

Phosphorus zoning reveals dendritic architecture of olivine

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ABSTRACT

The texture and composition of igneous minerals are unique recorders of the temperature, pressure, and composition of magma reservoirs, conduits, and lava flows. Decoding this information is predicated on the idea that magmatic crystals grow in a concentric pattern, and that any deviation from this model (such as anhedral crystal morphologies and complex chemical zoning) is the consequence of extrinsic processes such as magma mixing, dissolution, or deformation. Our analysis of the spatial distribution patterns of slowly diffusing impurities (phosphorus, aluminum) in volcanic, plutonic, and experimental olivine crystals reveals, however, that the crystallization record is not a straightforward time progression from crystal core to rim. We propose here an internal dendrite hypothesis that unites diverse manifestations of thermodynamic disequilibrium crystallization, and may be fundamental to interpreting chemical stratigraphy, subgrain domain structures, and the formation of melt inclusions within olivine.

INTRODUCTION

The analysis of chemical information stored in magmatic phases is a basis of volcano petrology, which seeks to infer the evolution of magma properties in pursuit of the processes influencing eruptive behavior (Streck, 2008). Volcanoes provide the necessary raw data in the form of erupted glass and minerals, which are time-sensitive recorders of their thermochemical environment. The challenge is to interpret the record at the scale of individual crystals. The canonical approach is based on the idea that layers are added to crystals sequentially, as rings are added to the exteriors of growing trees. The compositions of these successive layers are dictated by stoichiometry and the chemical potentials of crystalline components dissolved in the melt, and thus the crystals provide chronologic records of the evolving local chemical environment. This conceptual model has been highly successful in providing insights into magmatic processes operating in a variety of tectonic settings (Ruprecht and Plank, 2013; Streck, 2008). However, discovery of rhythmic enrichments of the incompatible element phosphorus (P) in the otherwise compositionally monotonous olivine of ocean island basalts (OIBs), mid-oceanic ridge basalts (MORBs), arc lavas, komatiites, and Martian meteorites (Milman-Barris et al., 2008; Tschegg et al., 2010; Sakyi et al., 2012; Welsch et al., 2013) poses a conundrum. Viewed through the tree-ring model of crystal growth, the zoned olivine crystals seem to require large oscillations in growth rate caused by oscillations in temperature and/or melt composition to generate the layers of enrichment in P (Grant and Kohn, 2013; Milman-Barris et al., 2008).

Through the acquisition of P distribution maps by electron probe microanalysis, we test whether the geologic principle of superposition always applies to olivine crystals, and critically evaluate the underlying assumption that crystal-

lization controlled by the crystal-melt interface reaction operates throughout the growth history.

SAMPLES

Our investigation centers on a pillow lava (sections S690-A and S690-B from dive site S690) collected at 3064 m below sea level from a submarine slope of Hualalai volcano, Hawaii, during a 2002 JAMSTEC (Japan Agency for Marine–Earth Science and Technology) cruise (Hammer et al., 2006). The rock is composed of basaltic matrix glass, vesicles, and olivine phenocrysts. These crystals display a wide range of textures (Fig. 1; Figs. DR1 and DR2 in the GSA Data Repository¹) common in lavas worldwide (Helz, 1987; Streck, 2008; Welsch et al., 2013). Euhedral olivine crystals exhibit external growth faces that adhere to crystallographic laws. Spongy olivine crystals are characterized by embayments and rounded pockets of matrix material within the mineral. Deformed olivine crystals have internal subgrain domains apparent in cross-polarized light microscopy, separated by low-angle misorientations (2°–15°) that presumably represent planes of lattice defects. The presence of well-formed external facets on nearly all crystals (Fig. 1; Figs. DR1 and DR2) enables determination of crystallographic orientations in the section (Welsch et al., 2013); this in turn aids in deciphering the spatial distribution patterns of P. Although disparate in morphology, the olivine crystals are individually homogeneous in composition (<1% intracrystalline forsterite, Fo, variation), with intercrystalline variation of Fo_{90–82} (chemical compositions in Tables DR1–DR3 in the Data Repository).

¹GSA Data Repository item 2014307, analytical methods, crystal modeling, and experimental methods; Figures DR1 and DR2 (additional maps of phosphorus in Hualalai olivine); and Tables DR1–DR3 (composition of olivine, spinel, melt inclusions, and matrix glass in Hualalai samples), is available online at www.geosociety.org/pubs/ft2014.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

All the olivine crystals contain areas depleted in P (<0.04 wt% P₂O₅) and have narrow zones of enrichment (0.05–0.13 wt% P₂O₅), forming concentric or feathery patterns similar to those reported elsewhere (Milman-Barris et al., 2008; Sakyi et al., 2012; Welsch et al., 2013). The enriched areas are composed of thin lineations located at the outer edges, medial regions, and centers of crystals, and are oriented dominantly parallel to external faces. Standard stereological considerations suggest that such linear features observed in two-dimensional section planes represent lamellae in three dimensions. These observations form the basis of previous interpretations of P zoning as a marker of tree-ring style crystal growth (Milman-Barris et al., 2008). However, we propose that a full understanding of P enrichment in olivine requires consideration of feathery patterns of P zoning not explained by this model. Sections cut at fortuitous angles oblique to primary crystallographic axes expose P-enriched lineations propagating not parallel to external faces, but between the crystal center and its vertices. These lineations are especially apparent in the feathery zoning of Figure 1, in experiments performed in this study (Fig. 2), and in published maps (Milman-Barris et al., 2008, their figures 1a, 1e, 2a, and 3e–3f). We interpret these features as linear primary branches emanating from the crystal center and rooting lamellar secondary branches (Fig. 1). Because of their different spatial resolution, the zoning pattern may change from feathery to oscillatory when the section exposes only the secondary P-rich branches, and not the primary branches. In essence, the P-enriched olivine traces the outline of an inner dendrite that grows in a manner similar to snowflakes (Libbrecht, 2005).

SYMPTOMS OF RAPID GROWTH

The dendritic growth morphology is fully consistent with the requirement that compositional boundary layers around olivine crystals promote uptake of incompatible elements (Sangwal, 1996). Phosphorus is strongly rejected by olivine growing near chemical equilibrium with basaltic liquid (Grant and Kohn, 2013). However, high amounts of P₂O₅ (to 0.4 wt%; Milman-Barris et al., 2008) can be incorporated when its diffusion rate in the melt (Harrison and Watson, 1984) is surpassed by the advance of the growth surface (up to 10^{–6} m/s; Jambon et al., 1992). Unlike other incompatible elements, such as Al and Cr, that are simultaneously incorporated in olivine by coupled substitution (Milman-Barris et al., 2008), P diffuses extremely slowly in olivine (Spandler et al., 2007). Thus P zoning can be preserved over

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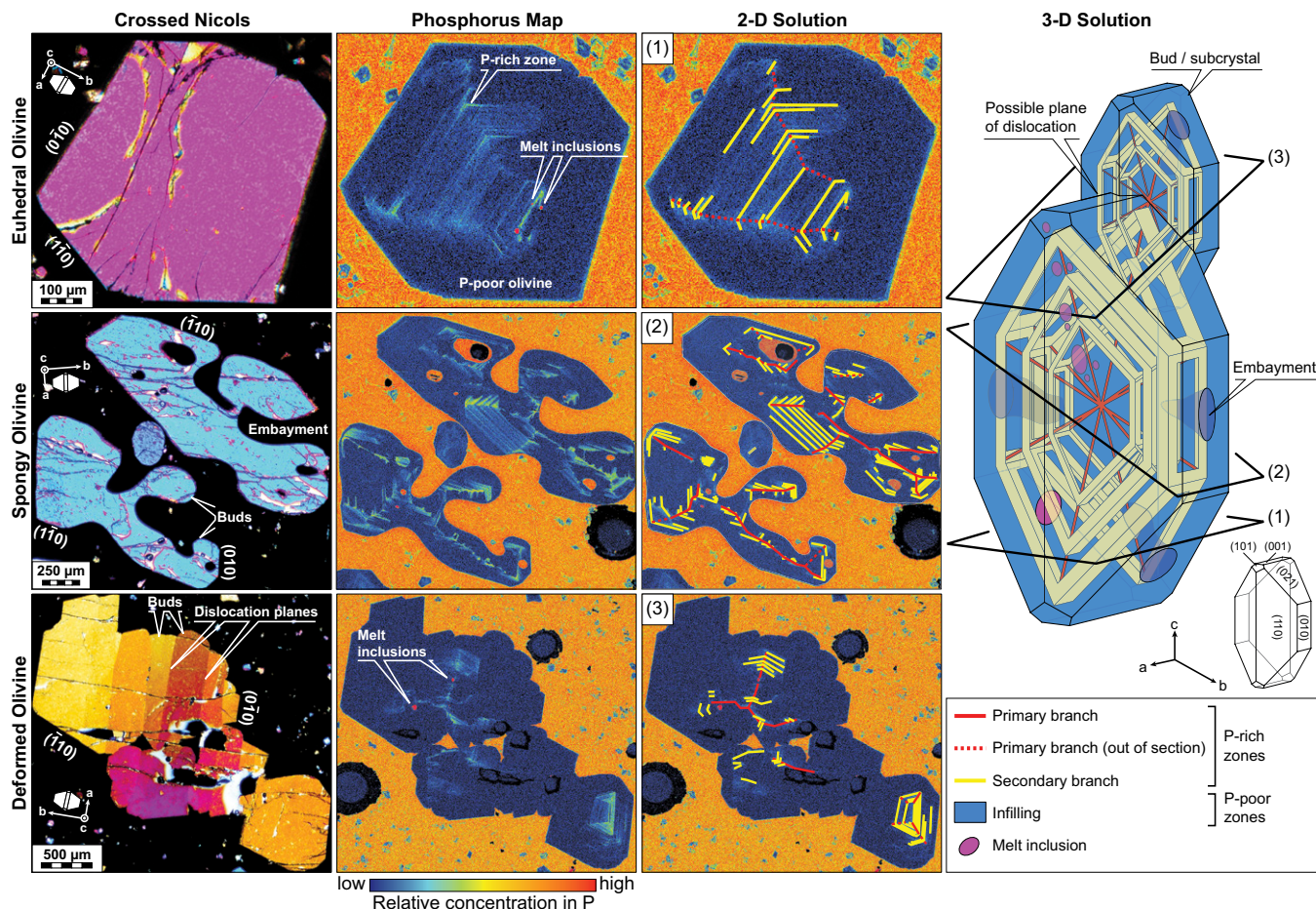


Figure 1. Euhedral, spongy, and deformed olivine crystals from oceanite sample S690-B, from the submarine slope of Hualalai volcano, Hawaii (see text). All the crystals show external growth faces and intact phosphorus (P) rich zones, regardless of the occurrence of embayments (in spongy olivine) or of dislocation planes (in deformed olivine). Figure DR1 (see footnote 1) provides imagery of additional examples, and Tables DR1–DR3 provide spot analyses. The primary and secondary branches forming the dendritic framework of olivine are outlined in red and yellow, respectively, in the two-dimensional (2D) solution interpretation maps and in the 3D-solution model. The P maps indicate that the primary P-rich branches propagate from the center of the crystal toward the apices. The secondary P-rich branches emerge from primary branches as planes (~10 μm thick) growing parallel to crystal faces (010), (110), and (021). Sections cut perpendicular to a crystallographic axis and far from the center (e.g., intersection type 1) expose only secondary branches, resulting in a concentric P-enrichment pattern. Sections cut at angles oblique to crystallographic axes and close to the center (e.g., types 2 and 3) are likelier to expose primary branches in addition to secondary branches, leading to a feathery pattern.

1–100 k.y. time scales, long after traces of other incompatible elements have been erased under magmatic conditions. Taking Al as a tracer of rapid, dendritic growth of olivine in our experiments, we reproduced the process of impurity uptake at low cooling rates (2 $^{\circ}\text{C}/\text{h}$) within a thermal gradient (Fig. 2). Importantly, skeletal and dendritic growths do not produce core-to-rim, oldest-to-youngest sequential layering characteristic of concentric compositional zoning. Rather, the oldest parts of a given crystal are the primary and secondary dendrite branches representing directions of fast, diffusion-controlled growth at high supersaturation. The polyhedral shapes of most olivine crystals and lack of P enrichment between dendrite arms indicate a slower stage of growth after relaxation of the melt boundary layer and cessation of dendritic growth.

Crystal growth experiments demonstrate that skeletal and dendritic crystals form during diffusion-controlled growth (Faure and Schiano,

2005) and that a crossover to interface control is essential for trapping inclusions of matrix melt (Kohut and Nielsen, 2004). The dual mechanism growth history proposed here is consistent with studies of melt inclusion entrapment in olivine. Because melt inclusions are typically sealed during the interface-controlled growth stage, they are representative of far-field melts, thus justifying their functionality as probes of the origin and evolution of magmas (Ren et al., 2005; Sobolev et al., 2005). Some melt inclusions may, however, have entrapped boundary layers enriched in elements incompatible with olivine (such as Ca and Al), and thus are not representative of the parental melts (Table DR3; Faure and Schiano, 2005). The presence of melt inclusions in the Hualalai olivines within or very near P enrichments (Fig. 1; Figs. DR1 and DR2) corroborates the inference that skeletal or dendritic growth is essential to melt inclusion formation (Figs. 2 and 3; see also Ni et al., 2014).

Rounded or spongy crystals often are interpreted as recording partial dissolution (Helz, 1987; Streck, 2008), a form of thermodynamic instability brought about by heating (Girard and Stix, 2010) or mingling of disparate magmas (Baggerman and DeBari, 2011). The P mapping technique applied to spongy crystals offers a means of evaluating this tenet for Hualalai olivine. If dissolution had occurred, there should be no correlation between the olivine P concentration and the position of the crystal-melt interface, and the internal dendrites should be truncated by dissolution surfaces. However, such cross-cutting relationships are not observed. High-P dendrites occur exclusively between embayments (Fig. 1; Figs. DR1 and DR2), suggesting that the curvature of crystal-melt interfaces represents a transitional morphology between diffusion-controlled growth, which amplifies protuberances, and interface-controlled growth, which flattens faces. Faceting on external sur-



Figure 2. Olivine crystal obtained by slow cooling of a synthetic magma along a thermal gradient (see the Materials and Methods section of the Data Repository [see footnote 1]). The crystal shows both external growth facets and rounded interfaces (embayments and melt inclusions) characteristic of spongy olivine in the Hualalai, Hawaii, oceanite (Fig. 1; Fig. DR1 [see footnote 1]). Aluminum enrichment patterns mimic those of phosphorus in natural olivine (Milman-Barris et al., 2008), revealing the initial dendritic structure before overgrowth of Al-poor olivine. In contrast with P zoning, Al zoning is weak to absent in natural samples because of its faster diffusion and longer subsolidus history at elevated temperature compared with short runs of experimental charges (Milman-Barris et al., 2008).

faces of these crystals and the presence of low-P olivine selvages enclosing each dendrite (Fig. 1; Fig. DR1) support our inference that euhedral morphologies would have developed, had these spongy crystals continued to grow.

Dislocation lamellae and undulose extinction in olivine are traditionally interpreted to have formed by plastic (subsolidus) deformation (Helz, 1987; Sakai et al., 2012). In shield-stage Hawaiian basalts, these features are taken as evidence for solid-state deformation in an olivine cumulate accommodating the spreading of volcanic edifices (Clague and Denlinger, 1994). However, the coincidence of dislocation planes with growth buds (Fig. 1; Fig. DR2) suggests that such defect structures may instead be associated with dendritic growth. Diffusion-controlled growth is known to produce a high density of lattice defects in minerals (Sunagawa, 2005), and has been shown experimentally to produce low-angle lattice misorientations in olivine (Faure et al., 2003). At magmatic temperature, these defects eventually migrate into the weakness planes of the mineral and form new dislocation planes. The delicate P enrichments of the Hualai

olivine crystals are not interrupted, crosscut, or displaced by subgrain domain boundaries (Fig. 1; Fig. DR2), and this is inconsistent with extensive shear deformation occurring after cessation of growth. The presence of matrix pockets between domains and the alignment of growth faces in adjacent crystals (Fig. 1; Fig. DR2) also argue against the interpretation that such crystals were disaggregated from a compacted cumulate pile. If growth phenomena can account for subgrain boundaries, the standard inferences regarding the origin of olivine rich basalts and the geometry of ocean island plumbing systems may require reevaluation.

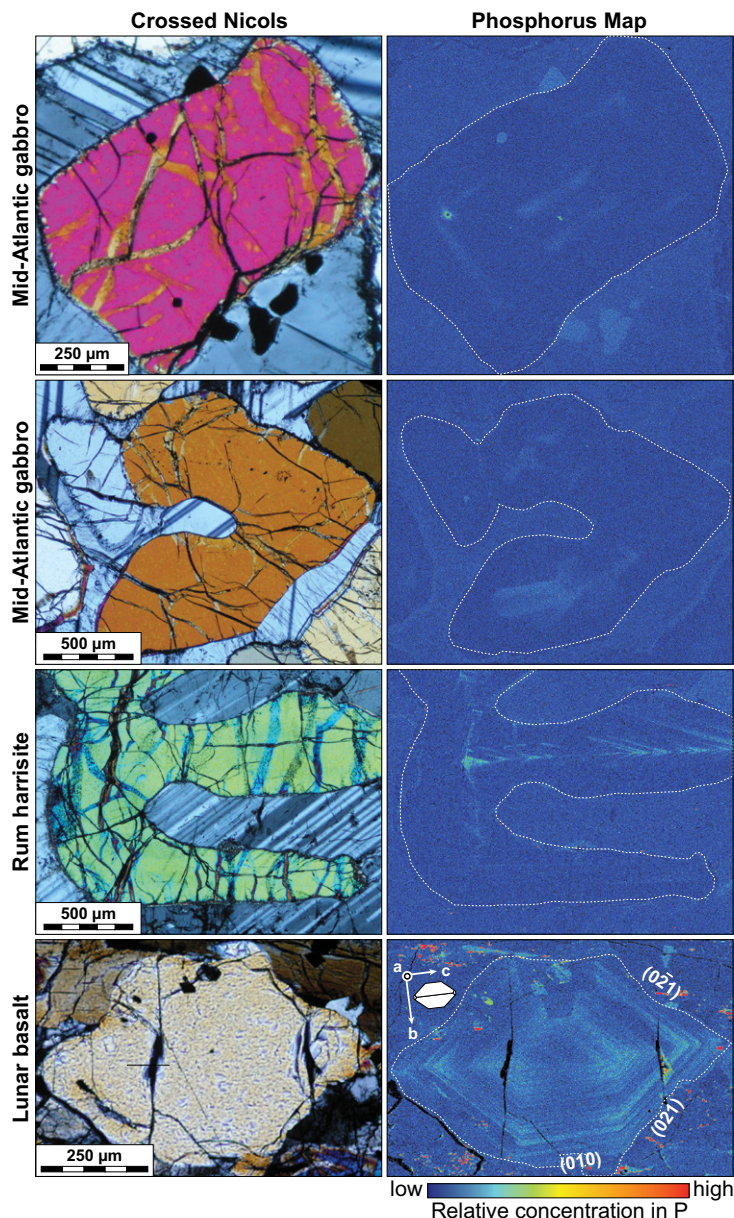


Figure 3. Occurrence of phosphorus (P) zoning in olivine crystals in gabbros from the Mid-Atlantic Ridge (30°N, Atlantis Massif, sample U1309D-247R3-002; see Suhr et al., 2008), harrisites from Rum Island (Scotland), and lunar basalts (sample 12002,162). Dotted lines in P maps demarcate the olivine crystals from surrounding phases. Note that P zoning is weaker in plutonic rocks than in volcanic samples because of its longer subsolidus history at elevated temperature.

IMPLICATIONS FOR IGNEOUS OLIVINE

We emphasize that euhedral, spongy, and deformed crystals can correspond to different stages and events of crystal growth, all derived from the initial diffusion-controlled crystallization of olivine. Laboratory crystal growth rate measurements (Jambon et al., 1992) suggest that the P-rich, Al-rich dendritic framework of an olivine phenocryst develops within a few minutes. Overgrowths poor in P and Al form over a few weeks, yielding a morphological evolution from spongy to euhedral, as the crystal fills embayments or seals off melt inclusions. Thus, initial rapid

growth of primary and secondary dendrite branches is followed by slow overgrowth and infilling. An important implication of the dendritic model is that the P-rich, Al-rich secondary branches located near the crystal rim are older than the P-poor, Al-poor zones close to the center. Thus, the zoning patterns observed in two-dimensional sections are dependent on both the stage of development and the section plane orientation (Fig. 1). Deviations from the simple geometry shown here are governed by local crystallization environment; e.g., crystals growing in a thermal flux will have one side more developed than the other, as shown in Figure 2.

The demonstration that magmatic phenocrysts are cored by large dendrites challenges a fundamental understanding of the relationship between melt supersaturation and specific magmatic environments. Rapidly grown dendrites are usually associated with situations where high supersaturation and high growth rate are driven by rapid cooling (e.g., pillow basalts, subaerial lava flows). However, rapid cooling is unlikely at depth because the heat transfer between the magma and its local environment is prohibitively slow. We performed additional mapping of P in olivine crystals from gabbros of the Mid-Atlantic Ridge and the Rum intrusion (Scotland), and confirmed the presence of dendritic P zoning in plutonic olivine (Fig. 3). This indicates that rapid, diffusion-controlled crystal growth is an important feature of magma crystallization, and can account for a variety of primary textural and compositional heterogeneities in igneous rocks. Dendritic olivine heralds rapid growth at high degrees of supersaturation in the magma, a process possible at depth by heat transfer to the country rock, i.e., slow conductive cooling (Donaldson, 1977; O'Driscoll et al., 2007). Dendritic growth may be also enhanced by exsolution of water, which increases the liquidus temperature of olivine (Donaldson, 1974; Almeev et al., 2007; Médard and Grove, 2008). We conclude that the paradigm of olivine growth in concentric layers from core to rim is not generally valid, and call for reevaluation of the related assumption of near-equilibrium crystallization as a general feature of mafic magmas.

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REFERENCES CITED

- Almeev, R.R., Holtz, F., Koepke, J., Parat, F., and Botcharnikov, R.E., 2007, The effect of H₂O on olivine crystallization in MORB: Experimental calibration at 200 MPa: *American Mineralogist*, v. 92, p. 670–674, doi:10.2138/am.2007.2484.
- Baggerman, T., and DeBari, S., 2011, The generation of a diverse suite of late Pleistocene and Holocene basalt through dacite lavas from the northern Cascade arc at Mount Baker, Washington: *Contributions to Mineralogy and Petrology*, v. 161, p. 75–99, doi:10.1007/s00410-010-0522-2.
- Clague, D.A., and Denlinger, R.P., 1994, Role of olivine cumulates in destabilizing the flanks of Hawaiian volcanoes: *Bulletin of Volcanology*, v. 56, p. 425–434, doi:10.1007/BF00302824.
- Donaldson, C.H., 1974, Olivine crystal types in harrisitic rocks of the Rum pluton and Archean spinifex rocks: *Geological Society of America Bulletin*, v. 85, p. 1721–1726, doi:10.1130/0016-7606(1974)85<1721:OCTIHR>2.0.CO;2.
- Donaldson, C.H., 1977, Laboratory duplication of comb layering in the Rum pluton: *Mineralogical Magazine*, v. 41, p. 323–336, doi:10.1180/minmag.1977.041.319.03.
- Faure, F., and Schiano, P., 2005, Experimental investigation of equilibration conditions during forsterite growth and melt inclusion formation: *Earth and Planetary Science Letters*, v. 236, p. 882–898, doi:10.1016/j.epsl.2005.04.050.
- Faure, F., Trolliard, G., and Soulestin, B., 2003, TEM investigation of forsterite dendrites: *American Mineralogist*, v. 88, p. 1241–1250.
- Girard, G., and Stix, J., 2010, Rapid extraction of discrete magma batches from a large differentiating magma chamber: The Central Plateau Member rhyolites, Yellowstone Caldera, Wyoming: *Contributions to Mineralogy and Petrology*, v. 160, p. 441–465, doi:10.1007/s00410-009-0487-1.
- Grant, T.B., and Kohn, S.C., 2013, Phosphorus partitioning between olivine and melt: An experimental study in the system Mg₂SiO₄-Ca₂Al₂Si₂O₉-NaAlSi₃O₈-Mg₃(PO₄)₂: *American Mineralogist*, v. 98, p. 1860–1869, doi:10.2138/am.2013.4237.
- Hammer, J.E., Coombs, M.L., Shamberger, P.J., and Kimura, J.-I., 2006, Submarine sliver in North Kona: A window into the early magmatic and growth history of Hualalai Volcano, Hawaii: *Journal of Volcanology and Geothermal Research*, v. 151, p. 157–188, doi:10.1016/j.jvolgeores.2005.07.028.
- Harrison, T.M., and Watson, E.B., 1984, The behavior of apatite during crustal anatexis: Equilibrium and kinetic considerations: *Geochimica et Cosmochimica Acta*, v. 48, p. 1467–1477, doi:10.1016/0016-7037(84)90403-4.
- Helz, R.T., 1987, Diverse olivine types in lava of the 1959 eruption of Kilauea volcano and their bearing on eruption dynamics, in Decker, R.W., et al., eds., *Volcanism in Hawaii: Volume 1: U.S. Geological Survey Professional Paper 1350*, p. 691–722.
- Jambon, A., Lussiez, P., and Clocchiatti, R., 1992, Olivine growth rates in a tholeiitic basalt: An experimental study of melt inclusions in plagioclase: *Chemical Geology*, v. 96, p. 277–287, doi:10.1016/0009-2541(92)90059-E.
- Kohut, E., and Nielsen, R.L., 2004, Melt inclusion formation mechanisms and compositional effects in high-An feldspar and high-Fo olivine in anhydrous mafic silicate liquids: *Contributions to Mineralogy and Petrology*, v. 147, p. 684–704, doi:10.1007/s00410-004-0576-0.
- Libbrecht, K.G., 2005, The physics of snow crystals: Reports on Progress in Physics, v. 68, p. 855–895, doi:10.1088/0034-4885/68/4/R03.
- Médard, E., and Grove, T.L., 2008, The effect of H₂O on the olivine liquidus of basaltic melts: Experiments and thermodynamic models: *Contributions to Mineralogy and Petrology*, v. 155, p. 417–432, doi:10.1007/s00410-007-0250-4.
- Milman-Barris, M., Beckett, J., Baker, M., Hofmann, A., Morgan, Z., Crowley, M., Vielzeuf, D., and Stolper, E., 2008, Zoning of phosphorus in igneous olivine: *Contributions to Mineralogy and Petrology*, v. 155, p. 739–765, doi:10.1007/s00410-007-0268-7.
- Ni, H., Keppler, H., Walte, N., Schiavi, F., Chen, Y., Masotta, M., and Li, Z., 2014, In situ observation of crystal growth in a basalt melt and the development of crystal size distribution in igneous rocks: *Contributions to Mineralogy and Petrology*, v. 167, p. 1–13, doi:10.1007/s00410-014-1003-9.
- O'Driscoll, B., Donaldson, C.H., Troll, V.R., Jerram, D.A., and Emeleus, C.H., 2007, An origin for harrisitic and granular olivine in the Rum layered suite, NW Scotland: A crystal size distribution study: *Journal of Petrology*, v. 48, p. 253–270, doi:10.1093/petrology/egl059.
- Ren, Z.-Y., Ingle, S., Takahashi, E., Hirano, N., and Hirata, T., 2005, The chemical structure of the Hawaiian mantle plume: *Nature*, v. 436, p. 837–840, doi:10.1038/nature03907.
- Ruprecht, P., and Plank, T., 2013, Feeding andesitic eruptions with a high-speed connection from the mantle: *Nature*, v. 500, p. 68–72, doi:10.1038/nature12342.
- Sakay, P.A., Tanaka, R., Kobayashi, K., and Nakamura, E., 2012, Inherited Pb isotopic records in olivine antecryst-hosted melt inclusions from Hawaiian lavas: *Geochimica et Cosmochimica Acta*, v. 95, p. 169–195, doi:10.1016/j.gca.2012.07.025.
- Sangwal, K., 1996, Effects of impurities on crystal growth processes: *Progress in Crystal Growth and Characterization of Materials*, v. 32, p. 3–43, doi:10.1016/0960-8974(96)00008-3.
- Sobolev, A.V., Hofmann, A.W., Sobolev, S.V., and Nikogosian, I.K., 2005, An olivine-free mantle source of Hawaiian shield basalts: *Nature*, v. 434, p. 590–597, doi:10.1038/nature03411.
- Spandler, C., O'Neill, H.S., and Kamenetsky, V.S., 2007, Survival times of anomalous melt inclusions from element diffusion in olivine and chromite: *Nature*, v. 447, p. 303–306, doi:10.1038/nature05759.
- Streck, M.J., 2008, Mineral textures and zoning as evidence for open system processes: *Reviews in Mineralogy and Geochemistry*, v. 69, p. 595–622, doi:10.2138/rmg.2008.69.15.
- Suhr, G., Hellebrand, E., Johnson, K., and Brunelli, D., 2008, Stacked gabbro units and intervening mantle: A detailed look at a section of IODP Leg 305, Hole U1309D: *Geochemistry Geophysics Geosystems*, v. 9, Q10007, doi:10.1029/2008GC002012.
- Sunagawa, I., 2005, *Crystals: Growth, morphology and perfection*: Cambridge, UK, Cambridge University Press, 308 p.
- Tschegg, C., Ntaflou, T., Kiraly, F., and Harangi, S., 2010, High temperature corrosion of olivine phenocrysts in Pliocene basalts from Banat, Romania: *Austrian Journal of Earth Sciences*, v. 103, p. 101–110.
- Welsch, B., Faure, F., Famin, V., Baronnet, A., and Bachèlery, P., 2013, Dendritic crystallization: A single process for all the textures of olivine in basalts?: *Journal of Petrology*, v. 54, p. 539–574, doi:10.1093/petrology/egs077.

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