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**Petrogenetic implications of chromite-seeded boninite crystallization experiments:
Providing a basis for chromite-melt diffusion chronometry in an oxybarometric context**

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ABSTRACT

Boninites are rare high magnesium andesites that often contain trace chromites. These chromites precipitate from primitive boninitic melts and are thought to be carried to the surface in melts that continue to crystallize a significant volume of silicate minerals. Such magmatic differentiation drives primitive chromite out of equilibrium with the residual melt with respect to both divalent and trivalent cation proportions. Diffusion then operates to alter primitive chromite toward a composition in equilibrium with residual melt. To simulate this process, we have performed internally heated pressure vessel experiments, providing insights into the processes of chromite-melt re-equilibration through time. While Fe-Mg exchange at magmatic temperatures equilibrates the tetrahedrally coordinated divalent cations in chromite in less than 6 hours, equilibration of trivalent cations in octahedral coordination with residual melts is slower. Our experimental results show that chromite Al concentrations are ubiquitously lower, and $\text{Fe}^{2+}/\text{Fe}^{3+}$ values are ubiquitously higher than modelled equilibrium values, indicating that there was insufficient time for significant Al and Fe^{3+} replacement of Cr. Similar observations can be made for natural chromite compositions in the extrusive sequence of the Troodos ophiolite (Cyprus). Based on a simple model of diffusive equilibration, we estimate that microphenocrystic chromites up to 60 μm in diameter take between 60 days and *c.* 170 years to equilibrate under conditions analogous to the physiochemical state of melt immediately prior to eruption. For the Troodos ophiolite extrusive sequence, this implies that mafic magmas are erupted less than *c.* 170 years after extraction from the mantle for disequilibrium textures and compositions to be preserved.

1. INTRODUCTION

Boninites are rare high magnesium andesites that are produced by the melting of highly depleted mantle (harzburgite) under shallow and hydrous conditions (Pearce and Reagan, 2019). The paucity of this rock type in the geologic record may be attributed to the exotic

nature of these petrogenetic conditions and/or the tendency of boninites to erupt in places with a low preservation potential (e.g. forearc regions, Stern and Bloomer, 1992). Nevertheless, boninites are generated in several tectonic settings including intraoceanic arcs (Meijer, 1980), intracontinental arcs (Tatsumi, 2006), back-arc basins (Falloo et al., 1992), and oceanic plateaus (Golowin et al., 2017). Additionally, several boninites have been found in ophiolite terranes (e.g. Bédard, 1999; Cameron, 1985; Dilek and Thy, 2009; Ishikawa et al., 2002; Meffre et al., 1996), though the tectonic settings of some ophiolites are topics of rigorous debate (cf. Gass, 1968; Metcalf and Shervais, 2008; Miyashiro, 1973; Moores et al., 2000; Pearce and Robinson, 2010; Regelous et al., 2014; Woelki et al., 2020; Woelki et al., 2018).

A cogenetic relationship between boninitic melt and podiform chromitite deposits found in some ophiolitic mantle sections has been hypothesized (Arai, 1997; Arai and Yurimoto, 1994, 1995; Rollinson, 2008; Rollinson et al., 2018; Zhou and Robinson, 1997; Zhou et al., 1994). With regard to podiform chromitite formation, it has been suggested that primitive hydrous melts react with depleted mantle, become silica-enriched via the incongruent melting of orthopyroxene (implying olivine crystallization), and crystallize a large volume of high-Cr# chromite due to change in the number of available melt octahedral sites (Edwards et al., 2000). Separately, mechanisms of chromitite formation have been experimentally explored assuming immiscibility between melt-melt or melt-fluid components (Ballhaus, 1998; Matveev and Ballhaus, 2002). Initial immiscibility has been observed in other experimental studies that focused on the formation of boninitic melts via the same petrogenetic mechanism (i.e. incongruent melting, Fisk, 1986), and the boninitic composition of melts are preserved in equilibrium experiments that simulate melt-peridotite reactions (Mitchell and Grove, 2016). It is noteworthy that one experiment (C608) of Mitchell and Grove (2016) not only produced boninite melt in equilibrium with a dunite residual mantle mineral assemblage, but that the

composition of the residual mineral assemblage overlaps with the most depleted end of the olivine-spinel mantle array in compositional space (Arai, 1994). Ultimately, few studies have explicitly attempted to reconcile the links between boninite magma genesis, chromitite formation, and/or, more generally, chromite crystallization (Arai, 1997; Arai and Yurimoto, 1994, 1995; Rollinson, 2008; Rollinson et al., 2018; Zhou et al., 1994; Zhou et al., 1996).

If boninitic melts are generated during concomitant olivine and chromite precipitation as described above, then the appearance of high-Cr# chromite (and forsteritic olivine) in boninites may be due to their removal from a mantle domain rather than crystallization from extracted melts in the crustal domain, where chromite has not been observed to crystallize under experimental conditions analogous to those that are realistic for primitive melt differentiation (e.g. pressures > 1 bar, Umino and Kushiro, 1989).

It is important to specify the full implications of this model of boninite + chromitite petrogenesis, namely that boninite and chromitite appear to be linked by a cogenetic relationship based on observations of each in ophiolitic assemblages, that the underlying relationship is essentially a reactive transport process that occurs in the shallow subarc mantle, and that information on such processes may be inferred by detailed studies of chromite-melt or chromite-olivine-melt geochemistry; the systematics of which are preserved to different degrees in natural volcanic and plutonic suites (e.g. Kamenetsky et al., 2001). Further, if chromites are plucked from the melt-mantle petrogenetic system, then their melt inclusions (e.g. Kamenetsky et al., 2002; Umino et al., 2018; Umino et al., 2015) may give valuable information regarding the nature of magma genesis in the reactive transport regime.

In the present study, we conducted a series of high-pressure (*c.* 2 kbar) experiments to create systems wherein high silica boninite crystallized over brief time periods in the presence of stable chromite. The data presented here demonstrate that chromite is little affected by

crystallization processes over short timescales unless unrealistically oxidizing conditions are imposed. Silicate mineral assemblages form via equilibrium crystallization in hydrous melts without significantly altering chromite compositions save for Mg-Fe exchange when buffered near the nickel-nickel oxide (NNO) buffer. We propose that the systems represented by these experiments may be regarded as approximations of what occurs in natural chromite-bearing primary melts during their crustal differentiation (Scowen et al., 1991). Similar observations on partial chromite-melt equilibration in natural samples from the Troodos ophiolite (Cyprus) allow a coarse quantification of the extraction time for the mafic magmas of the extrusive suite, but more detailed diffusion chronometry on the chemical zonation patterns of natural chromites will be required to provide tight constraints.

2. MATERIALS AND EXPERIMENTAL METHODS

Crystallization experiments were performed using internally heated pressure vessels (IHPVs) at the Institut des Sciences de la Terre d'Orléans (ISTO), Université d'Orléans, France, as well as at the Geological Survey of Japan (GSJ) in Tsukuba, Japan. Additional sample preparation took place at ISTO and at the Japan Agency for Marine-Earth Science and Technology (JAMSTEC) in Yokosuka, Japan.

2.1. *Starting materials*

Table 1 provides major element data for the starting materials as well as the bulk composition of the mixture used for the experiments. Analyses of the starting materials are given alongside sample data in the supplemental Tables S1 and S2. A fragment of high-Si boninite taken via dredging from the Mariana forearc (sample YK0612 974-R6, Reagan et al., 2010) was chosen as a suitable starting material based on observed chromite phenocrysts and microphenocrysts in thin section, which indicated chromite stability. The fragment was powdered and fluxed to form glass, which was analysed during our routine spectrometric

analysis (BO-G, Table S1) and re-powdered for sample loading. Chromite seeds sourced from the mantle section of the Troodos Ophiolite were added to glass powders with the intent of fostering further growth of chromite from boninitic melts. These seeds are unzoned and are homogeneous (avg. $Mg\# = 62$, $Cr/[Al+Cr+Fe^{3+}] = 70$). Two sample mixtures were made by mixing powdered glass with one size fraction of chromite (either $>160\ \mu m$ or $<32\ \mu m$ in size), and each starting mixture contained 2% added chromite (by mass). The size of the seeds added to powdered glass were initially varied in order to test if seed size affects the resultant modal mineralogy of the sample.

Nominally pure platinum capsules were used as sample containers. Sample mixtures were first loaded and then hydrated with heavy water (2H_2O) using a microsyringe before the capsules were welded shut. Each capsule contained *c.* 1 wt% 2H_2O prior to welding (Table 2). 2H_2O was used instead of 1H_2O to allow future analysis of water using secondary ion mass spectrometry, with this substitution enabling easy distinction between added water and background hydrogen. The quality of the welds was checked by immersing each capsule in hot oil. All capsules were adequately sealed (poor welds emit a bubble stream, indicating an inadequate seal).

NiO+NiPd redox sensors added to each experiment allowed for the hydrogen fugacity (fH_2) imposed by the IHPV pressure medium to be evaluated, as redox sensors accurately reflect the oxygen fugacity (fO_2) imposed by the gas buffer (Pownceby and O'Neill, 1994; Taylor et al., 1992). These sensors were made by packing two pellets into inert ZrO_2 powder within a platinum capsule so that the pellets are not in contact with the capsule wall. One pellet was made of 50% NiO and 50% Ni_xPd_{1-x} and the other was made of 50% NiO and 50% Ni_yPd_{1-y} , with $x = 0.5$ and $y = 0.85$. Deionized water was added until the capsule interior became

visibly saturated. Then the capsule was welded shut. Welds were checked in the same way for the sensors as they were for the sample capsules.

2.2. Experimental design

The IHPVs used at ISTO and GSJ both employed molybdenum furnaces to perform the high temperature experiments described here. Since the same amount of water was initialized in each sample, by varying the temperature of the experiments between 1200, 1150, and 1100°C, variable degrees of crystallinity are achieved in each sample. This determines the concentration of water in residual melts, as the crystallization of nominally anhydrous mafic minerals enriches the melt volume in incompatible volatile elements. The experiments were performed under isobaric conditions, which means the final variable to consider is the fO_2 of the system.

Target oxygen fugacities were *c.* 1-3 log units above the NNO buffer, which are analogous to magmas generated in subduction zone settings (Brandon and Draper, 1996; Evans et al., 2012; Kelley and Cottrell, 2009; Parkinson and Arculus, 1999). The oxidation states were either left unbuffered or buffered by pressurizing the IHPV with an Ar-H₂ gas mixture (pH_2^{added} , Table 2). Pt capsules are permeable to hydrogen, which diffuses through the capsule wall to bond with oxygen in the melt so that reduction of the sample volume occurs (Chou et al., 1978; Shaw, 1963). Since the volume of the pressure medium is much greater than the volume of the sample capsule, the pressure medium is effectively an infinite reservoir with respect to hydrogen. Thus, the effective concentration of hydrogen available to each capsule during a given experiment, fH_2 , may be considered constant. Unbuffered experiments cause the redox state of melts to approach a condition known as the intrinsic fO_2 of the IHPV. The intrinsic fO_2 of IHPV systems is highly oxidizing (NNO+2 to NNO+4, Scaillet et al., 1992; Taylor et al., 1992, see further discussion in Supplemental Text 1).

The experiments described here each lasted less than 6 hours. The utility of short-period experiments is multifaceted. From a volcanological perspective, fast ascending magmas are extracted from their crustal domains and extruded onto the surface in as little as tens of minutes (Lloyd et al., 2016) when melts are hot ($>1000^{\circ}\text{C}$) and volatile rich. Short timescales of the order of hours to days have also been inferred for volatile poor arc magmas (Lormand et al., 2020). In a rapidly ascending melt, a variety of concomitant processes may alter the physiochemical state of the melt volume, including syn-eruptive mixing (e.g. Tomiya et al., 2013; Wolf and Eichelberger, 1997), crystallization (e.g. Blundy and Cashman, 2005; Cashman and Blundy, 2000), and whole-rock contamination (e.g. Mattioli et al., 2006). Such processes, along with subtleties such as the inclusion of antecrystic minerals, produce disequilibrium mineral assemblages that provide valuable insight into the latest stages of magmatism (Couch et al., 2001; La Spina et al., 2016; Ubide et al., 2014; Zellmer et al., 2016; Zellmer et al., 2014). Thus, for natural magmatic systems, brief durations on the order of hours represent an end member in an ascent period context, and disequilibrium characteristics may be useful if properly placed into a petrogenetic context. Given boninite petrogenesis occurs at relatively shallow depths and generates hot and hydrous melts, sometimes in extensional settings (Reagan et al., 2017), rapid ascent rates cannot be precluded. Furthermore, since it is possible that chromites preserved in boninite matrices may have been generated within the source regions of the melts, knowledge of how these minerals react to changes in the physiochemical states of the melts (i.e. experimental observation) is needed in order to assess and contextualize natural sample materials. These considerations provide an incentive to perform experiments on brief timescales and to analyse disequilibrium features.

3. ANALYTICAL METHODS

Analytical facilities at Victoria University of Wellington, Hokkaido University, Massey University, and The University of Iowa were utilized to gather the data presented here.

Following removal of the sample holder from the IHPV, each capsule was weighed to assess for mass loss during the experiment. The capsules were then mounted in epoxy and ground to expose their interiors. Ni-Pd alloys recovered from each sensor capsule was separated from powdered ZrO_2 and mounted in epoxy. These sample materials were then polished for imaging and microprobe analysis, using SiC lapwheels and diamond grit paste.

3.1. Electron microbeam techniques

Samples produced at ISTO were imaged using an FEI Quanta 200 Environmental scanning electron microscope (SEM) at the Manawatu Microscopy and Imaging Centre (Massey University). This SEM was also used to perform semi-quantitative analyses of calcic silicate minerals using an attached EDAX energy dispersive spectroscope (EDS). Samples produced at GSJ were imaged at the Creative Research Institute of Hokkaido University using a JEOL JSM-7000F Field Emission SEM. An attached XMAX 150 EDS was used here to analyse the capsule Pt walls in contact with sample melts in order to detect iron loss after each experiment (Supplemental Text 2, Table S3). Quantification of Fe in Pt was achieved by calibrating signal intensity to pure Co.

Electron probe microanalysis (EPMA) occurred at multiple laboratories: at Victoria University of Wellington and The University of Iowa, JEOL JXA-8230 Superprobes were used. Additional chromite analyses were performed at Hokkaido University on a JEOL JXA-8800R. Glass analyses were performed using Na-migration mitigation techniques. In addition to using diffuse beam conditions (spot sizes of 5-10 μm), two Na acquisitions are totalled. If analyses return low concentrations (determined using secondary standards), then sodium loss may be corrected by either: removing the second acquisition (if Na is lost), removing either

point (if either indicates loss), or back-calculating time-resolved intensity to correct for Na loss. No analyses reported here experienced significant sodium migration as indicated by multiple analyses of both sample and standard materials.

Secondary standards provided by the Smithsonian Institution Department of Mineral Sciences and/or the Max Planck Institute for Chemistry were included in all glass and mineral analyses. Ni-Pd sensor compositions were quantified using metal standards by Astimex. Repeat analyses of secondary standards provided a basis to assess the accuracy of data gathered during EPMA (Tables S1-S2, and S4). The accuracies associated with glass analyses have been determined to be within 1% for SiO_2 , Al_2O_3 , MgO , and CaO , 5% for TiO_2 , FeO , and K_2O , 10% for Na_2O , and 20% for MnO . For analyses of silicate minerals, SiO_2 , MgO , CaO , and Na_2O are accurate to within 1%, while FeO , Cr_2O_3 , MnO , and Al_2O_3 are better than 2%. Chromite standardization was achieved using several mineral and oxide standards. Replicate standard analyses demonstrated that all major elements given are accurate to within 5%, while MnO is accurate to within 40%. Secondary standard compositions are taken from Jarosewich et al. (1980); Jochum et al. (2006); and Jochum et al. (2005).

To ensure analyses of pyroxene were of high quality, raw EPMA data were normalized prior to formulae recalculation using the methods described by Putirka (2008). Analyses that returned cation totals much greater than or less than 4 (on an $\text{O} = 6$ basis) were discarded. In a similar manner, raw chromite analyses were recalculated to cation proportions per 4 oxygens. Recalculation of ferric iron proportions used the equation of Droop (1987). No other multivalent cations (e.g. Mn , Cr) were considered.

3.2. Determination of phase proportions

In order to provide high-precision phase proportion data, a computationally inexpensive machine learning tool enabled the analysis of backscattered electron (BSE) images and

produced segmented images that we interpreted in terms of phase proportions using Adobe Photoshop. Segmented images are images that have been petrographically interpreted using a machine learning algorithm and are color-coded based on which phase each pixel represents (Supplemental Text 3). The machine learning tool used is called Trainable Weka Segmentation, and was developed by Arganda-Carreras et al. (2017). The algorithm requires limited user input (5-8 user-defined groups of pixels) to “train” the computer-generated classifier, which segments as many mineral phases as the user defines. This tool produced the segmented images used to infer the phase proportions given in Table 2. The tool is provided as a plugin on the Fiji Is Just ImageJ (FIJI) platform (Schindelin et al., 2012). A minimum of 5 training sessions were conducted for each analysis, and the data derived from each segmented image were averaged to produce the given proportions with the calculated standard deviation providing the precision of each phase classification. Images representative of the sample textures were used for segmentation. See Supplemental Text 3 for more information and an example of a segmented image.

3.3. *Determination of oxygen fugacities from the solid sensors*

Fugacity calculations were performed following the methodology of Scaillet et al. (1995). Sensor compositions, X_{Ni} ($Ni/[Ni+Pd]$ calculated using cation proportion), were determined following EPMA. Further discussion of fugacity, including the calculation methodology, is provided in the Supplemental Text 1.

4. RESULTS

Weighing the capsules after quench indicated that no mass was lost during any experiment. Table 2 gives information on each sample including the mixture used, initial water concentration, experimental conditions, resultant phase proportions inferred for each sample, sensor compositions, and fO_2 data.

The capsule interiors of every sample except for Bon1200Ub were analysed via EDS in order to assess the degree of iron loss from the melt to the Pt of the capsule wall. Line analyses from the sample-wall contact into the capsule wall yielded no detectable iron *c.* 30 μm from the interface. Integrating concentration profiles demonstrates that iron loss in unbuffered experiments is limited to 10% or lower (of bulk sample Fe), while buffered experiments lost 20-35% Fe over experiment durations (Supplemental Text 2, Table S3). However, we will demonstrate that none of our discussion topics have been significantly affected by iron loss.

4.1. Petrographic observations

Euhedral-subhedral orthopyroxene (opx) is abundant and is the only silicate phase present at 1200°C and 1150°C (Figure 1A). In BSE images, these crystals often have bright caps that form at the apices of euhedral crystal forms (Figure 1B). At 1100°C, a petrographically distinct trace silicate phase was observed along with abundant opx in Bon1100U (Figure 1C). Semi-quantitative EDS analyses of this phase demonstrate that this silicate is rich in Ca, Mg, and Fe. If it is a pyroxene, it is likely augite (*c.* $\text{Wo}_{31}\text{En}_{57}\text{Fs}_{12}$). Chromite is stable in all boninitic samples, and BSE images of moderate-sized grains show that chromite mantles have become brighter than cores (Figure 1D), indicating that diffusive equilibration was interrupted by quenching in large grains. In general, all chromites appear as anhedral grains with sharp-subrounded corners. These are not indications of chromite growth, suggesting that all observed chromites are the original seeds added to each experiment. Likewise, there is no evidence of dissolution, which indicates that chromite was a stable phase for the full duration of each experiment. This implies that our experiments only produced pyroxene crystallization in the presence of stable chromite.

A small number of micro-vesicles occur in all boninitic samples (e.g. Figure 1A). The vesicles are spherical and show no indication of clustering. They appear randomly distributed within the sample volume. No vapour films were observed along any of the capsule walls.

4.2. Redox sensors and calculation of imposed fO_2

Average X_{Ni} values were calculated for each sensor and used to infer sensor fO_2 for each experiment. For water undersaturated sample melts, a_{H_2O} must be modelled in order to accurately calculate fO_2 . To this end, the activity model of Burnham (1979) was used in conjunction with major element data and inferred melt water concentrations (Supplemental Text 1) to model a_{H_2O} . The uncertainties reported here for fO_2 are similar to those reported elsewhere for the solid sensor technique (Jégo et al., 2010; Scaillet et al., 1995). The solubility model of Zhang et al. (2007) was used to calculate maximum water concentrations in residual melts under the experimental conditions, which correspond to c. 5.3-5.4 wt%. According to these model constraints, boninitic melts did not reach saturation (Table 2), and the ubiquitous presence of micro-vesicles (Figure 1A) is therefore not due to water saturation (exsolution) but likely due to the inclusion of atmospheric gas in the sample capsules during preparation.

Complexities associated with quench crystallization were observed in samples Bon1200Ua, Bon1200Ub, Bon1200Ba and Bon1200Bb and are discussed later. A principal effect of quench crystallization is to raise a_{H_2O} in residual melts. Thus, for these high-T samples, the reported fO_2 data are considered maxima.

4.3. Compositional Data

Representative compositional data are given in Table 3. Full sample datasets for each phase, including secondary standard analyses, data compiled from the literature, and model data, are given in Tables S1-S2 and S4. Literature data cited for comparison are provided in Table S5.

4.3.1. Glass compositions

Residual melts formed andesitic glasses, the compositions of which are given with other experimental products in Table 3. These glasses are depleted in FeO, MnO, MgO, and Cr₂O₃ relative to both the initial boninite glass as well as the bulk composition of the system (Table 1). SiO₂, CaO, Al₂O₃, Na₂O, K₂O, and TiO₂ are enriched in residual melt during every experiment, which is consistent with extensive opx crystallization.

The two experiments conducted at high temperature (Bon1200U and Bon1200B) returned four samples with glasses containing low MgO concentrations relative to those from experiments conducted at 1150°C. This is counterintuitive, because the crystallization of opx at higher temperature should produce a lower proportion of minerals relative to lower temperatures, and overall depletion of MgO and FeO relative to the initial glass composition should be smaller. Additionally, glass compositions inferred for sample Bon1200Ua indicate a high degree of heterogeneity beyond the limit of analytical uncertainty, consistent with inefficient quenching producing local melt heterogeneity. These data, along with relatively high melt K₂O concentrations and the presence of abundant rim formation on opx grains within these samples (Figure 1B) indicate that a significant degree of quench crystallization has occurred in the high temperature experiments. These observations are absent from all experiments conducted at 1150-1100°C, which suggests that quenching was efficient in these latter experiments and that no quench crystallization occurred.

4.3.2. Pyroxene compositions

Opx formed under every temperature and redox condition imposed by the IHPV. In order to confirm the identity of low-Ca pyroxenes as opx and not pigeonite, we calculated calcium molar fractions for an opx-clinopyroxene (cpx) dividing line using equation 38 of Beattie et al. (1991) with the experimental temperatures imposed within the IHPV as the single independent variable. All pyroxene data presented here fall below these model values, which confirms their identity as opx. Opx compositions are graphically illustrated in Figure 2. Plotted alongside these data are data taken from other experiments conducted using boninitic bulk compositions (Tatsumi, 1981; Umino and Kushiro, 1989) and natural opx compositions sourced from boninitic rocks (Mariana trench, Bloomer and Hawkins, 1987; Troodos ophiolite, Cameron, 1985; and Chichijima, Umino, 1986; Yajima and Fujimaki, 2001).

Opx Mg# (molar $\text{Mg}/[\text{Mg}+\text{Fe}_{\text{Total}}]$) positively correlates with temperature, and under buffered redox conditions is lower than in unbuffered products (Figure 2). Differences in MgO and FeO concentrations observed in samples processed at 1200°C but different $f\text{O}_2$ are on the order of 1-2 wt% for each element. Thus, lower Mg# is associated both with lower temperature as well as lower $f\text{O}_2$. Minor oxide components in opx include CaO, Na₂O, Cr₂O₃, MnO, TiO₂, and Al₂O₃. The concentrations of each of these oxides are < 5 wt%, with variation of some concentrations correlating with changes in the intensive parameters of the IHPV. Higher cation proportions of Ca, Al, and Mn are observed in samples synthesized under lower temperatures (Figure 2). Cr₂O₃, Na₂O and TiO₂ concentrations are extremely low in all pyroxenes, and potential variations in these oxides due to changes in temperature or redox condition are imperceptible when considering the detection limits for these elements. The effects of imposing variable redox conditions on the melt-opx partitioning of Ca, Al, and Mn cannot be discerned for a given temperature interval because, with regard to these elements, the mean core compositions for all opx synthesized at a given temperature are not observed to significantly change between high and low $f\text{O}_2$.

When natural and other experimental opx compositions are compared to the experimentally synthesized opx presented here, the majority of natural and experimental opx compositions are similar to opx synthesized at 1200°C and under buffered fO_2 conditions in terms of their Mg#. Mn proportions broadly overlap with products of high temperature crystallization, while Al and Ca cation proportions from the literature are, respectively, somewhat lower and higher than our experimental products.

4.3.3. Chromite compositions

Initial seed chromite fragments were analysed by EPMA in order to determine if the chromite pod could be considered homogeneous. Representative data are given in Table 1 with other starting material compositions. A single analysis revealed minimal enrichment of FeO and TiO_2 (Table S2). Because the level of enrichment is low and rarely observed, we consider the seed chromite to be homogeneous.

Experimental chromite compositions are chromium-rich, typically with $70 < Cr\# < 81$ ($Cr\# =$ molar $Cr/[Cr+Al]$, Table 3), and compositional data are illustrated in Figure 3. Priority was given to small seed chromites (*c.* 10-15 μm in diameter) that were able to be analysed without significant Si-contamination of the analysis volume from adjacent glass. This was because the initial goal of adding seed chromite was to foster mineral growth from the boninitic liquid. Since this likely did not occur, then the next best action was to analyse material that most likely equilibrated with residual melts by the end of each experiment. Two samples seeded with large chromite fragments (Bon1200Ua and Bon1200Ba) were observed to also contain several small anhedral chromite fragments distributed among the opx crystals (possibly chromite powder contamination from the sieving process). Several of these were analysed in Bon1200Ua, but no analyses of chromite in Bon1200Ba were determined to be

free of glass contamination based on high observed concentrations of Si, Ca, and, in some cases, Na. These data were rejected.

Compositions taken from the literature on boninite-hosted chromites sourced from the Mariana trench wall (Bloomer and Hawkins, 1987), the Troodos ophiolite (Bailey et al., 1991; Cameron, 1985; Flower and Levine, 1987; MacLeod, 1988; Thy and Xenophontos, 1991), Guam (Reagan and Meijer, 1984), and Chichijima (Umino, 1986) are provided for comparison. Note that the chromites from Thy and Xenophontos (1991) are olivine-hosted mineral inclusions.

In terms of trivalent cation proportions (i.e. Fe^{3+} , Al, and Cr), $f\text{O}_2$ buffered experiments produced chromites with compositions that did not significantly change from the initial seed composition (Figure 3A). Chromium is efficiently oxidized above NNO in iron-bearing melts (Hanson and Jones, 1998). Thus, all Cr in chromite is Cr^{3+} . However, some of these chromites have bright mantles that clearly indicate Fe enrichment (e.g. Figure 1D). Under intrinsic $f\text{O}_2$ conditions corresponding to *c.* 3.2-4.0 log units above the NNO buffer and at temperatures of 1200-1150°C (red and yellow diamonds on Fig. 3), significant amounts of Fe^{3+} were added to chromite, resulting in an enrichment of total FeO with concentrations > 20 wt%. For these samples, their trend on Figure 3A illustrates significant Fe^{3+} -Al exchange between chromite and melt, as the trend of core compositions runs sub-parallel to lines of equal Cr proportion (which caused the observed increase in Cr# for these chromites). Because this trend is linear and the samples do not cluster, it is likely that the Fe^{3+} -Al exchange reaction failed to reach equilibrium. It is noteworthy that chromite grains in sample Bon1100U appear to have lost very little Al during the experiments, as Al_2O_3 concentrations are ≤ 1 wt% different from concentrations in the seed chromite, consistent with the observed invariance of their inferred Fe^{3+} contents. TiO_2 was consistently low in all chromites,

398 reaching a maximum value of 0.14 wt% under the lowest temperature setting (Bon1100U).
 399 NiO concentrations were nearly constant throughout the dataset at *c.* 0.11 wt%.

400 The literature data lie on a separate trend on Figure 3A that is sub-parallel to lines of constant
 401 Fe^{3+} proportion. Of these data, chromite inclusions in olivine from the Kythreotis locality
 402 (Troodos, Thy and Xenophontos, 1991) and matrix chromite from Guam appear to be the
 403 most aluminous, while sample material from the Mariana Trench and Chichijima plot
 404 together near the extreme Cr end of the ternary diagram along with other Troodos chromites.
 405 In fact, chromite compositions from Troodos boninites and tholeiites span a wide range on
 406 this diagram, plotting between the Kythreotis samples and the highly chromian composition
 407 observed for the Kapilio locality (Cameron, 1985). The similarity between some of the
 408 chromites observed in Troodos boninites/tholeiites and the seed chromites from the plutonic
 409 chromitite is noted, as it was by Cameron (1985).

410 In Figure 3B, Mg# (chromite $\text{Mg\#} = \text{Mg}/[\text{Mg} + \text{Fe}^{2+}]$ using molar proportions) is plotted
 411 against $\text{Fe}^{3+}/[\text{Fe}^{3+} + \text{Cr} + \text{Al}]$ (also calculated using molar proportions) in order to visualize the
 412 effects of iron enrichment in a compositional space that is more representative of the spinel
 413 (*sensu lato*, hereafter *s.l.*) solid solution. Again, it is evident that buffered experiments
 414 (squares) have the same Fe^{3+} proportion as seed chromite. However, it is apparent that some
 415 Mg- Fe^{2+} exchange has occurred at 1150°C, which represents the rim formation reaction
 416 observed in BSE images (yellow square). Thus, in $f\text{O}_2$ buffered experiments conducted at
 417 1150°C, Fe^{2+} has been added to chromite and Mg has been lost to the melt. For a given
 418 temperature, Mg# appears to decrease with Fe^{3+} incorporation. This is observed for samples
 419 recovered from experiments Bon1200U and Bon1150U, which plot to higher Fe^{3+} relative to
 420 products of buffered experiments. Interestingly, natural chromite compositions observed in
 421 the Troodos ophiolite span a slightly greater range of Mg# than the experimental products.

Included in these data are additional olivine-hosted chromite inclusion data from Sobolev et al. (1993) and Golowin et al. (2017).

5. DISCUSSION

5.1. *Assessment of divalent cation distribution and equilibrium state between chromite-opx-melt*

Because the experiments described here did not produce any discernible chromite growth, instead of discussing chromite crystallization, the following sections discuss the state and kinetics of chromite equilibration. The physiochemical states imposed upon the boninite system are analogous to a shallow-mid crust setting, and thus these experiments are ideally suited to study the effects of chemical disequilibrium on compositional change as a function of temperature and fO_2 over brief timescales in this setting.

Based on textural evidence, it is apparent that large seed chromites in the samples presented here failed to reach chemical equilibrium with their residual melts (Figure 1D). Since opx crystallization is the process that altered the major element composition of melts during each experiment, it is also the process that determines the extent to which chromite would have to interact with residual melt in order to reach an equilibrium state under the conditions imposed within the IHPV. Thus, it is important to qualify the relationship between opx and residual melt so that chromite-melt relationships can be confidently explored.

In order to test for opx-melt equilibrium, the methodology of Putirka (2008) was used. Specifically, for a given sample, melt cation fractions were calculated (X_d^{liq} , Table S1) for each glass analysis. From these values, X_{Si}^{liq} was used to calculate model equilibrium Fe-Mg exchange coefficients (K_D , Table 4, Figure 4A) using the following relationship given by Putirka (2008):

$$K_D(\text{Fe} - \text{Mg})^{\text{opx} - \text{liq}} = 0.4805 - 0.3733X_{\text{Si}}^{\text{liq}} \quad \text{Equation 1}$$

An uncertainty (1σ) of ± 0.06 was attributed to these modelled K_D values, which is an order of magnitude higher than the 1σ associated with the distribution of modelled K_D values given in Table 4 and is illustrated as areas on Figure 4A. Observed K_D calculations employed molar proportions for opx core analyses and average molar proportions for glass compositions. Average K_D values (including 2σ error bars) for samples Bon1150U and Bon1150B plot completely within their model areas, indicating that the opx sampled in these charges were in equilibrium with their respective residual melts at the time of quenching. K_D values calculated for three opx cores in sample Bon1100U produce an average K_D that is positioned just outside of the model area. However, since the lower error bar stretches into the uncertainty envelope as illustrated, it is reasonable to say that these crystals also equilibrated with their residual melt. There are two negative effects of quench crystallization that impacted K_D calculations and prevented us from determining whether opx in samples processed at 1200°C were able to reach equilibrium or not. The first is the effect of raising $X_{\text{Si}}^{\text{liq}}$, which occurred as quench crystals removed Mg, Fe, and Ca from residual melts. This lowers model K_D values (Equation 1). The other effect is the removal of Mg and Fe from the melt phase, which precluded realistic K_D values from being observed (Figure 4A). Since opx-melt K_D s indicate an equilibrium condition for experiments conducted at $1150\text{--}1100^\circ\text{C}$, none of the iron loss observed in these samples had an observable effect on the equilibrium partitioning of Fe-Mg between opx and melt. This indicates that our equilibration considerations are not significantly affected by this process.

In order to assess for chromite-opx equilibrium, the model of Liermann and Ganguly (2003) was applied. This model was calibrated at higher pressures than imposed in our experiments. However, because changes between partial molar volumes (of end-member compositions at

the standard state) associated with the Fe²⁺-Mg exchange reaction between chromite and opx appear to exhibit ideal mixing behaviour and because both Fe²⁺ and Mg endmembers exhibit similar and predictable pressure dependencies, Liermann and Ganguly (2003) assumed a pressure normalization scheme (their equation 5) to process their K_D values and formulate a thermometer for opx-chromite pairs that may be applied under a wide range of pressure conditions. We have rearranged this thermometer (their equation 8) to predict chromite-opx K_D (Fe²⁺-Mg, Table 4) at 2 kbar (0.2 GPa):

$$K_D(\text{Fe}^{2+} - \text{Mg})^{\text{chrom} - \text{opx}} = \exp \left[\frac{AT(K) + B + 122P(\text{GPa}) - CX_{\text{Al}}^{\text{opx}} + DY_{\text{Cr}}^{\text{chrom}}}{T(K)} \right] \quad \text{Equation 2}$$

This K_D equation utilizes opx Al molar proportion ($X_{\text{Al}}^{\text{opx}}$), chromite Cr/[Cr+Al+Fe³⁺] ($Y_{\text{Cr}}^{\text{chrom}}$), and constants derived for Al-Fe³⁺ system correction using the charge balance method: A = -0.351±0.102, B = 1217±120, C = 1863, and D = 2345±188 (Table 4 of Liermann and Ganguly, 2003). Uncertainties associated with the model K_Ds were calculated to be ±0.157 (i.e. better than ±7%, 2σ relative) based on propagating the uncertainties provided for coefficients A, B, and D. Assuming the compositional parameter for opx does not significantly change, and since Cr proportions for the synthetic chromites are not observed to change significantly between any of the samples (Figure 3A), this equation predicts the equilibrium state of chromite-opx with regard to Fe²⁺-Mg exchange for each experimental condition at the time of quenching (Figure 4B, observed K_D values were calculated using molar proportions with chromite X_{FeO} multiplied by molar Fe²⁺/ΣFe inferred from stoichiometry).

As illustrated on Figure 4B, the Fe²⁺-Mg subcomposition of chromite (given as Mg# in Figure 3B) in several samples has equilibrated with the opx-melt subsystem over the brief timescale of these experiments. The relatively large seed shown in Figure 1D has a rim that is *c.* 8-10 μm wide. Because our analyses prioritized small chromites that were *c.* 10-15 μm in

diameter, we consider it likely that EPMA sampled chromite that completely equilibrated with respect to Fe^{2+} -Mg through diffusion.

Thus, since a self-consistent determination of equilibrium has been established using empirical relationships, then the Fe^{2+} -Mg data provided here describe the equilibrium condition of the melt + opx + chromite system under high temperature and $f\text{O}_2$ conditions analogous to those in sub-arc crust. Interestingly, significant degrees of iron loss should raise the Mg# of the sample bulk composition even when the ratio of Fe^{2+} to Fe^{3+} in melt is maintained by hydration (Supplemental Text 2). This effect should be observable in product opx compositions, as higher melt Mg# should result in higher opx Mg#. Since this is not observed (Figure 2, Table 3), then the observed iron loss (in the case of Bon1150B, 20% bulk Fe) does not significantly affect the equilibrium distribution of Fe^{2+} -Mg under our experimental conditions.

5.2. *Assessing chromite-melt equilibrium based on model equilibrium trivalent cation proportions*

Since Fe^{2+} -Mg has now been accounted for, it is prudent to also examine the equilibrium state of the trivalent cations in chromite. To this end, multiple modelling methods were integrated to predict equilibrium chromite compositions (with respect to trivalent cation proportions). Our method modelled system compositional data using the alphaMELTS front end (Smith and Asimow, 2005) and the MELTS thermodynamic model (Ghiorso and Sack, 1995) with Rhyolite-MELTS system corrections enabled (Gualda et al., 2012). Nested modelling utilized SPINMELT-2.0 (Nikolaev et al., 2018a, b), which calculated an alternative stable chromite composition for each intermediate MELTS step. These models are likely to bookend actual trivalent cation proportions in spinel (*s.l.*) compositional space (see Davis and Cottrell, 2018; Nikolaev et al., 2018a, for information and discussion on how individual models behave

when predicting chromite compositions). A detailed description of the modelling methodology is included in Supplemental Text 4. SPINMELT-2.0 cannot make sense of MELTS-modelled liquid compositions at NNO+3 because the liquid composition at this condition lies outside of the calibration range for the SPINMELT-2.0 algorithm. Thus, SPINMELT-2.0 data are not available under highly oxidizing conditions.

Figure 5 illustrates the relationship between MELTS and SPINMELT-2.0 models and the difference between modelled compositions and the synthetic chromites produced in our experiments. Alternative models were created to observe the effect of 30% iron loss on the system (empty symbols, Figure 5). It appears that under highly oxidizing conditions and 1150-1200°C, experimental chromite $\text{Fe}^{3+}/[\text{Fe}^{3+}+\text{Cr}+\text{Al}]$ values approach values that are attained at NNO+2 in the MELTS models. Still, given the distance on the ternary diagram between modelled chromite compositions and our experimental data, none of the experimental chromites are in equilibrium based on observed trivalent cation proportions. This includes model data that were generated under conditions where iron loss was accounted for. The principal effect of iron loss is to reduce the proportion of iron in equilibrium chromite. The trend to high Fe^{3+} concentrations observed for the oxidized samples illustrated in Figures 3A and 5 are likely to represent a segment of a diffusion trend in ternary space. The concept of diffusion in this compositional space is explored below. Since the volume of chromite in the charges is invariant (i.e. no resorption or crystallization has been observed), then the process by which chromite equilibrates can exclusively be attributed to diffusion.

Differences between MELTS and SPINMELT-2.0 output data are surprisingly large but may be attributed to both our modelling strategy (Supplemental Text 4) as well as inherent limitations of the model platforms. Models in the MELTS family tend to overpredict spinel (*s.l.*) Fe^{3+} proportion and underpredict Cr proportion (Davis and Cottrell, 2018; Nikolaev et

al., 2018a), and the creators of SPINMELT-2.0 claim that their model reproduces several petrologically important chemical aspects of chromite chemistry to better than 20% (Cr/Al and Mg/Fe²⁺, Nikolaev et al., 2018a). What MELTS does describe accurately is Fe-Al exchange within the system during melt evolution and thus likely provides a best fit topology in compositional space (Davis and Cottrell, 2018). Because of these observations, we reiterate that our modelling method likely bookends equilibrium chromite compositions; keeping in mind that multiple experiments were performed beyond the calibration range of SPINMELT-2.0.

In the case where Fe²⁺ in chromite is in equilibrium with the co-existing melt/silicate mineral assemblage, the interdiffusion of trivalent cations should occur in chromite with Fe²⁺/Fe³⁺ higher than that in coexisting melt, as melt Fe²⁺/Fe³⁺ should always be higher than spinel Fe²⁺/Fe³⁺ (Maurel and Maurel, 1982). Using equation 7 of Kress and Carmichael (1991), model melt Fe²⁺/Fe³⁺ values were generated (Table S1) using glass compositions and the intensive parameters imposed by the IHPV to show that most if not all experimental chromites must incorporate more Fe³⁺ before reaching an equilibrium Fe²⁺/Fe³⁺ threshold (Figure 6). That is, in order to reach an equilibrium condition, the observed Fe²⁺/Fe³⁺ in chromite must incorporate more Fe³⁺ so that their ratio values fall below the grey lines on Figure 6. The exception is sample Bon1200Bb, the chromite Fe²⁺/Fe³⁺ values of which are distributed (mostly) beneath the modelled melt Fe²⁺/Fe³⁺ value.

The diffusion of major cations within spinel (*s.l.*, e.g. Figure 19 of Van Orman and Crispin, 2010) are ranked by order of decreasing diffusivity (log D, m²/s) at 1100°C (10⁴/K = *c.* 7.3): Mg-Al (extrapolated, *c.* -13.5), Fe (self-diffusion, *c.* -16), Mg (self-diffusion, *c.* -16.5), and Cr-Al (below x-axis, see below). Thus, D_{Cr-Al} is likely the limiting factor in chromite-melt diffusive equilibration, though uncertainties associated with D_{Cr-Al} are reportedly large at high

Cr# (Suzuki et al., 2008) and $f\text{O}_2$ affects D_{Fe} (Vogt et al., 2015). As stated by Vogt et al. (2015) this behaviour is not well constrained under high-T and high-P conditions. Our results corroborate this inference. Since spinel (*s.l.*) is an isometric mineral, the given diffusivities do not vary with crystallographic orientation, which is convenient for the purpose of textural analysis (Supplemental Text 5).

As demonstrated in Figure 3A, when buffered at NNO+0.4, +1 and +2.5, chromite compositions did not significantly change from the original seed composition with respect to trivalent cation proportion. Only change in Mg# is observed for these chromites (Figure 3B). Significant Fe^{3+} incorporation was only observed in unbuffered samples at $T > 1100^\circ\text{C}$ and occurred at the expense of Al, since trivalent cation proportions for these samples are distributed along lines of equal Cr proportion (Figure 3A). Thus, Al counter-diffusion facilitated Fe^{3+} incorporation in chromite under highly oxidizing conditions at 1150-1200°C; although it is unlikely these minerals completely equilibrated during the experiments (Figure 5).

The Fe-Mg and Fe-Al exchange reactions have also been observed in natural samples that are allowed to equilibrate over decadal timescales (Scowen et al., 1991). Importantly, the observations of Scowen et al. (1991) confirm the rank of the diffusivities outlined above and establish that even though Cr is the most sluggish element to diffuse, eventually Cr diffusion does occur in natural settings to equilibrate chromite following Fe-Al interdiffusion.

Based on our observations, we hypothesize that Fe^{3+} -Al interdiffusion operates principally as a function of $f\text{O}_2$ to equilibrate chromite $\text{Fe}^{2+}/\text{Fe}^{3+}$ (after equilibration of chromite Mg#) on a shorter timescale than is required to equilibrate Cr in the system. This scenario of diffusive re-equilibration may be conceptualized within a multi-step chemical reaction (Figure 7). The first step concerns Fe^{2+} -Mg exchange between chromite and melt. This is the only reaction

observed in samples processed under buffered fO_2 (and in sample Bon1 100U), and since the observed changes in chromite composition are more complex under higher fO_2 conditions, we combine this exchange with the observed increase in Fe^{3+} in trivalent cation proportion as reaction 1 (Figure 7). Thus, a relatively high $Fe^{2+}/Mg + Fe^{3+}/Al$ composition is generated as a magnetite component ($FeFe_2O_4$) is added to the starting chromite composition. This exchange is facilitated by the counter-diffusion and exchange of Mg and Al, and the spinel (*sensu stricto*, hereafter *s.s.*) component thus diminishes (see Table S2 for modelled end-member component compositions). With reaction 1, the chromite composition approaches a tie line between $Fe(Al,Cr)_2O_4$ and $Mg(Fe,Cr)_2O_4$ in the compositional space of the spinel (*s.l.*) prism (dashed grey line in Figure 7A). Importantly, the chromite compositional trend will not approach the Cr-magnetite solid solution in the prism space but a spinel (*s.l.*) composition intermediate between Cr-magnetite and the $Mg(Fe,Cr)_2O_4$ solid solution, as spinel (*s.l.*) Mg concentration is only being diluted by reaction 1 (i.e. Mg is rearranged within the chromite matrix with some flux across the crystal-melt boundary). In order to equilibrate Cr proportion, which is expected to decrease under all imposed experimental conditions (Figure 5), compositions should evolve along lines of equal Fe^{3+}/Al (dashed grey line in Figure 7B; reaction 2) in the isothermal state as Cr is lost to the melt phase. An added component with higher Fe^{2+}/Mg is required because $Mg\#$ in chromite was not observed to increase in any experiment (Figure 3B) and because this is necessary for chromite to equilibrate with the silicate mineral assemblage (Figure 4B).

The difference in diffusivities between mineral species provides an interesting constraint on the origin of the polyminerale microlite assemblages described here. In particular, Fe-Mg interdiffusion in opx occurs more slowly ($\log D = -19.5$ at QFM and high T, Klügel, 2001) than interdiffusion of any of the major cations in chromite. If, in natural samples, it is found that microlitic silicates like opx are in equilibrium with residual melts and matrix chromites

are not, then the likely explanation for this observation is that the microlitic silicate formed from the melt it is in (i.e. an equilibrium crystallization process). Crystallization of ferrous phases is one of several oxidizing mechanisms in arc magmatic systems (see Cottrell et al., 2020). This process provides an impetus for diffusive re-equilibration of chromite to begin, and the grounds for oxyspeedometric analysis of the chromite-melt subsystem in a diffusion chronometric context. Chromite crystals sampled from Chichijima (Umino, 1986), the Troodos ophiolite (Bailey et al., 1991), and Guam (Reagan and Meijer, 1984) exhibit chemical zonation consistent with pre-eruptive oxidation, as chromite rim-mantle zone analyses return more ferric compositions than analyses of their cores. Such features are unique to the pre-eruptive regime but may be confused with compositional trends that are attributable to chemical weathering. Thus, it is important to discern here oxidation of chromite that occurs in this scenario and oxidation that occurs post-eruption (i.e. chemical weathering or metamorphism of chromite). In the literature on the zoned chromites described above, there is no mention of textures consistent with porous-chromite oxidation (Gervilla et al., 2019; Hodel et al., 2020). The volcanic rocks sampled by the studies cited above were observed to be fresh with little to no evidence of alteration, which is not consistent with a weathering environment capable of significantly modifying chromite compositions in either hydrothermal (Hodel et al., 2020) or metamorphic (Gervilla et al., 2019) regimes. Instead, since the chromite FeO and Al₂O₃ concentrations are observed to increase from core to rim (which is a geochemical signature of magmatic oxidation in our model, i.e. reaction 2 of Figure 7), we maintain that these zonation patterns are of magmatic rather than secondary origin. With this in mind, the next sections assess natural chromite and glass compositions recovered from the extrusive suite of the Troodos ophiolite in a similar manner as our experimental products, and data available from the literature are used to constrain ascent rates for these lavas.

5.3. *Experimental observations vs. natural processing in the crustal column*

Mafic Troodos glass compositions were taken from the literature for the following localities: the Kalavassos Mine (eastern end of the Limassol Forest Complex), Margi (northern part of the extrusive sequence), and Kapilio (western end of the Limassol Forest Complex). All data were taken from Woelki et al. (2020) with an additional two glass analyses from Golowin et al. (2017) for the Kalavassos Mine locality. The studies cited used laser ablation inductively coupled plasma mass spectrometry to quantify minor-trace concentrations of Cr for these samples. Data on mineral compositions for these locations are sparse. However, multiple compositions were found and taken from Cameron (1985), Bailey et al. (1991), Flower and Levine (1987), and MacLeod (1988). Here, we assess these data to determine if the aforementioned minerals and melts were in equilibrium at the time of eruption. Chromite data were found neither for the Akaki River Canyon section nor for the Arakapas Fault Belt though Ohnenstetter et al. (1990) performed several analyses, no data are provided in the source. Thus, even though these locations have been widely studied, we are currently unable to assess for chromite-melt equilibrium for these parts of the extrusive sequence.

SPINMELT-2.0 was used to model equilibrium chromite compositions in a similar way as in the experimental scenario discussed above. Physiochemical variables were set to approximate eruption conditions with pressure set to 0.5 kbar, which corresponds to a water depth of 5000 meters (inferred eruption condition, Woelki et al., 2020), and the fO_2 of the system was set to QFM+0.25 (*c.* NNO-0.5), QFM+0.75 (*c.* NNO), and QFM+1.25 (*c.* NNO+0.5). This range compares well with the natural range of fO_2 for the Troodos magmas; crystallization of olivine + chromite occurred at fugacities slightly above QFM+0.25 (Golowin et al., 2017); and glasses recovered from a Troodos “upper pillow lava” (Rautenschlein et al., 1985) have Fe^{2+}/Fe^{3+} (recalculated to molar ratios) that return fO_2 values $\geq$ QFM+1.35 (NNO+0.6) using

a pressure of 0.5 kbar, a temperature of 1130°C (upper limit of eruption temperature given by Golowin et al., 2017), a rearranged equation 7 from Kress and Carmichael (1991), and the fugacity conversions of Frost (1991), providing a reasonable estimate for the upper limit for our fugacity setting.

SPINMELT-2.0 output was treated in a similar way as the experimental data (Supplemental Text 4). When $f\text{O}_2$ is provided, melt $\text{Fe}^{2+}/\text{Fe}^{3+}$ is calculated internally and used to model chromite composition. Since temperature is not provided to the program, it must be predicted by the algorithm to provide a chromite composition estimate for each input melt composition. For these lavas, liquid temperatures have been inferred to vary between *c.* 1030-1130°C (Golowin et al., 2017). These temperatures are consistent with temperatures inferred from viscosity models (Schouten and Kelemen, 2002) generated for lavas on the North side of the extrusive sequence and with independent thermometry (inferred to provide a quantification of closure temperature) performed by Dare et al. (2009) for the Kalavassos Mine locality. SPINMELT-2.0 output was observed to lie within 25°C of this temperature range for a majority of the glass samples (Table S6) for each $f\text{O}_2$ condition. Thus, we inferred that our models faithfully replicated equilibrium conditions for chromite-melt at the time of eruption.

Figure 8 illustrates the relationships between modelled and observed chromite compositions of the Troodos (cf. Figure 5). Sample glass recovered from the Kalavassos Mine produced one major cluster for each $f\text{O}_2$ condition and one Al-rich glass sample displaced modelled chromite compositions to higher Al and lower Cr. All glass samples were determined to be “tholeiitic” by Woelki et al. (2020). All of the matrix chromite compositions observed for this locality are similar to olivine-hosted chromite inclusions observed in these same lavas (Golowin et al., 2017). A single natural chromite composition is displaced to higher Al compared with the others. However, according to our models, all of these chromite

compositions are too Cr-rich and require $\text{Fe}^{3+}+\text{Al}$ incorporation to be in equilibrium with residual melts.

Woelki et al. (2020) determined that the glass samples recovered from the Kapilio locality range from boninitic to tholeiitic in composition. The chromite data from this locality include the most chromian spinel (*s.l.*) analysis from the Troodos sample suite (Cameron, 1985) and three relatively simple (number of elements reported = 4) analyses of chromite given by Flower and Levine (1987). These compositions are also far from the modelled chromite compositions. As with the samples from the Kalavassos Mine, $\text{Fe}^{3+}+\text{Al}$ incorporation is required for re-equilibration. If a tie line is drawn through the natural samples from the Cr apex, it would intersect the model array at the point where the data generated at QFM+0.75 touches the data generated at QFM+1.25.

Finally, chromites taken from the Margi locality exhibit a compositional trend that is similar to that observed in the data from the Kapilio suite. Glasses taken from this locality produced a high-Al and low-Al trend, which reflects a modest separation of the glass data into more and less differentiated populations, respectively. Chromite core analyses given by Bailey et al. (1991) lie in roughly the same area as those of the Kalavassos Mine. However, rim analyses reported in this study are displaced to higher Fe^{3+} concentrations with a single analysis reaching the Fe^{3+} proportion inferred for chromite in equilibrium with melt at QFM+0.75. However, for this mineral rim, Cr-Al interdiffusion must also occur to reach the Al concentration inferred to represent an equilibrium composition. Thus, we conclude that the chromites observed in the Troodos extrusive suite were not in equilibrium with their residual melt compositions at the time of eruption, but in multiple localities these minerals were likely in a state of active equilibration (via diffusion) at the time they were erupted.

Regarding Fe^{2+} , slowly cooled chromites lose Mg to coexisting ferromagnesian silicates
 (Ozawa, 1984), while rapidly quenched mineral pairs preserve high-temperature
 compositions (e.g. Scowen et al., 1991). Since the glasses sampled from the Troodos rapidly
 quenched upon eruption (e.g. Robinson et al., 1983), chromite Mg# may have been
 preserved. By focusing on a single locality where glass, opx, and chromite data exist, we may
 treat natural samples in the same way as the experimental products above and test for system
 Fe^{2+} -Mg equilibrium. To this end, we refocus on the Kapilio locality. Glass data from this site
 (Woelki et al., 2020) were processed to predict $K_D(\text{Fe-Mg})^{\text{opx-liq}}$ values using equation 1.
 Mineral data from this locality are from Flower and Levine (1987). In total, two opx and
 three chromite compositions were used (their sample AM-4, Table 5). Unfortunately, there is
 no way of determining if these materials come from the same outcrops as the glass, which is
 why all glass data were used in modelling. Based on model physiochemical constraints
 outlined above, the opx sampled by Flower and Levine (1987) is in equilibrium with residual
 melts (within 1σ of the mean model $K_D(\text{Fe-Mg})^{\text{opx-liq}}$ value). Using a median $Y_{\text{Cr}}^{\text{chrom}}$ for the
 matrix chromites (0.70), model $K_D(\text{Fe-Mg})^{\text{chrom-opx}}$ values (calculated using equation 2) are
 observed to vary between *c.* 4.68-4.96 at 1130°C and 0.5 kbar and 5.41-5.86 at 1030°C and
 0.5 kbar (Table 5). Varying $Y_{\text{Cr}}^{\text{chrom}}$ by 0.1 (the actual variation observed among the sample
 chromites) causes these model K_D values to vary by ± 0.07 (*c.* $\pm 3\%$), which is roughly one
 half of the magnitude of the uncertainty associated with the model parameters. Observed
 $K_D(\text{Fe-Mg})^{\text{chrom-opx}}$ values are found to vary between 4.8 and 7.3 depending on which
 chromite-opx pair is used. Two of the three chromite grains are seen to be in equilibrium with
 at least one of the opx grains based on these K_D models. One other chromite grain in this
 sample returned high observed K_D values for both opx grains, reflecting low MgO
 concentrations. This chromite also has a low total EPMA composition (94.79) compared to
 the other analyses (*c.* 98). Regardless, it is remarkable, given the dearth of mineral data

available for the Troodos extrusive sequence, that any equilibrium condition could be established at all. These findings further the point that more mineral data should be gathered from the Troodos ophiolite and other natural chromite-bearing rocks to assess for mineral-mineral/mineral-melt equilibrium.

The effects of natural quench crystallization and syn-eruptive microlite growth on modelling equilibrium chromite composition also needs to be considered. Depending on the Fe-Mg ratio of the minerals that crystallize, Fe^{2+} may be enriched or depleted in the residual melt. Using equilibrium exchange coefficients (e.g. Putirka, 2008), the crystallization of ferromagnesian silicates like olivine and opx are expected to enrich melts in FeO relative to MgO, and the differentiation of melt by these minerals should modestly enrich Fe^{3+} over Fe^{2+} (Birner et al., 2018; Kelley and Cottrell, 2012; O'Neill et al., 2018; Shorttle et al., 2015). Melt Al_2O_3 is expected to increase with the equilibrium crystallization of ferromagnesian silicates. Based on observations of the experimental products made at 1200°C, melt Al_2O_3 concentrations were not significantly affected by quench crystallization (Table 3). Although this effect will depend on the volume of crystallization produced during quenching, which was not constrained, we do not expect minor degrees of quench crystallization to significantly affect melt Al_2O_3 unless an aluminous phase crystallizes. In some relatively differentiated Troodos lavas, plagioclase feldspar is observed (Flower and Levine, 1987; Schmincke et al., 1983). Feldspar crystallization is expected to reduce melt Al_2O_3 and thus modelled chromite Al_2O_3 concentrations, which would cause observed chromite compositions to appear closer to equilibrium. Instead, we propose that (i) the higher chromite Al concentrations predicted by our modelling (Figure 8) reflect Al_2O_3 enrichment in the magmas (and thus the absence of plagioclase in glasses sampled by Woelki et al., 2020) that comprise the Troodos extrusive sequence, which is consistent with the predominate silicate mineral assemblages observed therein; namely olivine, olivine+cpx, or olivine+opx+cpx (Flower and Levine, 1987; Malpas

and Langdon, 1984; Schmincke et al., 1983), and that (ii) quench crystallization does not significantly affect these data. Since the most primitive glasses sampled by Woelki et al. (2018) were observed to classify as boninite liquids, we infer that the most Cr-rich equilibrium chromite compositions in our models (Figure 8), which correspond to these relatively primitive melt compositions, represent chromite compositions that genuinely reflect the equilibrium composition of chromite in melts unaffected by quench/syn-eruptive crystallization.

5.4. *Estimation of maximum/minimum ascent time through diffusion modelling*

Since stable chromite was driven into chemical disequilibrium during magmatic differentiation, remained in a state of disequilibrium with respect to trivalent cation proportions at the time of eruption, and equilibrated with co-existing silicate minerals with respect to Fe-Mg exchange (divalent cation proportion), magma ascent time may be estimated on the basis of disequilibrium/equilibrium between chromite and the equilibrium condition defined by the physiochemical state of the residual melts. Here, the maximum ascent time was modelled based on the lowest interdiffusivity for the chromite compositional system (D_{Cr-Al}), and minimum ascent time was modelled based on the highest interdiffusivity (D_{Fe-Mg}).

Based on chromite-melt behaviour modelled above and observed in the mafic lavas of the extrusive suite of the Troodos ophiolite, we estimated the maximum and minimum ascent times by calculating the time (t) it would take to equilibrate a hypothetical groundmass chromite microphenocryst [30-60 μm diameter with a composition similar to those of primitive chromite microphenocryst cores and mineral inclusions from the Kalavassos Mine locality (Figure 8, Golowin et al., 2017; Sobolev et al., 1993)] with residual melt under the inferred eruptive conditions using the following relationship from Crank (1975):

784 $\tau = Dt/a^2$ Equation 3

785 where a is the crystal radius, t is time, τ is non-dimensional time, and D is the interdiffusion
786 coefficient.

787 D_{Cr-Al} , the interdiffusivity coefficient of Cr-Al in chromite, is positively correlated with both
788 temperature and Cr# (Suzuki et al., 2008). For this reason, we calculated D_{Cr-Al} for chromite
789 with Cr# = 80 at 1030°C and 1130°C by extrapolating the relationships illustrated in Figures 5
790 and 10 of Suzuki et al. (2008) to low temperatures. In detail, we reproduced the Arrhenius
791 plot of Suzuki et al. (2008) for chromite with Cr# = 80 and fit linear equations to their
792 diffusivity data to predict $\log D_{Cr-Al}$ as a function of temperature (Supplemental Text 5). The
793 following equation was recovered:

794 $\log D_{Cr-Al} = -2.4199\left(\frac{10^4}{T(K)}\right) + 2.3902$ Equation 4

795 Using this equation, we estimate $\log D_{Cr-Al}$ (cm²/s) to be -16.2 at 1030°C and -14.9 at 1130°C
796 (Table 6).

797 We elected to use self-diffusion coefficients from Liermann and Ganguly (2002) to estimate
798 $\log D_{Fe-Mg}$ at the same conditions as $\log D_{Cr-Al}$. We also reproduced their Arrhenius plots for
799 both Fe and Mg self-diffusion (Supplemental Text 5) and then used their equation 4 to
800 calculate an interdiffusivity coefficient, $\log D_{Fe-Mg}$. For this calculation, we used the following
801 linear equations recovered from their Arrhenius plots:

802 $\log D_{Fe} = -1.0322\left(\frac{10^4}{T(K)}\right) - 4.7506$ Equation 5

803 $\log D_{Mg} = -1.0545\left(\frac{10^4}{T(K)}\right) - 4.7125$ Equation 6

804 Using these equations and equation 4 of Liermann and Ganguly (2002), $\log D_{\text{Fe-Mg}}$ was
805 calculated to be -12.7 at 1030°C and -12.2 at 1130°C (Table 6).

806 With these D values, we calculated maximum ascent time using the simple equation for
807 diffusion in a sphere (equation 3) by assuming $\tau = 0.04$ (i.e. insignificant change in core
808 composition) and minimum ascent time by assuming $\tau = 0.4$ (i.e. complete re-equilibration,
809 Table 6). At 1030°C, in order to preserve a matrix chromite core whose Cr# = 80, a maximum
810 of *c.* 170 years can pass before the core of the chromite begins to equilibrate, which means
811 that the mafic lavas of the Troodos ophiolite, once extracted from their mantle source,
812 crystallized their silicate cargo and erupted in less than *c.* 170 years. If T is raised to 1130°C,
813 the maximum amount of time is reduced to 8 years. Since the interdiffusivity coefficient is
814 positively correlated with Cr#, if chromite has a lower Cr# than 80, then maximum ascent
815 time increases. In fact, when Cr# approaches 0, $D_{\text{Cr-Al}}$ approaches values two orders of
816 magnitude lower than when Cr# = 80 (Suzuki et al., 2008). Maximum ascent times would
817 increase accordingly. However, because the chromites of the Troodos presented here are
818 highly chromian, we expect our maximum ascent times to be within reason. We calculated
819 minimum ascent time (for the same hypothetical chromite grain) at 1030°C to be *c.* 220 days.
820 At 1130°C this value is lowered to 60 days. These back-of-the-envelope calculations
821 demonstrate that it will be possible to constrain the ascent rate of boninitic magmas through
822 study of diffusion profiles in matrix chromite crystals that they carry, and this should be done
823 systematically in future research.

824 Overall, the melt temperature data cited as independent observations for the Troodos
825 extrusive suite are corroborative, but it is important to discuss these data because temperature
826 exerts strong control over diffusion. The three methods of temperature estimation are based
827 on geochemical modelling (Dare et al., 2009; Golowin et al., 2017; Schouten and Kelemen,

2002). Golowin et al. (2017) used olivine-melt compositional data and the equilibrium relationships given by Ford et al. (1983) and Almeev et al. (2007) to quantify minimum crystallization temperatures, which they interpreted as eruption temperatures. Schouten and Kelemen (2002) used the geothermometer of Sisson and Grove (1993) to estimate temperature for their viscosity models. Finally, Dare et al. (2009) calculated temperature using the olivine-spinel thermometer of Ballhaus et al. (1991) and inferred this temperature as a closure temperature for chromite. Taken together, since the present discussion is focused on the kinetics of chromite-melt re-equilibration at pre-eruptive conditions, the estimates of Golowin et al. (2017) represent our preferred liquid temperatures because they are most likely to constrain melt temperatures prior to significant syn-eruptive crystallization of microlitic pyroxene. Granted, when significant pyroxene crystallization occurs, melt water concentrations assumed by Golowin et al. (2017) for Troodos glasses (*c.* 3 wt%) represent maxima and their temperatures minima following the liquidus depression relationships given by Almeev et al. (2007). Woelki et al. (2020) quantified water concentrations in boninite glasses to be 1.7-2.7 wt%, which is slightly below the value provided by Golowin et al. (2017). This means our models may use temperatures that are slightly underestimated. The consequence of this is that our model ascent rates may be minima under high-temperature conditions and that ascent times for the Troodos extrusive sequence may be higher than modelled here. The likelihood of lower liquid temperatures are low due to the high closure temperature of 1100°C inferred by Dare et al. (2009).

Additional complexity is added when considering the effect of changing Cr# during oxidation. Since $\log D_{\text{Cr-Al}}$ becomes lower as chromite loses Cr (Suzuki et al., 2008), since we elected to regress data provided for the highest Cr# chromites in the study of Suzuki et al. (2008) in order to estimate maximum ascent rate, and since natural chromites have slightly

less Cr (Table S5), our maximum ascent times may be underestimated. This is an additional knowledge gap that should be addressed with future experimental work.

Because primitive compositional characteristics of the oxide mineral cargo are retained in several chromite crystals in the matrices of lavas of the Troodos ophiolite extrusive sequence and because, in some cases, mineral textures relating to diffusive equilibration seem to be preserved, we propose that chromites in such boninitic-tholeiitic lavas are products of either (i) crystallization from primary magmas or the incongruent melting reaction that is known to produce olivine + chromite in the shallow sub-arc mantle, or (ii) crystallization in complex fluid-melt or melt-melt mixtures in the same part of the magmatic system. In either case, chromite is likely precipitated prior to extensive pyroxene crystallization, as melt fractionation by pyroxene tends to compromise chromite stability in some igneous systems (e.g. layered mafic intrusions or ocean island basalts, Irvine, 1967; Roeder, 1994). Such behaviour appears to be absent in boninites and tholeiites associated with ophiolitic terranes such as the Troodos or the forearc regions of intra-oceanic arc systems (e.g. Whattam et al., 2020). In these rocks, matrix chromite appears with stable pyroxene minerals as euhedral-subhedral mineral grains with no signs of resorption or breakdown. Thus, chromite is most likely a primitive component of the boninite-tholeiite petrogenetic system that perseveres through differentiation in arc systems and likely records compositional traits that reflect the full range of physiochemical states these magmas undergo prior to eruption (Figure 9).

In our petrogenetic model, synthesized in Figure 9, chromite forms in equilibrium with primitive boninitic melt prior to the growth of many silicate minerals (Figure 9B) and has a primitive composition characterized by high Mg# and Y_{Cr} (Stage 1). Once silicate minerals nucleate (Figure 9C), chromite Mg# will immediately begin to re-equilibrate, as this parameter is highly sensitive to the presence of ferromagnesian silicates (Stage 2). As these

silicates grow, melt oxidation occurs, and Fe^{3+} -Al exchange begins (Stage 3, Figure 9D). Finally, Cr exchange begins to occur with Fe^{3+} and Al (such that chromite Fe^{3+}/Al remains constant, Figure 7B) and the volume of chromite at the edge of the grain reaches an equilibrium state with melt prior to eruption (Stage 4). If this chromite grain is entrained in an ascending melt that is quenched upon eruption, then the differential diffusivities of the major trivalent cations in chromite can be interpreted in a chronometric context (Figure 9E). Careful analysis of chromite should include a quantification of Fe-speciation (see EPMA methodology of Davis and Cottrell, 2018) so that precise thermometry and fugacity information can be inferred from natural samples.

6. CONCLUSIONS

- 1) The experiments presented here enabled us to infer the kinetic behaviour of chromite in boninitic melt. Pyroxene is a ubiquitous component of the experimentally synthesized boninites, and residual melts are andesitic in composition. Matrix glasses preserved in natural boninites (Coulthard Jr et al., 2021; Woelki et al., 2020) demonstrate that olivine $\pm$ pyroxene crystallization commonly generates residual melts that are basaltic andesitic to andesitic in composition, similar to the products of these crystallization experiments.
- 2) The fact that these same natural glasses are enriched in Fe^{3+} upon eruption (Brounce et al., 2019; Rautenschlein et al., 1985) suggests that primitive boninitic melts (i) crystallize chromite under less oxidizing conditions than those characteristic of the pre-eruptive crustal column and within what are likely complex melt-fluid/melt-melt mixtures present in the sub-arc or back-arc mantle, (ii) crystallize olivine/pyroxene phenocrysts under magmatic conditions without significant chromite crystallization in the crust, and (iii) entrain most of their chromite crystal cargo prior to microlitic

growth during ascent and eruption, to produce natural boninites and derived andesitic-basaltic andesitic glasses.

- 3) If chromite, including microlitic matrix chromite, were to crystallize from these residual liquids, then they would incorporate more Fe^{3+} and Al than observed, as shown by the natural samples taken from the extrusive sequence of the Troodos Ophiolite. Thus, most chromites are products of primitive melt crystallization in the crustal domain or of the incongruent melting of orthopyroxene in the mantle domain. When entrained in an evolving magma, melt oxidation perturbs the equilibrium chromite composition to higher Fe^{3+} . If sufficiently oxidizing conditions are achieved, Fe^{3+} replaces Al efficiently such that $\text{Fe}^{2+}/\text{Fe}^{3+} + \text{Fe}^{3+}/\text{Al}$ chromite-melt equilibrium is approached. The disequilibrium textures and compositions preserved in some phenocrystic-microphenocrystic chromites should be examined closely to ascertain ascent rates using Fe^{3+} diffusivity.
- 4) In chromite, Cr-Al/ Fe^{3+} equilibrium is achieved over much longer timescales. If considered the limiting factor of chromite-melt equilibration, natural microphenocrystic chromite observed in the extrusive suite of the Troodos ophiolite would equilibrate with residual melts in less than *c.* 170 years. Diffusion may be much more rapid, and future work on the diffusive equilibration of both experimental and natural chromites should provide tighter constraints.

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927 **REFERENCES**

- 928 Almeev, R.R., Holtz, F., Koepke, J.r., Parat, F. and Botcharnikov, R.E. (2007) The effect of
 929 H₂O on olivine crystallization in MORB: Experimental calibration at 200 MPa. *American*
 930 *Mineralogist* 92, 670-674.
- 931 Arai, S. (1994) Characterization of spinel peridotites by olivine-spinel compositional
 932 relationships: Review and interpretation. *Chemical Geology* 113, 191-204.
- 933 Arai, S. (1997) Origin of podiform chromitites. *Journal of Asian Earth Sciences* 15, 303-310.
- 934 Arai, S. and Yurimoto, H. (1994) Podiform chromitites of the Tari-Misaka ultramafic
 935 complex, southwestern Japan, as mantle-melt interaction products. *Economic Geology* 89,
 936 1279-1288.
- 937 Arai, S. and Yurimoto, H. (1995) Possible sub-arc origin of podiform chromitites. *Isl. Arc* 4,
 938 104-111.
- 939 Arganda-Carreras, I., Kaynig, V., Rueden, C., Eliceiri, K.W., Schindelin, J., Cardona, A. and
 940 Sebastian Seung, H. (2017) Trainable Weka Segmentation: a machine learning tool for
 941 microscopy pixel classification. *Bioinformatics* 33, 2424-2426.
- 942 Bailey, D.G., Langdon, G.S., Malpas, J. and Robinson, P.T. (1991) Ultramafic and related
 943 lavas from the Margi area, Troodos ophiolite, in: Gibson, I.L., Malpas, J., Robinson, P.T.,
 944 Xenophontos, C. (Eds.), *Cyprus Crustal Study Project: Initial Report, Holes Cy-1 and 1a*.
 945 *Geological Survey of Canada*, pp. 187-202.
- 946 Ballhaus, C. (1998) Origin of podiform chromite deposits by magma mingling. *Earth and*
 947 *Planetary Science Letters* 156, 185-193.
- 948 Ballhaus, C., Berry, R.F. and Green, D.H. (1991) High pressure experimental calibration of
 949 the olivine-orthopyroxene-spinel oxygen geobarometer: implications for the oxidation state
 950 of the upper mantle. *Contributions to Mineralogy and Petrology* 107, 27-40.
- 951 Beattie, P., Ford, C. and Russell, D. (1991) Partition coefficients for olivine-melt and
 952 orthopyroxene-melt systems. *Contributions to Mineralogy and Petrology* 109, 212-224.
- 953 Bédard, J.H. (1999) Petrogenesis of Boninites from the Betts Cove Ophiolite, Newfoundland,
 954 Canada: Identification of Subducted Source Components. *Journal of Petrology* 40, 1853-
 955 1889.
- 956 Birner, S.K., Cottrell, E., Warren, J.M., Kelley, K.A. and Davis, F.A. (2018) Peridotites and
 957 basalts reveal broad congruence between two independent records of mantle fO₂ despite local
 958 redox heterogeneity. *Earth and Planetary Science Letters* 494, 172-189.
- 959 Bloomer, S.H. and Hawkins, J.W. (1987) Petrology and geochemistry of boninite series
 960 volcanic rocks from the Mariana trench. *Contributions to Mineralogy and Petrology* 97, 361-
 961 377.
- 962 Blundy, J. and Cashman, K. (2005) Rapid decompression-driven crystallization recorded by
 963 melt inclusions from Mount St. Helens volcano. *Geology* 33, 793-796.

- Brandon, A.D. and Draper, D.S. (1996) Constraints on the origin of the oxidation state of mantle overlying subduction zones: An example from Simcoe, Washington, USA. *Geochimica et Cosmochimica Acta* 60, 1739-1749.
- Brounce, M., Reagan, M.K., Coulthard Jr., D.A., Kelley, K.A. and Cottrell, E. (2019) The oxidation states of iron and volatile compositions of Expedition 352 glasses, Goldschmidt 2019, Barcelona, Spain.
- Burnham, C.W. (1979) The importance of volatile constituents, in: Yoder, H.S., Jr. (Ed.), *The evolution of the igneous rocks*. Princeton University Press, Princeton, New Jersey, pp. 439-482.
- Cameron, W.E. (1985) Petrology and origin of primitive lavas from the Troodos ophiolite, Cyprus. *Contributions to Mineralogy and Petrology* 89, 239-255.
- Cashman, K. and Blundy, J. (2000) Degassing and crystallization of ascending andesite and dacite. *Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences* 358, 1487-1513.
- Chou, I.M., Eugster, H.P., Berens, P. and Weare, J.H. (1978) Diffusion of hydrogen through platinum membranes at high pressures and temperatures. *Geochimica et Cosmochimica Acta* 42, 281-288.
- Cottrell, E., Birner, S., Brounce, M., Davis, F.A., Waters, L.E. and Kelley, K.A. (2020) Oxygen Fugacity Across Tectonic Settings, in: Neuville, D.R., Moretti, R. (Eds.), *AGU Geophysical Monograph Redox variables and mechanisms in magmatism and volcanism*. Wiley.
- Couch, S., Sparks, R.S.J. and Carroll, M.R. (2001) Mineral disequilibrium in lavas explained by convective self-mixing in open magma chambers. *Nature* 411, 1037-1039.
- Coulthard Jr, D.A., Reagan, M.K., Shimizu, K., Bindeman, I.N., Brounce, M., Almeev, R.R., Ryan, J., Chapman, T., Shervais, J. and Pearce, J.A. (2021) Magma Source Evolution Following Subduction Initiation: Evidence From the Element Concentrations, Stable Isotope Ratios, and Water Contents of Volcanic Glasses From the Bonin Forearc (IODP Expedition 352). *Geochemistry, Geophysics, Geosystems* 22, doi: [10.1029/2020GC009054](https://doi.org/10.1029/2020GC009054).
- Crank, J. (1975) *The Mathematics of Diffusion*. Oxford University Press, London.
- Dare, S.A.S., Pearce, J.A., McDonald, I. and Styles, M.T. (2009) Tectonic discrimination of peridotites using fO_2 -Cr# and Ga-Ti-Fe^{III} systematics in chrome-spinel. *Chemical Geology* 261, 199-216.
- Davis, F.A. and Cottrell, E. (2018) Experimental investigation of basalt and peridotite oxybarometers: Implications for spinel thermodynamic models and Fe³⁺ compatibility during generation of upper mantle melts. *American Mineralogist* 103, 1056-1067.
- Dilek, Y. and Thy, P. (2009) Island arc tholeiite to boninitic melt evolution of the Cretaceous Kizildag (Turkey) ophiolite: Model for multi-stage early arc-forearc magmatism in Tethyan subduction factories. *Lithos* 113, 68-87.

- 1002 Droop, G.T.R. (1987) A general equation for estimating Fe^{3+} concentrations in
 1003 ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria.
 1004 Mineralogical Magazine 51, 431-435.
- 1005 Edwards, S.J., Pearce, J.A. and Freeman, J. (2000) New insights concerning the influence of
 1006 water during the formation of podiform chromitite. Geological Society of America Special
 1007 Papers 349, 139-148.
- 1008 Evans, K.A., Elburg, M.A. and Kamenetsky, V.S. (2012) Oxidation state of subarc mantle.
 1009 Geology 40, 783-786.
- 1010 Falloon, T.J., Malahoff, A., Zonenshaina, L.P. and Bogdanova, Y. (1992) Petrology and
 1011 geochemistry of back-arc basin basalts from Lau Basin spreading ridges at 15°, 18° and 19°S.
 1012 Mineralogy and Petrology 47, 1-35.
- 1013 Ferracutti, G.R., Gargiulo, M.F., Ganuza, M.L., Bjerg, E.A. and Castro, S.M. (2015)
 1014 Determination of the spinel group end-members based on electron microprobe analyses.
 1015 Mineralogy and Petrology 109, 153-160.
- 1016 Fisk, M.R. (1986) Basalt magma interaction with harzburgite and the formation of high-
 1017 magnesium andesites. Geophysical Research Letters 13, 467-470.
- 1018 Flower, M.F.J. and Levine, H.M. (1987) Petrogenesis of a tholeiite-boninite sequence from
 1019 Ayios Mamas, Troodos ophiolite: evidence for splitting of a volcanic arc? Contributions to
 1020 Mineralogy and Petrology 97, 509-524.
- 1021 Ford, C., Russell, D., Craven, J. and Fisk, M. (1983) Olivine-liquid equilibria: temperature,
 1022 pressure and composition dependence of the crystal/liquid cation partition coefficients for
 1023 Mg, Fe^{2+} , Ca and Mn. Journal of Petrology 24, 256-266.
- 1024 Frost, B.R. (1991) Introduction to oxygen fugacity and its petrologic importance. Reviews in
 1025 Mineralogy and Geochemistry 25, 1-9.
- 1026 Gass, I.G. (1968) Is the Troodos Massif of Cyprus a Fragment of Mesozoic Ocean Floor?
 1027 Nature 220, 39-42.
- 1028 Gervilla, F., Asta, M.P., Fanlo, I., Grolimund, D., Ferreira-Sánchez, D., Samson, V.A.,
 1029 Hunziker, D., Colas, V., González-Jiménez, J.M., Kerestedjian, T.N. and Sergeeva, I. (2019)
 1030 Diffusion pathways of Fe^{2+} and Fe^{3+} during the formation of ferrian chromite: a μXANES
 1031 study. Contributions to Mineralogy and Petrology 174, 65.
- 1032 Ghiorso, M.S. and Sack, R.O. (1995) Chemical mass transfer in magmatic processes IV. A
 1033 revised and internally consistent thermodynamic model for the interpolation and
 1034 extrapolation of liquid-solid equilibria in magmatic systems at elevated temperatures and
 1035 pressures. Contributions to Mineralogy and Petrology 119, 197-212.
- 1036 Golowin, R., Portnyagin, M., Hoernle, K., Sobolev, A., Kuzmin, D. and Werner, R. (2017)
 1037 The role and conditions of second-stage mantle melting in the generation of low-Ti tholeiites
 1038 and boninites: the case of the Manihiki Plateau and the Troodos ophiolite. Contributions to
 1039 Mineralogy and Petrology 172, 104.

- 1040 Gualda, G.A., Ghiorso, M.S., Lemons, R.V. and Carley, T.L. (2012) Rhyolite-MELTS: a
 1041 modified calibration of MELTS optimized for silica-rich, fluid-bearing magmatic systems.
 1042 *Journal of Petrology* 53, 875-890.
- 1043 Hanson, B. and Jones, J.H. (1998) The systematics of Cr^{3+} and Cr^{2+} partitioning between
 1044 olivine and liquid in the presence of spinel. *American Mineralogist* 83, 669-684.
- 1045 Hodel, F., Macouin, M., Trindade, R.I.F., Araujo, J.F.D.F., Respaud, M., Meunier, J.F.,
 1046 Cassayre, L., Rousse, S., Drigo, L. and Schorne-Pinto, J. (2020) Magnetic Properties of
 1047 Ferritchromite and Cr-Magnetite and Monitoring of Cr-Spinels Alteration in Ultramafic and
 1048 Mafic Rocks. *Geochemistry, Geophysics, Geosystems* 21, doi: [10.1029/2020GC009227](https://doi.org/10.1029/2020GC009227).
- 1049 Irvine, T.N. (1967) Chromian spinel as a petrogenetic indicator. Part 2. Petrologic
 1050 applications. *Canadian Journal of Earth Sciences* 4, 71-103.
- 1051 Ishikawa, T., Nagaishi, K. and Umino, S. (2002) Boninitic volcanism in the Oman ophiolite:
 1052 Implications for thermal condition during transition from spreading ridge to arc. *Geology* 30,
 1053 899-902.
- 1054 Jarosewich, E., Nelen, J.A. and Norberg, J.A. (1980) Reference Samples for Electron
 1055 Microprobe Analysis*. *Geostandards Newsletter* 4, 43-47.
- 1056 Jégo, S., Pichavant, M. and Mavrogenes, J.A. (2010) Controls on gold solubility in arc
 1057 magmas: An experimental study at 1000 C and 4 kbar. *Geochimica et Cosmochimica Acta*
 1058 74, 2165-2189.
- 1059 Jochum, K.P., Stoll, B., Herwig, K., Willbold, M., Hofmann, A.W., Amini, M., Aarburg, S.,
 1060 Abouchami, W., Hellebrand, E., Mocek, B., Raczek, I., Stracke, A., Alard, O., Bouman, C.,
 1061 Becker, S., Dücking, M., Brätz, H., Klemm, R., de Bruin, D., Canil, D., Cornell, D., de Hoog,
 1062 C.-J., Dalpé, C., Danyushevsky, L., Eisenhauer, A., Gao, Y., Snow, J.E., Groschopf, N.,
 1063 Günther, D., Latkoczy, C., Guillong, M., Hauri, E.H., Höfer, H.E., Lahaye, Y., Horz, K.,
 1064 Jacob, D.E., Kasemann, S.A., Kent, A.J.R., Ludwig, T., Zack, T., Mason, P.R.D., Meixner,
 1065 A., Rosner, M., Misawa, K., Nash, B.P., Pfänder, J., Premo, W.R., Sun, W.D., Tiepolo, M.,
 1066 Vannucci, R., Vennemann, T., Wayne, D. and Woodhead, J.D. (2006) MPI-DING reference
 1067 glasses for in situ microanalysis: New reference values for element concentrations and
 1068 isotope ratios. *Geochemistry, Geophysics, Geosystems* 7.
- 1069 Jochum, K.P., Willbold, M., Raczek, I., Stoll, B. and Herwig, K. (2005) Chemical
 1070 Characterisation of the USGS Reference Glasses GSA-1G, GSC-1G, GSD-1G, GSE-1G,
 1071 BCR-2G, BHVO-2G and BIR-1G Using EPMA, ID-TIMS, ID-ICP-MS and LA-ICP-MS.
 1072 *Geostandards and Geoanalytical Research* 29, 285-302.
- 1073 Kamenetsky, V.S., Crawford, A.J. and Meffre, S. (2001) Factors controlling chemistry of
 1074 magmatic spinel: An empirical study of associated olivine, Cr-spinel and melt inclusions
 1075 from primitive rocks. *Journal of Petrology* 42, 655-671.
- 1076 Kamenetsky, V.S., Sobolev, A.V., Eggins, S.M., Crawford, A.J. and Arculus, R.J. (2002)
 1077 Olivine-enriched melt inclusions in chromites from low-Ca boninites, Cape Vogel, Papua
 1078 New Guinea: evidence for ultramafic primary magma, refractory mantle source and enriched
 1079 components. *Chemical Geology* 183, 287-303.

- 1080 Kelley, K.A. and Cottrell, E. (2009) Water and the Oxidation State of Subduction Zone
1081 Magmas. *Science* 325, 605-607.
- 1082 Kelley, K.A. and Cottrell, E. (2012) The influence of magmatic differentiation on the
1083 oxidation state of Fe in a basaltic arc magma. *Earth and Planetary Science Letters* 329-330,
1084 109-121.
- 1085 Klügel, A. (2001) Prolonged reactions between harzburgite xenoliths and silica-
1086 undersaturated melt: implications for dissolution and Fe-Mg interdiffusion rates of
1087 orthopyroxene. *Contributions to Mineralogy and Petrology* 141, 1-14.
- 1088 Kress, V.C. and Carmichael, I.S.E. (1991) The compressibility of silicate liquids containing
1089 Fe_2O_3 and the effect of composition, temperature, oxygen fugacity and pressure on their
1090 redox states. *Contributions to Mineralogy and Petrology* 108, 82-92.
- 1091 La Spina, G., Burton, M., de' Michieli Vitturi, M. and Arzilli, F. (2016) Role of syn-eruptive
1092 plagioclase disequilibrium crystallization in basaltic magma ascent dynamics. *Nature*
1093 *Communications* 7, 13402.
- 1094 Liermann, H.-P. and Ganguly, J. (2002) Diffusion kinetics of Fe^{2+} and Mg in aluminous
1095 spinel: experimental determination and applications. *Geochimica et Cosmochimica Acta* 66,
1096 2903-2913.
- 1097 Liermann, H.P. and Ganguly, J. (2003) Fe^{2+} -Mg fractionation between orthopyroxene and
1098 spinel: experimental calibration in the system $\text{FeO-MgO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-SiO}_2$, and
1099 applications. *Contributions to Mineralogy and Petrology* 145, 217-227.
- 1100 Lloyd, A.S., Ferriss, E., Ruprecht, P., Hauri, E.H., Jicha, B.R. and Plank, T. (2016) An
1101 Assessment of Clinopyroxene as a Recorder of Magmatic Water and Magma Ascent Rate.
1102 *Journal of Petrology* 57, 1865-1885.
- 1103 Lormand, C., Zellmer, G.F., Kilgour, G.N., Németh, K., Palmer, A.S., Sakamoto, N.,
1104 Yurimoto, H., Kuritani, T., Iizuka, Y. and Moebis, A. (2020) Slow ascent of unusually hot
1105 intermediate magmas triggering Strombolian to sub-Plinian eruptions. *Journal of Petrology*.
- 1106 MacLeod, C.J. (1988) The tectonic evolution of the Eastern Limassol Forest Complex,
1107 Cyprus, Department of Earth Sciences. The Open University.
- 1108 Malpas, J. and Langdon, G. (1984) Petrology of the Upper Pillow Lava suite, Troodos
1109 ophiolite, Cyprus. Geological Society, London, Special Publications 13, 155-167.
- 1110 Mattioli, M., Renzulli, A., Menna, M. and Holm, P.M. (2006) Rapid ascent and
1111 contamination of magmas through the thick crust of the CVZ (Andes, Ollagüe region):
1112 Evidence from a nearly aphyric high-K andesite with skeletal olivines. *Journal of*
1113 *Volcanology and Geothermal Research* 158, 87-105.
- 1114 Matveev, S. and Ballhaus, C. (2002) Role of water in the origin of podiform chromitite
1115 deposits. *Earth and Planetary Science Letters* 203, 235-243.
- 1116 Maurel, C. and Maurel, P. (1982) Étude expérimentale de l'équilibre Fe^{2+} - Fe^{3+} dans les
1117 spinelles chromifères et les liquides silicatés basiques coexistants, à 1 atm. *Comptes Rendus*
1118 *des Séances de l'Académie des Sciences* 295.

- 1119 Meffre, S., Aitchison, J.C. and Crawford, A.J. (1996) Geochemical evolution and tectonic
1120 significance of boninites and tholeiites from the Koh ophiolite, New Caledonia. *Tectonics* 15,
1121 67-83.
- 1122 Meijer, A. (1980) Primitive arc volcanism and a boninite series: examples from western
1123 Pacific island arcs, in: Hayes, D.E. (Ed.), *The Tectonic and Geologic Evolution of Southeast*
1124 *Asian Seas and Islands*. American Geophysical Union, pp. 269-282.
- 1125 Metcalf, R.V. and Shervais, J.W. (2008) Suprasubduction-zone ophiolites: Is there really an
1126 ophiolite conundrum? *Special Papers-Geological Society of America* 438, 191.
- 1127 Mitchell, A.L. and Grove, T.L. (2016) Experiments on melt–rock reaction in the shallow
1128 mantle wedge. *Contributions to Mineralogy and Petrology* 171, 107.
- 1129 Miyashiro, A. (1973) The Troodos ophiolitic complex was probably formed in an island arc.
1130 *Earth and Planetary Science Letters* 19, 218-224.
- 1131 Moores, E.M., Kellogg, L.H. and Dilek, Y. (2000) Tethyan ophiolites, mantle convection,
1132 and tectonic" historical contingency": A resolution of the" ophiolite conundrum". *Geological*
1133 *Society of America Special Papers* 349, 3-12.
- 1134 Nikolaev, G.S., Ariskin, A.A. and Barmina, G.S. (2018a) SPINMELT-2.0: Simulation of
1135 spinel–melt equilibrium in basaltic systems under pressures up to 15 kbar: I. model
1136 formulation, calibration, and tests. *Geochemistry International* 56, 24-45.
- 1137 Nikolaev, G.S., Ariskin, A.A. and Barmina, G.S. (2018b) SPINMELT-2.0: Simulation of
1138 Spinel–Melt Equilibrium in Basaltic Systems under Pressures up to 15 Kbar: II. Description
1139 of the Program Package, the Topology of the Cr-spinel–Melt Model System, and Petrological
1140 Implications. *Geochemistry International* 56, 125-135.
- 1141 O'Neill, H.S.C., Berry, A.J. and Mallmann, G. (2018) The oxidation state of iron in Mid-
1142 Ocean Ridge Basaltic (MORB) glasses: Implications for their petrogenesis and oxygen
1143 fugacities. *Earth and Planetary Science Letters* 504, 152-162.
- 1144 Ohnenstetter, M., Bechon, F. and Ohnenstetter, D. (1990) Geochemistry and mineralogy of
1145 lavas from the Arakapas Fault Belt, Cyprus: Consequences for magma chamber evolution.
1146 *Mineralogy and Petrology* 41, 105-124.
- 1147 Ozawa, K. (1984) Olivine-spinel geospeedometry: Analysis of diffusion-controlled Mg-Fe²⁺
1148 exchange. *Geochimica et Cosmochimica Acta* 48, 2597-2611.
- 1149 Parkinson, I.J. and Arculus, R.J. (1999) The redox state of subduction zones: insights from
1150 arc-peridotites. *Chemical Geology* 160, 409-423.
- 1151 Pearce, J.A. and Reagan, M.K. (2019) Identification, classification, and interpretation of
1152 boninites from Anthropocene to Eoarchean using Si-Mg-Ti systematics. *Geosphere* 15, 1008-
1153 1037.
- 1154 Pearce, J.A. and Robinson, P.T. (2010) The Troodos ophiolitic complex probably formed in a
1155 subduction initiation, slab edge setting. *Gondwana Research* 18, 60-81.

- 1156 Pownceby, M.I. and O'Neill, H.S.C. (1994) Thermodynamic data from redox reactions at
 1157 high temperatures. III. Activity-composition relations in Ni-Pd alloys from EMF
 1158 measurements at 850–1250 K, and calibration of the NiO+Ni-Pd assemblage as a redox
 1159 sensor. *Contributions to Mineralogy and Petrology* 116, 327-339.
- 1160 Putirka, K.D. (2008) Thermometers and Barometers for Volcanic Systems. *Reviews in*
 1161 *Mineralogy and Geochemistry* 69, 61-120.
- 1162 Rautenschlein, M., Jenner, G.A., Hertogen, J., Hofmann, A.W., Kerrich, R., Schmincke, H.U.
 1163 and White, W.M. (1985) Isotopic and trace element composition of volcanic glasses from the
 1164 Akaki Canyon, Cyprus: implications for the origin of the Troodos ophiolite. *Earth and*
 1165 *Planetary Science Letters* 75, 369-383.
- 1166 Reagan, M.K., Ishizuka, O., Stern, R.J., Kelley, K.A., Ohara, Y., Blichert-Toft, J., Bloomer,
 1167 S.H., Cash, J., Fryer, P., Hanan, B.B., Hickey-Vargas, R., Ishii, T., Kimura, J.-I., Peate,
 1168 D.W., Rowe, M.C. and Woods, M. (2010) Fore-arc basalts and subduction initiation in the
 1169 Izu-Bonin-Mariana system. *Geochemistry Geophysics Geosystems* 11.
- 1170 Reagan, M.K. and Meijer, A. (1984) Geology and geochemistry of early arc-volcanic rocks
 1171 from Guam. *GSA Bulletin* 95, 701-713.
- 1172 Reagan, M.K., Pearce, J.A., Petronotis, K., Almeev, R.R., Avery, A.J., Carvallo, C.,
 1173 Chapman, T., Christeson, G.L., Ferré, E.C., Godard, M., Heaton, D.E., Kirchenbaur, M.,
 1174 Kurz, W., Kutterolf, S., Li, H., Li, Y., Michibayashi, K., Morgan, S., Nelson, W.R., Prytulak,
 1175 J., Python, M., Robertson, A.H.F., Ryan, J.G., Sager, W.W., Sakuyama, T., Shervais, J.W.,
 1176 Shimizu, K. and Whattam, S.A. (2017) Subduction initiation and ophiolite crust: new insights
 1177 from IODP drilling. *Int. Geol. Rev.* 59, 1439-1450.
- 1178 Regelous, M., Haase, K.M., Freund, S., Keith, M., Weinzierl, C.G., Beier, C., Brandl, P.A.,
 1179 Endres, T. and Schmidt, H. (2014) Formation of the Troodos Ophiolite at a triple junction:
 1180 Evidence from trace elements in volcanic glass. *Chemical Geology* 386, 66-79.
- 1181 Robinson, P.T., Melson, W.G., O'Hearn, T. and Schmincke, H.-U. (1983) Volcanic glass
 1182 compositions of the Troodos ophiolite, Cyprus. *Geology* 11, 400-404.
- 1183 Roeder, P.L. (1994) Chromite; from the fiery rain of chondrules to the Kilauea Iki lava lake.
 1184 *The Canadian Mineralogist* 32, 729-746.
- 1185 Rollinson, H. (2008) The geochemistry of mantle chromitites from the northern part of the
 1186 Oman ophiolite: inferred parental melt compositions. *Contributions to Mineralogy and*
 1187 *Petrology* 156, 273-288.
- 1188 Rollinson, H., Mameri, L. and Barry, T. (2018) Polymineralic inclusions in mantle
 1189 chromitites from the Oman ophiolite indicate a highly magnesian parental melt. *Lithos* 310-
 1190 311, 381-391.
- 1191 Scaillet, B., Pichavant, M. and Roux, J. (1995) Experimental crystallization of leucogranite
 1192 magmas. *Journal of Petrology* 36, 663-705.
- 1193 Scaillet, B., Pichavant, M., Roux, J., Humbert, G. and Lefevre, A. (1992) Improvements of
 1194 the Shaw membrane technique for measurement and control of fH₂ at high temperatures and
 1195 pressures. *American Mineralogist* 77, 647-655.

- 1196 Schindelin, J., Arganda-Carreras, I., Frise, E., Kaynig, V., Longair, M., Pietzsch, T.,
 1197 Preibisch, S., Rueden, C., Saalfeld, S. and Schmid, B. (2012) Fiji: an open-source platform
 1198 for biological-image analysis. *Nature methods* 9, 676.
- 1199 Schmincke, H.-U., Rautenschlein, M., Robinson, P.T. and Mehegan, J.M. (1983) Troodos
 1200 extrusive series of Cyprus: A comparison with oceanic crust. *Geology* 11, 405-409.
- 1201 Schouten, H. and Kelemen, P.B. (2002) Melt viscosity, temperature and transport processes,
 1202 Troodos ophiolite, Cyprus. *Earth and Planetary Science Letters* 201, 337-352.
- 1203 Scowen, P.A.H., Roeder, P.L. and Helz, R.T. (1991) Reequilibration of chromite within
 1204 Kilauea Iki lava lake, Hawaii. *Contributions to Mineralogy and Petrology* 107, 8-20.
- 1205 Shaw, H.R. (1963) Hydrogen-Water Vapor Mixtures: Control of Hydrothermal Atmospheres
 1206 by Hydrogen Osmosis. *Science* 139, 1220-1222.
- 1207 Shorttle, O., Moussallam, Y., Hartley, M.E., MacLennan, J., Edmonds, M. and Murton, B.J.
 1208 (2015) Fe-XANES analyses of Reykjanes Ridge basalts: Implications for oceanic crust's role
 1209 in the solid Earth oxygen cycle. *Earth and Planetary Science Letters* 427, 272-285.
- 1210 Sisson, T.W. and Grove, T.L. (1993) Temperatures and H₂O contents of low-MgO high-
 1211 alumina basalts. *Contributions to Mineralogy and Petrology* 113, 167-184.
- 1212 Smith, P.M. and Asimow, P.D. (2005) Adibat_1ph: A new public front-end to the MELTS,
 1213 pMELTS, and pHMELTS models. *Geochemistry, Geophysics, Geosystems* 6.
- 1214 Sobolev, A., Portnyagin, M., Dmitriev, L., Tsameryan, O., Danyushevsky, L., Kononkova,
 1215 N., Shimizu, N. and Robinson, P. (1993) Petrology of ultramafic lavas and associated rocks
 1216 of the Troodos massif, Cyprus. *Petrology* 1, 331-361.
- 1217 Stern, R.J. and Bloomer, S.H. (1992) Subduction zone infancy: Examples from the Eocene
 1218 Izu-Bonin-Mariana and Jurassic California arcs. *GSA Bulletin* 104, 1621-1636.
- 1219 Suzuki, A.M., Yasuda, A. and Ozawa, K. (2008) Cr and Al diffusion in chromite spinel:
 1220 experimental determination and its implication for diffusion creep. *Phys. Chem. Miner.* 35,
 1221 433.
- 1222 Tatsumi, Y. (1981) Melting experiments on a high-magnesian andesite. *Earth and Planetary
 1223 Science Letters* 54, 357-365.
- 1224 Tatsumi, Y. (2006) High-Mg Andesites in the Setouchi Volcanic Belt, Southwestern Japan:
 1225 Analogy to Archean Magmatism and Continental Crust Formation? *Annual Review of Earth
 1226 and Planetary Sciences* 34, 467-499.
- 1227 Taylor, J.R., Wall, V.J. and Pownceby, M.I. (1992) The calibration and application of
 1228 accurate redox sensors. *American Mineralogist* 77, 284-295.
- 1229 Thy, P. and Xenophontos, C. (1991) Crystallization Orders and Phase Chemistry of Glassy
 1230 Lavas from the Pillow Sequences, Troodos Ophiolite, Cyprus. *Journal of Petrology* 32, 403-
 1231 428.

- 1232 Tomiya, A., Miyagi, I., Saito, G. and Geshi, N. (2013) Short time scales of magma-mixing
1233 processes prior to the 2011 eruption of Shinmoedake volcano, Kirishima volcanic group,
1234 Japan. *Bulletin of Volcanology* 75, 750.
- 1235 Ubide, T., Galé, C., Larrea, P., Arranz, E. and Lago, M. (2014) Antecrysts and their effect on
1236 rock compositions: The Cretaceous lamprophyre suite in the Catalanian Coastal Ranges (NE
1237 Spain). *Lithos* 206-207, 214-233.
- 1238 Umino, S. (1986) Magma mixing in boninite sequence of Chichijima, Bonin Islands. *Journal*
1239 *of Volcanology and Geothermal Research* 29, 125-157.
- 1240 Umino, S., Kanayama, K., Kitamura, K., Tamura, A., Ishizuka, O., Senda, R. and Arai, S.
1241 (2018) Did boninite originate from the heterogeneous mantle with recycled ancient slab? *Isl.*
1242 *Arc* 27, e12221.
- 1243 Umino, S., Kitamura, K., Kanayama, K., Tamura, A., Sakamoto, N., Ishizuka, O. and Arai, S.
1244 (2015) Thermal and chemical evolution of the subarc mantle revealed by spinel-hosted melt
1245 inclusions in boninite from the Ogasawara (Bonin) Archipelago, Japan. *Geology* 43, 151-154.
- 1246 Umino, S. and Kushiro, I. (1989) Experimental studies on boninite petrogenesis, in:
1247 Crawford, A.J. (Ed.), *Boninites: And Related Rocks*. Unwin and Hyman, London, pp. 89-
1248 111.
- 1249 Van Orman, J.A. and Crispin, K.L. (2010) Diffusion in Oxides. *Reviews in Mineralogy and*
1250 *Geochemistry* 72, 757-825.
- 1251 Vogt, K., Dohmen, R. and Chakraborty, S. (2015) Fe-Mg diffusion in spinel: New
1252 experimental data and a point defect model†. *American Mineralogist* 100, 2112-2122.
- 1253 Whattam, S.A., Shervais, J.W., Reagan, M.K., Coulthard Jr., D.A., Pearce, J.A., Jones, P.,
1254 Seo, J., Putirka, K., Chapman, T., Heaton, D., Li, H., Nelson, W.R., Shimizu, K. and Stern,
1255 R.J. (2020) Mineral compositions and thermobarometry of basalts and boninites recovered
1256 during IODP Expedition 352 to the Bonin forearc. *American Mineralogist*.
- 1257 Woelki, D., Michael, P., Regelous, M. and Haase, K. (2020) Enrichment of H₂O and fluid-
1258 soluble trace elements in the Troodos Ophiolite: Evidence for a near-trench origin. *Lithos*
1259 356-357, 105299.
- 1260 Woelki, D., Regelous, M., Haase, K.M., Romer, R.H.W. and Beier, C. (2018) Petrogenesis of
1261 boninitic lavas from the Troodos Ophiolite, and comparison with Izu–Bonin–Mariana fore-
1262 arc crust. *Earth and Planetary Science Letters* 498, 203-214.
- 1263 Wolf, K.J. and Eichelberger, J.C. (1997) Syneruptive mixing, degassing, and crystallization
1264 at Redoubt Volcano, eruption of December, 1989 to May 1990. *Journal of Volcanology and*
1265 *Geothermal Research* 75, 19-37.
- 1266 Yajima, K. and Fujimaki, H. (2001) High-Ca and low-Ca boninites from Chichijima, Bonin
1267 (Ogasawara) archipelago. *Japanese Magazine of Mineralogical and Petrological Sciences* 30,
1268 217-236.
- 1269 Zellmer, G.F., Sakamoto, N., Hwang, S.-L., Matsuda, N., Iizuka, Y., Moebis, A. and
1270 Yurimoto, H. (2016) Inferring the Effects of Compositional Boundary Layers on Crystal

- 1271 Nucleation, Growth Textures, and Mineral Chemistry in Natural Volcanic Tephra through
1272 Submicron-Resolution Imaging. *Frontiers in Earth Science* 4.
- 1273 Zellmer, G.F., Sakamoto, N., Iizuka, Y., Miyoshi, M., Tamura, Y., Hsieh, H.-H. and
1274 Yurimoto, H. (2014) Crystal uptake into aphyric arc melts: insights from two-pyroxene
1275 pseudo-decompression paths, plagioclase hygrometry, and measurement of hydrogen in
1276 olivines from mafic volcanics of SW Japan. *Geological Society, London, Special*
1277 *Publications* 385, SP385. 383.
- 1278 Zhang, Y., Xu, Z., Zhu, M. and Wang, H. (2007) Silicate melt properties and volcanic
1279 eruptions. *Reviews of Geophysics* 45.
- 1280 Zhou, M.-F. and Robinson, P.T. (1997) Origin and tectonic environment of podiform
1281 chromite deposits. *Economic Geology* 92, 259-262.
- 1282 Zhou, M.F., Robinson, P.T. and Bai, W.J. (1994) Formation of podiform chromitites by
1283 melt/rock interaction in the upper mantle. *Mineralium Deposita* 29, 98-101.
- 1284 Zhou, M.F., Robinson, P.T., Malpas, J. and Li, Z. (1996) Podiform chromitites in the
1285 Luobusa ophiolite (Southern Tibet): Implications for melt-rock interaction and chromite
1286 segregation in the upper mantle. *Journal of Petrology* 37, 3-21.
1287

Figure Captions

Figure 1: A) BSE image of Bon1150U. This image is representative of the “general” texture observed in the boninitic charges. This includes several examples of euhedral prismatic opx (dark mineral grains) and platy elongated opx (same colour) set in a relatively homogeneous glass with anhedral chromite (bright grains). The black orb-shaped parts are vapour bubbles. B) Close up of an opx cut parallel to the (010) plane exhibiting a ghost core (red ellipse). The core is likely related to crystallization occurring within the melt/glass phase before stable thermal conditions were achieved within the IHPV. The arrow points to bright caps that form at the apices of most if not all opx in this sample (from experiment Bon1200B). These caps are thought to have grown during quench. The glass adjacent to these minerals is darker, indicating the loss of iron to the quench-grown rim. C) Broad view of sample Bon1100U with calcic pyroxene highlighted (red ellipses). Several opx are aligned here, with their c-axes sub-perpendicular to the image plane. D) BSE image of chromite in Bon1150B after thresholding brightness and contrast to isolate and amplify Fe enrichment textures.

Figure 2: Cation proportion ($O = 6$) vs $Mg\#$ (calculated using Fe_{total}) for opx core analyses. Literature data are taken from sources listed in the text. Point uncertainties are within the boundaries of the symbol.

Figure 3: Chromite compositional data. A) A portion of a conventional ternary diagram illustrating the relative proportions of octahedrally coordinated trivalent cations after recalculation (dimensions of the ternary are illustrated on the inset). Literature data are taken from sources listed in the text. B) Diagram that illustrates Fe incorporation into both octahedral and tetrahedral sites using $Mg\#$ and the $Fe^{3+}/(Fe^{3+}+Al+Cr)$ parameter. Symbols same as Figure 2. Analytical uncertainties associated with each composition lie within the symbol boundaries.

Figure 4: A) Equilibrium exchange coefficients calculated for opx and residual melt. B) Equilibrium exchange coefficients for opx and chromite. Symbols as in Figure 2.

Figure 5: Results from MELTS and SPINMELT-2.0 modelling compared to experimental data (the edge of the ternary diagram from Figure 3A is shown as a dashed line). Lines are drawn in the direction of decreasing temperature from 1200°C to 1100°C. Solid symbols represent model data that do not account for iron loss, while empty symbols represent data generated using models with 30% imposed iron loss.

Figure 6: Comparison between average chromite $\text{Fe}^{2+}/\text{Fe}^{3+}$ observed in experimental charges and modelled equilibrium glass values of the same ratio (grey lines). For equilibrium conditions to be met, the symbols for each sample would need to lie below the grey lines.

Figure 7: Graphical representation of the chemical evolution of chromites within the compositional space of the spinel prism (inset). Hypothesized relationship: Fe-Mg interdiffusivity > Fe-Al interdiffusivity > Cr-(Al, Fe) interdiffusivity. If Fe-Mg and Fe-Al equilibrate chromite $\text{Mg}^\#$, $\text{Fe}^{2+}/\text{Fe}^{3+}$, and Fe^{3+}/Al , with Cr equilibration following, then re-equilibration is a process that may be approximated by reactions 1 and 2 in a multi-step fashion. A) Reaction 1 displaces chromite compositions to higher Fe^{2+}/Mg and Fe^{3+}/Al as the spinel (s.s.) component in chromite decreases. In ternary space, this reaction causes a shift to higher Fe^{3+} concentrations along lines of equal Cr proportion (B). Reaction 2 proceeds along lines of equal Fe^{3+}/Al (dashed grey line in B) as Cr is lost to the melt phase. Reaction 2 proceeds in a direction perpendicular to the page (up) in A.

Figure 8: Partial ternary diagrams (see inset) generated to compare trivalent cation proportions of natural chromite minerals from the Troodos ophiolite (green triangles) with modelled chromite compositions generated using SPINMELT-2.0. The grey-bordered green area underlying the green triangles on the Kalavassos Mine section represents the

1336 compositional range of olivine-hosted chromite inclusions taken from Golowin et al. (2017)
1337 and MacLeod (1988).

1338 **Figure 9:** Diagram summarizing the petrogenetic model wherein disequilibrium textures are
1339 preserved in phenocrystic-microphenocrystic chromite as a function of differences between
1340 the diffusivities of the major divalent and trivalent cations in chromite. A) Spinel octahedron.
1341 Subsequent images use a cross section of this hypothetical mineral form. B) A schematic of
1342 the initial condition of chromite in primitive boninite melt without a large proportion of
1343 silicate minerals. C) Silicate mineral nuclei form, immediately depleting the surrounding melt
1344 in Fe^{2+} and Mg. D) Silicate minerals grow and completely alter the surrounding melt. The
1345 melt has acquired an evolved residual composition rich in Fe^{3+} . E) Hypothetical diffusion
1346 trends for all major cations in chromite from a-a' (transect shown in D).

Table 1: Starting material compositions

	<i>High-Si Boninite</i> *YK0612 974-R6	<i>Troodos Chromitite</i> **Chromite Seed	<i>Boninite Glass</i> **BO-G	<i>Normalized Mixture Composition</i> BO-G with 2 wt% added Chromite
SiO ₂	56.74	0.05	57.92	55.51
TiO ₂	0.17	0.05	0.04	0.17
Cr ₂ O ₃	***0.19	53.81	0.19	1.26
Al ₂ O ₃	10.66	15.11	10.69	10.73
FeO	8.75	15.34	8.38	8.87
MnO	0.23	0.24	0.16	0.23
MgO	15.04	14.01	14.62	15.01
CaO	5.54	-	6.16	5.42
Na ₂ O	2.01	-	1.86	1.97
K ₂ O	0.82	-	0.46	0.80
P ₂ O ₅	0.03	-	0.08	0.03
Total	100.18	98.72	100.48	100.00

*Composition from Reagan et al. (2010, XRF Analysis)

**All analyses of starting materials are provided in the supplemental Tables S1 and S2

***Converted from ppm Cr to wt% Cr₂O₃

- = not quantified

Table 2: Sample identification and characterization, experiment descriptions, and preliminary results

Capsule ID	IHPV Lab	Initial Composition		Experimental Conditions			
		Seed Size (μm)	wt% D ₂ O (1 σ)	T ($^{\circ}\text{C}$)	P (kbar)	$p\text{H}_2^{\text{added}}$ (bars)	Duration (hrs)
Bon1200Ua	ISTO	$x < 32$	1.136 (0.142)	1200	2.13	0.0	4.0
Bon1200Ub	ISTO	$160 < x < 250$	1.395 (0.155)	1200	2.13	0.0	4.0
Bon1200Ba	ISTO	$x < 32$	0.916 (0.153)	1200	2.12	1.9	1.4
Bon1200Bb	ISTO	$160 < x < 250$	0.763 (0.191)	1200	2.12	1.9	1.4
Bon1150U	ISTO	$x < 32$	0.770 (0.128)	1150	2.16	0.0	4.2
Bon1150B	ISTO	$x < 32$	0.705 (0.141)	1150	2.14	1.4	3.2
Bon1100U	GSJ	$x < 32$	1.280 (0.142)	1100	2.00	0.0	5.1

Names: *U* = intrinsic $f\text{O}_2$, *B* = buffered $f\text{O}_2$, *a* and *b* designate a difference in the seed size of the chromite added

1348

Table 2 (continued)

Capsule ID	Product Phase Proportions (1 σ)			Activity Model		Oxygen Fugacity		
	Orthopyroxene	Chromite	Glass	Final wt% $^2\text{H}_2\text{O}$ (1 σ)	aH ₂ O (1 σ)	Sensor X_{Ni} (1 σ)	$\log f\text{O}_2$ (bars)	ΔNNO (1 σ)
Bon1200Ua	0.49 (0.01)	0.02 (0.01)	0.49 (0.02)	2.32 (0.30)	0.34 (0.07)	0.020 (0.004)	-3.69	3.81 (0.17)
Bon1200Ub	0.50 (0.03)	0.02 (0.00)	0.48 (0.03)	2.91 (0.37)	0.48 (0.08)	0.020 (0.004)	-3.39	4.11 (0.17)
Bon1200Ba	0.59 (0.07)	0.01 (0.00)	0.40 (0.07)	2.29 (0.55)	0.31 (0.11)	0.256 (0.003)	-6.77	0.73 (0.26)
Bon1200Bb	0.55 (0.01)	0.01 (0.01)	0.44 (0.01)	1.73 (0.44)	0.22 (0.08)	0.256 (0.003)	-7.07	0.43 (0.27)
Bon1150U	0.40 (0.08)	0.02 (0.00)	0.58 (0.08)	1.33 (0.29)	0.17 (0.07)	0.020 (0.004)	-4.88	3.21 (0.29)
Bon1150B	0.60 (0.06)	0.02 (0.00)	0.38 (0.05)	1.86 (0.44)	0.26 (0.09)	0.194 (0.003)	-7.09	1.00 (0.26)
Bon1100U	0.45 (0.05)	0.01 (0.01)	0.54 (0.05)	2.37 (0.34)	0.32 (0.07)	0.069 (0.009)	-6.21	2.52 (0.16)

Table 3: Representative compositional data of experiment products (average composition)

<i>Sample</i>	<i>Phase</i>	<i>No. Analyses</i>	SiO ₂	TiO ₂	Cr ₂ O ₃	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	NiO	Total	Mg#	Cr#	*Fe ²⁺ /Fe ³⁺
Bon1200Ua	Glass	6	61.36	0.07	bdl	16.34	5.90	0.10	2.43	6.51	3.08	0.81	-	96.63	-	-	0.77
	Orthopyroxene	15	55.99	bdl	0.69	1.66	6.59	0.20	33.87	1.09	bdl	-	-	100.14	0.90	0.22	-
	Chromite	4	0.27	bdl	48.62	8.49	24.89	0.36	12.57	-	-	-	0.10	95.36	0.47	0.79	1.17
Bon1200Ub	Glass	8	60.57	0.20	bdl	15.98	7.51	0.14	2.79	6.11	2.52	0.69	-	96.52	-	-	0.76
	Orthopyroxene	13	56.35	bdl	0.67	1.49	6.09	0.18	34.30	0.93	bdl	-	-	100.04	0.91	0.23	-
Bon1200Ba	Glass	5	62.08	0.18	bdl	17.90	5.24	0.13	1.64	6.13	2.99	0.84	-	97.17	-	-	3.35
	Orthopyroxene	13	56.34	bdl	0.71	1.88	7.31	0.20	32.68	1.32	0.05	-	-	100.50	0.89	0.22	-
Bon1200Bb	Glass	2	60.95	0.18	bdl	18.14	5.13	0.14	1.11	6.16	2.92	0.84	-	95.56	-	-	3.84
	Orthopyroxene	9	54.99	bdl	0.68	1.56	7.18	0.20	32.28	1.20	0.15	-	-	98.25	0.89	0.23	-
	Chromite	4	0.12	0.05	50.66	14.36	16.20	0.29	13.16	-	-	-	0.11	95.02	0.59	0.70	3.48
Bon1150U	Glass	4	58.52	0.06	0.05	14.47	7.04	0.11	6.12	8.13	2.59	0.65	-	97.74	-	-	1.00
	Orthopyroxene	8	55.02	bdl	0.64	2.47	8.46	0.23	31.23	1.69	0.06	-	-	99.84	0.87	0.15	-
	Chromite-Core	4	0.11	0.04	51.17	11.86	21.57	0.39	11.62	-	-	-	0.12	96.95	0.49	0.74	2.44
	Chromite-Rim	3	0.15	bdl	48.96	9.34	26.09	0.38	10.89	-	-	-	0.15	96.07	0.43	0.78	1.61
Bon1150B	Glass	3	60.34	0.08	bdl	16.20	5.21	0.10	4.63	7.01	2.94	0.75	-	97.29	-	-	2.74
	Orthopyroxene	2	54.98	bdl	0.70	2.37	9.04	0.24	31.57	1.89	bdl	-	-	100.83	0.86	0.16	-
	Chromite	1	0.08	0.05	51.93	14.45	19.41	0.35	11.5	-	-	-	0.10	97.93	0.51	0.71	4.51
Bon1100U	Glass	5	58.96	0.18	0.14	14.75	6.11	0.13	5.97	8.18	2.59	0.68	-	97.71	-	-	1.31
	Orthopyroxene	3	55.20	0.05	0.44	3.33	9.13	0.29	30.01	2.67	0.10	-	-	101.24	0.85	0.08	-
	Chromite	6	0.07	0.14	50.93	14.41	22.28	0.32	10.96	-	-	-	0.09	99.42	0.47	0.70	3.50

*Calculated using either stoichiometric recalculation (after Droop, 1987) for chromite or the model of Kress and Carmichael (1991) for glass

bdl = below detection limit, - = not analyzed/calculated

Table 4: Predicted and observed equilibrium compositional data for orthopyroxene (opx) and chromite (chrm)

<u>Modelled</u>	<u>$K_D(Fe-Mg)^{opx-liq} (1\sigma)$</u>	<u>$*K_D(Fe-Mg)^{chrm-opx}$</u>
Bon1200Ua	0.209 (0.007)	4.594
Bon1200Ub	0.211 (0.003)	-
Bon1200Ba	0.201 (0.005)	-
Bon1200Bb	0.199 (0.002)	4.639
Bon1150U	0.233 (0.001)	4.936
Bon1150B	0.219 (0.003)	4.957
Bon1100U	0.231 (0.009)	5.098
<u>Observed</u>		
Bon1200Ua	0.080 (0.004)	5.475 (0.260)
Bon1200Ub	0.066 (0.003)	-
Bon1200Ba	0.070 (0.005)	-
Bon1200Bb	0.048 (0.001)	4.279 (0.110)
Bon1150U	0.236 (0.011)	5.103 (0.237)
Bon1150B	0.246 (0.013)	4.863 (0.238)
Bon1100U	0.298 (0.010)	5.194 (0.171)

1 σ is a quantification of the distribution of modelled/observed values based on analytical precision and detected heterogeneity

**Model uncertainty = c. ± 0.157 (1 σ) using error propagation*

Table 5: Assessment of Fe-Mg equilibrium between opx, chromite, and melt in Kapilio lavas

<i>Opx data (norm.)</i>	SiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	<i>Moles MgO</i>	<i>Moles FeO</i>	X_{Al}^{opx}
*AM-4 opx-a	55.38	2.71	9.01	0.00	32.43	0.47	0.805	0.125	0.112
*AM-4 opx-b	56.14	1.65	8.15	0.00	32.63	1.43	0.810	0.113	0.068
<i>Chromite data</i>	Cr ₂ O ₃	Al ₂ O ₃	FeO	MgO	Total				<i>Average Y_{Cr}^{chrn}</i>
*AM-4 chrn-a	51.65	9.82	23.73	9.59	94.79		0.238	0.244	0.70
*AM-4 chrn-b	52.71	9.98	23.43	11.60	97.72		0.288	0.216	
*AM-4 chrn-c	53.80	10.18	23.46	11.25	98.69		0.279	0.228	
<i>Glass data and model K_D</i>	<i>**Average Model $K_D(Fe-Mg)^{opx-liq}$ (1σ)</i>					<i>**Average melt molar MgO (1σ)</i>		<i>**Average melt molar FeO (1σ)</i>	
	0.292 (0.004)					0.232 (0.024)		0.108 (0.004)	
<i>Modelled $K_D(Fe-Mg)^{chrn-opx}$</i>	opx-a	opx-b	<i>***(1σ)</i>						
1030°C (0.5 kbar)	4.676	4.955	0.157						
1130°C (0.5 kbar)	5.408	5.755	^						
	* Taken from Flower and Levine (1987)								
	** Compiled from all available analyses of Kapilio glass from Woelki et al. (2020)								
<i>Observed K_D Values</i>	$K_D(Fe-Mg)$	<i>****(1σ)</i>		<i>Equilibrium?</i>		<i>*** Same model uncertainty as in previous table</i>			
opx-a and average melt	0.334	0.041		yes		**** Calculated using error propagation methods applied to average melt composition			
opx-b and average melt	0.300	^		yes		^ = Same as above			
chrn-a and opx-a	6.587	-		no		- = Cannot be calculated using available data			
chrn-a and opx-b	7.324	-		no					
chrn-b and opx-a	4.827	-		yes (1030°C)					
chrn-b and opx-b	5.367	-		yes (mod T)					
chrn-c and opx-a	5.238	-		yes (mod T)					
chrn-c and opx-b	5.824	-		yes (opx-b 1130°C)					

Table 6: Ascent time calculations

<i>Chromite Radius (μm)</i>	<i>Maximum Ascent Time from Cr-Al Diffusion (years)</i>		<i>Minimum Ascent Time from Fe-Mg Diffusion (days)</i>	
	<i>at 1030 °C</i>	<i>at 1130 °C</i>	<i>at 1030 °C</i>	<i>at 1130 °C</i>
15	43	2	56	15
20	77	4	99	27
25	120	6	155	42
30	173	8	223	60
<i>log D (cm^2/sec)</i>	-16.2	-14.9	-12.7	-12.2

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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