral crystals as growth becomes interface limited. If this growth model is correct, then olivine phenocrysts may experience the entire range in growth rates determined experimentally, high during their skeletal phase, and gradually lower as crystals mature (e.g., Faure

et al., 2007). For example, growing a crystal by $x = 10$ μm or diffusing through a low-Fo crystal by the same distance takes about the same time ($t \sim 30$ h) if values of slow growth rates are used [i.e., extracting x from diffusion and growth rate expressions, $x = (Dt)^{1/2}$ and $x = Gt$; D is the diffusivity and G is the growth rate]. Thus, establishing whether zoning in olivine is dominated by growth or diffusion poses a challenge that is difficult to resolve using simple rate arguments.

To better understand the roles of growth and diffusion in determining olivine zoning patterns, X-ray maps for slow- and fast-diffusing elements within a remarkable skeletal olivine are presented. Skeletal phenocrysts are potentially ideal candidates to isolate growth-related from diffusion-related zoning because they presumably indicate a recent stage of rapid growth prior to eruption (e.g., Faure and Schiano, 2004). Contrary to expectations, we show that skeletal olivines indicative of rapid growth may record dominantly diffusion-related rather than growth-related major element zoning, and that their morphology can be preserved at magmatic temperatures for several months without being significantly modified. It is argued that either (1) olivine crystallization is a rapid process that does not result in zoning with respect to fast-diffusing elements (Fe-Mg, Ni), or that (2) any zoning of these elements during growth is rapidly erased and not preserved. In both cases, the implication is that diffusion dominates major element zoning in olivine; this lends support to diffusion-based studies aiming to extract time scales from concentration gradients.

COMPLEXITY OF CHEMICAL ZONING IN A SINGLE CRYSTAL

Methods: Selecting and Analyzing the Right Crystal

To examine the effects of growth and diffusion in generating chemical zoning patterns, olivines from the ongoing eruption at Kīlauea, Hawai'i, were examined (Garcia et al., 2000). Only crystals exhibiting skeletal and hopper morphologies indicative of rapid growth (Faure et al., 2007) were considered, to focus on potential growth-related zoning and minimize diffusion-induced modifications. An archetypal, well-oriented ~1 mm skeletal olivine was found within a sample from the Pu'u' Ō'ō eruption collected in July 1983. Spot analyses, transects, and X-ray element maps for fast-diffusing (Fe,
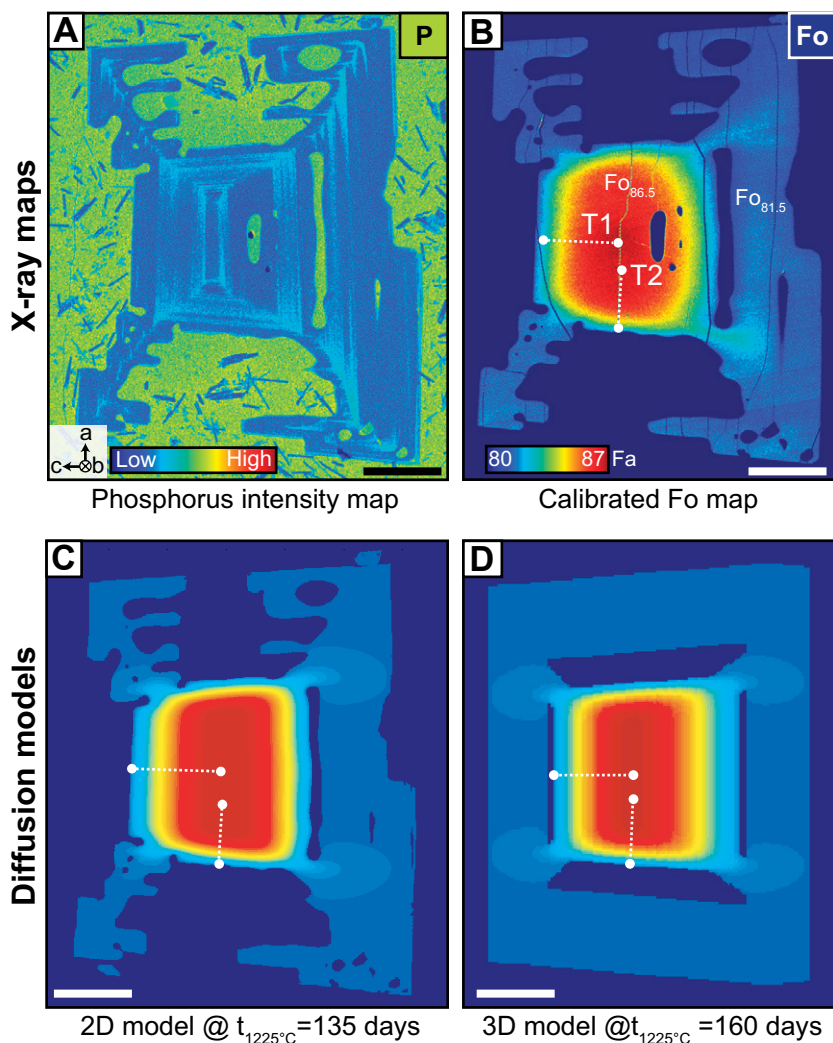
Figure 1. Comparison between zoning in a natural Kīlauea olivine and best-fit two-dimensional (2-D) and 3-D diffusion models. A: Phosphorous X-ray intensity map; map preserves the initial growth history of the olivine. Small inset at bottom left shows the approximate orientation of the section with respect to the crystallographic axes. B: Fe-Mg (Fo) X-ray intensity map; map indicates a later phase of diffusive reequilibration. C, D: Best-matching 2-D and 3-D diffusion models of Fe-Mg, and corresponding time scales. The 2-D model employs the same geometry as the Fo map, whereas the 3-D model requires simplifications in the crystal shape but accounts for diffusive fluxes from all directions. Mismatches occur near the melt inclusions, which are not accounted for in the models. The section in D was sampled slightly oblique to the *a-c* plane to match the orientation of the natural crystal. White dotted lines show the locations of electron probe microanalysis traverses T1 and T2 used to calibrate Fo maps, and utilized as output constraints for the 2-D and 3-D models (see text for details). Scale bars represent 200 μm.

Mg, Ni) and slow-diffusing elements (P, Al) in this olivine were acquired using an electron microprobe following methods described in the GSA Data Repository[1]. The Fe-Mg elements maps were calibrated using high-precision spot analyses.

Development of Compositional Zoning in the Chosen Olivine

The orientation of a crystal controls the zoning patterns exposed in thin section (Shea et al., 2015). The selected olivine was sectioned close to the principal *a* and *c* crystallographic axes (Fig. 1A; for details, see the Data Repository). Four antler-shaped branches project from the corners of a nearly equant crystal center, with several trapped melt inclusions.

Phosphorus zoning in the chosen crystal tracks the geometry of the main skeletal branches, and is more concentric within the core (Fig. 1A). The P-rich zones appear to be interconnected along the four branching directions, suggesting a history of rapid growth and partial infilling of the early crystal framework (e.g., Faure et al., 2003; Welsch et al., 2014). In contrast, Fo and Ni show concentric normal zoning (Fig. 1B; Fig. DR1 in the Data Repository), with two finger-shaped, higher Fo, higher Ni incursions into the rim. The discordance between the direction of these incursions and the direction of P-rich zones argues for a period of diffusive reequilibration subsequent to growth of the skeletal branches. Therefore, the crystallization of this particular olivine must have occurred in two distinct steps (Fig. 2). The core first grew with a composition close to $Fo_{86.5}$, and was later put in contact with a more evolved melt (e.g., during magma mixing), crystallizing the $Fo_{81.5}$ branches. A certain period of time was subsequently necessary for the core and antler-shaped
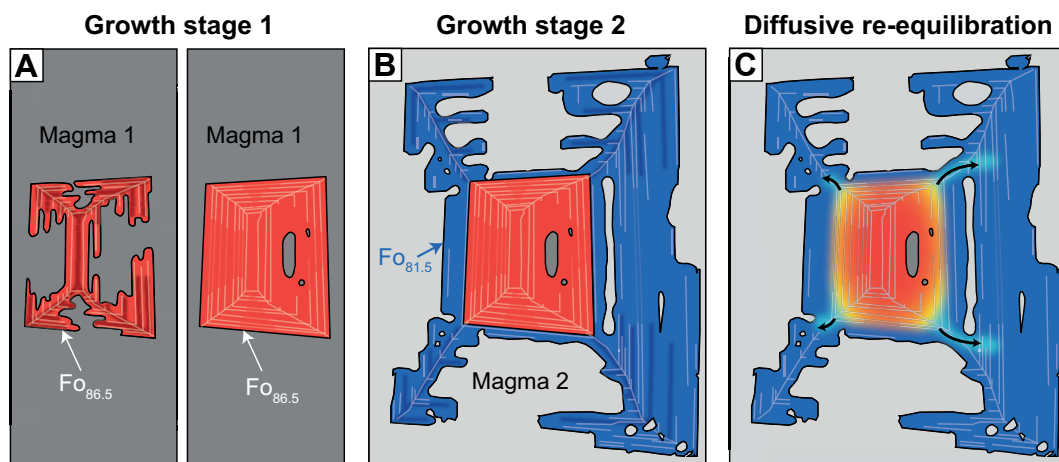
Figure 2. Interpretative petrological narrative. A: The olivine initially grows in a magma at equilibrium with a $Fo_{86.5}$ olivine composition (red), with or without fine-scale Fo zoning (dark red), matures, and homogenizes. B: The olivine is later incorporated into a different magma olivine and grows a $Fo_{81.5}$ skeletal rim (blue), with fine-scale Fo zoning or not (darker blue). C: The core and rim of the crystal reequilibrate diffusively for a certain period, without any significan changes in the crystal morphology. Thin white lines represent the framework marked by phosphorous zoning (see Fig. 1A).

rim to reequilibrate diffusively and the high Fo fingers to develop along the *c*-axis direction into the rim. This interpretation is further supported by the asymmetry in Fe-Mg and Ni zoning around the core (i.e., the concentration gradient is more extended along the *c* axis than along *a*; see Fig. 1B; Fig. DR1), which is symptomatic of anisotropic diffusion (e.g., Costa et al., 2008).

Time Scale of Diffusive Reequilibration

Two-dimensional (2-D) and 3-D diffusion models were used to determine the time scales necessary to produce the complex Fe-Mg zoning patterns of the Kīlauea olivine (for modeling details, see the Data Repository). The 2-D simulation was performed using a crystal geometry and initial and final concentrations based on the X-ray maps. A best-fit time was calculated corresponding to the minimum concentration mismatch between the model and the measured Fo map (Fig. DR2). The 3-D model employed a crystal template that incorporated commonly observed sets of olivine forms, as well as the main features of the skeletal crystal examined (Fig. DR3). The olivine then underwent diffusion, and sections sampled near the *a*-*c* orientation were compared with the calibrated X-ray map at each time step. Model parameters were set to match natural magma storage conditions under Kīlauea, with f_{O_2} at ΔQFM-1 (Rhodes and Vollinger, 2005) and P = 85 MPa (~2.5–3 km; e.g., Garcia et al., 2000). Two temperatures were investigated: a minimum temperature T = 1170 °C was first calculated based on the olivine-liquid thermometer of Beattie (1993), using the composition of the glass measured away from the olivine. This value likely corresponds to the eruption and not the storage temperature, because the glass contains microlites. A maximum temperature T = 1225 °C was also calculated based on a more primitive liquid composition in equilibrium with the $Fo_{81.5}$ rim (assuming an Fe-Mg partition coefficient K_D^{Fe-Mg} = 0.33), taken from the data set of Garcia et al. (2000). The time scales corresponding to the best-matching Fo zoning patterns in the 2-D and 3-D models are referred to as $t_{1225 °C}$ and $t_{1170°C}$.

The Fo zoning is well replicated at $t_{1225°C}$ = 135 days or $t_{1170°C}$ = 250 days of diffusion in the 2-D model (Fig. 1C). The fit between the model and the X-ray map is excellent within the olivine core (average Fo mismatch with measured analytical profile is <0.03% relative; see Fig. DR4). The higher Fo finger-like features observed in the natural sample are also well replicated. The 3-D model reproduces the main zoning features after $t_{1225°C}$ = 160 days of diffusion (or $t_{1170°C}$ = 300 days) (Fig. 1D). These simulations demonstrate that in order to obtain the Fe-Mg zoning features observed in the natural olivine, at least 4–5 months of diffusive reequilibration were necessary after growth of the skeletal rim around the crystal core.

IMPLICATIONS FOR MAGMATIC PROCESSES INVOLVING OLIVINE

Our understanding of solidification, residence, transit, and eruption of magmas is largely reliant on the textural and chemical record preserved in minerals. The complex zoning history inferred for the Kīlauea olivine, initially selected to minimize diffusive reequilibration, has several important bearings on petrological interpretations based on crystal morphology and composition: (1) skeletal phenocrysts can result from several stages of rapid growth; (2) skeletal morphologies can survive for months under magmatic conditions; (3) diffusion dominates major element zoning in olivine; and (4) growth-induced chemical zoning of fast-diffusing elements (Fe, Mg) may seldom be preserved.

Rapid Crystal Growth Can be a Multistage Process

The distinct distribution patterns of slow-diffusing elements such as phosphorus (Fig. 1A) and fast-diffusing elements in the Kīlauea olivine (Fig. 1B) indicate two stages of rapid growth within compositionally distinct magmas (Fig. 2). The continuity of the P enrichment along the main branches during the two crystallization stages implies a constancy in the propagation of growth directions. Skeletal growth branches systematically initiate at the crystal corners, consistent with previous observations (e.g., Faure et al., 2007). At the high degrees of undercooling required for skeletal growth (ΔT > 60 °C), the melt surrounding corner locations is expected to be more supersaturated in olivine-forming components than the melt at the center of crystal faces. These higher levels of supersaturation, combined with the fact that corner locations are energetically favorable for attachment of growth units, promote development of new protrusions that extend the main branches of the olivine skeleton. This behavior explains the permanence in preferential growth directions inferred from the P maps through all stages of crystallization. A corollary of this permanence is that P zoning patterns alone may yield valuable information on the kinetics of olivine crystallization (fast versus slow), but not necessarily on the number of major growth episodes.

Crystal Resilience: Survival of Rapid-Growth Morphologies in Magmas

Skeletal crystal morphologies are often expected to record and preserve chemical zoning from a recent phase of rapid growth. The inferred minimum 4–5 month period needed to produce the Fe-Mg zoning pattern with high-Fo fingers in the Kīlauea olivine refutes the notion, based on its morphology, that it grew just prior to eruption. Instead, these time scales imply that the skeletal morphology of this olivine was not significantly modified by textural maturation (infilling of the skeletal framework) after

initial growth (e.g., Faure et al., 2007; Welsch et al., 2014). The shift from diffusion-controlled to interface-controlled growth was initiated (i.e., the skeletal branches are partially infilled), but maturation did not progress to completion even after 4–5 months. During this period, the surrounding melt probably maintained a nearly constant temperature and composition after crystal growth, otherwise diffusive reequilibration would have modified the rim at the contact with the magma. Preserving this skeletal morphology within a high-*T* melt (1170–1225 °C) for months also requires that undercooling rapidly decreased after the fast growth phase (otherwise textural maturation would have progressed further). Infilling of the crystal framework may thus require additional cooling or even successive heating-cooling cycles, as suggested by the experiments of Faure et al. (2003). Thus, skeletal morphologies are useful indicators of part of olivine growth history, but do not imply that rapid growth was a recent event.

Diffusion Controls Fo Zoning

Our results confirm that phenocryst growth, as revealed by P zoning, can be rapid, and produces skeletal morphologies (Welsch et al., 2014). The nonconcentric nature of this growth process has further implications on major element zoning in olivine: if the spatial distribution of Fo does not conform to the patterns displayed by P-rich zones, then either (1) the growth stage examined (i.e., here, the branching rim) did not result in Fo zoning, or (2) this initial zoning was rapidly erased by diffusive reequilibration (see Fig. DR5). In either case, the outcome is that even in an olivine displaying a morphology reminiscent of rapid growth, the Fo gradients preserved are likely associated with diffusion, not growth. For the Kīlauea olivine, this conclusion is further supported by the good correspondence between observed and modeled zoning. If growth-related Fo zoning was significant between the rim and core, the step-wise concentration change imposed as initial conditions in the diffusion models (e.g., see Fig. DR2) would yield a poor match to the natural olivine after diffusion, particularly with respect to the Mg-rich finger-like incursions (Fig. 1B). The notion that diffusive reequilibration dominates zoning observed in olivine is consistent with the agreement between time scales derived from multiple elements in other studies (e.g., Costa and Dungan, 2005), and is further supported by examinations of Fe-Mg isotopes (Oeser et al., 2015). Collectively, there is mounting evidence to suggest that growth-induced development of Fe-Mg gradients in olivine is either very limited or seldom preserved. These conclusions lend support to time scales extracted via diffusion modeling, which typically assumes that diffusion is the main zoning process controlling compositional zoning of elements such as Fe-Mg, Ni, or Ca in olivine.

Can Crystal Growth Induce Major Element Zoning in Olivine?

The emerging view that major element zoning in olivine results dominantly from diffusive reequilibration of distinct zones with uniform or step-wise concentration changes generated by a rapid growth spurt contrasts markedly with the conventional idea that zoning is progressive and produced by slow fractional crystallization (e.g., Pearce, 1987). If rapid growth is the rule rather than the exception (Welsch et al., 2014), the question is then whether there are instances where major element gradients in olivine can be demonstrated to be unequivocally produced by crystal growth. Watson and Müller (2009) showed that the formation of boundary layers around a rapidly growing crystal strongly affects element partitioning. For olivine, boundary layers will be rapidly depleted in Fo and enriched in incompatible elements such as P, thus favoring crystallization of less forsteritic crystals with high P (for details, see Figs. DR5 and DR6). As growth transitions from diffusion to interface controlled, boundary layers are relaxed and, assuming that the far-field melt composition has not changed, the olivine becomes more forsteritic. In this scenario, the crystal would have a multiply zoned Fo skeleton, similar in aspect to that defined by P zoning. Because Fe-Mg diffusion is rapid, such zoning would be erased rapidly, and may be difficult to preserve and/or detect in natural samples. Experimental studies of olivine crystallization are needed to elucidate the conditions necessary to preserve growth-induced zoning.

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