

Phosphorus zoning as a recorder of crystal growth kinetics: application to second generation olivine in mantle xenoliths from the Cima Volcanic Field

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ABSTRACT

Composite mantle xenoliths from the Cima Volcanic Field (California, USA) contain glassy veins that cross-cut lithologic layering and preserve evidence of lithospheric melt infiltration events. Compositions and textures of minerals and glasses from these veins have the potential to place constraints on the rates and extents of reaction during infiltration. We studied glass-bearing regions of two previously undescribed composite xenoliths, including optical petrography and chemical analysis for major and trace elements by electron probe microanalysis and laser-ablation inductively coupled plasma mass spectrometry. The petrogenetic history of each vein involves melt intrusion, cooling accompanied by both wall-rock reaction and crystallization, quench of melt to a glass, and possibly later modifications. Exotic secondary olivine crystals in the veins display concentric phosphorus (P)-rich zoning, P-rich glass inclusions, and zoning of rapidly diffusing elements (e.g., Li) that we interpret as records of rapid disequilibrium events and cooling rates on the order of 10°C/h. Nevertheless, thermodynamic modelling of the diversity of glass compositions recorded in one of the

samples demonstrates extensive reaction with Mg-rich olivine from the matrix before final quench. Our results serve as a case study of methods for interpreting the rates and processes of lithospheric melt-rock reactions in many continental and oceanic environments.

Keywords: olivine rapid growth; phosphorus zoning; boundary layer; diffusive relaxation; mantle xenoliths; metasomatism

INTRODUCTION

A direct means of learning about the geochemical state and geologic evolution of the lithospheric mantle is the study of olivine and pyroxene-rich xenoliths — including harzburgites, lherzolites, and various pyroxenites — brought to the surface by deeply-sourced, rapidly-erupted lavas (e.g. Hawkesworth et al. 1984; Menzies et al. 1987; Downes 2001; Liu et al. 2009; Howarth et al. 2014). Xenolith studies complement remote geophysical methods (e.g., Soedjatmiko and Christensen 2000; Schulte-Pelkum et al. 2011; Allison et al. 2013; Behr and Hirth 2014) and studies of exposed mantle terranes such as massif peridotites (Le Roux et al. 2007; Lagabrielle and Bodinier 2008; Lorand et al. 2010) and ophiolites (Benn et al. 1988; Boudier and Nicolas 1995; Boudier et al. 1996; Nicolas and Prinzhofer 1983; Gass 1968; Gass and Masson-Smith 1963; Moores and Vine 1971). The prime strength of xenoliths relative to tectonically emplaced peridotites is their freshness, whereas their prime weakness is the lack of geologic context. A partial solution to the context problem lies in composite xenoliths, which carry more than one lithology in direct contact in the same hand sample (e.g. Nielson et al. 1993; Witt-Eickschen and Kramm 1998; Grégoire et al. 2010; Zhang et al. 2010a).

One challenge in mantle xenolith studies is obtaining meaningful bounds not just on the age but also on the durations and rates of chemical and thermal events (e.g. melting) that have affected the lithosphere. Such events are generally too short to be resolved by radiometric geochronology methods and, instead, kinetic constraints are needed (e.g., Ionov et al. 1994; Ducea et al. 2002). Although the relatively easy relaxation of major-element signatures such as Fe/Mg gradients over magmatic and post-magmatic timescales at mantle temperatures often erases most evidence of past processes, the minor and trace elements in xenoliths include both fast and slow diffusing species that represent a promising set of tools for constraining petrogenetic processes on multiple

time scales (Foley et al. 2013). Realizing such promise requires well-described samples with textures amenable to robust interpretation, sensitive analyses at the appropriate scale, experimental data on partition and diffusion coefficients, and quantitative modelling.

Distributions of the highly mobile tracer hydrogen, for example, offer constraints on the last few hours to days of the high-temperature history of mantle xenoliths, associated with ascent and eruption (Demouchy et al. 2006; Peslier et al. 2008; Hilchie et al. 2014; Peslier and Bizimis 2014; Warren and Hauri 2014; Demouchy et al. 2015). By contrast, phosphorus (P; N.B. we will use P for pressure) is a moderately incompatible and very slowly diffusing element in olivine (Watson et al. 2015) that can act as a sensitive and easily-preserved tracer of mineral growth histories and as a useful monitor of the timescales of pre-eruption petrogenetic processes (e.g. Boesenberg and Hewins 2010). Phosphorus can be hosted as a major constituent of minor phosphate phases or as a trace species in major phases such as pyroxene and olivine. As olivine and pyroxene represent the major constituents of the Earth's upper mantle and also the main crystallization products of mafic magmas *en route* to the surface, histories of these minerals inferred from P distributions may define the major events in the history of a lithospheric sample.

Several authors have identified P-rich zones in olivine from a variety of rocks, including terrestrial basalts, andesites, dacites, troctolites, and komatiites (Milman-Barris et al. 2008; Sakyi et al. 2012; Tschegg et al. 2010; Welsch et al. 2013, 2014, 2015; Maisonneuve et al. 2016); in metasomatized peridotites and mantle xenoliths (Mallmann et al. 2009); in meteorites including martian shergottites, lunar basalts, ordinary chondrites, and pallasites (Boesenberg et al. 2012; Shearer et al. 2013; Elardo and Shearer 2014; Ennis and McSween 2014; First and Hammer 2016; McCanta et al. 2016); in partially melted metapelitic gneisses (Tropper et al. 2004); and in experimentally produced olivine crystals (Toplis et al. 1994; Milman-Barris et al. 2008; Boesenberg and Hewins 2010). Explanations offered for P-rich zones in olivine have included non-equilibrium incorporation, melt composition, temperature, oxygen fugacity, and apatite saturation conditions (Toplis and Carroll 1995; Mallmann et al. 2009; Boesenberg and Hewins 2010; Grant and Kohn 2013; Welsch et al. 2014). In igneous olivine in particular, P-rich zones may primarily reflect incorporation of P in

excess of equilibrium partitioning during rapid growth, in which case zoning patterns primarily record crystal growth rate variations (Milman-Barris et al. 2008; Watson et al. 2015).

In this study, we report micro-scale petrological and geochemical analyses on constituent minerals and glass within “dark-colored” veins cross-cutting the lithological layering in two previously undescribed samples from the H. G. Wilshire collection of xenoliths from the Cima Volcanic Field (CVF - California, USA). Several hypotheses have been proposed for the origin of similar veins in mantle xenoliths worldwide: (1) remnants of an externally-derived CO₂- or H₂O-rich metasomatic silicate melt (Kempton 1987; Wulff-Pedersen et al. 1996), (2) material grown from hydrous or CO₂-rich fluids passing through the sampled volume (Ionov et al. 1994, 2002), (3) residues after breakdown of *in situ* hydrous phases such as phlogopite or amphibole (e.g. Yaxley and Kamenetsky 1999; Shaw and Klügel 2002), (4) internally-derived low-degree partial melts of the host rock (Baker et al. 1995; Kinzler and Langmuir 1995; Draper and Green 1997; Pilet et al. 2010), and (5) disequilibrium reaction products between infiltrating magma and the host xenolith (Wulff-Pedersen et al. 1999; Shaw et al. 2006).

The veins in our xenolith samples are dominated by glass and secondary phases (readily distinguished from equivalents in the matrix) such as olivine, clinopyroxene, plagioclase, apatite, spinel, and ilmenite. We used a range of complementary techniques — optical microscopy, micro-scale X-ray fluorescence (μ -XRF), electron probe microanalysis (EPMA), high-resolution field emission scanning electron microscopy (FE-SEM), and laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) — to characterize the xenoliths and the glasses and minerals in their veins. This paper focuses on the P concentration and zoning in exotic second-generation P-rich olivine found in the veins. We examine whether the olivine P concentrations are anomalous given the budget of P in the veins and test whether enrichment in the olivine is connected with particular metasomatic episodes. Finally, we propose a zonation model for the olivine and quantitative constraints on its growth process, extent of disequilibrium relative to the glass, and the cooling and reaction rates of the veins.

GEOLOGICAL SETTING AND SAMPLE DESCRIPTION

Geological Setting

The CVF (Figs. 1a,b), located in the Mojave Desert, southeastern California, USA, is one of many small, isolated late Cenozoic basaltic fields distributed across the southern Basin and Range province. Neogene extension of the Basin and Range has been accommodated in the crust by range-bounding normal faults and Cordilleran metamorphic core complexes with synchronous felsic volcanism and in the mantle by lithospheric thinning associated with subsequent mafic volcanism. Extension of the area ended at ~12 Ma (Davis et al. 1993). Mafic volcanism in the CVF began at ~7.5 Ma and continued until ~3 Ma. After a hiatus, reactivation of the field began at ~1 Ma and continued into the Holocene (Turrin et al. 1985). Although volcanic fields in the eastern Mojave region of California and Arizona range from basalt to rhyolite (Nealey and Sheridan 1989), the CVF contains only trachybasalt (hawaiite) and basaltic trachyandesite. For more details and context on the CVF and the Mojave Desert, refer to Luffi et al. (2009) and references therein.

Sample Description

The CVF xenolith suite is known to contain numerous composite samples with contacts among different lithologies. Such diverse lithologies as spinel peridotite, websterite, gabbro, clinopyroxenite and wehrlite have been described (Irving 1980; Wilshire et al. 1991; Farmer et al. 1995). Wilshire et al. (1991), modified by Wilshire and McGuire (1996), divided the xenoliths into three main groups: (1) “Cr-diopside” group (peridotite, websterite, phlogopite \pm pargasite clinopyroxenite); (2) “low-Cr green-pyroxene” group (Mg-rich websterite, two-pyroxene gabbro, microgabbro); and (3) “Al-augite” group (Fe-rich websterite, clinopyroxenite, gabbro, microgabbro). A fourth group includes composite xenoliths with two or more of the previous lithologies and peridotites with thick (1-15 mm wide) hornblendite \pm plagioclase \pm phlogopite veins. We studied two samples from this fourth, composite group. Sample *Ci-1-196* (NMNH 118016-209) is amphibole-bearing and contains multiple lherzolite, websterite, and dunite layers; sample *Ki-5-301* (NMNH 118016-1067) is amphibole-free and contains alternating orthopyroxenite and lherzolite layers. The xenoliths were collected in the Cima area within alkaline basalts of composition similar to hawaiite (Wilshire et al. 1988, 1991; Mukasa and Wilshire 1997) (Fig. 2), but no vestige of the host lavas was preserved in our samples. The primary mineralogical layering in the two xenoliths is cross-cut by “dark-colored” veins (Wilshire and McGuire 1996). The criteria for the selection of these two composite xenoliths were freshness, integrity of specimens, and

the presence of visible veins and lithologic layering at hand-sample scale. Polished thin sections were cut normal to the lithologic layering and, as much as possible, to the general trend of the veins.

ANALYTICAL METHODS

Scanning Electron Microscope (FE-SEM)

The California Institute of Technology (Caltech) GPS Zeiss 1550VP field-emission scanning electron microscope is equipped with an angle-sensitive backscattered electron detector, a 150 mm² active area Oxford X-Max Si-drift-detector energy-dispersive X-ray spectrometer (EDS), and an HKL electron backscatter diffraction (EBSD) system. Imaging, mapping, semi-quantitative EDS analysis, and EBSD were conducted using the SmartSEM, AZtec, and Channel 5 software packages. Analyses used a 15 kV accelerating potential and a 120 μm field aperture in high-current mode (~ 4 nA probe current), yielding imaging resolution better than 3 nm and an activation volume for EDS analysis $\sim 1 \mu\text{m}^3$.

Major elements

Major element compositions were determined in polished thin sections using a CAMECA SX-100 EPMA with four wavelength-dispersive spectrometers (WDS) and one EDS detector at the University of Vienna, Department of Lithospheric Research (Austria). Additional analyses used a JEOL JXA8530F Field Emission EPMA (FE-EPMA) with five wavelength-dispersive spectrometers (WDS) and one energy-dispersive spectrometer (EDS) at the Institut für Mineralogie, University of Münster, Germany. All analyses used 15 kV accelerating voltage. Initial survey of minerals used a 20 nA focused beam, 20 s on-peak counting time and 10 s for each background. Phosphorus concentrations in olivines were then re-analysed at 50 nA beam current with 20 s peak and 10 s background counting time. Published P concentrations (Jochum et al. 2005) for a set of reference materials match the results obtained using the analytical conditions described above, showing linearity from 118 to 1615 ppm P (Supplemental Fig. S1 and Supplemental Table S1). The detection limit for P with this protocol is 71 ppm (1σ). For glass analyses, a slightly defocused (5 μm diameter) beam and 10 s counting time were used. Natural mineral standards used were albite (Na, Si, Al), wollastonite (Ca), olivine (Mg), almandine (Fe), spessartine (Mn), orthoclase (K),

rutile (Ti), chromite (Cr), Ni-oxide (Ni) and Durango apatite (P) with ZAF matrix correction. Representative mineral compositions are given in Tables 1-2.

Micro-X-Ray Fluorescence (μ -XRF) maps

Micro-XRF element maps were collected using the Bruker M4 Tornado micro-XRF instrument at the Quaternary Dating Laboratory, Roskilde University, Denmark. A 50 kV, 600 μ A, \sim 25 μ m diameter excitation beam was generated by a Rh X-ray tube. Characteristic X-rays were collected on a 30 mm² xflash® Silicon Drift EDS detector. The full spectrum was collected during mapping with a motorized stage that moved the sample in steps of 30 to 80 μ m per pixel (depending on sample size) with a 10 ms/pixel dwell time, giving map collection times between 1 and 5 hours. Composite XRF maps are shown here for navigation and reference; detailed results of XRF mapping are not our focus.

Trace elements

Trace element measurements were performed on polished sections after EPMA analysis using LA-ICP-MS at the State Key Laboratory of Geological Processes and Mineral Resources (GPMR) of the China University of Geosciences in Wuhan and at the Institut für Mineralogie, University of Münster. Representative trace element analyses are given in Tables 3-4.

Trace element analyses at the GPMR used an Agilent 7500a ICP-MS and a 193 nm ArF excimer laser operating with ca. 14 J/cm² laser fluence and a repetition rate of 6-10 Hz (GeoLas 2005). Helium was the carrier gas. Argon was the make-up gas, mixed with the carrier gas via a T-connector before entering the plasma. Each analysis included 20–30 s of background acquisition (from a gas blank) followed by 50 s of sample data acquisition. Ablation spot diameters for mineral analyses were between 40 and 60 μ m. Element concentrations were calibrated against multiple reference materials (BCR-2G, BIR-1G and BHVO-2G), a summed metal oxide normalization was applied (Liu et al. 2008), and ten unknown measurements were always bracketed by measurement of SRM 610 glass. The preferred values of element concentrations for USGS reference glasses are in the GeoReM database (<http://georem.mpch-mainz.gwdg.de/>). Si, Mg and Ca served as internal standards for olivine/orthopyroxene, spinel and clinopyroxene/amphibole, respectively. The data reduction software ICPMSDataCal

was used for off-line selection and integration of the background and analyte signals, time-drift correction and quantitative calibration (Liu et al. 2008, 2010a).

Trace element analyses at University of Münster used a Thermo Fisher Scientific Element 2 sector-field ICP-MS and a Photon Machines Analyte G2 Excimer laser system operating with ca. 5 J/cm² laser fluence and a repetition rate of 6-10 Hz. We used a large-volume ablation cell with fast signal response and short wash-out times (< 1 s) that holds up to 6 conventional thin sections and additional reference materials. Prior to sample analyses, the system was tuned with NIST SRM 612 glass for high sensitivity, stability, and low oxide-interference rates ($^{232}\text{Th}^{16}\text{O}/^{232}\text{Th} < 0.2\%$). Spot diameters for the mineral analysis were between 12 and 60 μm ; in most cases 40 μm gave the best compromise between laser signal strength and spatial resolution. Counting times were 40 seconds for the peak and 20 seconds for the background. Wash-out time between individual spots was 10 seconds. NIST SRM 612 glass (Jochum et al. 2011) was used as an external standard and BIR-1G glass (Jochum et al. 2005) as an unknown to monitor precision and accuracy; internal standards were the same as in the GPRM analyses. Five to ten sample measurements were always bracketed by three measurements of NIST SRM 612 glass and two measurements of BIR-1G glass. Linearity of results with this protocol against accepted values in standards BHVO-2G and BCR-2G of elemental concentrations ranging from 0.5 ppm to 10⁵ ppm is documented in Supplemental Table S2 and Supplemental Figs. S2a-c. Furthermore, the linearity in a plot of measured Li concentrations of a set of standards against the GeoRem accepted values is remarkable, with the exception of BCR2-G using ²⁶Mg as internal standard (Supplemental Table S3 and Supplemental Fig. S2d).

PETROGRAPHY

Primary phases (matrix)

The two studied xenoliths are composites juxtaposing centimetric-scale layers of different ultramafic lithologies; the studied regions are from interior cuts of the xenoliths and are not in contact with the host basalt.

Sample *Ci-1-196* consisting of three predominant layers (from left to right; see Figs. 2a-c): dunite, websterite and amphibole-bearing lherzolite. The dunite layer is protogranular to porphyroclastic, whereas the websterite and lherzolite layers are

mainly of mosaic equigranular subtype (Fig. S3; Mercier and Nicolas 1975). The relative grain size of olivine crystals decreases from dunite through lherzolite to websterite and of orthopyroxene crystals from websterite to lherzolite. Spinel in the lherzolite matrix commonly shows a sieve texture at grain margins (Fig. S4). Ti-rich pargasite in the lherzolite matrix may have crystallized from infiltrating melts, but there is no evidence of reaction between the amphibole and the peridotite minerals (see Wilshire et al. 1991). However, the amphibole is partly decomposed to a glass-bearing symplectite (Fig. S5). A discrete “dark-colored” vein clearly cross-cuts the layering and has mostly sharp contacts against each matrix lithology (Figs. 2a-c; see below for petrography of the vein). There is no evident relationship between the distribution of matrix amphibole (and its decomposition products) and the dark vein.

Sample *Ki-5-301* consists of alternating layers of orthopyroxenite and lherzolite (Figs. 2d-f). The studied section captures one layer of each composition. Both lithologies display a transition from protogranular to porphyroclastic texture (Mercier and Nicolas 1975). The orthopyroxenite layer consists of >95 vol.% >1 mm orthopyroxene crystals, with <300 μm interstitial clinopyroxene grains and sulfide blebs included in orthopyroxene (Fig. S6a). The lherzolite layer is amphibole-free. Its constituent grains are euhedral to mostly anhedral in shape; the olivine crystals have dimensions <500 μm . Subhedral to anhedral spinels at boundaries between olivine and clinopyroxene in the lherzolite layer commonly show thin sieve-textured rims and non-sieve cores (Fig. S6b). Two discrete “dark-colored” veins occur in this sample, cross-cutting the lithologic layering; the first vein penetrates the lherzolite-orthopyroxenite contact whereas the second is found only in the lherzolite (Figs. 2d-f). We focused on the first vein (“P-rich MV” in Figs. 2d-f) due to its high P budget.

“Dark-colored” veins

In sample *Ci-1-196*, a vein (~200 μm wide) crosses Cpx-rich bands (average ~20 μm in width) that define a partly diffuse contact between lherzolite and websterite (Figs. 2a-c, 3a). It contains olivine + glass + plagioclase + spinel + clinopyroxene + ilmenite + apatite (Figs. 3a,b). Olivine contains apatite and spinel inclusions and is in contact with plagioclase and glass (Figs. 3a-c). Glass is widespread (~15 vol.%) in the vein and forms a contiguous, connected pool along the plane of the layer in addition to apparently isolated small patches in contact with olivine. Plagioclase occurs as prismatic, oriented

crystals parallel to the elongation of the layer or as intergranular crystals between olivine and/or clinopyroxene (Fig. 3d). Spinel shows anhedral and euhedral shapes and is found as inclusions in olivine in a preferential band near (but not at) the olivine rims and as free grains associated with plagioclase and glass (Figs. 3b,c). When spinel is in contact with glass, the spinel grains have sieve-textured outer rims (Figs. 3a,b). Clinopyroxene is present both as rims with well-developed crystal faces replacing wall-rock matrix minerals (orthopyroxene or olivine) and as isolated crystals within the melt layer (Figs. 3a,b). Ilmenite occurs as euhedral crystals within the layer or as thin rims (<2-3 μm) on plagioclase (Fig. 3d). Apatite is found mostly as inclusions near olivine rims and in plagioclase (Fig. 3a).

In sample *Ki-5-301*, a “dark-colored” area of irregular shape (average ~ 200 μm wide) crosses the contact between lherzolite and orthopyroxenite (Fig. 2d-f). In places, it resembles a planar vein, but it is connected to patches of various shapes. It consists of olivine + plagioclase + glass + clinopyroxene + spinel + ilmenite + apatite. Olivine occurs both as 30-150 μm euhedral crystals free of inclusions and as ~ 100 μm euhedral to subhedral grains that contain glass and spinel inclusions (Figs. 4a-f); both olivine types are embedded in glass. Normal Fe-Mg zoning is present at the rims of most olivine grains of all sizes and shapes. Plagioclase occurs as prismatic crystals; most are randomly oriented, but there is a fabric defined by crystals elongated parallel or sub-parallel to the plane of the layer (Fig. 4g). Two groups of glasses – based on textural criteria – are observed in the vein in *Ki-5-301*. The first group occurs in apatite-free areas where the vein progressively thins from ~ 50 μm wide down to nothing; as the matrix minerals approach each other, strong melt-matrix reaction between Mg-rich olivine and a melt apparently produced Fe-rich olivine (F_{074-75}) and clinopyroxene (Fig. S7a). Evidence for this reaction is preserved in irregular lobate crystal shapes and strong zonation at the olivine rim (Figs. 4f, S7a). The second group of glasses is observed in apatite-bearing areas. Clinopyroxene is found both within the vein and as a probable reaction product between melt and matrix orthopyroxene (Fig. 4c). Spinel occurs as inclusions in the olivine or in association with plagioclase and glass, with euhedral to anhedral shapes (Figs. 4b,d,f). Ilmenite occurs as euhedral crystals within the layer or as thin rims on plagioclase (Figs. 4d, S7b). Both spinel and ilmenite are limited to crystals <20-30 μm and likely either formed late or had very low growth rates compared to other phases in the veins. Apatite occurs as subhedral to anhedral crystals (~ 100 μm

in diameter) with mostly cusped or rounded faces at the contact with olivine or glass, as inclusions (<2 μm diameter) near the rim of P-rich olivine (Fo_{84}), and as prismatic crystals (5-30 μm diameter) embedded in glass (Figs. 4b,c,e, 5a).

MINERAL CHEMISTRY

Major and trace element compositions of minerals within glass-bearing veins and pockets are presented in this section and compared to mineral compositions from the matrix of the xenoliths where appropriate. Due to the size of several grains (less than $\sim 10\text{-}20\ \mu\text{m}$), some of the mineral phases were difficult or impossible to analyze. We emphasize those results that confidently represent single grain analyses.

Olivine

In sample *Ci-1-196* the vein contains olivine crystals ($\text{Fo}_{83\text{-}89}$) with 0.03-0.62 wt% P_2O_5 ; the P-rich olivine crystals ($\text{P}_2\text{O}_5 > 0.1$ wt%) are Fo_{85} to $\text{Fo}_{89.3}$. Due to the small grain size ($\sim 50\ \mu\text{m}$) within the vein, only a few LA-ICP-MS spots yield clear olivine analyses (Fig. S8a). The phosphorus content of the vein olivines is distinct from that of the matrix olivines, which are mostly below 0.08 wt%, except for two olivines on the edge of a vein that have P_2O_5 content up to 0.12 wt% by electron probe; the LA-ICP-MS measurements of P in matrix olivine are consistently low, close to our detection limit of 71 ppm, varying from 81 to 118 elemental ppm. Li concentrations are less than 3.84 ppm for olivine cores within the vein, whereas olivine rims adjacent to glass have up to 4.90 ppm (note the internal uncertainty of the Li analyses is ± 0.37 ppm). The Li is significantly higher in the matrix olivines, ranging from 4.58 to 5.51 ppm. The B content of olivine in the vein is variable (1.00-1.27 ppm), but typically less so than B contents of matrix olivine (0.42-2.25 ppm). Ba is much higher in vein olivine (up to 128.8 ppm) compared to matrix olivine (0.03-1.67 ppm). The V, Sc and Cr contents for the vein olivine cores are in the range of 31.9-92.6 ppm, 6.32-16.0 ppm and 98.5-2591 ppm. The olivine crystals adjacent to and within the vein have variable Ni content from 1373-3275 ppm. The ΣREE concentration in olivine crystals along the edge of the vein is as low as 0.197 ppm close to glass and 0.474 ppm farther from glass. Chondrite-normalized REE patterns for olivine are characterized by enrichment in LREE [(La/Yb)_N=3.06], flat MREE [(Gd/Yb)_N=1.06] and a concave downward overall pattern

resembling that of associated clinopyroxene rather than that of the highly LREE-enriched surrounding glass (Fig. S9a).

In sample *Ki-5-301* the glass-associated olivine crystals have Fo contents ranging up to 90 in the cores with normal zoning and well-defined rims a few microns wide, in contact with glass, extending down to 74.5 (Fig. 4c). These olivine crystals have variable P₂O₅ content; values up to 2.0 wt% are typical and the maximum is 3.5 wt%, much higher than in the matrix olivine from this xenolith (0.02-0.06 wt%). Elevated P₂O₅ concentrations (>0.5 wt%) can be found throughout the vein-associated olivine grains, but the highest concentrations are often in a well-defined band parallel to crystal rims but set back several microns from the rim (Fig. 11). Peak P occurs where the olivine is ~Fo₈₄, well-resolved from the most Fe-rich rims. Due to the small grain size (~50 μm) of the studied vein, only a few LA-ICP-MS spots yield clear olivine, in which the Li concentrations for discrete olivine crystals vary from 2.80 to 6.35 ppm. Li from the matrix olivines is more homogeneous (between 3.66 and 4.43 ppm). In one vein olivine sufficiently large to permit core and rim analyses, Li increases from the core (5.23 ppm) to the rim (6.35 ppm), which is well-resolved relative to the ±0.37 1σ internal precision of the Li analyses. The core and rim analyses of Li overlap at the 2σ level, but the probability that 5.23 ± 0.37 ppm and 6.35 ± 0.37 ppm are two samples of the same concentration is 0.004, which is negligible. The B content is variable (0.79-1.92 ppm) but typically 2-3 times higher than in the matrix olivine from this xenolith (0.56-0.94 ppm). Ba is much higher in vein olivine (0.43-4.81 ppm) compared to the matrix olivine (<0.14 ppm). V displays a large variation from 9.61 to 42.1 ppm, whereas Sc shows less variation, from 5.13 to 11.12 ppm (Fig. S8). The olivine crystals have Ni content in the range 1967-2741 ppm, Cr mostly in the range 134-337 ppm with one high value (990 ppm), Zn between 55.6 and 89.7 ppm and relatively uniform Co (107-135 ppm). The REE budget is low but extremely variable (Fig. S9a), ranging from 0.55 ppm to 5.71 ppm.

Clinopyroxene

In *Ci-1-196* the secondary clinopyroxene crystals (Fig. 3) are divided according to their textural relationships into those: (1) in the vein, (2) between the vein and matrix olivine, (3) in isolated glassy pockets, and (4) in glass surrounding matrix amphibole. Most of them are diopsides with some augites (Fig. S10). Clinopyroxene inside the vein projects

into the ternary Wo-En-Fs in the range $Wo_{38-45}En_{46-57}Fs_{4-10}$ (Fig. S10). Those apparently derived from reaction between melt and matrix olivine are slightly more calcic at $Wo_{39-47}En_{50-55}Fs_{3-7}$ (Fig. 3a). Clinopyroxene from isolated glassy pockets has a restricted composition in the range $Wo_{40-43}En_{49-52}Fs_{4-8}$. The clinopyroxene in melt surrounding amphiboles has a broader range of Ca contents compared to those in the isolated glassy pockets, projecting in the range $Wo_{40-46}En_{47-55}Fs_{4-7}$.

In *Ki-5-301*, we analyzed clinopyroxene crystals inside a glass-rich pocket connected to the vein and around its edges. The clinopyroxene from the glassy pocket projects at $Wo_{40}En_{55}Fs_5$ (Fig. S10). Those around the edges are similar, $Wo_{41-43}En_{50-54}Fs_{5-8}$. The P_2O_5 abundances are low from all clinopyroxene crystals, 0.04 to 0.08 wt%. Due to the small grain size only one grain was analyzed by LA-ICP-MS, and its low Ca content indicates slight influence from adjacent orthopyroxene (Fig. S8b). Nevertheless, the trace element values are unreasonable for fertile or residual mantle clinopyroxene: Li is 3.33 ppm and Ba 136 ppm. The REE budget is 144.11 ppm and the chondrite-normalized REE pattern is enriched in LREE [(La/Sm)_N=4.39] – in contrast to typical depleted mantle LREE patterns in primary cpx – with a small negative Eu anomaly (Eu/Eu*=0.83; Fig. S9b).

Plagioclase

In *Ci-1-196*, plagioclase extends over a substantial range of composition ($An_{45-57}Ab_{39-49}Or_{3-7}$). In contrast, *Ki-5-301* plagioclase exhibits a more restricted intermediate range $An_{51-56}Ab_{42-47}Or_{2-3}$. Plagioclase compositions are rather sodic for mantle plagioclases.

Glass

Glass in *Ci-1-196* displays a wide range of compositions, with P_2O_5 up to 1.2 wt%, K_2O 4-6 wt%, CaO 3-6 wt%, Na_2O 3-5 wt%, and SiO_2 48-65 wt% (Figs. 6, S11). In MgO variation diagrams, the glass compositions fall into three groups: a single, isolated analysis at 5.2 wt% MgO; a group extending from 3.67 wt% to 1.47 wt% MgO that forms a fairly coherent linear trend in all oxides against MgO; and a cluster with <0.3 wt% MgO (Fig. 6). An important feature of the variation diagrams is a steep positive slope in FeO^* vs. MgO that, when recast as Mg# vs. MgO, shows increasing Mg# as MgO decreases from 3.67 wt% to 1.47 wt%.

The analyzed glass compositions are compared in a TAS diagram (Fig. 6a) to a survey of mantle xenolith glasses sorted into various genetic categories by previous authors. The more primitive (i.e., low SiO₂) glasses plot in the region of overlap between the fields of “infiltrating basaltic melt” (Wulff-Pederson et al. 1999) and the “amphibole-related” glasses (Demény et al. 2004). Textural criteria are more helpful in this sample than broad groupings in the TAS diagram for discriminating amphibole breakdown from basalt infiltration. The variation in total alkalis with increasing SiO₂ is unusual compared to literature suites, with much slower increase in alkali content than observed in basalt-infiltration derived glasses and no evidence of the negative correlation apparent in the amphibole-derived field.

When comparing the more primitive *Ci-1-196* glass analyses with specific published xenolith glass analyses, the closest match is with interstitial glasses from La Palma xenoliths (Wulff-Pedersen et al. 1999) and with the Ib interstitial glasses in veins from Way-eu-Namus (Miller et al. 2012). Both the La Palma and Way-eu-Namus glasses were assigned by the original authors to origin via basaltic melt infiltration and reaction with the rock. Although the higher-SiO₂ *Ci-1-196* glasses bear some resemblance to *in situ* Si-rich glasses in a global xenolith survey (Schiano and Clocchiatti 1994), the examples in the global survey are typically found in isolated pockets with no association with more primitive glasses such as those found in *Ci-1-196*. Hence, this resemblance is probably incidental.

The primitive mantle (PM) normalized trace-element patterns for *Ci-1-196* vein glass are characterized by small positive Nb anomalies, variable Sr, overall enrichment in LILE, and negative V-Sc anomalies (Fig. S8c). Li content varies from 8.22 to 10.36 with one measurement as high as 20.0 ppm; similarly, B varies from 3.02 to 5.15 ppm except for the same point that yielded highest Li, which has 13.6 ppm B; Ba content is in the range of 509 to 643 ppm and Rb is 61.2 to 124 ppm. The REE patterns are characterized by strong LREE enrichment [(La/Yb)_N=9.86-12.73], moderately negative to small positive Eu anomalies (Eu/Eu* = 0.69-1.17), and enriched MREE compared to HREE [(Gd/Yb)_N=2.40-2.81; Fig. S9c].

In *Ki-5-301*, glass is widespread in the vein layer. These glasses have variable compositions divided into two distinct populations, systematically distributed in accordance with the textural distinction mentioned above: (1) P₂O₅ 0.89-1.76 wt% with

SiO₂ ranging from 48.7 to 53.4 wt% and Mg# from 32 to 53 and (2) P₂O₅ 1.62-2.59 wt% with SiO₂ ranging from 51.7 to 57.1 wt% and Mg# from 48 to 71 (Fig. S12). In MgO variation diagrams, the glass compositions display roughly linear trends with Al₂O₃ (linear correlation coefficient $r^2 = 0.5$), Na₂O (0.51), K₂O (0.66), P₂O₅ (0.71) and Mg# (0.6), while the other oxides are more scattered. In the TAS diagram, in contrast to *Ci-1-196* glasses, most of the *Ki-5-301* glass analyses plot in the amphibole-related field defined by Demény et al. (2004), well outside the overlap area with the infiltrating basaltic melt field defined by Wulff-Pedersen et al. (1999) (Fig. S12a).

The trace element chemistry also separates the same two groups of glass analyses in *Ki-5-301*: one glass from the first group (low P₂O₅; 0.89 wt% by EPMA) has low REE content ($\Sigma\text{REE}=279.2$ ppm) and a large positive Eu anomaly (Eu/Eu*=1.43), whereas points from the second group (high P₂O₅; 1.97-2.31 wt% by EPMA) are enriched in REE ($\Sigma\text{REE}=565.7-630.9$ ppm) with small negative Eu anomalies (Eu/Eu*=0.85-0.95; Figs. S8, S9). Additionally, the Li content is as low as 3.66 ppm in the first group and 3-4× higher (9.64-13.3 ppm) in the second group (Fig. S8). We also obtained four electron microprobe analyses of glass inclusions in olivine with P₂O₅ 1.64-3.57 wt%, SiO₂ 47.1-53.7 wt% and Mg# 44-68; the maximum P₂O₅ of 3.57 wt% is associated with SiO₂ 53.7 wt% and Mg# 57.

Apatite

In *Ci-1-196* apatite inclusions are present near the rim of P-rich olivine (Fo₈₅) and in plagioclase (An₅₄). Due to the small size (<1-2 μm) of apatite compared to the laser beam size (<30-40 μm), we were not able to analyze it for trace elements.

In apatite from sample *Ki-5-301*, the PM-normalized trace-element patterns are characteristic of the strongly fractionating crystal chemistry of apatite; Th–U abundances are ~700-800× PM (Fig. S8d). The chondrite-normalized REE patterns are higher in ΣREE , up to ~5500 ppm and strongly LREE enriched [(La/Yb)_N=62-109] (Fig. S9d).

Spinel

In *Ci-1-196*, secondary spinel composition varies from chromite to Ti-chromite from core to rim, with an outer rim rich in ulvöspinel; Al# ranges from 0.61-0.82 and Cr#

from 0.15 to 0.36. In *Ki-5-301*, secondary spinel composition is more variable compared to the matrix with Al# = 0.69-0.80 and Cr# = 0.17-0.27. In both samples, Fe³⁺ contents of spinel are low; Fe³⁺/(Cr+Al+Fe³⁺) based on electron probe stoichiometry is strictly less than 0.07 and typically ~0.03.

DISCUSSION

Phosphorus and trace element partitioning in olivine

Before discussing the petrogenetic implications of P partitioning between olivine and melt, it is important to establish that the data reflect analyses of single and not mixed phases. Hence, we examined the areas probed by EPMA with high-resolution SEM imaging at Caltech. In *Ci-1-196*, the ~50 µm long olivine (shown in Figs. 3a, 3c, 10 and 11a,b) is homogeneous in backscattered electron contrast at the maximum resolution of the FE-SEM. We see no evidence for included phases even at magnifications up to ×20000, which resolves features smaller than 0.2 µm and EDS analysis yield P₂O₅ content up to 0.51 wt%, identical to the maximum value obtained by WDS spot analysis with the EPMA. Similarly, FE-SEM analysis and imaging of *Ki-5-301* olivine in the glassy vein shows homogeneous back-scattered electron contrast, no evidence for included phases, and P concentrations by EDS that reproduce the EPMA concentrations (Figs. 12, S13). Moreover, the highest P contents in the olivines in the glassy veins are not at the crystal-glass interface, which argues against any analytical artifact involving contamination of the olivine analysis by surrounding glass or secondary fluorescence (Fig. 5a). The extreme enrichments in P in olivine are found only in the glassy veins, with only modest and occasional enrichment in the far-field matrix olivine. The P₂O₅ contents of matrix olivine are in the range 0.001-0.117 in *Ci-1-196* (based on 552 EPMA analyses) and 0.001-0.144 (based on 149 points) in *Ki-5-301*. Although much lower than in the vein-associated crystals, the ranges for matrix olivine do extend above literature values for well-equilibrated spinel lherzolites: P₂O₅ from 0.005-0.016 by EPMA (Witt-Eickschen and O'Neill 2005) or 0.002-0.031 (Mallmann et al. 2009) by LA-ICP-MS.

In summary, our measurements of elevated P concentrations in the vein olivines in both xenoliths have been confirmed by three analytical methods (EPMA, FE-SEM, and LA-ICP-MS). They are well above detection limits in all three methods and standard analyses in similar concentration ranges match expectation. Concentrations measured

at sub- μm , $\sim\mu\text{m}$, and 50 μm scales agree within uncertainty and imaging shows no inclusions, demonstrating that the P is structurally bound in the olivine. Only the vein olivines show these enrichments, although matrix olivines were analyzed in the same analytical sessions, and the highest P values in vein olivines are not found in contact with glass and so are unlikely to represent phase overlap or other boundary artifacts.

For glass analyses, we took data systematically along profiles moving away from olivine-glass interfaces. We did not observe P enrichment in any resolvable boundary layer; if there was a boundary layer during olivine growth it may have relaxed before quench or it might be too narrow to resolve by electron probe. In any case, the glass P concentrations we use in our partitioning estimates represent the melt far enough from the olivine interface to be apparently unaffected by boundary-layer enrichment.

Given that P appears to be present in the olivine structure, we examine several pairs of analyses of P in olivine and glass in direct contact to determine phenomenological partition coefficients which can then be compared to available natural and experimental constraints on equilibrium partitioning (see next section *Assessment of trace element partition model*). Expressing these pairs as apparent olivine/melt partition coefficients for P, K_d^* [wt% P_2O_5 in olivine / wt% P_2O_5 in glass], 15 olivine-liquid pairs in sample *Ci-1-196* exhibit a range from 0.03-0.55. In *Ki-5-301*, 19 olivine-liquid pairs show a range from 0.06-0.94, with three outlying pairs of high-P olivine and glass yielding ratios of 1.25-1.62.

Published, nominally equilibrium partition coefficients (for which we use the symbol K_d) from slow-growth experiments in basaltic and basaltic-andesitic liquids are in the range 0.051-0.1 (Brunet and Chazot 2001), 0.172-1.128 (Taura et al. 1998) and 0.049-0.916 (Fonseca et al. 2014). Published P K_d for basaltic liquids are in the range 0.038-0.05 (Adam and Green 2006). K_d for P in the range 0.051-1.41 have been reported for highly polymerized and silica-rich trachyandesitic melt by Grant and Kohn (2013). In the three studies that report order of magnitude variations in P olivine/liquid K_d , the reported values cannot all be equilibrium partition coefficients. Furthermore, as melt diffusion coefficients decreasing rapidly with increasing SiO_2 content, it becomes more difficult to achieve equilibrium growth conditions in higher SiO_2 melts. Given the common tendency for olivine to incorporate excess P, we suspect that the lowest reported values in these studies are most likely correct. In this light, the lowest values

of K_d^* (0.03-0.28) that we observe in the Cima xenolith glassy veins, found in olivine crystals on the margins of the glassy veins and pockets, are consistent with equilibrium with liquids parental to the glasses. In contrast, the K_d^* values in the range 0.3-0.94 and locally up to 1.62 are significantly higher than probable equilibrium olivine/liquid K_d . As the experimental data suggest a possible correlation with SiO_2 , we plot K_d and K_d^* from our samples against SiO_2 in the glass (Fig. 7). Experimental K_d does sometimes correlate with liquid SiO_2 , notably in the data of Grant and Kohn (2013) and Gee and Sack (1988). In other studies, there is no clear relation between K_d and SiO_2 content of the glass (e.g. Nekvasil et al. 2004). The estimated apparent partition coefficients, K_d^* , for sample *Ci-1-196* are not correlated with SiO_2 in the glass ($R^2 = 0.0143$). In contrast, in sample *Ki-5-301*, the high-Si/low-P glasses display a good positive correlation ($R^2 = 0.52$) between K_d^* and SiO_2 . In contrast, the high-Si/high-P group of glasses display an equally good negative correlation ($R^2 = -0.53$). Many observed pairs plot in the region of K_d - SiO_2 space occupied only by the highest experimental values from studies that also report low values at similar conditions, suggesting, despite some overlap between observed K_d^* and experimental K_d , that P concentrations in the studied olivine reflect significant disequilibrium growth.

Trace elements more rapidly diffusing in silicate melts than P (Zhang et al. 2010b; Holycross and Watson 2016) and not extremely incompatible, however, show patterns in the vein-associated olivines that are at least qualitatively consistent with equilibrium growth. The REE patterns (Fig. S9) generally resemble those that would be expected from equilibrium growth from a highly LREE-enriched liquid similar to the surrounding glass (except for one core olivine spot, black line in Fig S9a, that shows a concave-downward REE pattern resembling that of associated clinopyroxene from Fig. S9b). The Li concentrations in the olivines in the vein increase outwards from 3.84 ppm (cores) to 4.90 ppm (rims adjacent to glass), which is consistent with equilibrium incorporation during progressive crystal growth from a small melt pool. Preservation of this easily relaxed gradient, we suggest, places bounds on the time and temperature history of the glassy areas after the end of olivine growth.

Assessment of trace element partition model

Quantitatively, an assessment of olivine-melt trace element disequilibrium and the mechanism leading to disequilibrium is shown in Figs. 8, 9, which plots the observed

concentrations in olivine compared to those computed from coexisting glass analyses and published K_d partition coefficients using three different orderings of the elements suggested by three different models of disequilibrium growth as detailed below.

In addition to experimental sources cited above, we compiled phenocryst-matrix (Villemant 1988; Dunn and Sen 1994), and phenocryst-glass (Laubier et al. 2014) K_d values from the Geochemical Earth Reference Model (GERM) included in the Earthref database, focusing on those appropriate for liquid compositions spanning our observed glasses (basaltic andesite to basanite). We first took the median of compiled K_d values for each element for nominally similar basaltic andesite and basanite liquid compositions. We then plotted the median values in Onuma diagrams ($\log K_d$ vs. ionic radius) to ensure that the resulting sets of partition coefficient are internally consistent with the expectations of lattice strain theory (Blundy and Wood 1994; Wood and Blundy 2001). Inconsistent elements were adjusted to fit on smooth Brice model curves with other elements of the same valence; the two adopted sets of K_d values and the underlying references are given in Table 5.

Figures 8a,b and 9a,b for samples *Ci-1-196* and *Ki-5-301*, respectively, show observed K^*_d against estimated equilibrium K_d on a log-log plot; the expectation of equilibrium is that all data should plot along the 1:1 line. Panels 8c,d and 9c,d show the ratio (measured concentration in olivine)/(predicted concentration in olivine), which is equivalent to K^*_d/K_d , plotted against K_d ; in this view the elements are plotted in order of increasing compatibility as in a Coryell-Masuda diagram (“spidergram”) and the expectation of equilibrium is that all data should plot at a y -value of unity. Many olivine/liquid pairs show near-equilibrium values for the least incompatible elements and systematically increasing disequilibrium towards the most incompatible elements, approaching in some cases a plateau of constant apparent K^*_d for the most incompatible elements. This pattern admits at least two interpretations. The first is that most of the olivine LA-ICP-MS analyses are contaminated by a very small amount of glass, which nevertheless comes to dominate the analyzed trace element budget for the most incompatible elements. The other is that there is a systematic relationship between degree of disequilibrium and equilibrium partition coefficient, tending towards a maximum (in fact, infinite) degree of relative enrichment as K_d approaches zero.

Next, we considered a simple model controlled by growth rate and by differences in diffusivity of different elements in the melt. The simplest prediction of such a model is that the degree of disequilibrium for each element in a given crystal, which grew with a particular growth rate affecting all elements equally, should scale with the diffusion coefficient of that element in the melt. Figs. 8e,f and 9e,f test this prediction by plotting the degree of disequilibrium in order of increasing diffusivity. We used the recent experimental trace element diffusion coefficients in basaltic melts from Holycross and Watson (2016), assuming a temperature of 1250 °C. No particular order emerges in these plots. Although diffusivity may be one controlling factor on development of disequilibrium between rapidly growing crystals and far-field melt, it does not by itself appear to predict the relative degree of disequilibrium among various elements.

Finally, we look at the diffusive snowplow (DSP) model (Watson and Müller 2009), in order to check whether the theory leads to a function of both partition coefficient K_{di} and diffusivity D_i (in melt) that predicts the relative magnitude of disequilibrium for various elements. The DSP case with dynamical stirring approximated by a fixed-width boundary layer suggests that the steady state concentration $C_i^{ol}(diseq.)$ and the equilibrium concentration $C_i^{ol}(eq.)$ of an incompatible element in a solid growing at growth rate G when the boundary layer thickness is BL are related by

$$C_i^{ol}(diseq.) = \frac{C_i^{ol}(eq.)}{1 - (1 - K_{di}) \frac{G}{D_i} BL} . (1)$$

For a given crystal that grew at a certain rate surrounded by a certain boundary layer, G and BL would be the same for all elements, suggesting that the degree of disequilibrium for various elements i should scale as $(1-K_{di})/D_i$. Fig. 8g,h and 9g,h plot the degree of disequilibrium computed with each of the two sets of adopted partition coefficients in the sequence of decreasing $(1-K_{di})/D_i$, using the same set of diffusion coefficients from Holycross and Watson (2016) at 1250 °C. This model also produces no particularly compelling ordering of the elements. In fact, this model has great difficulty producing large degrees of disequilibrium without special tuning, since too small a value of D_i triggers a singularity. Because the partition coefficient appears as $(1-K_d)$, the sequence in this model is very similar to the diffusivity sequence except for a handful of elements with K_d close to unity. Since, furthermore, the most reasonable interpretation of the plots in compatibility order is that the most incompatible elements

probably suffer from contamination of their olivine analyses, it is best to evaluate the snowplow model using only the least incompatible elements in our data: P, Lu, Yb, V, Li and Sc. Indeed, for several olivine-glass pairs in each sample, particularly when using the basanite K_d set, these elements plot in a nearly monotonic sequence of increasing enrichment with increasing $(1-K_{di})/D_i$. The results suggest that a dynamically stirred snowplow model may be able to explain the observations of the more compatible and slowly diffusing elements such as P.

Relationship of P enrichment to other elements

Here we attempt to construct a petrogenetic history of the preserved glassy veins with consideration of time scales and evidence of equilibrium at each stage, combining qualitative and quantitative approaches. The qualitative approach is based on the spatial distributions of elemental zonation patterns in vein-hosted olivine. The quantitative approach includes liquid line of descent modeling and comparison to the vein glass compositions as well as disequilibrium trace element incorporation models based on available partition and diffusion coefficients of selected trace elements.

Spatial correlation of P with other elements

In an EPMA traverse across the most P-rich zones of an olivine from *Ci-1-196*, one mapped area with minimum P in olivine is surrounded by P-rich planes parallel to crystal edges (Fig. 10). The maximum thickness of such P-rich zones is less than 3-7 μm . In rim-rim profiles, MgO shows normal zoning toward the rim (Fig. 11a,b) and variations in P are uncorrelated with other elements (e.g. Al and Ca). Similar P zoning patterns in olivine have been described before, although previous authors mostly focused on large (mm-size) olivine phenocrysts, whereas the zoned crystals in the Cima xenolith veins are $\sim 50 \mu\text{m}$ across. For example, Milman-Barris et al. (2008) described P zoning in olivine from terrestrial basalts and a martian meteorite, with P_2O_5 contents up to 0.4 wt% and no correlation with Fo content. Elardo and Shearer (2014) described olivine phenocrysts from the basaltic lunar meteorite NWA 032 with relatively P-rich bands up to 0.06 wt% irregularly spaced between P-depleted zones and no correlation between P and any other elements. The absence of correlation between P and other elements might be due to later relaxation of zoning in more mobile elements, but this is unlikely in the present case given preservation of gradients in very rapidly diffusing elements. Conversely, where P has been observed to correlate with Cr and Al, this has

been attributed to similar diffusive controls on incorporation of these elements during disequilibrium rapid-growth conditions (Milman-Barris et al. 2008).

In *Ki-5-301*, X-ray maps of two olivine grains show narrow (<2-3 μm) P-rich bands uncorrelated with the normal zoning of MgO or other oxides (Fig. 12). Rim-to-rim profiles of two other olivine grains in *Ki-5-301* (Figs. 4b,c) show normal zoning of MgO, decreasing SiO₂ and NiO, and increasing CaO toward the rim (profile #15 is located in Fig. 4c and plotted in Fig. 11d; profile #17 in Fig. 5b and 11c). The most extreme P enrichment, in some cases up to 3.5 wt%, is near but not at the outermost Mg-poor rim. The most P-rich points are not contaminated by either matrix glass (P-rich olivines have lower SiO₂ than other olivine analyses) or any inclusions at FE-SEM scale (Figs. 4, 5). The outer rim, visible in most of the high-resolution FE-SEM maps (Figs. 4h, 5a), is also captured at EPMA scale in profile #17 (Fig. 11c), where the last point on the right end of the profile shows reversal of all the zoning trends. Helpfully, this last point demonstrates that the rest of the profile is unlikely to reflect simple contamination of the analyses by increasing proximity to melt. Petrologically, this point could be associated with minor olivine growth from a new melt or with a rapid quench phase upon eruption. In olivine crystals stored after growth at magmatic conditions, such fine details of growth zoning would be erased by rapid Fe-Mg inter-diffusion. The preservation of core-rim Li zoning, small-scale Fe-Mg gradients at the rim, and the presence of glass in veins all show that this sample had a short residence time at magmatic temperatures after olivine growth and a rapid quench during or shortly before eruption.

Point-wise correlation of P with other elements

The mechanism of P substitution into olivine, which can be inferred from correlated deviations from nominal olivine stoichiometry, may carry distinctive kinetic information. Within the current suite, in sample *Ci-1-196*, P⁵⁺ cations per formula unit is negatively correlated with Si⁴⁺ ($R^2 = 0.40$) and poorly ($R^2 = 0.11$) with Mg²⁺ + Fe²⁺ + Ca²⁺ + Mn²⁺ + Ni²⁺ (Fig. 13a-c). In contrast, P shows a slightly positive relation with Al (Figs. 13c). In sample *Ki-5-301*, the P-rich olivine crystals from the melt layer show good correlations of P⁵⁺ vs. Si⁴⁺ ($R^2 = 0.86$) and P⁵⁺ vs. Mg²⁺ + Fe²⁺ + Ca²⁺ + Mn²⁺ + Ni²⁺ ($R = 0.42$) (Fig. 13d,e). The prominent anti-correlation of P⁵⁺ and Si⁴⁺ (mainly in *Ki-5-301*; Fig. 13d-f) suggests a predominant substitution of P⁵⁺ for Si⁴⁺ balanced by M

site vacancies (e.g. $\text{Mg}_2\text{SiO}_4 + \frac{1}{2}\text{P}_2\text{O}_5 \rightarrow \text{Mg}_{1.5}[\text{P}]_{0.5}\text{PO}_4 + \frac{1}{2}\text{MgO} + \text{SiO}_2$, Agrell et al. 1988). The correlation of P with Al, though weak ($R^2 = 0.10$; Fig. 13f), suggests some activation of reaction $2\text{IVSi}^{4+} = \text{IVP}^{5+} + \text{IVR}^{3+}$ or else a more complicated scheme involving coupled substitution in tetrahedral sites balanced by vacancies in octahedral sites (Milman-Barris et al. 2008; Grant and Kohn 2013). In the case that both element concentrations are a function of growth rate, this would produce a perfect correlation between P and Al, unless Al diffusively relaxed afterwards, which we think is disproven by the Li distribution.

Although there are likely energetic differences and hence thermodynamic preference for one P substitution mechanism, it is also probable that the site occupancy is flexible enough that correlations (or lack thereof) among trace species might be better explained by differing kinetic behavior during crystal growth. The relation or interplay between P incorporation mechanism in olivine, growth rate, and growth process (equilibrium vs. disequilibrium) is described in the recent literature. Incorporation of P is enhanced by rapid far-from-equilibrium growth, whether due to highly polymerized melt (Grant and Kohn 2013), high cooling rate (Milman-Barris et al. 2008) or thermal gradient (Welsch et al. 2014). Two oft-cited physical mechanisms that are favored by any of these imposed conditions are (1) solute-trapping (STR) and (2) diffusive boundary-layer pile-up or DSP effect (e.g. Watson et al. 2015 and references therein). STR refers to growth at such high rates that incompatible components are overrun by the moving crystal boundary and incorporated without regard to their equilibrium partitioning. DSP describes the more moderate case where diffusion of compatible elements towards the growing crystal interface and of incompatible elements away from it may be too slow to maintain homogeneous liquid composition in the melt pool. In this case, crystal growth leads to depletion of compatible elements and enrichment of normally incompatible elements in the boundary layer that surrounds the crystal and from which it grows, incorporating (in the pure DSP model) elements according to equilibrium partitioning with the interfacial melt. Thus, enrichment of the boundary layer in slowly diffusing incompatible components leads to incorporation in the crystal at higher concentration than expected for equilibrium with the far-field liquid. The depletion of the boundary layer in some essential structural constituents of the crystal may eventually slow the growth rate and allow the boundary layer composition to relax towards the far-field composition. Similar boundary layer and structural constituent

delivery consideration affect the shape of the growing olivine grains as well, as argued for example by Jambon *et al.* (1992).

Welsch *et al.* (2014) examined natural magmatic olivine crystals grown from mafic liquids and found deviations from near-equilibrium crystallization to be commonplace in dendritic or skeletal olivine crystals that indicate rapid crystal growth at high degrees of supersaturation (Lofgren 1980 and reference therein). At high growth rates, Welsch *et al.* (2014) propose a dendritic model in which observed core to rim profiles do not record progressive growth in a simple stratigraphy. Nevertheless, the weak correlation between P and Al in the present samples suggests decoupling of the excess incorporation of these species. This could be due to diffusive relaxation of Al gradients after crystal growth but the preservation of Li gradients argues against relaxation of the much more slowly-diffusing Al^{3+} . A more promising explanation is crystal growth at cooling rates sufficiently fast to generate disequilibrium solute trapping of P but sufficiently slow for near-equilibrium incorporation of Al (e.g. Boesenberg and Hewins 2010). Judging by the dynamic experiments of Grant and Kohn (2013), this would be consistent with cooling rates near 10 °C/h. Similarly, in olivine phenocrysts from lunar basalts, P variation interpreted in the context of an STR model suggests that growing olivine crystals moving around a convecting magma chamber experienced cooling rates in the broad range of 2-30 °C/h (Elardo and Shearer 2014).

The STR mechanism seems to have gone to completion in one of the studied P-rich olivine crystals from sample *Ki-5-301* (Fig. 4). In this olivine, a glassy inclusion with P_2O_5 3.57 wt% is trapped in an olivine whose rim concentration of P is also 3.5 wt%. We cut a second section plane through this inclusion, and it remained an enclosed feature; hence, if it is an embayment connected to the surrounding melt, any connection is at least 50 μm from the analyzed spot and hence outside the boundary layer for growth of the local olivine. Our observation seems like direct evidence that the olivine was growing fast enough to quantitatively incorporate the P content of its boundary layer, which is represented by the quenched melt inclusion. An apparent partition coefficient of unity is the logical extreme case for STR at a temporarily very high growth rate. Due to possible equilibration between boundary layer melt and the melt inclusion after olivine formation, this value could be tentatively regarded as the upper limit of the actual partition coefficient in our rocks. Similarly high partition coefficients have been

suggested by other authors from both natural rocks (e.g. Welsch et al., 2013 reported zones in olivine with 1.01 wt% P₂O₅ coexisting with matrix melts in the range 0.3-0.6 wt% P₂O₅) and experiments (e.g. Grant and Kohn, 2013 reported 2.89 wt% P₂O₅ in olivine for a melt with 2.05 wt% P₂O₅).

Petrogenetic history of melt veins

Our data suggest a petrogenetic history involving the following stages: 1) melt intrusion, 2) reaction with matrix minerals and rapid cooling, 3) crystallization of mineral assemblage in the sequence of Ol → Ap → Cpx → Pl → Fe-Ox and 4) quench of glass. Stages 2 and 3 may in fact be simultaneous and coupled by energy conservation constraints. That is, during the first stages of evolution after a hot melt vein is placed in contact with walls of colder rock, the thermal and chemical disequilibrium will drive exchanges of mass and enthalpy among the phases that lead to coupled changes in the temperature, phase abundance, and phase chemistry of the vein and its immediate environs. Stage 4 may have followed shortly after the other stages, or it may have been somewhat later, perhaps upon ascent and eruption of the xenolith and its host lava.

The first stage, melt intrusion, is indicated by the planar shape of some of the glassy regions examined. Most of the glassy regions cross-cut the fabric of matrix minerals. Although glass in mantle xenoliths has, in other settings, been attributed to other mechanisms such as *in situ* partial melting (e.g. Schiano and Clochiatti 1994), such glasses are found as isolated inclusions or healed fractures in mantle minerals. Chemically exotic glass organized into cross-cutting planar veins is difficult to explain except by intrusion. Sample *Ci-1-196* also hosts glass-clinopyroxene-spinel-olivine symplectites around amphibole that most likely formed by destabilization of amphibole after external melt intrusion. Amphibole breakdown might have been driven by increased temperature, onset of decompression, or chemical potential changes brought by the melt. In parts of sample *Ki-5-301*, glass-rich veins are planar but are also connected to glassy patches infiltrating the host rock. We infer that there may have been easily fusible heterogeneities or melt-rock reactions with negative volume change that drew melt into the pockets. Alternatively, the area between grain boundaries may open during decompression and draw melt into the empty space.

The rapid cooling stage is apparently required by the trace element evidence of disequilibrium growth discussed above. The earliest crystallized phase was olivine, which grew rapidly enough to cause sluggish P to experience boundary layer enrichment but not so fast as to over-enrich other elements. Clinopyroxene formed later, either as euhedral crystals or reaction rims (Figs. 3a, 4c). Plagioclase is commonly observed as crystals parallel to the flow of the melt. Apatite, found as inclusion in plagioclase, presumably formed before plagioclase fractionation (Fig. 3a; sample *Ci-1-196*). Furthermore, the onset of apatite crystallization after olivine core nucleation but before the end of olivine growth is suggested by its presence as inclusions in olivine rims (samples *Ci-1-196* and *Ki-5-301*). The slight negative Eu anomalies ($\text{Eu}/\text{Eu}^*=0.79\text{-}0.86$) observed in large apatites may be inherited from the parental melt and not require plagioclase fractionation before apatite growth. It is important to distinguish between the onset of apatite saturation in the boundary layers around growing crystals and in the bulk melt pool. Apatite saturation requires both a certain level of enrichment in P_2O_5 and also sufficient volatile abundances (approximately 200 ppm F, 800 ppm Cl or 1 wt% H_2O ; McCubbin et al. 2014; 2015). Boundary layer enrichment is common for slow-diffusing P but these volatiles diffuse much faster and prevent very early apatite saturation in the boundary layer. Hence P-enrichment is accommodated in the crystal structure of the silicates through the various mechanisms discussed before. Only later, once progressive differentiation processes have concentrated incompatible volatile components in the bulk melt to a sufficient level, does the P-enriched boundary layer also reach apatite saturation — still before onset of apatite saturation in the lower-P bulk melt — leading to the incorporation of apatite in the olivine rims and pyroxene and feldspar grains. Free apatite growth occurs still later if there is time before quenching of the glass. According to McCubbin et al. (2015), the P solubility in silicate liquids increases with increasing temperature and decreasing silica activity. This may explain the definite evidence for dissolution of the large matrix apatites (Figs. 4c and 4e), which likely occurred during olivine dissolution following melt injection.

MELTS modeling

The observed glass compositions within each sample are interpreted in the context of crystal fractionation and assimilation processes using thermodynamic equilibrium modelling. The alphaMELTS software (<http://magmasource.caltech.edu>) was used to

track the behavior of both major and trace elements (Ghiorso and Sack 1995; Asimow and Ghiorso 1998; Asimow 1999; Ghiorso et al. 2002; Asimow et al. 2001, 2004; Smith and Asimow 2005). The thermodynamic approach differs from simple mass balance modelling of fractionation by assuring that crystallizing phases are, at least in the context of a particular set of solution models, saturated in the liquid composition as it evolves, under well-defined conditions of pressure, temperature, water content, and oxygen fugacity. The approach tests whether a suite of glasses are related to each other by fractional crystallization. We begin with the most primitive, highest MgO glass composition and assess whether its liquid line of descent passes through the more evolved compositions.

Sample Ci-1-196 – The single analysis with 5.2 wt% MgO and Mg# = 68 was tested first, but it appears to be unrelated to any other glass analysis. Consequently, we began instead with the most primitive of the group of analyses forming a coherent linear trend from 3.67 to 1.47 wt% MgO. We first examined simple, f_{O_2} -buffered, isobaric fractional crystallization in 1 °C steps. Over a wide range of pressure, f_{O_2} , and H₂O-content settings, the liquidus phase is clinopyroxene and the fractionation trend displays gently increasing FeO* and sharply decreasing Mg# as MgO decreases. Upon Fe-Ti-oxide saturation, FeO* turns over and begins decreasing with MgO; the position of oxide saturation is f_{O_2} sensitive. However, in no case does oxide saturation fractionate FeO* strongly enough to cause Mg# to increase with decreasing MgO as observed in the data. We were unable to find conditions under which the trend of glass compositions could be modelled as a fractional crystallization trend.

Therefore we examined models in which the hot liquid injected into a vein in a colder host rock experiences simultaneous cooling, crystallization, and equilibration with material from the host rock. The host around the melt vein and pockets in *Ci-1-196* is dominated by Fo_{87.5} olivine, so we simulated incorporation of such olivine into the equilibrating assemblage (Table 6). If the net reaction simply dissolved the host olivine, this process should clearly be called assimilation, but instead the process involves net precipitation of olivine at all stages, so the term “assimilation” is used loosely here. In cases where the system of cooling/crystallizing melt and heating/melting host rock can be treated as an isolated system, it makes sense to carry out such a calculation isenthalpically. In this case, however, the vein is so narrow that it is certainly losing heat by conduction to far-field country rock, so the energy constraint is unrealistic.

Instead we explored fixed ratios of mass assimilated to decrease in temperature. Beginning with 100 g of liquid, we examined a range of assimilation rates during cooling from 0.1 g/K to 1.0 g/K. The result at 0.1 g/K of assimilation is fairly similar to the simple fractionation case. The result at 1.0 g/K of assimilation forms a trend that decreases too steeply in FeO* and increases too steeply in Mg#, compared to the data (Fig. 6). Our best model begins with 0.1 g/K assimilation for the first 15 °C of cooling from the liquidus at 1200 °C, followed by 0.5 g/K of assimilation as cooling continues to 1075 °C, which is similar to the host rock temperature inferred from thermobarometry. The resulting evolution line agrees well with the slope of the data trend in Mg# and in all oxides except Na₂O (supplementary material). The data are essentially flat at 5 wt% Na₂O, whereas it is difficult to avoid an increase of 1-3 wt% Na₂O in model liquids as MgO decreases from 3.67 to 1.47 wt%. It may be that Na, being among the most rapidly diffusing species in silicate liquids, was able to diffusively homogenize across the melt vein during cooling (diffusion coefficients for Na in basaltic melts at 1200 °C are $\sim 10^{-9}$ m² s⁻¹ (Zhang et al. 2010b), suggesting homogenization across a 500 μm vein on a timescale of ~ 250 s), whereas other oxides are able to preserve a progressive evolution trend on scales of 100s of micrometers. An estimate of the timescale of equilibration of the vein with its host based simply on thermal diffusivity ($\sim 10^{-7}$ m² s⁻¹ at magmatic temperature for both olivine and silicate melt, Eriksson et al. 2003; Pertermann and Hofmeister 2015) is also about 250 s if equilibration extends to 5 vein widths in each direction, but this is difficult to quantify because of latent heat effects and other issues.

We note that this model does not explain the cluster of glasses with <0.3 wt% MgO; no model we examined could generate these glasses, most notably in that they contain ~ 7 wt% CaO, 4 wt% TiO₂, and 1 wt% P₂O₅ and are therefore grossly oversaturated in clinopyroxene, ilmenite, and apatite. It appears that these must be quench-modified disequilibrium glasses.

Our success in finding a petrogenetic evolution process that relates many of the observed glass compositions to one another, without modification by diffusion or mixing (except for Na₂O), is consistent with the timescales we have inferred for growth of the newly formed, P₂O₅-rich olivine in this sample. It requires that host olivine, too cold and too high in FeO to be in equilibrium with the injected liquid, was dissolving

as it approached thermal equilibrium with the melt, driving rapid crystallization of new olivine and pyroxene crystals and overgrowths (all the setup files to reproduce our calculations are given in the supplement in file *Setup files for Ci-1-196.zip*).

Sample Ki-5-301 – We did not find satisfactory models for evolution of glass compositions because they were too diverse and scattered to recognize well-defined trends on variation diagrams.

Proposed model for olivine growth

In most natural olivine crystals formed from magmatic processes, the re-equilibration of relatively fast-diffusing components erases growth zoning in ~4-5 months at temperatures of 1170-1225 °C (~350 μm diffusion length scale in olivine; Shea et al. 2015). A tentative application of this approach to the CVF olivine crystals drives us to propose a shorter period of re-equilibration (2-3 months), based on observation of olivine crystals from 50 to 200 μm across. Further, Watson *et al.* (2015) modeled diffusive relaxation at constant temperature of a ~5 μm wide P-rich band and suggested an upper limit of a few months at magmatic temperatures for preservation of such bands. We attempted to simulate the variations in forsterite component, phosphorus, and Li for olivine grown at various rates and stored for various times using the recent model presented in detail by Watson et al. (2015) and Watson and Müller (2009) (Fig. 14). The concentrations of incompatible elements (P, Al, and Li) during the growth phase are given by equation (1) above, whereas for compatible elements (Mg, Fe),

$$C_i^{ol}(diseq.) = \frac{C_i^{ol}(eq.)}{(K_{di}-1) \cdot \frac{G}{D_i} \cdot BL+1} \quad (2).$$

In our case, the equilibrium olivine composition was Fo₈₄ with 3 ppm Li and 0.01 wt% P₂O₅. We assumed diffusivities $D_{Fe-Mg}=10^{-11}$ m²/s (Zhang et al. 2010b), $D_P=10^{-12}$ m²/s (Watson et al. 2015), and $D_{Li}=10^{-10}$ m²/s (Dohmen et al. 2010). Although post-growth storage is not explicitly modeled here, its effect is only to relax gradients developed during growth and so our estimated growth rates are minima. Any storage between formation of the glass vein and eruption would imply more rapid growth during the formation of the vein. For the quantity *BL*, we use the 12.5 μm radius of the glass inclusion in an olivine in *Ki-5-301* whose observed P₂O₅ content is equal to the rim composition of adjacent olivine. With these parameters, a ratio of highest-to-lowest

observed P_2O_5 concentration greater than two, as observed in our samples, corresponds to a predicted growth rate greater than 10^{-7} m/sec (Fig. DR6 in Shea et al. 2015).

We have observed concentric (Fig. 10) and nonconcentric (Fig. 12) P zoning in olivine crystals from *Ci-1-196* and *Ki-5-301*, respectively. Both types of P zoning are associated with homogenous cores and normally-zoned outer rims in Mg#. The concentric rhythmic pattern of P-rich zones in *Ci-1-196* is consistent with a cut through the concentric terraces of a skeletal cavity (Faure et al. 2003; Welsch et al. 2013; Welsch et al. 2014). During olivine growth, both progressive Fe-enrichment of the residual liquid and depletion of forsterite component in the boundary layer of a very rapidly growing olivine might manifest as normal zoning (Figs. 14, 15). However, olivine from volcanic rocks (e.g. Hawaii) demonstrate that growth-induced development of Fe-Mg gradients in olivine is either very limited or seldom preserved (Shea et al. 2015). Furthermore, Fe-Mg inter-diffusion rates in olivine are 2-4 orders of magnitude faster than chemical diffusion of P (Spandler et al. 2007; Watson et al. 2015). But Li diffusion is even faster, and gradients in Li are preserved (Dohmen et al. 2010). We note the possibility, though, that the Li gradients could be related to a “late-stage” infiltration process wherein Li in olivine diffused inward post-magmatically.

In relation to the different categories of hypotheses proposed in the introduction for the origin of veins in mantle xenoliths, the most favored here is #5, wherein such glasses are due to disequilibrium reaction between infiltrating magma and the host xenolith. The most consistent interpretation is that growth zoning in Fe/Mg did not develop in this case, perhaps due to assimilation of homogenous matrix olivine during melt vein evolution. This is consistent with the nearly constant Mg# observed in the main body of *Ci-1-196* glass analyses. However, at the very end of growth, as suggested by olivine profile #17 (Fig. 11c) and the modeling in Fig. 14, the growth may have switched from diffusion control to interface control, forming the Mg-enriched olivine rim and the quenched glass, over a very short time during or shortly before the eruption of the basalt.

CONCLUSIONS

Analysis of major and trace-element geochemical data for glass-bearing areas of mantle xenoliths from the Cima Volcanic Field leads to a number of inferences and conclusions about growth processes and disequilibrium phenomena. Glassy veins are the products

of rapidly cooled injected melt, with crystallization coupled in at least some cases to reaction with host minerals. The geochemical and textural characteristics of olivine constrain the cooling rate and the mechanism of formation. In particular, the presence of alternating P-rich and P-poor areas in olivine grains suggests rapid growth with diffusion-controlled boundary-layer enrichment. The weak correlation between P and Al, sharp Fe enrichment zones at grain boundaries, and preservation of Li gradients together imply crystal growth at cooling rates on the order of 10 °C/h, sufficiently fast to generate disequilibrium STR of P and to preserve growth zoning of Li but sufficiently slow for near-equilibrium incorporation of Al. An end-member STR mechanism is difficult to avoid for the case of a P-rich glassy inclusion in an olivine with similar P concentration at the rim. The success of MELTS modeling of the observed family of glass compositions and mineral assemblages in one sample shows that, even on the rapid timescale of evolution of this vein, there was assimilation of matrix olivine.

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Figure Captions

Fig.1 (a) Simplified map showing the locations of Cenozoic volcanics (in orange) in the Mojave Desert region, including Cima Volcanic Field (Map modified after Farmer et al. 1995). Inset gives larger context, with area of map indicated by dashed black box. The black polygon labeled “B” shows the location of the more detailed geologic map shown in part b. (b) Generalized geological map of study area (modified from Ludington et al. 2007). Relatively young volcanic units are emphasized; all the xenoliths studied here were found in the Holocene volcanic flows within the Cima Volcanic Field

Fig.2 Hand-sample and thin-section scale appearance of the studied mantle xenoliths, emphasizing layered composite structures. Sample *Ci-1-196* (a-c). (a) The image at the top shows a photographed surface of the hand-specimen. (b) μ -XRF map colored to emphasize the different lithologic layers; at left is an Ol-rich layer (dunite), with a sharp boundary against a pyroxene-rich websterite in the middle, grading into a lherzolite layer towards the right. The melt vein is indicated near the far right. (c) The sketch map emphasizes that the melt vein crosses layering defined by cpx-rich bands in the lherzolite. Sample *Ki-5-301* (d-f). (d) Hand-specimen photograph at top shows the characteristic layered structure, from orthopyroxenite to lherzolite to orthopyroxenite. (e,f) Thin section image in middle and sketch at bottom capture only one layer of each composition, together with position and cross-cutting relations of melt veins

Fig.3 Backscattered (BSE) images of *Ci-1-196*. (a) General view of glassy vein and host matrix. Matrix olivine (at left) is rimmed by newly-crystallized clinopyroxene (Cpx) with interstitial glass (Gl). Small apatite crystals occur as inclusions in olivine and plagioclase. (b) Glass-rich area of vein-matrix interface emphasizing progressive iron-enrichment of olivine rim. Scattered spinels occur as inclusions in olivine and as free grains associated with plagioclase and glass. (c) Large olivine crystal enriched in P. A small spinel inclusion is shown. (d) Prismatic plagioclase crystals, rimmed in some cases by ilmenite, show a flow-oriented texture parallel to the elongation of the layer. (e) Enlarged panel of (c) using high-res SEM. The number 0.51 corresponds to the P₂O₅ content in wt% by EDS. (f) Enlarged panel of (e) showing a 200 nm scale area free of inclusions (the bright circle at bottom is an EPMA analysis spot, not an inclusion)

Fig.4 BSE images of *Ki-5-301*. (a) Typical glassy vein composed mostly of olivine (Ol) and clinopyroxene (Cpx) embedded in a glassy (Gl) matrix. (b) A P-rich olivine grain exhibiting a thick rim rich in phosphorus ($P_2O_5 \sim 3.0$ wt%) and iron ($Fe_{0.82}$). Also present are: glass (light grey), spinel (white euhedral crystals included in Ol or in the glassy matrix), apatite (also white at this contrast, both large and small crystals are present), and plagioclase (dark grey). Glass (Gl) inclusion in olivine has P_2O_5 3.7 wt%, very similar to that of the olivine rim. (c) A P-rich olivine with bright rim, surrounded by glass, apatite, and plagioclase. Small euhedral clinopyroxene crystals and a single rounded iron sulfide are found in the glass. (d) A P-rich olivine with rim reaching up to 3.57 wt% P_2O_5 . (e) Small area corresponding an one end of a melt-rich area containing P-rich olivine that was intensively studied. Large rounded apatite is also shown. (f). A P-rich olivine from the left rim of the glassy area in (e), with rounded glassy (former melt) inclusions. (g) Prismatic plagioclase crystals are oriented parallel to the elongation of the layer. (h) Enlarged part of olivine shown in (f). The numbers indicate the P_2O_5 content in wt% by EDS; no inclusions are visible

Fig.5 (a) Enlarged part of olivine shown in (Fig. 4c). (b) The two line scans (#1 from A to B and #2 from C to D) for P_2O_5 , MgO and FeO^* denoted in (a) are plotted against distance (in μm). Both scans are characterized by increase in P counts – due to the existence of P-rich band – near, but not at the olivine rim. Values plotted here show the full EDS quantification for MgO (wt%) and FeO (wt%), but for P_2O_5 we used an empirical linear scaling as P_2O_5 (wt%) = $[3.5 \times (\text{counts} - 50)/110]$. (c) X-ray maps of the olivine rim for Mg, Al, Ca and P, revealing the presence of μm sized apatite at the rim (and its absence elsewhere) due to the nucleation of the latter just before the end of olivine growth

Fig.6 (a) Total Alkali-Silica (TAS) diagram and (b-c) MgO variation diagrams for SiO_2 and FeO^* (in wt%) and (d) Mg# for glass analyses in sample *Ci-1-196*. The TAS diagram includes glasses from the melt vein, from an amphibole-bearing melt pocket, and from an amphibole-free melt pocket. The MgO variation diagrams show only the melt vein, whose differentiation sequence was modeled. Three distinct glass populations within the melt vein are evident. MELTS modeling of possible differentiation processes that might explain the diversity of glass compositions in the main population of melt vein data are shown. Each curve shows isobaric fractional

crystallization beginning with a glass at 4 wt% MgO, together with a range of rates (in grams per degree K of cooling, added to 100 g of starting liquid) of assimilation of Fo_{87.5} olivine, as a proxy for reaction of liquid with the vein walls as they come to thermal equilibrium. The preferred model, in orange, assimilates 0.1 g/K for the first 15 K of cooling and then 0.5 g/K for the rest of the path. Abbreviations: Pi-Ba: Picrobasalt; BA: Basalt; Ba-An: Basaltic-andesite; AN: Andesite; DA: Dacite; Tr-BA/HAW: Trachy-basalt/Hawaiite; BA-TRAN/MUG: Basaltic Trachyandesite/Mugearite; Tr-AN: Trachy-andesite; TR: Trachyte; RHY: Rhyolite; Bas-TE: Basanite-Tephrite; Ph-TE: Phonotephrite; Te-PH: Tephri-phonolite; PH: Phonolite. FO: Foidite. Glass compositions assigned to various origins by the authors listed in the legend are given in coloured fields

Fig.7 Scatter plot of SiO₂ (in wt%) vs. K_d^* obtained from olivine-glass pairs using EPMA data from samples *Ci-1-196* and *Ki-5-301*. The observed data are compared with experimental datasets of SiO₂ against K_d for various glass compositions. Many of the observed pairs plot in the region occupied only by the highest experimental values from studies (e.g. Dunn 1987; Taura et al. 1998; Grant and Kohn 2013) that also report low values at similar conditions. This suggests, despite some overlap between observed K_d^* and experimental K_d , that elevated P concentration in some of the studied olivine mainly reflects significant disequilibrium growth. The black dashed line represents the manually estimated upper limit for equilibrium partitioning data based on the lowest values reported in each experimental study at similar conditions

Fig.8 Sample *Ci-1-196*. Assessments of disequilibrium between olivine and glass using the suite of analyzed trace elements. Observed concentrations in olivine relative to those computed from coexisting glass analyses and published partition coefficients are plotted using three different orderings of the elements suggested by three different models of disequilibrium growth. (a-b) Observed K_d^* vs experimentally determined K_d on a log-log plot. (c-d) show the ratio of the (measured concentration in olivine)/(predicted concentration in olivine) against K_d ; here the elements are plotted in order of increasing compatibility. (e-f) show the ratio of the (measured concentration in olivine)/(predicted concentration in olivine) against elements sorted by increasing diffusivity. (g-h) show the ratio of the (measured concentration in olivine)/(predicted concentration in olivine) against elements sorted by increasing $(1-K_d)/D$, the function

suggested by the form of the steady-state diffusive snow-plow model. In (a, c, e, g) we used the adjusted median basaltic-andesite K_d set. while in (b, d, f, h) we used the adjusted median basanite K_d set. The references and values for adopted K_d sets are given in Table 5. The different colors correspond to different –but adjacent– mineral-glass pairs

Fig.9 Sample *Ki-5-301*. Assessments of disequilibrium between olivine and glass with the same sequence of panels and partition coefficients as in figure 8. The different colors correspond to different –but adjacent– mineral-glass pairs

Fig.10 Qualitative X-ray maps of the olivine grain featured in Fig. 3c (sample *Ci-1-196*). Numbers on the P map indicate point analyses of P_2O_5 wt%. EPMA profile A-B is shown on BSE image (a) and detailed in Fig. 11a. Brighter grey-scale values in the X-ray maps indicate higher concentration of the indicated elements. We have hand-drawn with white dashed lines in the P map to demarcate P-rich planes preserving euhedral growth zoning and parallel to the crystal facets. The typical thickness of a P-rich band, $\sim 7 \mu m$, is shown

Fig.11 For sample *Ci-1-196* (a) EPMA profile A-B across the olivine grain shown in Fig. 10. P (as P_2O_5) enrichment in grain core is uncorrelated with other oxides (in wt%), which dominantly show normal zoning toward both rims. For sample *Ki-5-301* two EPMA rim-rim profiles across olivine crystals are shown: (c) Profile #17, location indicated in Fig. 4b and (d) Profile #15, location indicated in Fig. 4c

Fig.12 Qualitative X-ray maps of an olivine grain shown in Fig. 4f from sample *Ki-5-301*. The upper part is shown on panels a-c and the lower part on panels d-f. P-rich bands less than 5-10 μm wide are visible in the interiors of the olivine crystal. Decreases in Mg and enrichments in P towards the rims are visible while other oxides are uniform. Brighter grey-scale values indicate higher concentration of the indicated element. EPMA point analyses of P_2O_5 are shown in the P panel. Discrete spinel, apatite, and glass inclusions are visible in the olivine

Fig.13 Scatter plots of individual EPMA analysis spots in olivine, for sample *Ci-1-196* (a-c) and sample *Ki-5-301* (d-f) comparing P^{5+} to (a,d) Si^{4+} , (b,e) $Mg^{2+}+Fe^{2+}+Ca^{2+}+Mn^{2+}+Ni^{2+}$ and (c,f) Al^{3+} . The uncertainties given for *Ki-5-301* data

by vertical bars were calculated from actual counting statistics for data obtained from Münster EPMA and are considered to be typical of the precision achieved on both instruments (EPMA of Münster and Vienna)

Fig.14 Theoretical zoning of (a) Fo, (b) Li, (c) P₂O₅ for $K_d=0.01$ and (d) P₂O₅ for $K_d=0.1$ variations during olivine growth at various growth rates, calculated using the boundary layer (BL) theory of Watson and Müller (2009), in which BL thickness is a free parameter. The equilibrium values were Fo_{84.5}, Li 3 ppm and P₂O₅ 0.01 wt%

Fig.15 Proposed model for olivine growing from a melt intruded into a lherzolite host. Rapid cooling leads to significant undercooling and formation (at time $t=t_0$) of a dendritic skeleton of high-P (indicated by dark green shading) olivine (Welsch et al. 2013). Slower growth at t_1 allows infill of the skeleton with lower-P olivine, forming a euhedral overall crystal shape and giving the appearance of oscillatory zoning where profiles cross into and out of the early skeletal bands. A return to rapid cooling at t_2 leads to accelerated crystal growth from which the incompatible element P is unable to diffuse away from the rapidly moving crystal interface, forming another P-rich band parallel to euhedral faces. The system may be stored for some short time at near-magmatic temperature, and then quenched (at time t_3) with growth of an Fe-rich rim (yellow band), before or upon eruption. The olivine traps P-rich melt (light green glass inclusion) from a boundary layer before t_1 and P-poor melt (light blue glass inclusion) before t_2 . Apatite, plagioclase, and spinel saturation in the near-olivine boundary layer occurred after olivine core nucleation but before the end of olivine growth as suggested by their presence as inclusions (at $t=t_2$) only near olivine rims. Compare to observations in Figs. 3, 4c, 5a, and 11a,b.

Supplementary Figures

Fig.S1 Münster EPMA analyses of standard reference materials using the same analytical conditions as the EPMA P-in-Olivine analyses (15kV, 50 nA, 20 s peak and 10 s background counting time) compared to the published P-concentrations

Fig.S2 Münster LA-ICP-MS trace element analyses of the reference materials BCR2-G (a), BIR1-G (b) and BHVO2-G (c) using various internal standards, compared to preferred GeoRem concentrations. (d) Measured Li concentrations for reference materials compared to preferred published concentrations; all protocols tested are successful except for ^{26}Mg internal standard in BCR-2G

Fig.S3 Thin section mosaic for sample *Ci-1-196* showing the protogranular to porphyroclastic dunite layer at the left, and equigranular websterite and lherzolite layers in the middle

Fig.S4 Sample *Ci-1-196* BSE images. (a) Spinel with sieved margin between olivine crystals in the lherzolite matrix. (b) Enlarged view of part of the sieved margin in contact with plagioclase, olivine and glass

Fig.S5 Sample *Ci-1-196* BSE images. (a) Amphibole partly decomposed to a glass-bearing symplectite. (b) Enlarged view of symplectite, composed of glass, clinopyroxene, olivine and orthopyroxene

Fig.S6 Sample *Ki-5-301* BSE images. (a) Orthopyroxene crystals hosting rounded sulfide inclusions and interstitial clinopyroxene grains. (b) Large ($600 \times 1200 \mu\text{m}$) anhedral spinel occurring in the lherzolite layer showing thin sieved margins and non-sieve core

Fig.S7 Sample *Ki-5-301* BSE images. (a) Apatite-free area of vein with a maximum width $\sim 50 \mu\text{m}$; Fe-rich olivine formed as overgrowth on olivine and as discrete grains between pyroxene and glass (former melt). (b) Ilmenite crystals up to $\sim 20 \mu\text{m}$ occur within the glass layer or as thin rims on plagioclase

Fig.S8 Trace element patterns normalized to primitive mantle (PM) for (a) olivine, (b) clinopyroxene, (c) glass and (d) apatite. In (a), all analyses correspond to olivine crystals from MV

Fig.S9 Rare earth elements normalized to CI chondrite for (a) olivine, (b) clinopyroxene, (c) glass and (d) apatite. In (a), all analyses correspond to olivine crystals from MV. Symbols as in Fig. S6

Fig.S10 Pyroxene compositional range projected into Wo-En-Fs ternary. Analyses range from augite to diopside while covering a significant range in Fe content (triangles: sample *Ci-1-196*; boxes: *Ki-5-301*)

Fig.S11 MgO variation diagrams for major oxides (in wt%) for glass analyses in sample *Ci-1-196*. Abbreviations as in Fig. 5.

Fig.S12 TAS diagram and MgO variation diagrams for major oxides (in wt%) and Mg# for glass analyses in sample *Ki-5-301*. Abbreviations as in Fig. 5. Glass composition fields as in figure 6

Fig.S13 Qualitative X-ray maps (Ca, Na, Ti) of the olivine grain shown in Fig. 4f from sample *Ki-5-301* (the rest of the x-ray maps are given in fig.12). The upper part is shown on panels a-c and the lower part on panels d-f. Brighter grey-scale values indicate higher concentration of the indicated element. Discrete spinel, apatite, and glass inclusions are visible in the olivine