



Phosphorus and aluminum zoning in olivine: contrasting behavior of two nominally incompatible trace elements

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Received: 26 March 2019 / Accepted: 28 August 2019
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Abstract

Phosphorus zoning in olivine is receiving considerable attention for its capacity to preserve key information about rates and mechanisms of crystal growth. Its concentration can vary significantly over sub-micron spatial scales and form intricate, snowflake-like patterns that are generally attributed to fast crystal growth. Ostensibly similar aluminum enrichment patterns have also been observed, suggesting comparable incorporation and partitioning behavior for both elements. We perform 1-atm crystallization experiments on a primitive Kīlauea basalt to examine the formation of P and Al zoning as a function of undercooling $-\Delta T$ ($-\Delta T = T_{\text{liquidus}} - T_{\text{crystallization}}$) during olivine growth. After 24 h spent at $T_{\text{initial}} = 1290$ °C (10 °C above olivine stability), charges are rapidly cooled to final temperatures $T_{\text{final}} = 1220$ – 1270 °C, corresponding to undercoolings $-\Delta T = 10$ – 60 °C (with $T_{\text{liquidus}} = 1280$ °C). Compositional X-ray maps of experimental olivine reveal that only a small undercooling (≤ 25 °C) is required to produce the fine-scale enrichments in P and Al associated with skeletal growth. Concentration profiles indicate that despite qualitatively similar enrichment patterns in olivine, P and Al have contrasting apparent crystal/melt mass distribution coefficients of $K_{\text{P}}^{\text{ol/melt}} = 0.01$ – 1 and $K_{\text{Al}}^{\text{ol/melt}} = 0.002$ – 0.006 . Phosphorus can be enriched by a factor > 40 -fold in the same crystal, whereas Al enrichment never exceed factors of 2. Glass in the vicinity of synthetic and natural olivine is usually enriched in Al, but, within analytical uncertainty, not in P. Thus, we find no direct evidence for a compositional boundary layer enriched in P that would suffice to produce P enrichments in natural and synthetic olivine. Numerical models combining growth and diffusion resolve the conditions at which Al-rich boundary layers produce the observed enrichment patterns in olivine. In contrast, the same models fail to reproduce the observed P enrichments, consistent with our observation that P-rich boundary layers are insignificant. If instead, P olivine/melt partitioning is made to depend on growth rate, models adequately reproduce our observations of 40-fold enrichment without boundary layer formation. We surmise that near-partitionless behavior ($K_{\text{P}}^{\text{ol/melt}}$ close to 1) of P is related to the olivine lattice being perhaps less stiff in accommodating P during rapid crystallization, and/or to enhanced formation of vacancy defects during fast growth. Our results confirm that P is a robust marker of initial rapid growth, but reveal that the undercooling necessary to induce these enrichments is not particularly large. The near-ubiquitous process of magma mixing under volcanoes, for instance, is likely sufficient to induce low-to-moderate degrees of undercooling required for skeletal growth.

Keywords Olivine · Phosphorus · Aluminum · Growth kinetics · Trace-element partitioning

Communicated by Gordon Moore.

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s00410-019-1618-y>) contains supplementary material, which is available to authorized users.

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Phosphorus and aluminum in olivine: background

Phosphorus and aluminum are typically present in magmatic olivine as trace elements (< 0.1 wt%). Their spatial distribution in single olivine crystals has generated significant interest, since Milman-Barris et al. (2008) revealed that both elements display striking fine-scale, complex enrichment patterns within samples from various geological settings (ocean intraplate basalt, mid-ocean ridge

basalt, komatiites, arc andesites, and meteorites). These zoning patterns were interpreted to provide a blueprint of rapid olivine crystallization, wherein intrinsic factors (e.g., oscillating growth rates following undercooling) rather than multiple external forcings (e.g., repeated magma mixing) led to oscillatory zoning in P or Al. Subsequently, Welsch et al. (2013, 2014) examined olivine phenocrysts preserving morphological remnants of an earlier skeletal growth history (e.g., hopper cavities, steps), and provided a crucial link between fine-scale P and Al zoning and rapid crystallization: olivine may start its magmatic journey through skeletal growth, and progressively ripen and infilled into the faceted, polyhedral morphologies that characterize most phenocrysts (Fig. 1a). These findings are forcing reassessment of canonical ideas about the formation of phenocrysts and the interpretation of element zoning in olivine. First, phenocrysts may not always form via addition of concentric growth layers (i.e., the ‘tree ring’ model) (Welsch et al. 2013; Manzini et al. 2017; Baziotis

et al. 2017; Xing et al. 2017). Second, if skeletal growth dominates, then concentric zoning (i.e., does not display snowflake-like patterns) of major (Fe–Mg) or minor (Ni, Ca, Mn), or trace (Cr) elements is associated with progress toward equilibrium via diffusion rather than initial growth (Shea et al. 2015; de Maisonville et al. 2016; Lynn et al. 2018). Confirming these hypotheses is important for interpreting olivine compositional variation, as well as understanding the formation of melt inclusions. For example, younger inclusions may not be those closest to the core. Furthermore, diffusion chronometry is often predicated on the supposition that concentric growth-induced zoning can be neglected, which still needs to be experimentally validated. Finally, Al-in-olivine thermometers depend on the assumption of equilibrium partitioning and the associated analytical methodology (utilizing isolated spot analyses) implicitly requires that Al is homogeneously distributed within olivine grains (e.g., Coogan et al. 2014; Bussweiler et al. 2017).

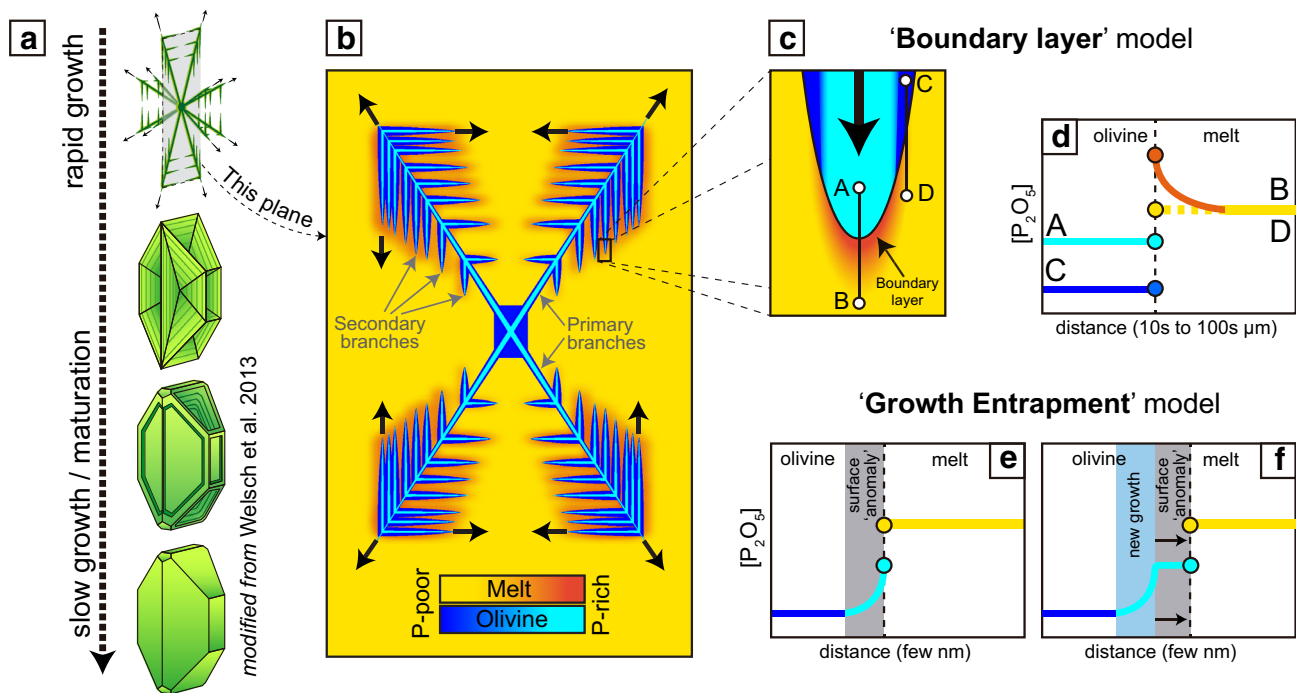


Fig. 1 Schematic representation and conceptual model used in this study to understand olivine growth and incorporation of trace elements. **a** Hypothetical growth sequence of an olivine crystal. Initial growth is rapid and leads to propagation of primary and secondary branches (skeletal morphology). As growth rates slow down, the initial framework is progressively interconnected and infilled, resulting in a typical polyhedral phenocryst after morphological ‘maturation’. **b** Section across the *a*–*c*-axis plane of the olivine in (a) showing the formation of P-rich zones along primary and secondary skeletal branches. A hypothesis commonly proposed to explain fine-scale P (and Al) enrichments in olivine (blue regions colored according to enrichment level) involves the formation of boundary layers in the melt around the complex growing interface (red regions in the melt).

If growth rates exceed diffusion rates of incompatible elements like P in the melt, those elements can accumulate at the melt–crystal interface and, with no change in partition coefficient, result in enrichments within the crystal (c and d) (e.g., Lasaga 1982). Transects A–B and C–D through P-rich and P-poor regions, respectively, are shown for illustration. An alternative model (Watson et al. 2015) postulates that the surface of the growing crystal (at the nm scale) has an anomalous structure (e), resulting in an anomalous concentration in P that gets trapped during growth (100% entrapment efficiency is represented here) (f). Diffusion of the element in the crystal must be slow enough for this enrichment to persist. Colored circles highlight the P concentrations at the interface

A number of questions and apparent paradoxes are prompted by these shifts in the olivine growth paradigm. First, the mechanism(s) for incorporation of high P or Al concentrations in olivine are still largely unidentified. Possibilities include: the ‘boundary layer’ model and the ‘growth entrapment’ model (e.g., Milman-Barris et al. 2008; Welsch et al. 2013; Watson et al. 2015). In the boundary layer model (Fig. 1b–d), the growth and advancement of crystal branches or faces is fast relative to the pace of diffusive relaxation of P and Al in the surrounding melt. The melt adjacent to the crystal becomes enriched in rejected elements, and their concentration in the olivine increases despite fixed (equilibrium) solid/melt partition coefficients (e.g., Smith et al. 1955; Albarède and Bottinga 1972; Watson and Müller 2009). Phosphorus-rich zones measured in natural olivine are at least 2–15 times the background levels within a single crystal, which, according to this model, would imply similar enrichments in the melt boundary layer (Shea et al. 2015; de Maisonneuve et al. 2016; Baziotis et al. 2017). In the growth entrapment model (Fig. 1e, f), growth rates are fast relative to diffusion in the crystal, and the outermost atomic layers of the advancing interface are sufficiently different from the bulk (interior) in structure and/or bond energies. These layers can incorporate incompatible elements or ‘impurities’ (e.g., P and Al) far in excess of the equilibrium partitioning concentration (e.g., Watson and Liang 1995). Depending on the growth rate and the rate of diffusion of the element of interest in the crystal, the trapped near-interface concentration anomaly in the crystal may or may not be dissipated before it is buried. In both cases, the growth rates required to form notable boundary layers or preserve trapped concentration anomalies are inferred to be very high, at least 10^{-7} m s^{-1} (Watson et al. 2015; Shea et al. 2015). The extent to which either of these models is able to reproduce enrichment patterns of P or Al in synthetic and natural samples has yet to be tested.

Second, rapid growth producing skeletal or dendritic crystals apparently requires $-\Delta T$ values in excess of 60°C , or fast cooling rates (Donaldson 1976; Jambon et al. 1992; Welsch et al. 2013). The growth rates of $> 10^{-7} \text{ m s}^{-1}$ required by the boundary layer and solute trapping models to reproduce large enrichments in P (Shea et al. 2015; Baziotis et al. 2017) correspond to undercoolings $-\Delta T > 75^\circ\text{C}$ according to the experimental data of Jambon et al. (1992). Such high undercoolings require olivine crystallization to take place under somewhat special circumstances (e.g., rapid cooling during lava flow or dike emplacement, thermal gradient at reservoir edges, mixing of magmas with very large temperature differences, or in response to prior superheating caused by adiabatic ascent) (e.g., Faure et al. 2006; Welsch et al. 2013). These conditions might be consistent with the thermal history of some samples (e.g., komatiites), but are not wholly satisfactory as explanations for the widespread

occurrence of olivine with internal snowflake P-enrichment patterns in typical OIB, Arc, and MORB samples (Milman-Barris et al. 2008; Welsch et al. 2014; Shea et al. 2015; de Maisonneuve et al. 2016; Manzini et al. 2017), or in intrusive olivine (Welsch et al. 2014; Xing et al. 2017) where crystallization at depth presumably occurs at lower undercooling.

Finally, incorporation of P^{5+} or Al^{3+} into the tetra- (4+) and octahedral (2+) olivine sites needs charge balancing that may affect how other elements are partitioned (e.g., Spandler and O’Neill 2010). Phosphorus is generally inferred to occupy the tetrahedral site and substitute for Si (e.g., Agrell et al. 1998; Boesenberg et al. 2004), and Al can occupy either tetrahedral or octahedral sites in olivine (Zhukova et al. 2017). P and Al may be involved in the same charge-balancing reaction or be accommodated by other elements (e.g., Cr^{3+} , Fe^{3+} , Na^+ , Li^+ , and H^+) and vacancies (Milman-Barris et al. 2008; McCanta et al. 2016). While a wide variety of possible exchange reactions can be written to satisfy charge balance, it is challenging to identify which are operative.

A series of olivine crystallization experiments was performed to examine the conditions for formation of P and Al enrichment in olivine. Distributions of these elements in experimental glass and olivine are compared with those in natural samples to tackle three guiding questions: (1) Are P and Al zoning patterns consistent with a model of initial skeletal growth for polyhedral olivine phenocrysts? (2) What are the degrees of undercooling required to produce skeletal growth and the sharp, snowflake-like enrichment patterns of P and Al? (3) What are the operative P and Al substitution reactions? (4) How are P and Al incorporated into olivine and what are the implications for equilibrium vs disequilibrium trace-element partitioning?

Experimental and analytical methods

Experimental strategy

Cooling experiments involving a natural basalt as starting material were conducted within a vertical 1-atm gas-mixing furnace at the University of Hawaii. The starting material is a ‘golden pumice’ (highly vesicular glassy basalt) consisting of undoped primitive Kīlauea tholeiite (~11.3 wt% MgO, see Table 1) erupted in 1820 CE (e.g., Garcia et al. 2003; Lynn et al. 2017). The starting material contains 6–7 vol.% percent olivine microphenocrysts (here defined as having sizes $< 200 \mu\text{m}$) and phenocrysts (sizes $> 200 \mu\text{m}$) with variable core and rim Fo ($100 \times \text{Mg}/[\text{Mg} + \text{Fe}]$) compositions (Fo ~81–89%, Lynn et al. 2017). This material was lightly crushed to preserve olivine grains that were, for the most part, picked out of the starting powder. Because olivine content can be variable across a hand sample, separating

Table 1 Summary of experiments and P and Al concentrations in the olivine

Experiment	t@ T _{initial} hr	T _{final} °C	-ΔT °C	t@T _{final} hr	Olivine compositions				Partition coefficients			
					Al ₂ O ₃ (min) ppm	Al ₂ O ₃ (max) ppm	P ₂ O ₅ (min) ppm	P ₂ O ₅ (max) ppm	K _{Al} (min)	K _{Al} (max)	K _P (min)	K _P (max)
k1820-ol2	26	1240	40	48	410	640	40	1670	0.0032	0.0049	0.02	0.86
k1820-ol3	24	1270	10	48	no new olivine formed							
k1820-ol4	24	1255	25	48	410	580	240	1790	0.0033	0.0046	0.11	0.83
k1820-ol13	24	1240	40	96	330	650	80	860	0.0025	0.005	0.041	0.46
k1820-ol14	24	1277	3	72	no new olivine formed							
k1820-ol15	24	1255	25	84*	380	520	90	970	0.0029	0.004	0.05	0.51
k1820-ol16	24	1255	25	6	450	660	240	1710	0.0036	0.0052	0.12	0.89
k1820-ol17	24	1270	10	87.6	320	500	20	650	0.0026	0.004	0.01	0.38
k1820-ol18	24	1255	25	12.33	380	580	190	1320	0.003	0.0046	0.09	0.67
k1820-ol19	24	1220	60	48	350	690	120	1590	0.0026	0.0052	0.07	0.9
k1820-ol20	24	1220	60	6	350	710	70	1870	0.0027	0.0055	0.04	0.92
k1820-ol21	24	1240	40	25.5	370	670	220	1790	0.0028	0.0052	0.11	0.87
k1820-ol22	24	1240	40	cc**	340	540	30	1780	0.0027	0.0042	0.02	0.94
k1820-ol25	8	1240	40	48	310	630	120	1740	final glass not analyzed			
k1820-ol26	24	1240	40	48	360	440	150	830	final glass not analyzed			
k1820_GR9	24	1220	60	1.5	only analyzed by x-ray mapping							
k1820_GR15	24	1220	60	0.33	450	810	210	1990	0.0036	0.0065	0.1	0.93

t@T_{initial}: time at the initial temperature T_{initial} = 1290 °CT_{final}: final temperature after cooling step-ΔT: Degree of undercooling between T_{liquidus} = 1280 °C and final experiment temperature T_{final}t@T_{final}: time spent at the final temperature before quench

*: time at the final conditions not known precisely due to unexpected early quench, known to be between 72 and 96h

**: continuous cooling experiment with ΔT/Δt = 1 °C/hr

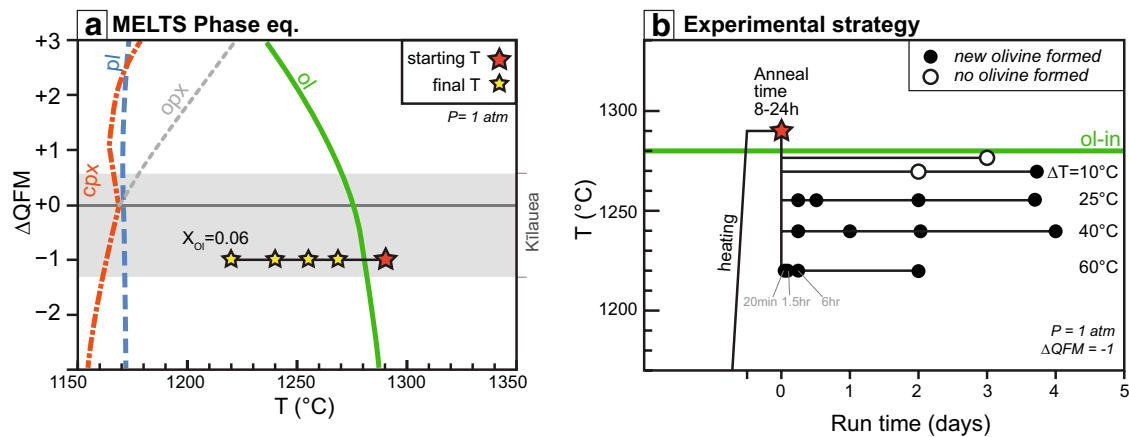


Fig. 2 **a** 1-atm phase equilibria diagram for the 1820CE Kīlauea starting material used for olivine crystallization experiments calculated using MELTS (Gualda et al. 2012). At fO_2 conditions relevant to Kīlauea basalt (grey box), olivine is the only forming phase for $-\Delta T = 100^\circ\text{C}$ below the liquidus. Experiments were performed at 1

log units below the QFM buffer. *cpx* clinopyroxene, *ol* olivine, *opx* orthopyroxene, *pl* plagioclase. **b** Temperature–time plot illustrating the experimental strategy and quench conditions for the runs examined herein

most crystals from the powder was done to avoid dealing with significant compositional variability in the bulk starting material.

Experimental charges were formed by mixing the crushed material with small amounts of polyvinyl alcohol, shaping the slurry into ~8 mm-diameter spheres ('beads') around coiled Re wire. The liquidus temperature for this tholeiite was verified experimentally to be 1280°C ($\pm 3^\circ\text{C}$) by holding at different temperatures for 24 h and examining the resulting beads for newly grown olivine. This value is in excellent agreement with the 1281°C predicted by MELTS (Gualda et al. 2012). Olivine is the liquidus mineral and the only phase to crystallize until $T = 1160\text{--}1170^\circ\text{C}$ ($-\Delta T > 110^\circ\text{C}$), where clinopyroxene and plagioclase begin to co-crystallize (Fig. 2a).

Each experiment was started with an initial 30 min period at 600°C to ensure mixing of gases and avoid Re oxidation during the subsequent temperature ramp-up. Then, temperature was increased continuously from 600°C to an initial value above the liquidus (1290°C) at 240°C/h . The charge was held at this temperature for 24 h (except for two experiments with shorter initial equilibration times of 8 h), after which the temperature was dropped as quickly as possible to final temperatures of 1270, 1255, 1240, or 1220°C , corresponding to undercoolings of $-\Delta T = 10, 25, 40, 60^\circ\text{C}$, respectively (Fig. 2b). Temperature was monitored with an S-type thermocouple ($\pm 3^\circ\text{C}$) suspended level with experimental charges. The final desired temperature was reached within $\sim 1^\circ\text{C}$ in < 5 min, corresponding to minimum cooling rates $-\Delta T/\Delta t = 120\text{--}720^\circ\text{C/h}$. The charges subsequently dwelled for durations between 20 min and 4 days. This cooling strategy imposes the driving force as a 'single-step', which is not necessarily most representative of cooling in

nature but the only way to quantify the relationship between undercooling and system response (see Hammer 2008 for more details). Rapid quenching was achieved without exposing samples to air by drop-quenching the charge into an attached water beaker by zap-melting the Pt wire holding the charges. One additional slower, continuous cooling experiment at $-\Delta T/\Delta t = 1^\circ\text{C/h}$ with final temperature of 1240°C (equivalent to a total $-\Delta T = 40^\circ\text{C}$) was also carried out to check whether cooling rate influenced resulting crystal morphology and P–Al content. Quenched charges were embedded in resin, serial-sectioned (typically 5 sections/charge) to maximize exposure of olivine crystals, and polished for electron microprobe (EMP) analysis. Newly grown olivine was easily distinguished from any pre-existing olivine seeds from the well-faceted and often skeletal morphologies, as well as the different Fo composition evident from simple observation in Backscatter Electron Imaging (BSE).

Oxygen fugacity (fO_2) in these experiments was set at one log unit below the quartz–fayalite–magnetite mineral redox buffer ($\Delta QFM = -1$) using a controlled mixture of flowing H_2 and CO_2 , monitored via a zirconia-based solid electrolyte oxygen sensor (uncertainty of $\pm 0.02\text{--}0.04$ log units fO_2 , cf. First and Hammer 2016). This value was chosen to simulate fO_2 conditions relevant to Hawaiian tholeiites, as generally accepted at the start of the project (Rhodes and Vollinger 2005). Recent findings by Helz et al. (2017) suggest that Kīlauea magmas may be slightly more oxidized ($\Delta QFM = +0\text{--}0.4$ log units). The difference in fO_2 is not anticipated to substantively affect our conclusions, since changes in phase equilibria are small across the range $\Delta QFM = -1$ to $\Delta QFM + 0.5$ (Fig. 2a), although melt Fe^{3+}/Fe^{2+} may influence the partition coefficients of some elements.

Analytical methods

The experiments, along with other natural samples selected for comparisons, were analyzed for olivine and glass compositions using a JEOL-8500F Hyperprobe at the University of Hawaii, using Probe for EPMA software and its built-in matrix correction schemes (e.g., Donovan and Tingle 1996; Armstrong 1988). Element profiles of major (Fe, Mg, Si), minor (Ca, Mn, Ni), and trace (Cr, P, Al, Na) elements were acquired within olivine using an accelerating voltage of 20 keV, a 250 nA beam current, and spot sizes of 2 μm .

On peak count times were either 40 s (Si, Fe, Mn, Ca, Na, and P) or 50 s (Mg, Ni, Al, Cr). Profiles were also collected within embayments and glass adjacent to the olivine interface to check for boundary layers. An average of six additional spot analyses was performed in glass regions from each charge, far away from olivine crystals, to obtain average interstitial glass compositions. For glass analyses, the accelerating voltage was 20 keV, the current 20 nA, with spot sizes of 2–4 μm and 10–15 μm for profiles and individual spots, respectively. On peak count times were 30 s (Si, Ti, Cr, Fe, Mn, Ca, Na, K, and P) or 68 s (Al, Ni, Mg), with half the peak times on the background. Si gains or Na losses during the glass analyses were monitored and corrected when necessary using the Time-Dependent Intensity (TDI) function implemented in the Probe for EPMA software. Gains and losses were undetected for spot analyses with large spot sizes and for profiles using smaller spot sizes, TDI corrections reached maximum values of 6% relative for Na loss and 0.5% relative for Si gain. Both mineral and glass standards were used for olivine and glass calibrations including San Carlos and Springwater olivine (Fe, Mg, Si), Kakanui Augite (Ca), two Caltech Ni and Mn olivine standards (Ni, Mn), F-apatite USNM 104021 (P), Amelia Albite (Na), Orthoclase (K), and basaltic glasses VG-2 and A99 (e.g., Jarosewich et al. 1980). Accuracy and precision for P and Al in olivine are hard to assess due to poor constraints on the homogeneity of standard olivine with respect to trace elements. Repeat measurements on San Carlos olivine yield $\text{P}_2\text{O}_5 = 56 \pm 25$ ppm (1 σ) and $\text{Al}_2\text{O}_3 = 265 \pm 20$ ppm (1 σ), comparable to the 50 and 330 ppm measured by Batanova et al. (2015) for the two elements. We adopt a conservative value of 30 ppm for precision, whereas accuracy cannot be robustly determined. Accuracy for glass measurements is estimated at 500 ppm for both P_2O_5 and Al_2O_3 , and relative precision ~ 12 and 0.5%, respectively. We note that the relatively low precision of P_2O_5 glass analyses compared to olivine precludes identification of small variations ($< 12\%$ relative) within transects aimed at resolving boundary layers close to the olivine interface. This analytical limitation limits our ability to measure P enrichments < 1.1 – 1.2 times the far-field melt concentration. As we discuss further below, such small variations are inconsequential for the purposes

of this study. In contrast, the higher precision achieved for Al allows resolving enrichments < 1.02 -fold. X-ray element maps of Mg, Ni, Ca, Cr, Al, and P were collected in selected experimental and natural crystals using 20 keV, 200–300 nA, resolutions of 0.5–2.5 $\mu\text{m}/\text{pixel}$, with dwell times of 80–200 ms/pixel. Microphotographs and analytical profiles and glass analyses of P and Al in the experiments are available in the Supplementary Material (Table A1).

Results

General characteristics of experimental charges

From the 17 experiments completed, 15 experiments contain newly grown olivine crystals varying in size from a few tens of micrometers to > 1 mm (Fig. 3). Olivine failed to grow in two experiments at low undercooling $-\Delta T = 3$ and 10°C and 48–72 h at the final conditions (Fig. 2b, Table 1). Olivine did form at $-\Delta T = 10^\circ\text{C}$ but only in a longer (88 h) run. In the majority of the experimental charges, larger crystals (e.g., Fig. 3b) are typically concentrated at the bottom. Smaller crystals ($< 200 \mu\text{m}$) are interspersed within the quenched bead, and, in some cases, distributed along the bead edges. Re is not spatially correlated with olivine, and, thus, does not seem to have any effect on its nucleation or growth, unlike Pt (e.g., Faure et al. 2003). A more detailed investigation of the sizes and morphologies of olivine in duplicate experiments quenched after different dwell times and measured in 3D by XRT (Mourey and Shea 2018) confirmed that growth rates increase depending on the degree of undercooling. Mass percent crystallized, calculated from differences in the glass MgO content in superliquidus (1290°C) experiments and runs quenched at different final temperatures, is 0.5, 1.5, 3, and 5.2 wt% at $-\Delta T = 10, 25, 40,$ and 60°C , respectively (Mourey and Shea 2018). In addition to newly grown olivine, a number of pre-existing seeds that were partially dissolved during the initial dwell stage at superliquidus conditions are overgrown by rims after cooling (Fig. 3a). These overgrown crystals (typically Fo 87–89, Lynn et al. 2018) are easily distinguishable from the newly grown rims (Fo 83–85) in Z-contrast (backscattered electron) images. Seeds were avoided in this study. The melt in the starting material contains $1900 (\pm 300)$ ppm P_2O_5 and 12.44 (± 0.03) wt% Al_2O_3 , and varies between 1700–2200 ppm P_2O_5 and 12.44–13.22 wt% Al_2O_3 in the glasses post-experiment.

Morphology and P and Al zoning of experimental olivine

As observed by prior studies (Donaldson 1976; Faure et al. 2007), olivine morphology progressively changes with the

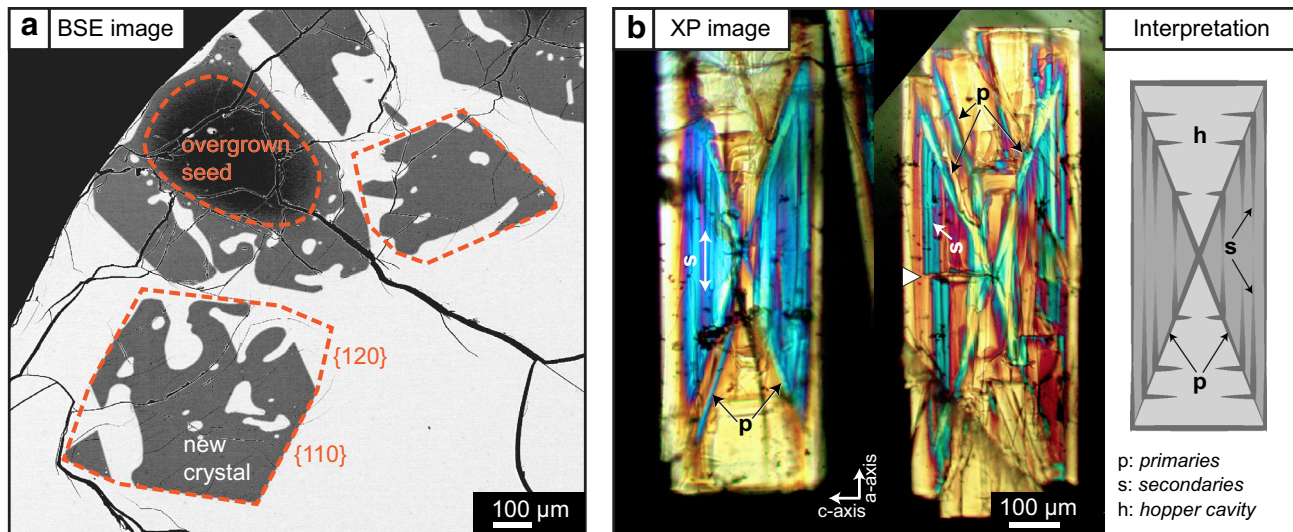


Fig. 3 Images of two experimental charges that underwent 1 day at superliquidus conditions, followed by a cooling step to **a** 1240 °C ($-\Delta T=40$ °C) and dwell for 4 days, and **b** 1220 °C ($-\Delta T=60$ °C) and dwell for 1.5 h at those final conditions. **a** Backscatter Electron image. Aside from newly grown crystals, a few olivine ‘seeds’ (pre-existing from the natural starting material) are present in the charge and easily distinguished by their darker shade in BSE images. **b** Cross-polarized photograph of two skeletal olivine crystals elongated along the *a*-axis. Primary (P) and secondary (S) growth branches

are labeled and an interpretative sketch is shown on the right. Note the higher blue birefringence colors on the left and right sides of the crystals. Higher birefringence is associated here with variations in thickness; hence, blue regions are thicker (contain more secondary branches) than pale yellow regions (thin olivine with hourglass hopper cavities). Also note that some of the secondary branches do not align perfectly as they join towards the center of the crystal (triangle on right image)

degree of undercooling, from faceted polyhedral shapes ($\pm$ hopper cavities) at low undercoolings ($-\Delta T=10$ –25 °C), to hopper and skeletal at moderate undercoolings ($-\Delta T=25$ –60 °C) (Figs. 4, 5 and 6). The most “mature” olivine morphologies (fewer inclusions, more polyhedral habits) are present in the longer runs at lower undercooling ($-\Delta T=25$ °C, 72–96 h), consistent with previous experimental results (Faure et al. 2003) (Fig. 5). At $-\Delta T=10$ °C, even after a long dwell period (88 h), very little crystallization was evident. The only two newly formed crystals observed in section are small (100–200 µm) and polyhedral (Fig. A1 in the supplementary material). Despite the tendency for morphologies to become skeletal with increasing undercooling, a wide spectrum (polyhedral to skeletal) occurs within a single charge, smaller crystals being more polyhedral (Fig. 6). Crystals with hopper/skeletal morphologies typically have a larger footprint (350–1000 µm) than the faceted crystals (150–500 µm) in a given run product. No dendritic morphologies (i.e., here defined as having fine-scale fibrous branches with irrational crystallographic orientation and lacking an overall predictable form, e.g., Donaldson 1976) were formed at the undercoolings investigated.

The inception of olivine crystallization is best observed in the time series at $-\Delta T=60$ °C (Fig. 4). Skeletal primary branches already formed after 20 min and continued to grow for several hours. Secondary branches originating from primaries appeared after 6 h, and had in some cases joined

their opposing counterparts from a nearby branch (e.g., Fig. 3b). The spacing between secondary branches is variable along a single, primary branch, but matched by other secondaries stemming from neighboring primaries (Fig. 4). Primary and secondary olivine branches are both marked by P enrichments, and less clearly Al enrichments, P and Al enrichments are strongest along the primary branches and progressively decrease along secondary branches.

Lower degrees of undercooling ($-\Delta T=25$ –40 °C) produce the same P and Al enrichment patterns as the 60 °C undercooling series (Fig. 5). Secondary skeletal branching is less obvious in the $-\Delta T=25$ °C series olivine crystals. P-rich zones are just as sharp as they are in the 40 °C and 60 °C series, though not as rigidly periodic.

The slower cooling experiment at $\Delta T/\Delta t=1$ °C/h grew large skeletal olivine similar to those in the 40 °C and 60 °C charges, with similar enrichments in P and Al (Fig. A1). Therefore, for these particular sets of experiments, cooling rate does not seem to influence our results at least down to 1 °C/h. The total undercooling, therefore, seems to drive morphology and element enrichment for the range of cooling rates examined.

Despite the more subtle zoning in Al compared to P, both are generally positively correlated along primary and secondary branches of crystals formed at all degrees of undercooling investigated (Figs. 4 and 5). Some growth sectors show seemingly opposite relationships, wherein

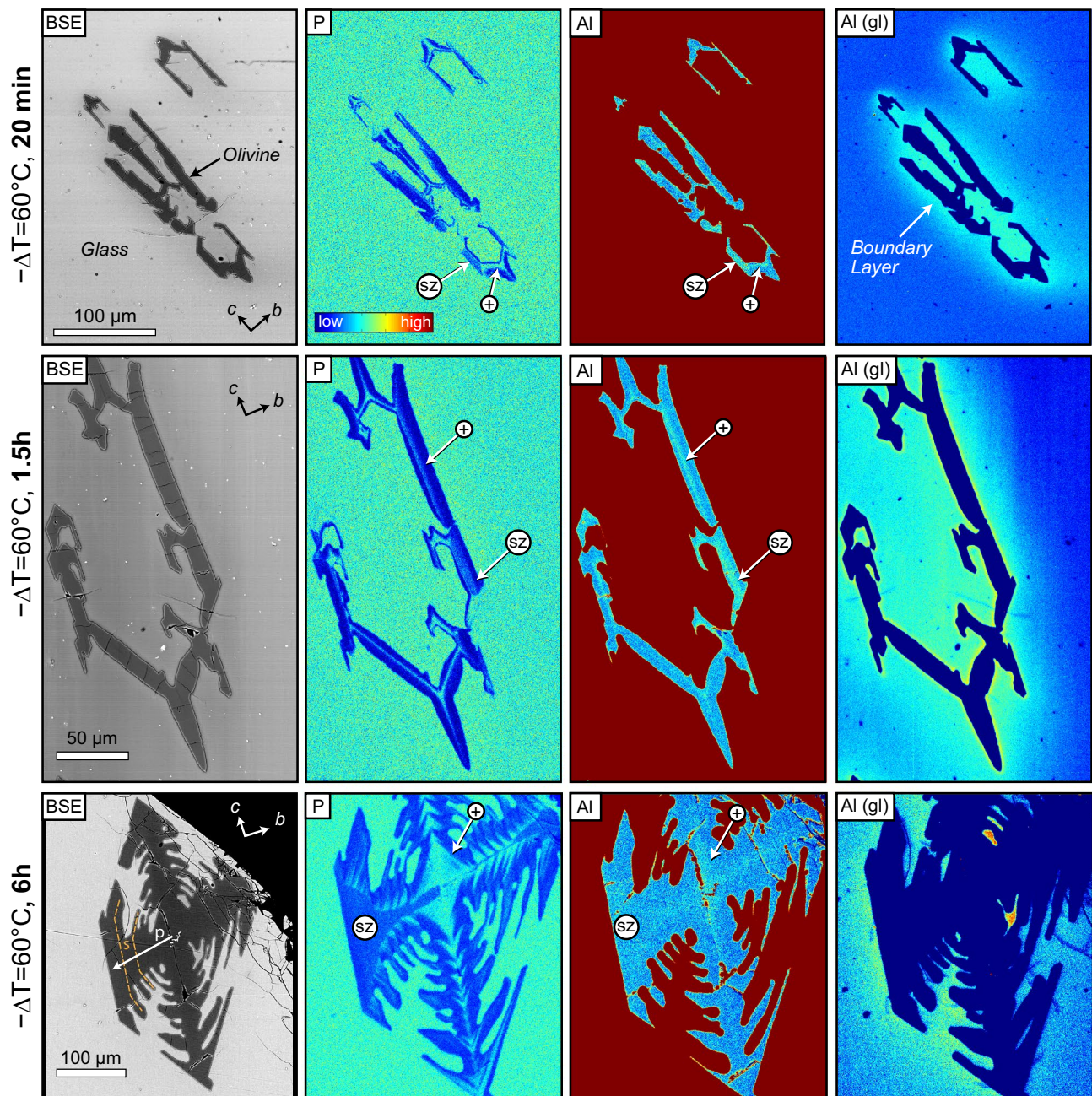


Fig. 4 Morphology and P and Al zoning of olivine during the first few hours of crystallization in runs at $-\Delta T=60^\circ\text{C}$ undercooling. From top to bottom, example of crystals obtained after 20 min, 1.5 h, and 6 h. From left to right, (1) BSE images, X-ray maps of (2) P with color intensities adapted to see zoning both in olivine and glass, (3) Al adapted for olivine, and (4) Al adjusted for the surrounding glass. Clear fine-scale enrichments are displayed by P in the olivine for all run times, whereas Al shows more subdued, yet still visible, changes.

P and Al are anticorrelated. This anticorrelation is only apparent, and results from the relatively low P enrichment in the sector compared to the surroundings. When sector-zoned regions are considered in isolation, P and Al are still positively correlated.

Note the presence of spatially correlated enrichments in both P and Al (plus signs) as well as frequent sector-zoned (sz) regions where P is still slightly enriched compared to the most P-poor parts of the olivine but far less than neighboring P-rich zones. Some of the sector zones by contrast show the high Al concentrations. No clear P enrichment or depletion is seen in the surrounding glass, while Al is enriched close to the crystal interface

The features in these experimental run products share characteristics with natural samples, both in terms of olivine morphology and P + Al zoning (Fig. 7). Skeletal and polyhedral olivine from Kīlauea and Lō'īhi show similar internal snowflake P and Al enrichment patterns, with primary and

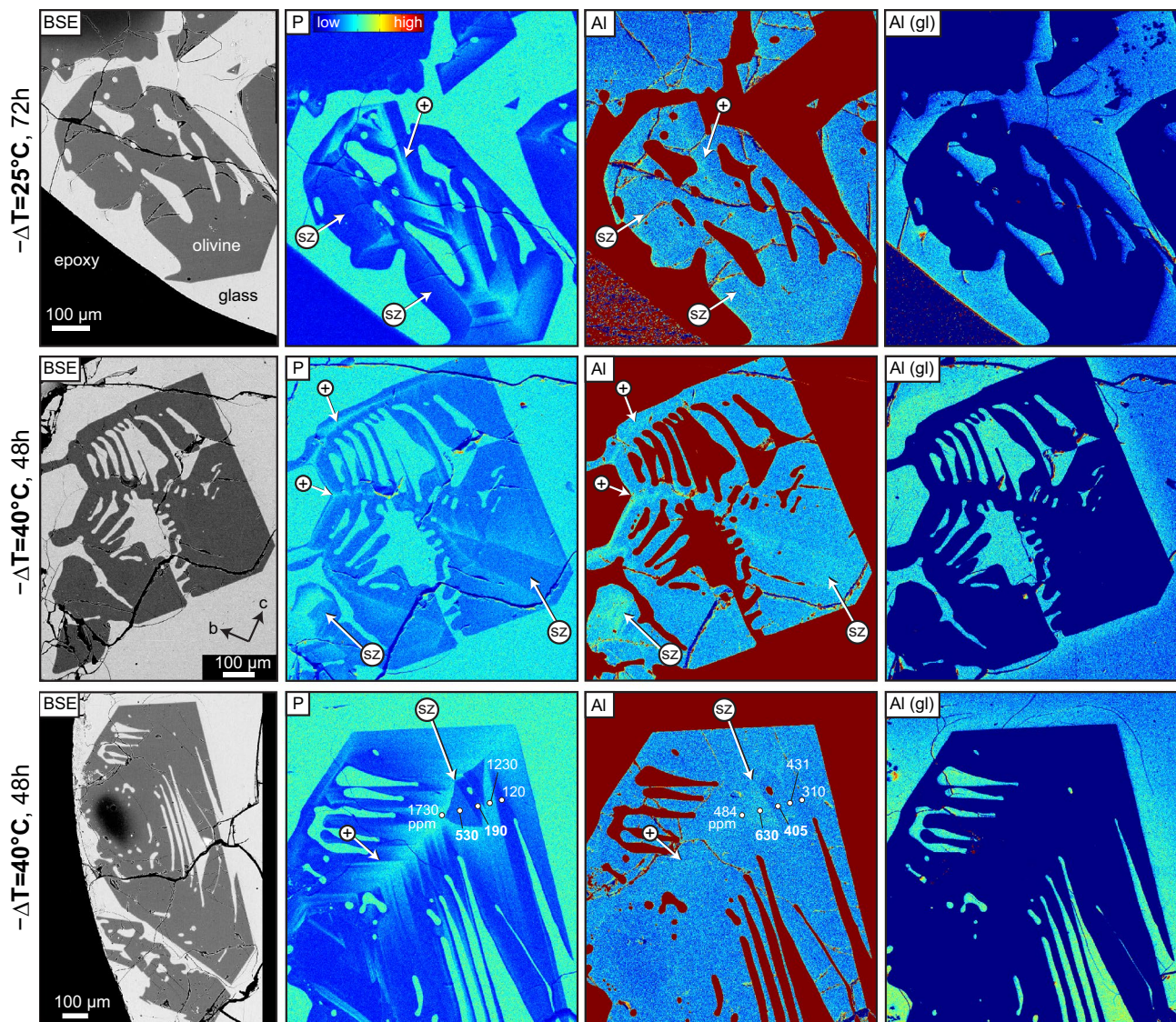


Fig. 5 Morphology and P and Al zoning of olivine in longer experiments (2–3 days) at $-\Delta T=25\text{--}40^\circ\text{C}$ undercooling. From left to right, (1) BSE images, X-ray maps of (2) P with color intensities adapted to see zoning both in olivine and glass, (3) Al adapted for olivine, and (4) Al adjusted for the surrounding glass. Similar to experiments performed at higher undercooling ($-\Delta T=60^\circ\text{C}$ cf. Figure 3), P always shows clear enrichments in the olivine, and Al enrich-

ments are more subtle. The glass around the olivine is not enriched or depleted in P, but it is clearly enriched in Al. Note that Al and P are often positively correlated (plus signs) except in certain crystal regions where their relationship is more complex (marked sz=sector zoning, see main text). The bottom olivine had a small pre-existing seed, which apparently did not influence the process of rapid growth (i.e., skeletal morphology and large size are maintained)

secondary branches. In these a–c sections, olivine has four primary branches, and spacing between secondaries is also similar between the different primaries (Fig. 7a). P zoning in the more mature olivine from Lō‘ihi illustrates that those secondaries merge imperfectly (i.e., misalignments between secondaries stemming from two different primaries are common), but closely enough to yield an apparent impression of ‘oscillatory’ zoning (Fig. 7b). The two natural olivine crystals also display sector-zoned regions. In the Kīlauea olivine, Al is strongly enriched and P not particularly enriched at the core (Fig. 7a), while in the Lō‘ihi olivine, relative Al

concentrations are at their lowest. In both cases, Al-enriched sectors appear to be related to the *a*-axis direction, along the {110} form.

Variations in P and Al concentrations in natural and experimental olivine

Phosphorus and aluminum in olivine from both experiments and natural samples range between 30–1950 ppm P_2O_5 and 300–750 ppm Al_2O_3 (corresponding to about 20–580 ppm P and 130–340 ppm Al) (Figs. 6 and 7, Table 1). Within

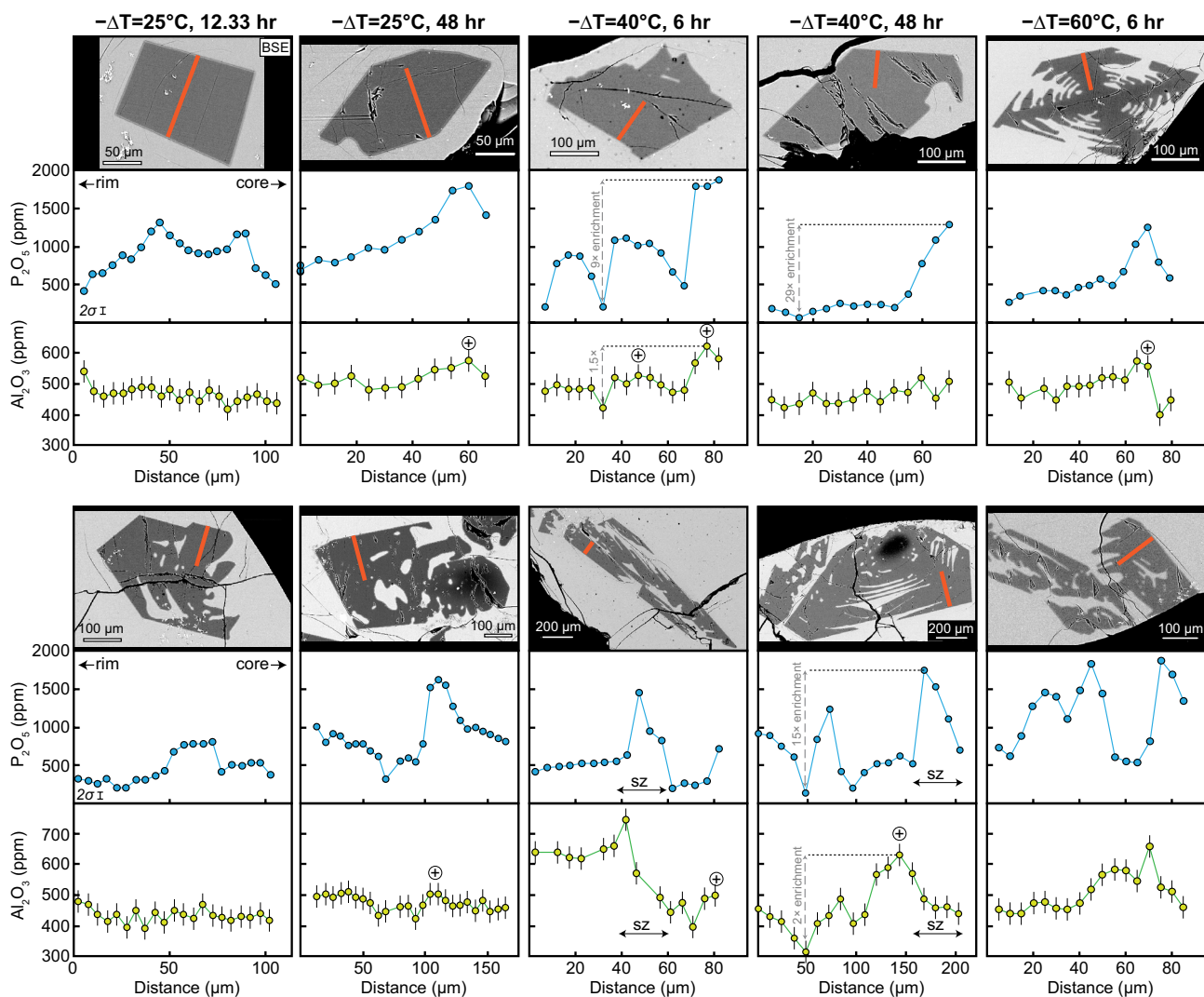


Fig. 6 Morphology of experimental olivine and P and Al concentration profiles. Top and bottom sets show two olivine crystals imaged and measured within a single charge, illustrating the range in morphologies generated during crystallization. Plus signs designate

regions where P and Al show similar enrichment behavior, whereas sector-zoned (sz) regions show more complex patterns. Analytical precision (2σ) for P_2O_5 is the same as the size of blue symbols

individual analytical profiles, P can increase by factors up to $\sim \times 30$ – 50 between P-poor and P-rich zones, whereas Al never exceeds enrichment of $\times 2$ between Al-rich and Al-poor regions (Figs. 6, 7 and Fig. A1). There is no clear relationship between degree of undercooling or run time and the maximum enrichment detected in the profiles. Given that skeletal branches enriched in P and Al enrichments are spatially limited features in 3D, sectioning effects matter greatly in determining the maximum measured concentrations. Within a single charge, P and Al thus vary considerably in maxima/minima values among different crystals (Fig. A1 in the Supplementary Material). Despite this variability, maximum values attained by both elements are equivalent at 25, 40, and 60 °C of undercooling ($Al_2O_3 = 500$ – 700 ppm, $P_2O_5 = 1300$ – 1900 ppm). Slightly lower maximum P

concentrations (500–1000 ppm) were measured in one run at $-\Delta T = 10$ °C (Fig. A1) and two longer experiments at $-\Delta T = 25$ and 40 °C, but it is not known whether this difference is significant or simply the result of not intersecting enrichments through their true maximum concentrations.

Boundary layers in natural and experimental melts

X-ray maps of experimental charges show systematic Al enrichment halos ~ 20 – 200 μm in thickness in the glass around olivine crystals for all undercoolings and run durations (excluding the $-\Delta T = 10$ °C charge, which was not mapped) (Figs. 4 and 5). These halos are still present but thinner and/or less pronounced in the long-duration experiments (≥ 72 h, Fig. 5). Thinning of the boundary layers with time may be

associated with declining olivine growth rates and the ability for Al to diffuse out in the far-field melt. Halo thickness is also variable even around a single grain, consistent with an incompatible element being accumulated around a growing crystal with complex morphology. Similar enrichments also occur in the glass of natural samples examined, where a thicker Al-rich zone is observed around the skeletal olivine, and only a thin enrichment is seen near the polyhedral olivine (Fig. 7). EPMA profiles in the glass surrounding experimental and natural olivine yield Al enrichments of $\times 1.05$ – 1.1 with respect to the far-field glass composition (Figs. 7 and 8). In contrast, there are no resolvable P enrichments in glass around any of the experimental or natural olivine. Measurements of glass at the interface oscillate around $P_2O_5 = 2000$ – 2500 ppm without a clear trend (Figs. 7 and 8). Given the low analytical precision for P in the glass ($\sim 15\%$ relative), we cannot completely rule out the presence of P enrichments $< 1.15\times$ that are similar in magnitude to Al. As we discuss further, such enrichments are far too small to have produced P-rich zones in the olivine (also see Fig. A2 in the supplementary material). Even so, glass pools partially trapped as inclusions have P contents indistinguishable from the outside glass (within uncertainty), whereas Al is clearly enriched (Fig. 8b). If anything, phosphorus in the glass around the natural skeletal olivine from Kilauea slightly decreases towards the interface (Fig. 7a). Settling of crystals during the experiment could possibly disrupt and partially erase P boundary layers (e.g., Watson and Müller 2009). In this case, however, boundary layers in Al would also be affected, contrary to what we observe (Figs. 4 and 5). Notably, in X-ray maps, maximum P intensities in glass and olivine are indistinguishable and have very similar concentrations (Figs. 4, 5, and 7); the far-field glass has a range ~ 1700 – 2200 ppm P_2O_5 , comparable to the most P-rich zones (1300–1900 ppm), yielding an apparent distribution coefficient of close to 1.

Discussion

The main results above demonstrate that: (1) Hopper/skeletal morphologies and P and Al zoning comparable to that observed in natural olivine can develop even at fairly low undercooling ($-\Delta T \leq 25$ °C); (2) P and Al differ vastly in relative concentration between ‘enriched’ and ‘normal’ zones in the crystal (up to $50\times$ and $2\times$ enrichment factors, respectively); (3) the maximum concentration in P attained in the olivine P-rich zones is comparable to the concentration of P in the melt; and (4) well-defined Al-rich boundary layers are present in glass around the olivine in natural and experimental olivine, but are absent or not resolved for P, despite the large enrichments measured in the neighboring olivine. Below we discuss the implications of these results for the development of P–Al zoning in natural olivine, and for their equilibrium or disequilibrium partitioning behavior.

We then explore the physical mechanisms for incorporating these trace elements into the crystal structure.

Development of P and Al zoning in olivine at low-to-moderate undercooling

The fine-scale zoning in P and Al within natural and experimental olivine measured in numerous studies (Milman-Barris et al. 2008; Welsch et al. 2013, 2014; Shea et al. 2015; de Maisonrouve et al. 2016; Manzini et al. 2017; Xing et al. 2017; Baziotis et al. 2017; Gordychik et al. 2018; Ersoy et al. 2019) is generally thought to originate from episodes of rapid crystal growth under conditions of high undercooling. Welsch et al. (2013) propose that strong, localized thermal gradients around reservoir walls may generate sufficient undercooling to crystallize P- and Al-zoned olivine. Alternatively, during intrusion of magma as dikes or small injection veins, the cooler country rock may absorb sufficient heat and provide the necessary conditions for skeletal olivine phenocryst growth (e.g., Baziotis et al. 2017). Olivine in chondrules also displays strong Al zoning consistent with rapid growth (Libourel and Portail 2018). There, the thermal fluctuations induce rapid cycles of crystallization–dissolution, and originate from gas–melt interactions in the solar nebula.

Quantifying the relationship between the degree of undercooling and the development of P and Al zoning is, however, challenging. Experiments presented in Milman-Barris et al. (2008) and Welsch et al. (2014) were performed under continuous cooling conditions (and under a thermal gradient for Welsch et al. 2014), making it difficult to relate formation of P or Al zoning directly to the total thermal driving force $-\Delta T$. While the relationship between undercooling and cooling rate is not easily quantified, our only continuous cooling experiment ($-\Delta T = 1$ °C/h for an integrated $-\Delta T = 40$) formed olivine indistinguishable in morphology and P–Al composition from those that crystallized within the equivalent single-step cooling experiment at $-\Delta T = 40$ °C. Thus, step-wise or continuous cooling may be comparable in this series down to 1 °C/h. In part based on relationships between morphology, growth rate, and undercooling obtained by Jambon et al. (1992); Welsch et al. (2013) proposed that the growth-rate conditions needed to produce skeletal to dendritic olivine, and thus P-enrichments, should be only met at a high $-\Delta T > 60$ °C. Newer growth-rate data obtained by a companion study utilizing experiments similar to those presented herein show that, even at $-\Delta T = 25$ – 60 °C, moderate growth rates between 0.5×10^{-8} and 6×10^{-8} m s $^{-1}$ are sufficient to initiate skeletal growth (Mourey and Shea 2018). The discrepancy between the experiments of Jambon et al. (1992) and ours with respect to the morphology $-\Delta T$ relationship may be a simple function of scaling: in their ingenious setup, olivine grew within plagioclase-hosted melt

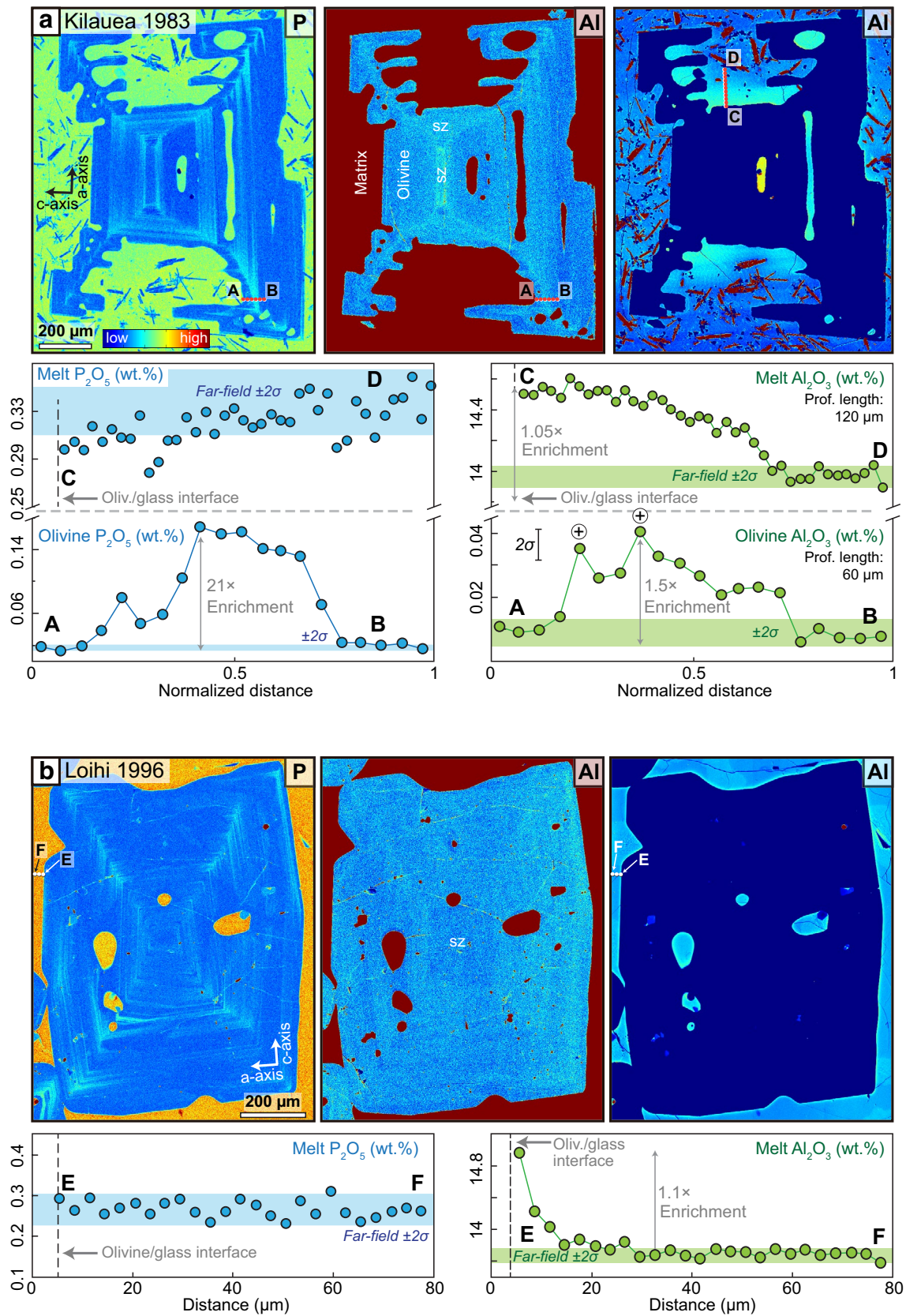


Fig. 7 P and Al zoning in natural olivine from Hawai'i. **a** A skeletal olivine from the Pu'u 'Ō'ō eruption at Kīlauea volcano (cf. Shea et al. 2015), and **b** a well-faceted, 'polyhedral' olivine from the 1996 eruption of Lō'ihi volcano. As in Figs. 4 and 5, X-ray maps of P and Al (adjusted to best visualize zoning in olivine and in the outside glass) show intricate enrichments in both elements along primary and secondary growth branches and sector-zoned regions where they appear anticorrelated. The plots below show P_2O_5 and Al_2O_3 in the surrounding glass, and (Kīlauea olivine only) in the crystal. Plus signs denote regions in the olivine that show similar enrichment behavior in P and Al

inclusions, which restricted their size ($\leq 50 \mu m$). Under low-to-moderate ΔT conditions, morphological instability (non-faceted growth) and development of skeletal branches may be more difficult to initiate. As is commonly done in material sciences for metal alloys, future detailed examinations of the relationships between undercooling, growth rate, and the spacing of skeletal branches (e.g., Grugel 1993) as recorded by P zoning in olivine could yield robust cooling-rate meters for basaltic magmas.

The P and Al zoning patterns produced in our olivine formed at $-\Delta T = 25\text{--}60^\circ C$ (Figs. 4 and 5) demonstrate that high undercooling is not a requirement for interface instability. Natural basaltic magmas, therefore, need not undergo extreme thermal histories (e.g., a strong, localized thermal gradient) to crystallize P- and Al-enriched olivine. Instead, we suggest that the nearly ubiquitous process of magma mixing under volcanoes erupting basalt (e.g., Costa and Dungan 2005; Kahl et al. 2015; Colman et al. 2016; Lynn et al. 2017) can easily create the moderate driving force needed: hotter recharge magma may be undercooled by several tens of degrees, depending on the temperature difference and relative volumes of the two end-members. Magma mixing also induces changes in phase equilibria, promoting chemical (constitutional) undercooling on the scale of the hybrid magma. In this fashion, even hybridizing end-members that might conceptually be at initially similar temperature conditions could grow skeletal olivine if their composition is different enough. Magma mixing may thus be a unifying phenomenon to explain the development of P and Al zoning in olivine from various geodynamic settings.

Distinct partitioning behavior of P and Al

Nernst partition coefficients for P and Al ($K_p^{ol/melt} = \frac{C_p^{oliv}}{C_p^{melt}}$ and $K_{Al}^{ol/melt} = \frac{C_{Al}^{oliv}}{C_{Al}^{melt}}$, noted 'K' to avoid confusion with diffusivity terms 'D' below, and where C is mass concentration), were calculated both for P- or Al-rich and P- or Al-poor regions of each experimental olivine using minimum and maximum measured concentrations (C_p^{oliv} and C_{Al}^{oliv}). The concentrations in the final melt were used for C_p^{melt} and C_{Al}^{melt} . The partition coefficients could also be calculated using the concentration

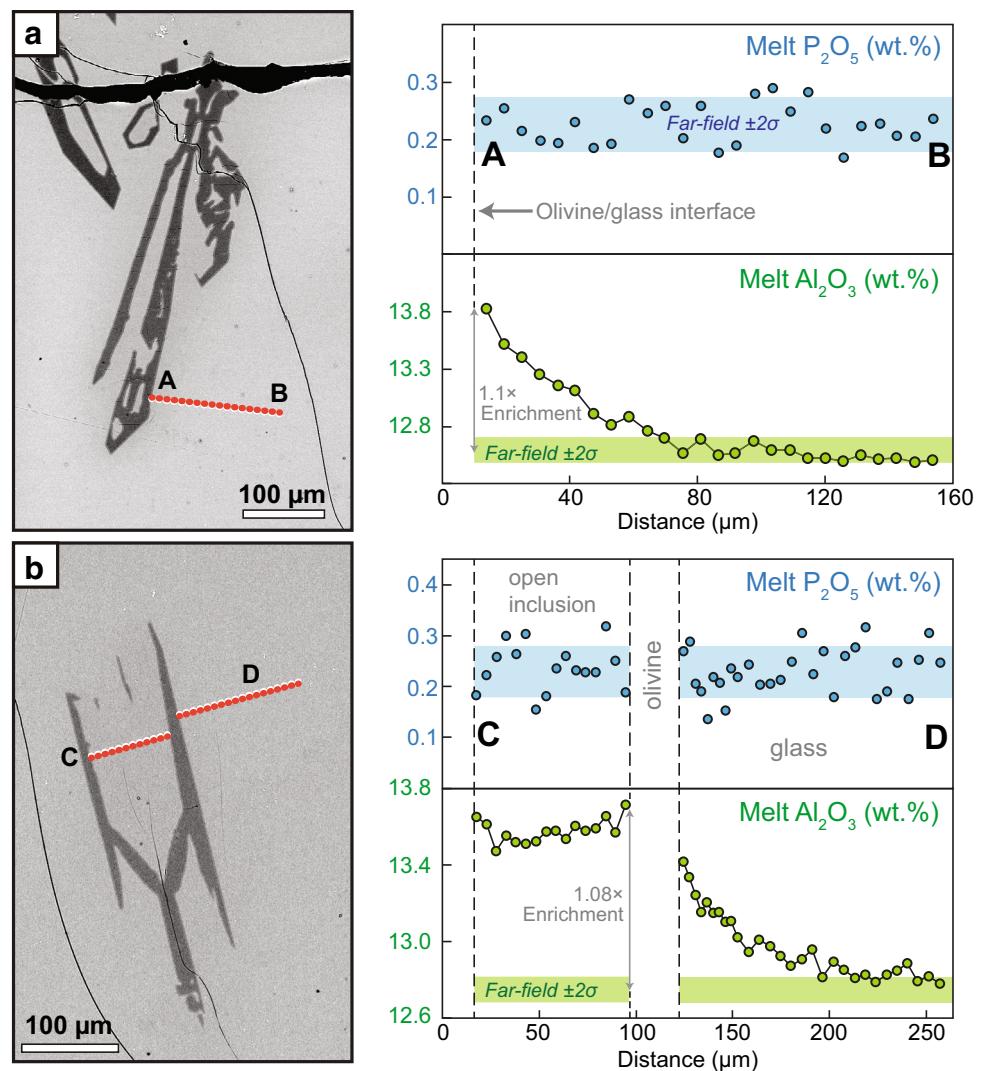
measured in the melt next to the olivine interface. However, because the olivine crystals in question are chemically heterogeneous, some zones of interest are not well represented by adjacent melt. In any case, given that boundary layers are not detectable for P and that they show enrichment of $\times 1.1$ in Al at most (Fig. 8), using the far-field melt composition will shift $K_p^{ol/melt}$ and $K_{Al}^{ol/melt}$ to higher values by $\sim 10\%$ relative or less.

Partition coefficients vary greatly for P and approach 1 in some olivine ($0.01 < K_p^{ol/melt} < 0.93$), whereas they vary much less for Al, which is largely incompatible throughout the experimental sets ($0.0025 < K_{Al}^{ol/melt} < 0.0068$) (Fig. 9 and Table 1). There is no clear relationship between P partition coefficients and undercooling as maximum values of $K_p^{ol/melt} > 0.9$ plateau at $-\Delta T = 25^\circ C$, Fig. 9a. In contrast, there may be a slight increase in maximum $K_{Al}^{ol/melt}$ with undercooling (Fig. 9b).

Values of $K_p^{ol/melt}$ between 1 and 1.4 were already reported in experimental studies (Dunn 1987; Taura et al. 1998; Grant and Kohn 2013; Fonseca et al. 2014) spanning the compositional range between peridotite and andesite. Kinetic crystallization experiments from Milman-Barris et al. (2008) also yield high partition coefficients (up to ~ 0.7), and several investigations of natural samples support the occurrence of such high $K_p^{ol/melt}$ values (see Baziotis et al. 2017 and references therein). Based on experiments performed using simplified Fe-free synthetic silicate melts (CMAS + $Na_2O + P_2O_5$), Grant and Kohn (2013) found that $K_p^{ol/melt}$ increased with SiO_2 content or, alternatively, with the degree of polymerization of the melt, NBO/T the ratio of non-bridging oxygens to tetrahedrally coordinated cations. According to their data set, olivine in our Kīlauea basalt (NBO/T = 1.1) should have a $K_p^{ol/melt} \approx 0.1$. It's likely that additional charge-balancing mechanisms occur when Fe is present in the melt due to its strong influence on equilibrium vacancy concentration in the octahedral site (e.g., Dohmen and Chakraborty 2007). Similarly, the presence of the variety of trace elements typically present in natural basalt also exerts some control on crystal chemistry (e.g., Spandler and O'Neill 2010), meaning that simple partitioning predictions based on major element composition of the melt are unlikely to succeed. Overall, our results suggest that P partitioning is much more sensitive to kinetics (growth rate) than melt composition.

The $K_{Al}^{ol/melt}$ values which we calculated compare reasonably well with other results from experimental studies of basalt (0.012 in Beattie 1994; 0.0044 in Yurimoto and Sueno 1984 and 0.01 in Matzen et al. 2011), though on the lower range. Given the low concentrations of Al in olivine, differences in analytical tools (SIMS vs. EPMA) and methods (e.g., low current vs. high current for EPMA) may cause some of the discrepancy in $K_{Al}^{ol/melt}$ measured. Aside from analytical uncertainty considerations, the complex nature of

Fig. 8 P and Al concentrations in the melt included in and surrounding experimental olivine. **a** and **b** Are two skeletal olivine crystals in charges that formed after 1.5 h at $-\Delta T = 60^\circ\text{C}$. Light blue and green bars show the variation expected from analytical precision. Al is enriched by about 10% within the open inclusion and boundary layers, whereas P does not show any obvious enrichment or depletion within uncertainty. Given that P is enriched by factors up to $50\times$ in olivine, a simple boundary layer model (i.e., where P is incompatible and piles up at the interface) would predict similar enrichments in the melt. By contrast, Al is enriched by factors $<2\times$ in the olivine and some boundary layer enrichment is also observed

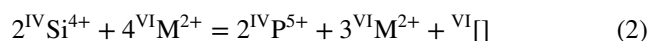


enrichments in both Al and P complicates calculation of partition coefficients. Because these enrichments are volumetrically small and complexly distributed within a 3D olivine crystal (e.g., Fig. 1), measuring the maximum concentration of fine-scale (e.g., 1–10 μm) enrichment zones within a 2D section is unlikely unless previous mapping has been done to characterize their distribution. This problem is exacerbated in crystals that have already matured to polyhedral morphologies, for which locations of fast growth (skeletal branches) are no longer obvious (cf. Figs. 5, 6 and 7, also Welsch et al. 2014). As a result, $K_{\text{P}}^{\text{ol/melt}}$ and $K_{\text{Al}}^{\text{ol/melt}}$ estimates reported in the literature may at times be underestimated.

P and Al substitution mechanisms in olivine

A main question arising from the existing partitioning data is why do P and Al display such different values in olivine? To evaluate this question, we consider the mechanisms and sites through which they may be incorporated in the

crystal lattice. A plethora of reactions have been proposed for accommodating P and Al in olivine (Agrell et al. 1998; Milman-Barris et al. 2008; Boesenberg and Hewins 2010) including:



where IV and VI represent the tetrahedral and octahedral sites, $\square$ is a vacancy, and M is the metal vacancy site in olivine.

In most proposed reactions (e.g., 1–3), P is thought to occupy the tetrahedral site, substituting for Si and forming $(\text{Mg,Fe})_2\text{PO}_4$ units. Al has been inferred to occupy either an octahedral or tetrahedral site or both depending on the reaction considered (e.g., Evans et al. 2008). We can evaluate

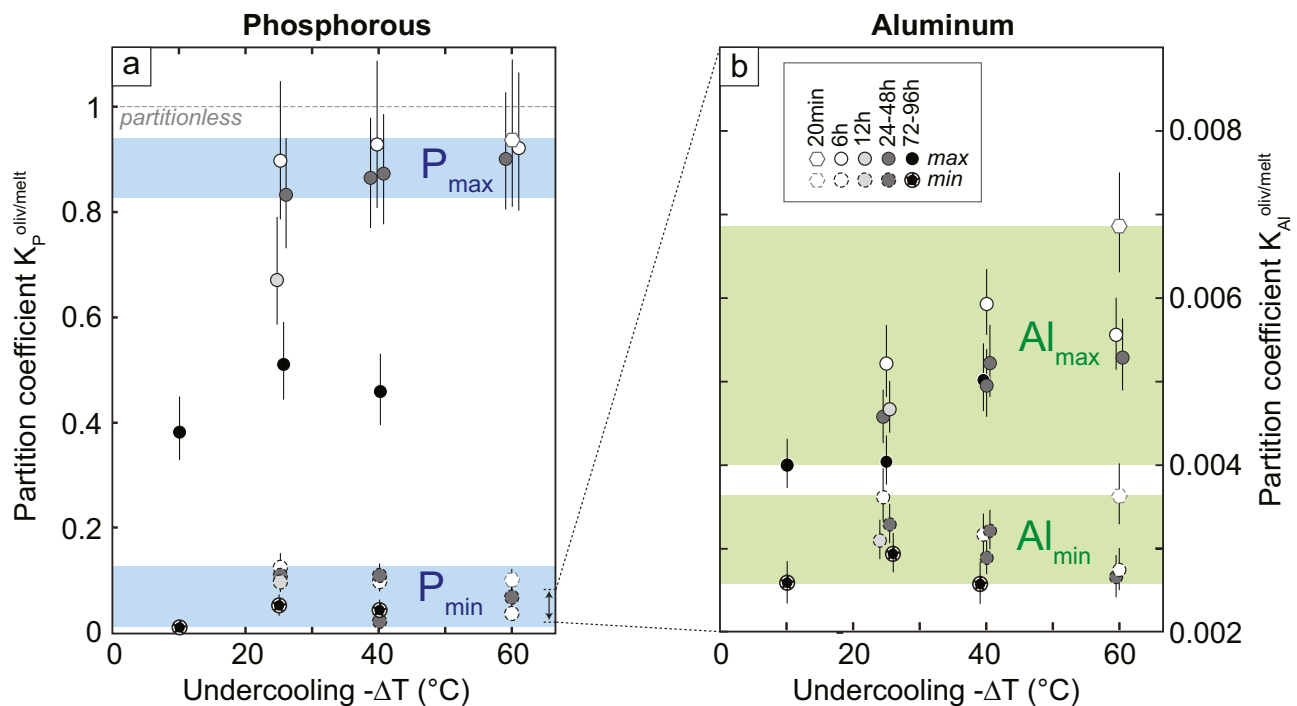


Fig. 9 Partitioning of P and Al between olivine and melt for the different experimental series as a function of undercooling. Minimum (dashed circles) and maximum (full circles) partition coefficients are calculated using, respectively, the lowest and highest measured concentration of P and Al in the crystal and their average concentration in the melt. Ranges in minimum and maximum values are shown as blue and green fields for each element. A remarkable difference in calculated values is obtained for P (more than one order of magni-

tude), while values are less variable for Al. The range in Al partition coefficients is also shown on the left plot for comparison (double arrow). P shows near-partitionless ($K_P = 1$) behavior in some cases. Partitioning of P in olivine does not seem to depend noticeably on initial undercooling (note: run at $-\Delta T = 10$ °C has slightly lower values, but only 1 small crystal could be analyzed), while there may be some dependence for Al

these mechanisms by examining covariations in various elements. P and Al measured from individual spots and analytical profiles covary positively in both experimental and natural olivine, with the exception of some sectors in which they appear anticorrelated (Fig. 10). In detail, there are two trends that emerge even when considering single profiles: a high P trend with a slope $P = 10 \times \text{Al}$, and a low P trend, with a slope $P = \text{Al}$ (Fig. 10a–c). The vast majority of the P-rich zones analyzed form the high P trend, where Al concentration alone is insufficient to satisfy charge balance (e.g., reaction 3). The low P trends are by contrast well explained by simple coupling between P and Al to substitute for two Si atoms (reaction 3). Interestingly, the most Al-rich spots often correspond to regions of the olivine that are sector-zoned (Figs. 5, 6 and 7). The apparent anticorrelation of P and Al in maps and profiles seems to contradict the positive covariation in elemental plots (Fig. 10). In reality, however, Al-rich zones are also more P-rich than the most P-poor and Al-poor zones (low P trends in Fig. 10, see Fig. 6 for an example), meaning that a positive covariation is maintained. The anomalously P-rich zones forming the high P trends in Fig. 10, therefore, swamp out the P-Al covariation present in

sector zones. No particular trend in P or Al with undercooling is obvious.

The direct substitution of Si by P indicated by reactions (1) and (2) has been well documented in phosphoran olivine (i.e. $\text{P}_2\text{O}_5 > 0.5$ wt%) in natural samples (Agrell et al. 1998; Baziotis et al. 2017). For more common olivine compositions such as those studied here (i.e. $\text{P}_2\text{O}_5 < 0.5$ wt%), the relationship between P and Si is more difficult to assess largely because in the lower Si content associated with high P within P-rich zones is overwhelmed by analytical uncertainty of SiO_2 . Despite the noise in the data and clear shifts in Si concentrations associated with analytical drift, plots of Si vs. P suggest that either reaction (1) or (2) could explain the trends observed for P-rich zones (Fig. A3). Other plots to evaluate reactions (3) and (4) did not yield trends supportive of these reactions and are not shown. Thus, we favor (1) incorporation of P in P-rich zones via Si substitution ($\pm$ creation of vacancies on the tetrahedral site or octahedral site, reaction 1), and (2) incorporation of Al in Al-rich zones by substitution of two Si atoms by both P and Al in the tetrahedral site (reaction 3).

The question of why P is preferred to Al during rapid growth of primary olivine branches still remains, and we

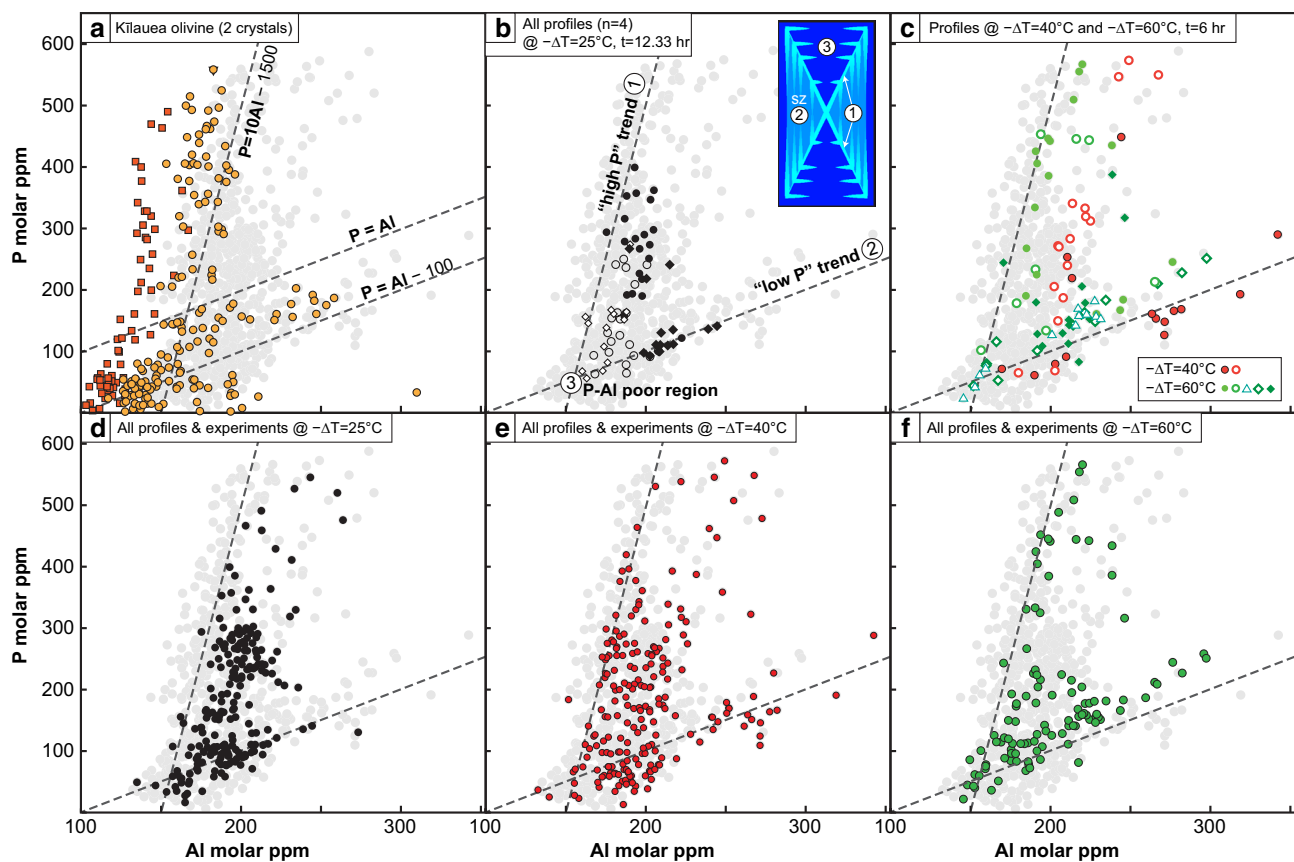


Fig. 10 Covariations between Al and P (expressed in molar concentrations) within **a** natural samples, **b**, **c** individual profiles, and **d–f** at different undercooling. Different symbols represent different profiles in the same sample unless specified. Grey circles show the entire experimental data set for comparison. Two main trends are visible, a “high P” trend (slope $P=10\times\text{Al}$) and a “low P” trend ($P=\text{Al}$). The

low trend is often associated with Al enrichment within sector zones, where P is comparatively not as enriched. The reaction $2\text{Si}=\text{P}+\text{Al}$ may be well depicted by this low P trend, whereas Al is clearly insufficient to charge balance P along the high P trend. Inset schematic of a P-zoned olivine in **(b)** shows the inferred location of the different trends and regions of the Al–P diagrams

propose two hypotheses: (A) P is preferentially incorporated over Al during rapid growth by virtue of its smaller ionic radius ($r_{\text{P}}^{5+}=0.17\text{ \AA}$ vs. $r_{\text{Al}}^{3+}=0.39\text{ \AA}$, in tetrahedral coordination, for a site with an optimum effective ionic radius close to that of Si $r_{\text{Si,IV}}^{4+}\sim 0.26\text{ \AA}$, Shannon 1976). The lattice strain model (Blundy and Wood 1994; Fig. 11 and see Supplementary Material for details) predicts that the elastic strain energy penalty for incorporating larger ions is slightly higher than the penalty for hosting smaller ions, but not to a great extent. In addition, it is possible that the optimum radius for 5+ elements in the tetrahedral (IV) site is smaller than that of 4+ elements like Si (r_{Si}^{4+}). For instance, the optimum effective radius for 4+ elements in octahedral coordination is shifted towards slightly smaller sizes ($r_{0,\text{VI}}^{4+}\sim 0.66\text{ \AA}$, where r_0 is optimum radius and VI denotes the octahedral site) than the optimum radius for 2+ and 3+ elements in the same site ($r_{0,\text{VI}}^{2+}\sim r_{0,\text{VI}}^{3+}\sim 0.71\text{ \AA}$ Spandler and O'Neill 2010) (Fig. 11). If 5+ elements also require a smaller optimum radius in tetrahedral coordination, P

would be easier to accommodate in the olivine lattice than 3+ elements like Al, but only during fast growth. Conceivably, rapid growth could produce a slightly less stiff lattice, which in turn leads to easier incorporation of P compared to the larger Al atoms (less energetic penalty for smaller cations). (B) Rapid growth could lead to enhanced formation of defects within the lattice. Such defects, in particular vacancies, are important for the incorporation of P (e.g., reactions 1 and 2 above), and this mechanism would activate and dominate the P vs. Al relationship (e.g., high P trend, Fig. 10) during periods of fast olivine growth. Al incorporation in the tetrahedral site may be less sensitive to vacancy concentration, since they are not required for substitutions involving Si (Coogan et al. 2014; Zhukova et al. 2017). By examining the nanoscale structure of P-rich vs. P-poor zones in natural or experimental olivine (Hammer et al. 2017), we may be able to determine whether any of these scenarios adequately explains uptake of P over Al during olivine growth.

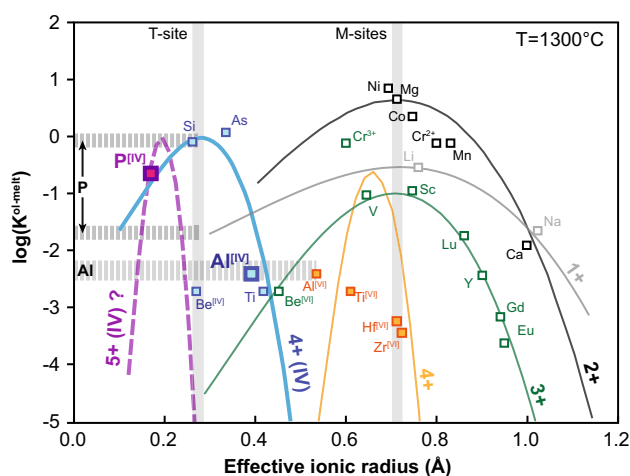


Fig. 11 Cation partitioning in olivine as a function of effective ionic radius (Onuma diagram). Ranges in partition coefficients calculated for the crystallization experiments presented herein are shown on the left. Partitioning data: P, Al, Si, As, Ti[IV] (Yurimoto and Sueno 1984), all other elements (Spandler and O'Neill 2010, and references therein). Effective ionic radii are from Shannon (1976). Curves on the diagram are calculated using the lattice strain model (e.g., Blundy and Wood 1994, see Supplementary Material for details). The curve calculated for P in tetrahedral coordination (dashed purple) is speculative

Models for P and Al enrichment during olivine growth

Two principal mechanisms have been proposed to explain disequilibrium incorporation of trace elements at enriched or depleted levels: the boundary layer (BL) model, and the growth entrapment (GE) model. The BL model is most prevalent in the literature (e.g., Albarède and Bottinga 1972; Lasaga 1982; Bacon 1989; Faure and Schiano 2005; Milman-Barris et al. 2008; Watson and Müller 2009; Welsch et al. 2013). Nonetheless, we briefly describe the GE model below as well and refer to Watson et al. (2015) and our supplementary material for more details and results.

Growth entrapment model

The GE model postulates the existence of a thin chemically anomalous layer at the surface of the growing crystal (Watson and Liang 1995; Watson 2004). In this thin interfacial layer (i.e. a few molecules wide), the structure and bonding of atoms is thought to be different from that of the regular lattice. Incorporation of trace elements can thus occur at concentrations different from predicted equilibrium. The efficiency of growth entrapment depends on (1) the partitioning of the element at the surface layer and in the bulk lattice (F in Watson and Liang 1995), and (2) the competition between crystal growth rate (V) and diffusivity (D) of the element in the crystal (Fig. A4). Higher V/D ratios favor higher entrapment efficiency, as higher

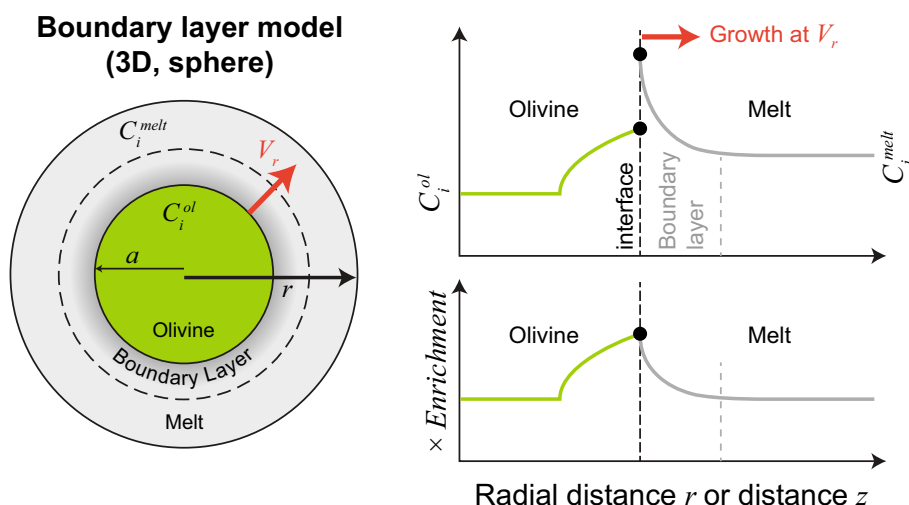
diffusion rates act to smear out the thin chemically anomalous layer. The model was used by Watson et al. (2015) to tackle the same problem of P enrichments in olivine. They adopted an effective partition coefficient (or surface enrichment factor) $F=10$ and concluded that the model effectively explained why tenfold P enrichments were preserved: under growth-rate conditions in the range 10^{-9} – 10^{-6} m/s, the diffusivity of P in olivine is slow enough to allow enrichments of factor 3–10× above equilibrium levels to survive diffusive relaxation during incorporation. We repeated similar models for P and Al, with enrichment factors $F=40$ and $F=2$, respectively, to model growth at 1240 °C ($-\Delta T=40$ °C). Under these conditions, enrichment factors between 18–37 and 1.2–1.8 are preserved for P and Al, respectively, under growth rates 10^{-8} – 10^{-7} m/s relevant to this degree of undercooling (Mourey and Shea 2018) (See Supplementary Material and Figs. A5 and A6). Therefore, it is possible to preserve high levels of enrichments through the GE mechanism, as diffusion in the crystal is not fast enough to erase the chemically anomalous surface layer. A difficulty with the GE model is that the enrichments are an a priori result of the model: they are controlled by F values, but these are not easily quantifiable (e.g., Watson 2004; Lanzillo et al. 2014).

Boundary layer model

In the boundary layer enrichment (BL) model, elements that are rejected in the crystal are enriched in the surrounding melt during growth (e.g., Tiller et al. 1953; Smith et al. 1955; Lasaga 1982; Watson and Müller 2009). Similarly, compatible elements are preferentially incorporated in the solid and depleted in the corresponding boundary layer. If the partition coefficient K remains constant, enrichment of an incompatible element in the melt boundary layer will induce a concurrent increase in the concentration of the element in the growing crystal (Fig. 12). In this scenario, it is, therefore, the compositional evolution of the melt that is modeled, and the incorporation of a given element in the crystal controlled by K . This model was proposed to explain the high concentrations of P and Al in olivine by several authors (Milman-Barris et al. 2008; Welsch et al. 2013, 2014; Shea et al. 2015; de Maisonneuve et al. 2016). In Shea et al. (2015), P-enrichment factors were based on relative X-ray map intensities between P-rich and P-poor regions, and thus vastly underestimated (factors of 1.5–2 $\times$). This led to the finding that enriching P by these amounts was possible given fast enough growth (e.g., Fig. A2). de Maisonneuve et al. (2016) obtained better estimates of these enrichment factors (6–12 $\times$) using Laser Ablation Inductively Coupled Mass Spectrometry, and found that the boundary layer model required unrealistically high growth rates ($> 10^{-6}$ m s $^{-1}$).

Using the revised enrichment factors extracted from our experiments, we explore two versions of the BL model: the traditional one, in which K is taken to be constant, and an

Fig. 12 Boundary layer (BL) numerical model setup. The growing olivine is approximated as a 3D sphere of radius a , surrounded by a melt envelope of radius r . V_r is the radial growth rate. Diagram on the right illustrates the enrichment of an incompatible element within the melt towards the melt–olivine interface. This region is termed the boundary layer. The pile-up of the incompatible element in the melt is translated into an enrichment factor within the growing crystal, assuming the solid–melt partition coefficient stays constant and at equilibrium



alternative one where K is assumed to depend on growth rate.

Following Zhang (2008), the 3D radial expression for diffusion and advection can be written as:

$$\frac{\partial C_i^{\text{melt}}}{\partial t} = D_i^{\text{melt}} \frac{\partial^2 C_i^{\text{melt}}}{\partial r^2} + \frac{2D_i^{\text{melt}}}{r} \frac{\partial C_i^{\text{melt}}}{\partial r} + V_r \left(\frac{\rho_c}{\rho_m(r=a)} - 1 \right) \frac{a^2}{r^2} \frac{\partial C_i^{\text{melt}}}{\partial r}, \quad (5)$$

where i is either P or Al, C_i^{melt} is their concentration in the melt, D_i^{melt} their diffusivity in the melt (assumed independent of their concentration), a the radial position of the interface, r the radial position ($r > a$ in the melt), V_r the radial growth rate, and $\frac{\rho_c}{\rho_m(r=a)}$ the density ratio between crystal and melt at the interface. The mass conservation condition at the interface is given by:

$$\left. \frac{\partial C_i^{\text{melt}}}{\partial r} \right|_{x=0} = \frac{(K_i^{\text{ol/melt}} - 1) V_r C_i^{\text{melt}}}{D_i^{\text{melt}}}. \quad (6)$$

At each time step, the concentration of P or Al in the solid is given by:

$$C_i^{\text{cryst}} = K_i^{\text{ol/melt}} C_i^{\text{melt}}. \quad (7)$$

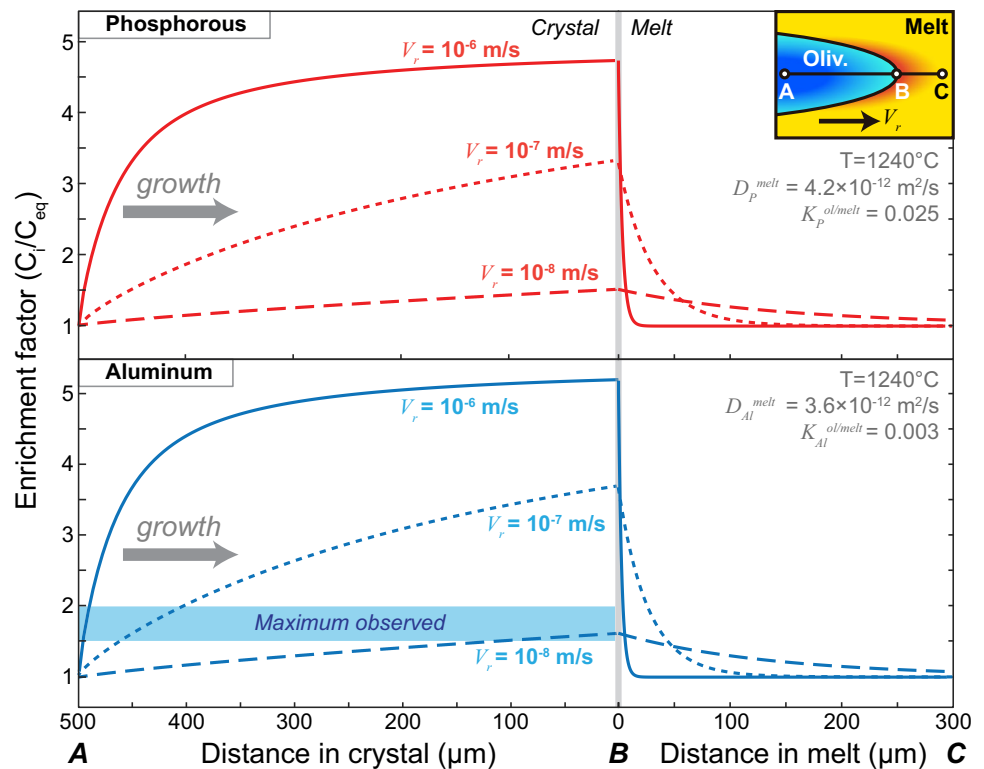
Models were all carried out at $T = 1240^\circ \text{C}$ ($-\Delta T = 40^\circ \text{C}$), for growth rates $V_r = 10^{-8}$ – 10^{-6} m s^{-1} , with D_P^{melt} calculated according to Watson et al. (2015) and $D_{\text{Al}}^{\text{melt}}$ from the expression in Zhang et al. (2010):

$$D_P^{\text{melt}} = 10^{-6.30} \exp \left(\frac{-147000}{RT} \right) \quad (8)$$

$$D_{\text{Al}}^{\text{melt}} = \exp \left((-0.88 - 18.02 X_{\text{Si}}) - \frac{23111 + 5918 X_{\text{Si}}}{T} \right). \quad (9)$$

We first adopted values $K_P^{\text{ol/melt}} = 0.025$ and $K_{\text{Al}}^{\text{ol/melt}} = 0.003$, which are on the lower end of those measured in the experiments (Fig. 9). Model results show that enrichments in both elements develop in the melt for growth rates between 10^{-6} and 10^{-8} m/s , and these enrichments get directly translated to higher concentrations in the olivine (Fig. 13). For growth rates within the range relevant to the experiments presented here (10^{-8} – 10^{-7} m s^{-1}), Al is enriched by a factor of 1.5–3.5 in the crystal. This value is close to, though slightly higher than, the maximum observed enrichments (~ 1.5 – 2). By contrast, P enrichments produced in this model (also 1.5–3.5) are clearly insufficient when compared to P concentrations in experimental and natural olivine. There are key additional contraindications regarding this model: first, boundary layers predicted develop for Al, but, within analytical uncertainty, not for P in the experimental olivine (Figs. 4, 5, 7 and 8). Second, formation of a $\sim 500 \mu\text{m}$ olivine crystal is unlikely to occur via growth at constant rates. Rather, growth rate is likely to decrease as undercooling decreases over the course of growth as undercooling declines. Third, the concentration profiles of P and Al in model olivine crystals (Fig. 13) show an increase in concentration with distance from core to rim, where experiments show that along a given skeletal branch, the concentration decreases with distance from the olivine center (e.g., Figs. 4, 5 and 7). Finally, the geometry of the model (spherical) is not well adapted to the inferred mode of propagation of skeletal olivine branches during the initial growth spurt. We expect the boundary layers forming around a propagating spherical interface to dissipate less rapidly than those that form at the front of a pointier (skeletal) tip (i.e., due to the near- 360° of melt surrounding the tip through which elements can dissipate). Despite those caveats, the 3D spherical geometry of the BL models is a substantial improvement over a 1D planar model, in that boundary layers are become diluted more rapidly in the surrounding melt (e.g., Watson and Müller 2009).

Fig. 13 Boundary layer (BL) model results for constant partition coefficients (K) and constant growth rates. Plots on the left show the concentration of both P and Al within the growing olivine (effectively a zoning pattern), and those on the right show the concentration in the melt. Faster growth rates lead to higher concentrations of incompatible elements in the boundary layer and thus enrichments in the olivine. Enrichment in Al predicted by this model match those measured in natural and experimental olivine, while enrichment in P is too low in the models to adequately reproduce measured concentrations (enrichments up to 50-fold)



The simple BL model discussed above fails to reproduce the enrichment factors in P, and we explore the alternative scenario where growth rates and the partition coefficient for P are growth rate and time-dependent. Other studies have reported growth-rate dependence of apparent element partitioning in various mineral phases (e.g., Conte et al. 2006; Lofgren et al. 2006; Mollo et al. 2011, 2013), although differentiating true disequilibrium partitioning from equilibrium partitioning in the presence of boundary layers is clearly a major challenge. As a starting point, we create a function that forces $K_P^{\text{ol/melt}} \sim 1$ at the onset of growth, in agreement with maximum partition coefficients observed (e.g., Figs. 9a). That function then lets $K_P^{\text{ol/melt}}$ decrease with time to a final value equal to the low end $K_P^{\text{ol/melt}} = 0.025$ according to a topology (Fig. A7 in the Supplementary Material) defined by an error function of the type:

$$K_P^{\text{ol/melt}}(t) = \frac{1}{2} \operatorname{erfc}\left(\frac{t - 3600}{2600}\right) + 0.025, \quad (10)$$

where t is time in seconds. In the absence of evidence for order-of-magnitude variations in $K_{\text{Al}}^{\text{ol/melt}}$ during growth (Fig. 9b), we maintain a constant partition coefficient:

$$K_{\text{Al}}^{\text{ol/melt}} = 0.003.$$

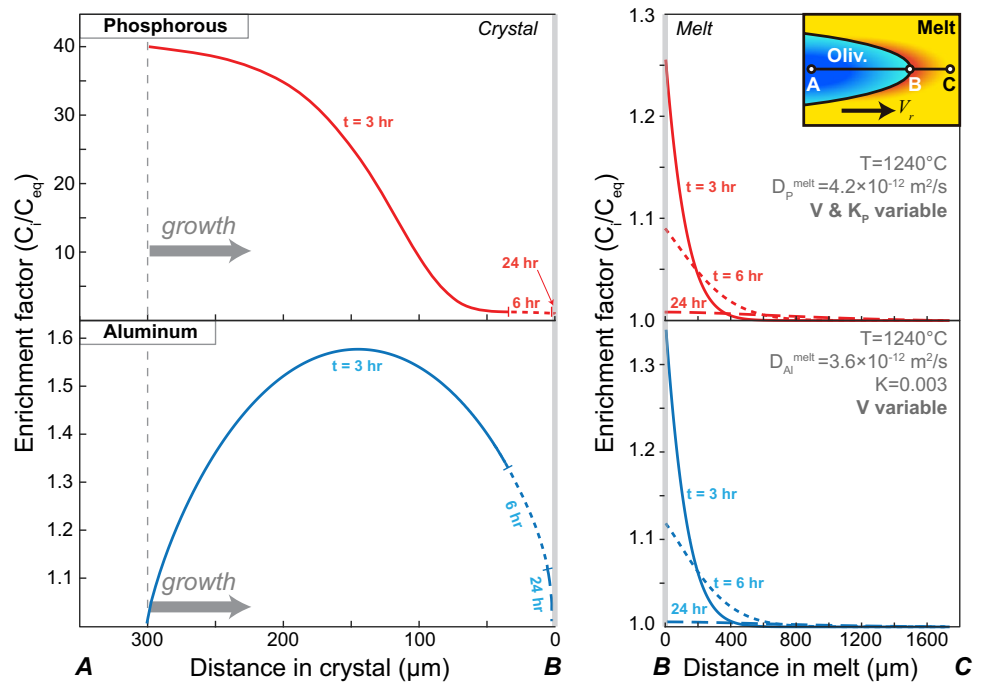
For both revised BL models, we assume that the growth rate also decreases with time, according to a simple exponential law:

$$V_r(t) = V_{r,\text{max}} \exp(-2 \times 10^{-4} t), \quad (11)$$

where $V_{r,\text{max}}$ is the maximum initial growth rate, taken to be 6×10^{-8} m/s for undercooling conditions in the range of the experimental series (Mourey and Shea 2018). A decelerating power law function was also tested and yielded very similar results. We did not test accelerating growth functions (e.g., Watkins et al. 2017), since the experiments show that growth rates decrease with time. In brief, the shape of the partition coefficient function will determine the enrichment pattern that results from the models, while the growth rate function controls the extent of the enriched zone along the growth direction.

Models incorporating variable partitioning (P) and growth-rate (P and Al) behaviors (Fig. 14) yield enrichment patterns that are better suited with observations. Olivine is initially enriched in P by $40\times$ —without requiring a similar enrichment in the surrounding melt—and the enrichment factor decreases with decreasing melt- and the enrichment factor decreases with decreasing growth rates. The model results are consistent with: (1) the lack of a strong P-rich boundary layer in the melt ($< 1.3\times$ after 3 h, and $\sim 1.1\times$ after 6 h, which is within analytical uncertainty), and the presence of a boundary layer in Al (also $\sim 1.3\times$ decreasing to measured enrichments of $1.1\times$ after 6 h (compare with Figs. 7 and 8), which is still larger than analytical uncertainty); (2) the tendency for P concentrations to decrease along a given growth branch (Figs. 4, 5, and 7). Since partitioning of Al was not made time-dependent in the model, its concentration

Fig. 14 Boundary layer (BL) model results for exponentially decreasing growth-rate- and time-dependent partition coefficients (K). Plots on the left show the zoning pattern obtained, and those on the right the element concentration in the melt (note the important change of y-scale for upper right P diagram). Most of the growth occurs within the first 3 h, and little additional growth subsequently as growth rates decrease. Enrichments predicted by this model satisfy observations made both in experimental and natural samples



increases along the first half of the crystal as growth rates are high and the boundary layer accumulates, and then decreases as growth rates slow further and the boundary layer dissipates. Like P, Al decreases in intensity along a given olivine branch; the initial increase predicted by the model, however, is not clearly observed in experimental and natural olivine (Figs. 4, 5 and 6). Either the growth rate implemented in the model is slightly too low and the boundary layer—and thereby the enrichments—builds up too slowly, or, alternatively, the P and Al enrichments intersected by the sections we use as ground truths are incomplete (i.e., the regions corresponding to the very beginning of growth are not exposed). Despite these small discrepancies, we favor a crystal growth model in which P partitioning depends sharply on growth rate, ultimately reaching near-partitionless behavior at high growth rate, while Al partitioning is comparatively insensitive.

Origin of sector zoning in olivine

Sector zoning also occurs both in our experiments and natural samples. Similar observations were made by Pack and Palme (2003) for Al and Ti in olivine and Milman-Barris et al. (2008) for P, Al, and Cr, and interpreted to partly result from buildup of boundary layers enriched in those elements (i.e., through the BL mechanism). Although more systematic observations of sector zoning and its dependence on crystallographic orientation are needed, our results are consistent with a BL enrichment mechanism: Al is more enriched in those sectors than in the rest of the crystal (Figs. 4, 5, 6, 7 and 10), while P is comparatively not. As discussed above,

Al enrichment depends mostly on the formation of boundary layers, while P enrichment is less sensitive to diffusion kinetics in the surrounding melt and more sensitive to the growth-rate-dependence of its partition coefficient.

Because olivine appears initially grow in a skeletal fashion, sector zoning cannot, however, be viewed as differential incorporation of elements through advancement of large crystal faces but rather as the end-result of secondary branches growing and merging preferentially within a given region. The hourglass appearance of some of the rapidly grown crystals in cross-polarized light (Fig. 3b) is associated with additional thickness and denser development of secondary branches. Therefore, sector zoning may simply develop where secondary branching is promoted during initial growth, and fail to appear in regions where secondary branching lags behind (also see Fig. 10). Consequently, sector zoning should essentially depend on the direction of fastest growth. In Pack and Palme (2003) and Milman-Barris et al. (2008), sector-zoned regions appeared along the three crystallographic directions. Our experiments and natural crystals confirm these observations. For instance, the Kīlauea olivine (Fig. 7a) appears to have the largest Al enrichment at the very core, possibly along the b direction. According to the P-enrichment patterns, growth may have been faster along the c -axis for a certain period (primary branches curve in the c -direction), and Al sector zoning follows an ‘apparent’ $\{011\}$ form (i.e., the secondary branches responsible for sector zoning actually grew along the c -direction). Finally, the growth of the skeletal rim of this olivine occurred faster along a (primaries curve towards the a -axis), and secondary branches are most developed along a . Based

on its generally morphology, the Lō'ihī olivine likely grew fastest along the *c*-direction, consistent with sector zoning occurring along the direction of *c*-axis secondaries (yielding an apparent {011} form for sector zoning) (Fig. 7b). Two of the experimental crystals also display apparent sector zoning on {010}, which would result from preferential formation of secondaries along the *c*-axis (Figs. 4 and 5). Sector zoning of Al and potentially other elements like Cr or Ti in olivine is, therefore, another marker of rapid growth, one that better captures the rapid propagation of secondary branches.

Implications for element coupling and thermometry

The disequilibrium incorporation of two 'nominally' incompatible trace elements like P and Al confirms the concerns expressed by a number of recent studies: crystallographic site preference and charge-balancing considerations are critical when interpreting trace-element variations in minerals, particularly in light of disequilibrium processes involving kinetics of crystal growth and diffusion (Spandler and O'Neill 2010; Jollands et al. 2014; Zhukova et al. 2017; Lynn et al. 2018; Tollan et al. 2018). As highlighted by the recent debates sparked by vastly differing results for diffusivity of REE in olivine (Cherniak 2010; Spandler and O'Neill 2010) or for differing results for diffusion vs. element coupling of Li in zircon (Trail et al. 2016; Tang et al. 2017; Sliwinski et al. 2018), crystal-chemical effects may dictate our ability to use equilibrium and disequilibrium thermodynamics to recover the P–T–X–t history of magmas (e.g., Rubin et al. 2017; Wilson et al. 2017). High disequilibrium P concentrations in the initial growth regions of an olivine lead to different charge-balancing considerations for other nearby non 2+ cations incorporated or diffusing through the octahedral sites. The availability of several hundreds of ppm of a 5+ cation like P can help to balance 1+ elements like Na, Li, H, or 3+ elements like Cr, Al, some of which are used for diffusion modeling (Lynn et al. 2018). Because P diffuses slowly in olivine, elements that are used for charge balance may end up also diffusing much slower than in zones where P is not so abundant.

Disequilibrium partitioning considerations are also critical when utilizing trace-element concentrations for the purpose of thermometry. Twofold differences in olivine Al concentrations, apparent only in maps, can have important consequences in temperature calculations based on Al alone (Bussweiler et al. 2017) or Al in olivine and spinel (Coogan et al. 2014). Similar caveats may be pertinent to REE elements used for thermometry in plagioclase-pyroxene (Sun and Liang 2017), or Ti in quartz (Huang and Audetat 2012). Verifying the absence of trace-element enrichments is thus a requirement to obtain temperatures that are meaningful. Detecting and quantifying trace-element zoning in minerals are, however, not always

straightforward despite recent advances in X-ray, LA-ICPMS, or FTIR mapping (e.g., Ubide et al. 2015), and can quickly become expensive (e.g., full olivine EPMA maps within this study took between 12 and 24 h). Fortunately, olivine is a beam-resistant mineral and most modern microprobes can resolve trace-element enrichments in P, Al, Cr, Ti, Co, Zn, or Na (Batanova et al. 2015). To minimize cost, we have adopted a strategy over the last few years where 'strip maps' about 10–20 pixels wide, several hundred pixels long, and 10 min in duration can be programmed vertically and horizontally (ideally both) across a given olivine grain, and generally prove sufficient to detect the presence or absence of strong enrichments and any coupling between P and Al. This method has often proven helpful in determining whether a grain might be interesting to investigate crystal growth and element coupling (e.g., Shea et al. 2015), or whether a region displays no detectable P or Al zoning and can thus be used for Li diffusion without worrying as much about coupling issues (e.g., Lynn et al. 2018).

Conclusions

The similarities and contrasts in behavior of two trace elements in olivine (P and Al) are now well documented by both experimental and natural crystals. Both trace elements display intricate fine-scale enrichment patterns that are unambiguously related to rapid olivine growth. There are important differences, however, in how the two elements are incorporated: a simple 'boundary layer' model where growth rates are sufficient to result in the accumulation of Al at the interface explains relatively well our experimental observations. In contrast, partitioning of P in olivine must be to some degree growth-rate dependent: during the same experiment, the effective partition coefficient varies by almost two orders of magnitude. This difference in behavior may be attributed to the smaller effective ionic radius of P compared to Al and the tendency for the olivine lattice to be slightly more flexible during periods of fast growth. An interesting outcome of these experiments is that above a certain threshold growth rate, the effective partition coefficient rises to a value of ~1, meaning that it is possible to recover the phosphorus content of a melt by measuring the maximum P content of the olivine (after verifying that it grew rapidly). This can be useful in cases where no glass or melt inclusion data can be extracted from an olivine-bearing igneous rock.

Our experiments demonstrate that growth rates relevant to moderate undercooling conditions (e.g., $> 10^{-8}$ m/s at 25–60 °C) are sufficient to generate P and Al enrichments. Localized thermal conditions (e.g., growth under a strong thermal gradient) are not needed to favor skeletal growth and

incorporation of higher concentrations of P or Al; the common process of magma mixing is likely sufficient to produce the moderate undercooling and rapid growth conditions. The presence and proportion of skeletal and P- and Al-enriched olivine may, therefore, point to the importance of magma mixing in the prior history of an erupted magma.

Acknowledgements This work was funded by National Science Foundation Grant EAR-17225321 to TS and by a National Research Foundation Investigatorship Award (Grant number NRF-NRFI2017-06) to FC. The authors acknowledge Benoît Welsch, Francois Faure, Caroline Bouvet-de-Maisonneuve, and Mike Garcia, for the conversations that stimulated some of the ideas presented in this work. Reviews by Bruce Watson and Youxue Zhang helped improve the clarity of the manuscript. We also thank the editor Gordon Moore for his timely handling of the manuscript. This is SOEST contribution 10796.

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