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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**

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

## 40 1. INTRODUCTION

41 Boninites are rare high magnesium andesites that are produced by the melting of highly  
42 depleted mantle (harzburgite) under shallow and hydrous conditions (Pearce and Reagan,  
43 2019). The paucity of this rock type in the geologic record may be attributed to the exotic

44 nature of these petrogenetic conditions and/or the tendency of boninites to erupt in places  
45 with a low preservation potential (e.g. forearc regions, Stern and Bloomer, 1992).  
46 Nevertheless, boninites are generated in several tectonic settings including intraoceanic arcs  
47 (Meijer, 1980), intracontinental arcs (Tatsumi, 2006), back-arc basins (Falloon et al., 1992),  
48 and oceanic plateaus (Golowin et al., 2017). Additionally, several boninites have been found  
49 in ophiolite terranes (e.g. Bédard, 1999; Cameron, 1985; Dilek and Thy, 2009; Ishikawa et  
50 al., 2002; Meffre et al., 1996), though the tectonic settings of some ophiolites are topics of  
51 rigorous debate (cf. Gass, 1968; Metcalf and Shervais, 2008; Miyashiro, 1973; Moores et al.,  
52 2000; Pearce and Robinson, 2010; Regelous et al., 2014; Woelki et al., 2020; Woelki et al.,  
53 2018).

54 A cogenetic relationship between boninitic melt and podiform chromitite deposits found in  
55 some ophiolitic mantle sections has been hypothesized (Arai, 1997; Arai and Yurimoto,  
56 1994, 1995; Rollinson, 2008; Rollinson et al., 2018; Zhou and Robinson, 1997; Zhou et al.,  
57 1994). With regard to podiform chromitite formation, it has been suggested that primitive  
58 hydrous melts react with depleted mantle, become silica-enriched via the incongruent melting  
59 of orthopyroxene (implying olivine crystallization), and crystallize a large volume of high-  
60 Cr# chromite due to change in the number of available melt octahedral sites (Edwards et al.,  
61 2000). Separately, mechanisms of chromitite formation have been experimentally explored  
62 assuming immiscibility between melt-melt or melt-fluid components (Ballhaus, 1998;  
63 Matveev and Ballhaus, 2002). Initial immiscibility has been observed in other experimental  
64 studies that focused on the formation of boninitic melts via the same petrogenetic mechanism  
65 (i.e. incongruent melting, Fisk, 1986), and the boninitic composition of melts are preserved in  
66 equilibrium experiments that simulate melt-peridotite reactions (Mitchell and Grove, 2016). It  
67 is noteworthy that one experiment (C608) of Mitchell and Grove (2016) not only produced  
68 boninite melt in equilibrium with a dunite residual mantle mineral assemblage, but that the

69 composition of the residual mineral assemblage overlaps with the most depleted end of the  
70 olivine-spinel mantle array in compositional space (Arai, 1994). Ultimately, few studies have  
71 explicitly attempted to reconcile the links between boninite magma genesis, chromitite  
72 formation, and/or, more generally, chromite crystallization (Arai, 1997; Arai and Yurimoto,  
73 1994, 1995; Rollinson, 2008; Rollinson et al., 2018; Zhou et al., 1994; Zhou et al., 1996).

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

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

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

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

## 103 **2. MATERIALS AND EXPERIMENTAL METHODS**

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

### 109 *2.1. Starting materials*

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

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

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

133 NiO+NiPd redox sensors added to each experiment allowed for the hydrogen fugacity ( $f_{\text{H}_2}$ )  
134 imposed by the IHPV pressure medium to be evaluated, as redox sensors accurately reflect  
135 the oxygen fugacity ( $f_{\text{O}_2}$ ) imposed by the gas buffer (Pownceby and O'Neill, 1994; Taylor et  
136 al., 1992). These sensors were made by packing two pellets into inert ZrO<sub>2</sub> powder within a  
137 platinum capsule so that the pellets are not in contact with the capsule wall. One pellet was  
138 made of 50% NiO and 50% Ni<sub>x</sub>Pd<sub>1-x</sub> and the other was made of 50% NiO and 50% Ni<sub>y</sub>Pd<sub>1-y</sub>,  
139 with  $x = 0.5$  and  $y = 0.85$ . Deionized water was added until the capsule interior became



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

## 142 2.2. *Experimental design*

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

151 Target oxygen fugacities were *c.* 1-3 log units above the NNO buffer, which are analogous to  
152 magmas generated in subduction zone settings (Brandon and Draper, 1996; Evans et al.,  
153 2012; Kelley and Cottrell, 2009; Parkinson and Arculus, 1999). The oxidation states were  
154 either left unbuffered or buffered by pressurizing the IHPV with an Ar-H<sub>2</sub> gas mixture  
155 ( $pH_2^{added}$ , Table 2). Pt capsules are permeable to hydrogen, which diffuses through the  
156 capsule wall to bond with oxygen in the melt so that reduction of the sample volume occurs  
157 (Chou et al., 1978; Shaw, 1963). Since the volume of the pressure medium is much greater  
158 than the volume of the sample capsule, the pressure medium is effectively an infinite  
159 reservoir with respect to hydrogen. Thus, the effective concentration of hydrogen available to  
160 each capsule during a given experiment,  $fH_2$ , may be considered constant. Unbuffered  
161 experiments cause the redox state of melts to approach a condition known as the intrinsic  $fO_2$   
162 of the IHPV. The intrinsic  $fO_2$  of IHPV systems is highly oxidizing (NNO+2 to NNO+4,  
163 Scaillet et al., 1992; Taylor et al., 1992, see further discussion in Supplemental Text 1).

164 The experiments described here each lasted less than 6 hours. The utility of short-period  
165 experiments is multifaceted. From a volcanological perspective, fast ascending magmas are  
166 extracted from their crustal domains and extruded onto the surface in as little as tens of  
167 minutes (Lloyd et al., 2016) when melts are hot ( $>1000^{\circ}\text{C}$ ) and volatile rich. Short timescales  
168 of the order of hours to days have also been inferred for volatile poor arc magmas (Lormand  
169 et al., 2020). In a rapidly ascending melt, a variety of concomitant processes may alter the  
170 physiochemical state of the melt volume, including syn-eruptive mixing (e.g. Tomiya et al.,  
171 2013; Wolf and Eichelberger, 1997), crystallization (e.g. Blundy and Cashman, 2005;  
172 Cashman and Blundy, 2000), and whole-rock contamination (e.g. Mattioli et al., 2006). Such  
173 processes, along with subtleties such as the inclusion of antecrystic minerals, produce  
174 disequilibrium mineral assemblages that provide valuable insight into the latest stages of  
175 magmatism (Couch et al., 2001; La Spina et al., 2016; Ubide et al., 2014; Zellmer et al.,  
176 2016; Zellmer et al., 2014). Thus, for natural magmatic systems, brief durations on the order  
177 of hours represent an end member in an ascent period context, and disequilibrium  
178 characteristics may be useful if properly placed into a petrogenetic context. Given boninite  
179 petrogenesis occurs at relatively shallow depths and generates hot and hydrous melts,  
180 sometimes in extensional settings (Reagan et al., 2017), rapid ascent rates cannot be  
181 precluded. Furthermore, since it is possible that chromites preserved in boninite matrices may  
182 have been generated within the source regions of the melts, knowledge of how these minerals  
183 react to changes in the physiochemical states of the melts (i.e. experimental observation) is  
184 needed in order to assess and contextualize natural sample materials. These considerations  
185 provide an incentive to perform experiments on brief timescales and to analyse  
186 disequilibrium features.

### 187 3. ANALYTICAL METHODS

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

190 Following removal of the sample holder from the IHPV, each capsule was weighed to assess  
191 for mass loss during the experiment. The capsules were then mounted in epoxy and ground to  
192 expose their interiors. Ni-Pd alloys recovered from each sensor capsule was separated from  
193 powdered ZrO<sub>2</sub> and mounted in epoxy. These sample materials were then polished for  
194 imaging and microprobe analysis, using SiC lapwheels and diamond grit paste.

### 195 3.1. *Electron microbeam techniques*

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

205 Electron probe microanalysis (EPMA) occurred at multiple laboratories: at Victoria  
206 University of Wellington and The University of Iowa, JEOL JXA-8230 Superprobes were  
207 used. Additional chromite analyses were performed at Hokkaido University on a JEOL JXA-  
208 8800R. Glass analyses were performed using Na-migration mitigation techniques. In addition  
209 to using diffuse beam conditions (spot sizes of 5-10 µm), two Na acquisitions are totalled. If  
210 analyses return low concentrations (determined using secondary standards), then sodium loss  
211 may be corrected by either: removing the second acquisition (if Na is lost), removing either

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

215 Secondary standards provided by the Smithsonian Institution Department of Mineral Sciences  
216 and/or the Max Planck Institute for Chemistry were included in all glass and mineral  
217 analyses. Ni-Pd sensor compositions were quantified using metal standards by Astimex.  
218 Repeat analyses of secondary standards provided a basis to assess the accuracy of data  
219 gathered during EPMA (Tables S1-S2, and S4). The accuracies associated with glass analyses  
220 have been determined to be within 1% for SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, and CaO, 5% for TiO<sub>2</sub>, FeO,  
221 and K<sub>2</sub>O, 10% for Na<sub>2</sub>O, and 20% for MnO. For analyses of silicate minerals, SiO<sub>2</sub>, MgO,  
222 CaO, and Na<sub>2</sub>O are accurate to within 1%, while FeO, Cr<sub>2</sub>O<sub>3</sub>, MnO, and Al<sub>2</sub>O<sub>3</sub> are better than  
223 2%. Chromite standardization was achieved using several mineral and oxide standards.  
224 Replicate standard analyses demonstrated that all major elements given are accurate to within  
225 5%, while MnO is accurate to within 40%. Secondary standard compositions are taken from  
226 Jarosewich et al. (1980); Jochum et al. (2006); and Jochum et al. (2005).

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

### 233 3.2. *Determination of phase proportions*

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

236 produced segmented images that we interpreted in terms of phase proportions using Adobe  
237 Photoshop. Segmented images are images that have been petrographically interpreted using a  
238 machine learning algorithm and are color-coded based on which phase each pixel represents  
239 (Supplemental Text 3). The machine learning tool used is called Trainable Weka  
240 Segmentation, and was developed by Arganda-Carreras et al. (2017). The algorithm requires  
241 limited user input (5-8 user-defined groups of pixels) to “train” the computer-generated  
242 classifier, which segments as many mineral phases as the user defines. This tool produced the  
243 segmented images used to infer the phase proportions given in Table 2. The tool is provided  
244 as a plugin on the Fiji Is Just ImageJ (FIJI) platform (Schindelin et al., 2012). A minimum of  
245 5 training sessions were conducted for each analysis, and the data derived from each  
246 segmented image were averaged to produce the given proportions with the calculated  
247 standard deviation providing the precision of each phase classification. Images representative  
248 of the sample textures were used for segmentation. See Supplemental Text 3 for more  
249 information and an example of a segmented image.

### 250 3.3. *Determination of oxygen fugacities from the solid sensors*

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

## 255 4. RESULTS

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

260 The capsule interiors of every sample except for Bon1200Ub were analysed via EDS in order  
261 to assess the degree of iron loss from the melt to the Pt of the capsule wall. Line analyses  
262 from the sample-wall contact into the capsule wall yielded no detectable iron *c.* 30  $\mu\text{m}$  from  
263 the interface. Integrating concentration profiles demonstrates that iron loss in unbuffered  
264 experiments is limited to 10% or lower (of bulk sample Fe), while buffered experiments lost  
265 20-35% Fe over experiment durations (Supplemental Text 2, Table S3). However, we will  
266 demonstrate that none of our discussion topics have been significantly affected by iron loss.

#### 267 4.1. *Petrographic observations*

268 Euhedral-subhedral orthopyroxene (opx) is abundant and is the only silicate phase present at  
269 1200°C and 1150°C (Figure 1A). In BSE images, these crystals often have bright caps that  
270 form at the apices of euhedral crystal forms (Figure 1B). At 1100°C, a petrographically  
271 distinct trace silicate phase was observed along with abundant opx in Bon1100U (Figure 1C).  
272 Semi-quantitative EDS analyses of this phase demonstrate that this silicate is rich in Ca, Mg,  
273 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  
274 boninitic samples, and BSE images of moderate-sized grains show that chromite mantles  
275 have become brighter than cores (Figure 1D), indicating that diffusive equilibration was  
276 interrupted by quenching in large grains. In general, all chromites appear as anhedral grains  
277 with sharp-subrounded corners. These are not indications of chromite growth, suggesting that  
278 all observed chromites are the original seeds added to each experiment. Likewise, there is no  
279 evidence of dissolution, which indicates that chromite was a stable phase for the full duration  
280 of each experiment. This implies that our experiments only produced pyroxene crystallization  
281 in the presence of stable chromite.

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

#### 285 4.2. *Redox sensors and calculation of imposed $fO_2$*

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

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

#### 302 4.3. *Compositional Data*

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

#### 306 4.3.1. Glass compositions

307 Residual melts formed andesitic glasses, the compositions of which are given with other  
308 experimental products in Table 3. These glasses are depleted in FeO, MnO, MgO, and Cr<sub>2</sub>O<sub>3</sub>  
309 relative to both the initial boninite glass as well as the bulk composition of the system  
310 (Table 1). SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, and TiO<sub>2</sub> are enriched in residual melt during every  
311 experiment, which is consistent with extensive opx crystallization.

312 The two experiments conducted at high temperature (Bon1200U and Bon1200B) returned  
313 four samples with glasses containing low MgO concentrations relative to those from  
314 experiments conducted at 1150°C. This is counterintuitive, because the crystallization of opx  
315 at higher temperature should produce a lower proportion of minerals relative to lower  
316 temperatures, and overall depletion of MgO and FeO relative to the initial glass composition  
317 should be smaller. Additionally, glass compositions inferred for sample Bon1200Ua indicate  
318 a high degree of heterogeneity beyond the limit of analytical uncertainty, consistent with  
319 inefficient quenching producing local melt heterogeneity. These data, along with relatively  
320 high melt K<sub>2</sub>O concentrations and the presence of abundant rim formation on opx grains  
321 within these samples (Figure 1B) indicate that a significant degree of quench crystallization  
322 has occurred in the high temperature experiments. These observations are absent from all  
323 experiments conducted at 1150-1100°C, which suggests that quenching was efficient in these  
324 latter experiments and that no quench crystallization occurred.

#### 325 4.3.2. Pyroxene compositions



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

336 Opx Mg# (molar  $\text{Mg}/[\text{Mg}+\text{Fe}_{\text{Total}}]$ ) positively correlates with temperature, and under buffered  
337 redox conditions is lower than in unbuffered products (Figure 2). Differences in MgO and  
338 FeO concentrations observed in samples processed at 1200°C but different  $f\text{O}_2$  are on the  
339 order of 1-2 wt% for each element. Thus, lower Mg# is associated both with lower  
340 temperature as well as lower  $f\text{O}_2$ . Minor oxide components in opx include CaO, Na<sub>2</sub>O, Cr<sub>2</sub>O<sub>3</sub>,  
341 MnO, TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>. The concentrations of each of these oxides are < 5 wt%, with  
342 variation of some concentrations correlating with changes in the intensive parameters of the  
343 IHPV. Higher cation proportions of Ca, Al, and Mn are observed in samples synthesized  
344 under lower temperatures (Figure 2). Cr<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and TiO<sub>2</sub> concentrations are extremely low  
345 in all pyroxenes, and potential variations in these oxides due to changes in temperature or  
346 redox condition are imperceptible when considering the detection limits for these elements.

347 The effects of imposing variable redox conditions on the melt-opx partitioning of Ca, Al, and  
348 Mn cannot be discerned for a given temperature interval because, with regard to these  
349 elements, the mean core compositions for all opx synthesized at a given temperature are not  
350 observed to significantly change between high and low  $f\text{O}_2$ .

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

#### 357 4.3.3. Chromite compositions

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

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

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

376 Compositions taken from the literature on boninite-hosted chromites sourced from the  
377 Mariana trench wall (Bloomer and Hawkins, 1987), the Troodos ophiolite (Bailey et al.,  
378 1991; Cameron, 1985; Flower and Levine, 1987; MacLeod, 1988; Thy and Xenophontos,  
379 1991), Guam (Reagan and Meijer, 1984), and Chichijima (Umino, 1986) are provided for  
380 comparison. Note that the chromites from Thy and Xenophontos (1991) are olivine-hosted  
381 mineral inclusions.

382 In terms of trivalent cation proportions (i.e.  $\text{Fe}^{3+}$ , Al, and Cr),  $f\text{O}_2$  buffered experiments  
383 produced chromites with compositions that did not significantly change from the initial seed  
384 composition (Figure 3A). Chromium is efficiently oxidized above NNO in iron-bearing melts  
385 (Hanson and Jones, 1998). Thus, all Cr in chromite is  $\text{Cr}^{3+}$ . However, some of these  
386 chromites have bright mantles that clearly indicate Fe enrichment (e.g. Figure 1D). Under  
387 intrinsic  $f\text{O}_2$  conditions corresponding to *c.* 3.2-4.0 log units above the NNO buffer and at  
388 temperatures of 1200-1150°C (red and yellow diamonds on Fig. 3), significant amounts of  
389  $\text{Fe}^{3+}$  were added to chromite, resulting in an enrichment of total FeO with concentrations > 20  
390 wt%. For these samples, their trend on Figure 3A illustrates significant  $\text{Fe}^{3+}$ -Al exchange  
391 between chromite and melt, as the trend of core compositions runs sub-parallel to lines of  
392 equal Cr proportion (which caused the observed increase in Cr# for these chromites). Because  
393 this trend is linear and the samples do not cluster, it is likely that the  $\text{Fe}^{3+}$ -Al exchange  
394 reaction failed to reach equilibrium. It is noteworthy that chromite grains in sample  
395 Bon1100U appear to have lost very little Al during the experiments, as  $\text{Al}_2\text{O}_3$  concentrations  
396 are  $\leq 1$  wt% different from concentrations in the seed chromite, consistent with the observed  
397 invariance of their inferred  $\text{Fe}^{3+}$  contents.  $\text{TiO}_2$  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  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  proportion as seed chromite. However, it is apparent that some  
415 Mg- $\text{Fe}^{2+}$  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,  $\text{Fe}^{2+}$  has been added to chromite and Mg has been lost to the melt. For a given  
418 temperature, Mg# appears to decrease with  $\text{Fe}^{3+}$  incorporation. This is observed for samples  
419 recovered from experiments Bon1200U and Bon1150U, which plot to higher  $\text{Fe}^{3+}$  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.

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

## 424 5. DISCUSSION

### 425 5.1. *Assessment of divalent cation distribution and equilibrium state between chromite-* 426 *opx-melt*

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

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

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

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

446 An uncertainty ( $1\sigma$ ) of  $\pm 0.06$  was attributed to these modelled  $K_D$  values, which is an order  
447 of magnitude higher than the  $1\sigma$  associated with the distribution of modelled  $K_D$  values given  
448 in Table 4 and is illustrated as areas on Figure 4A. Observed  $K_D$  calculations employed molar  
449 proportions for opx core analyses and average molar proportions for glass compositions.

450 Average  $K_D$  values (including  $2\sigma$  error bars) for samples Bon1150U and Bon1150B plot  
451 completely within their model areas, indicating that the opx sampled in these charges were in  
452 equilibrium with their respective residual melts at the time of quenching.  $K_D$  values  
453 calculated for three opx cores in sample Bon1100U produce an average  $K_D$  that is positioned  
454 just outside of the model area. However, since the lower error bar stretches into the  
455 uncertainty envelope as illustrated, it is reasonable to say that these crystals also equilibrated  
456 with their residual melt. There are two negative effects of quench crystallization that  
457 impacted  $K_D$  calculations and prevented us from determining whether opx in samples  
458 processed at  $1200^\circ\text{C}$  were able to reach equilibrium or not. The first is the effect of raising  
459  $X_{\text{Si}}^{\text{liq}}$ , which occurred as quench crystals removed Mg, Fe, and Ca from residual melts. This  
460 lowers model  $K_D$  values (Equation 1). The other effect is the removal of Mg and Fe from the  
461 melt phase, which precluded realistic  $K_D$  values from being observed (Figure 4A). Since opx-  
462 melt  $K_D$ s indicate an equilibrium condition for experiments conducted at  $1150\text{-}1100^\circ\text{C}$ , none  
463 of the iron loss observed in these samples had an observable effect on the equilibrium  
464 partitioning of Fe-Mg between opx and melt. This indicates that our equilibration  
465 considerations are not significantly affected by this process.

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

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

$$476 \quad K_D(\text{Fe}^{2+} - \text{Mg})^{\text{chrom} - \text{opx}} = \exp \left[ \frac{AT(\text{K}) + B + 122P(\text{GPa}) - CX_{\text{Al}}^{\text{opx}} + DY_{\text{Cr}}^{\text{chrom}}}{T(\text{K})} \right] \quad \text{Equation 2}$$

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

489 As illustrated on Figure 4B, the Fe<sup>2+</sup>-Mg subcomposition of chromite (given as Mg# in  
 490 Figure 3B) in several samples has equilibrated with the opx-melt subsystem over the brief  
 491 timescale of these experiments. The relatively large seed shown in Figure 1D has a rim that is  
 492 *c.* 8-10 μm wide. Because our analyses prioritized small chromites that were *c.* 10-15 μm in

493 diameter, we consider it likely that EPMA sampled chromite that completely equilibrated  
494 with respect to Fe<sup>2+</sup>-Mg through diffusion.

495 Thus, since a self-consistent determination of equilibrium has been established using  
496 empirical relationships, then the Fe<sup>2+</sup>-Mg data provided here describe the equilibrium  
497 condition of the melt + opx + chromite system under high temperature and  $fO_2$  conditions  
498 analogous to those in sub-arc crust. Interestingly, significant degrees of iron loss should raise  
499 the Mg# of the sample bulk composition even when the ratio of Fe<sup>2+</sup> to Fe<sup>3+</sup> in melt is  
500 maintained by hydration (Supplemental Text 2). This effect should be observable in product  
501 opx compositions, as higher melt Mg# should result in higher opx Mg#. Since this is not  
502 observed (Figure 2, Table 3), then the observed iron loss (in the case of Bon1150B, 20% bulk  
503 Fe) does not significantly affect the equilibrium distribution of Fe<sup>2+</sup>-Mg under our  
504 experimental conditions.

505 *5.2. Assessing chromite-melt equilibrium based on model equilibrium trivalent cation*  
506 *proportions*

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



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

522 Figure 5 illustrates the relationship between MELTS and SPINMELT-2.0 models and the  
523 difference between modelled compositions and the synthetic chromites produced in our  
524 experiments. Alternative models were created to observe the effect of 30% iron loss on the  
525 system (empty symbols, Figure 5). It appears that under highly oxidizing conditions and  
526 1150-1200°C, experimental chromite  $\text{Fe}^{3+}/[\text{Fe}^{3+}+\text{Cr}+\text{Al}]$  values approach values that are  
527 attained at NNO+2 in the MELTS models. Still, given the distance on the ternary diagram  
528 between modelled chromite compositions and our experimental data, none of the  
529 experimental chromites are in equilibrium based on observed trivalent cation proportions.  
530 This includes model data that were generated under conditions where iron loss was accounted  
531 for. The principal effect of iron loss is to reduce the proportion of iron in equilibrium  
532 chromite. The trend to high  $\text{Fe}^{3+}$  concentrations observed for the oxidized samples illustrated  
533 in Figures 3A and 5 are likely to represent a segment of a diffusion trend in ternary space.  
534 The concept of diffusion in this compositional space is explored below. Since the volume of  
535 chromite in the charges is invariant (i.e. no resorption or crystallization has been observed),  
536 then the process by which chromite equilibrates can exclusively be attributed to diffusion.

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

541 al., 2018a), and the creators of SPINMELT-2.0 claim that their model reproduces several  
542 petrologically important chemical aspects of chromite chemistry to better than 20% (Cr/Al  
543 and Mg/Fe<sup>2+</sup>, Nikolaev et al., 2018a). What MELTS does describe accurately is Fe-Al  
544 exchange within the system during melt evolution and thus likely provides a best fit topology  
545 in compositional space (Davis and Cottrell, 2018). Because of these observations, we  
546 reiterate that our modelling method likely bookends equilibrium chromite compositions;  
547 keeping in mind that multiple experiments were performed beyond the calibration range of  
548 SPINMELT-2.0.

549 In the case where Fe<sup>2+</sup> in chromite is in equilibrium with the co-existing melt/silicate mineral  
550 assemblage, the interdiffusion of trivalent cations should occur in chromite with Fe<sup>2+</sup>/Fe<sup>3+</sup>  
551 higher than that in coexisting melt, as melt Fe<sup>2+</sup>/Fe<sup>3+</sup> should always be higher than spinel  
552 Fe<sup>2+</sup>/Fe<sup>3+</sup> (Maurel and Maurel, 1982). Using equation 7 of Kress and Carmichael (1991),  
553 model melt Fe<sup>2+</sup>/Fe<sup>3+</sup> values were generated (Table S1) using glass compositions and the  
554 intensive parameters imposed by the IHPV to show that most if not all experimental  
555 chromites must incorporate more Fe<sup>3+</sup> before reaching an equilibrium Fe<sup>2+</sup>/Fe<sup>3+</sup> threshold  
556 (Figure 6). That is, in order to reach an equilibrium condition, the observed Fe<sup>2+</sup>/Fe<sup>3+</sup> in  
557 chromite must incorporate more Fe<sup>3+</sup> so that their ratio values fall below the grey lines on  
558 Figure 6. The exception is sample Bon1200Bb, the chromite Fe<sup>2+</sup>/Fe<sup>3+</sup> values of which are  
559 distributed (mostly) beneath the modelled melt Fe<sup>2+</sup>/Fe<sup>3+</sup> value.

560 The diffusion of major cations within spinel (*s.l.*, e.g. Figure 19 of Van Orman and Crispin,  
561 2010) are ranked by order of decreasing diffusivity (log D, m<sup>2</sup>/s) at 1100°C (10<sup>4</sup>/K = *c.* 7.3):  
562 Mg-Al (extrapolated, *c.* -13.5), Fe (self-diffusion, *c.* -16), Mg (self-diffusion, *c.* -16.5), and  
563 Cr-Al (below x-axis, see below). Thus, D<sub>Cr-Al</sub> is likely the limiting factor in chromite-melt  
564 diffusive equilibration, though uncertainties associated with D<sub>Cr-Al</sub> are reportedly large at high

565 Cr# (Suzuki et al., 2008) and  $fO_2$  affects  $D_{Fe}$  (Vogt et al., 2015). As stated by Vogt et al.  
566 (2015) this behaviour is not well constrained under high-T and high-P conditions. Our results  
567 corroborate this inference. Since spinel (*s.l.*) is an isometric mineral, the given diffusivities do  
568 not vary with crystallographic orientation, which is convenient for the purpose of textural  
569 analysis (Supplemental Text 5).

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

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

584 Based on our observations, we hypothesize that  $Fe^{3+}$ -Al interdiffusion operates principally as  
585 a function of  $fO_2$  to equilibrate chromite  $Fe^{2+}/Fe^{3+}$  (after equilibration of chromite Mg#) on a  
586 shorter timescale than is required to equilibrate Cr in the system. This scenario of diffusive  
587 re-equilibration may be conceptualized within a multi-step chemical reaction (Figure 7). The  
588 first step concerns  $Fe^{2+}$ -Mg exchange between chromite and melt. This is the only reaction

589 observed in samples processed under buffered  $fO_2$  (and in sample Bon1100U), and since the  
590 observed changes in chromite composition are more complex under higher  $fO_2$  conditions, we  
591 combine this exchange with the observed increase in  $Fe^{3+}$  in trivalent cation proportion as  
592 reaction 1 (Figure 7). Thus, a relatively high  $Fe^{2+}/Mg + Fe^{3+}/Al$  composition is generated as a  
593 magnetite component ( $FeFe_2O_4$ ) is added to the starting chromite composition. This exchange  
594 is facilitated by the counter-diffusion and exchange of Mg and Al, and the spinel (*sensu*  
595 *stricto*, hereafter *s.s.*) component thus diminishes (see Table S2 for modelled end-member  
596 component compositions). With reaction 1, the chromite composition approaches a tie line  
597 between  $Fe(Al,Cr)_2O_4$  and  $Mg(Fe,Cr)_2O_4$  in the compositional space of the spinel (*s.l.*) prism  
598 (dashed grey line in Figure 7A). Importantly, the chromite compositional trend will not  
599 approach the Cr-magnetite solid solution in the prism space but a spinel (*s.l.*) composition  
600 intermediate between Cr-magnetite and the  $Mg(Fe,Cr)_2O_4$  solid solution, as spinel (*s.l.*) Mg  
601 concentration is only being diluted by reaction 1 (i.e. Mg is rearranged within the chromite  
602 matrix with some flux across the crystal-melt boundary). In order to equilibrate Cr  
603 proportion, which is expected to decrease under all imposed experimental conditions  
604 (Figure 5), compositions should evolve along lines of equal  $Fe^{3+}/Al$  (dashed grey line in  
605 Figure 7B; reaction 2) in the isothermal state as Cr is lost to the melt phase. An added  
606 component with higher  $Fe^{2+}/Mg$  is required because Mg# in chromite was not observed to  
607 increase in any experiment (Figure 3B) and because this is necessary for chromite to  
608 equilibrate with the silicate mineral assemblage (Figure 4B).

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

614 are not, then the likely explanation for this observation is that the microlitic silicate formed  
615 from the melt it is in (i.e. an equilibrium crystallization process). Crystallization of ferrous  
616 phases is one of several oxidizing mechanisms in arc magmatic systems (see Cottrell et al.,  
617 2020). This process provides an impetus for diffusive re-equilibration of chromite to begin,  
618 and the grounds for oxyspeedometric analysis of the chromite-melt subsystem in a diffusion  
619 chronometric context. Chromite crystals sampled from Chichijima (Umino, 1986), the  
620 Troodos ophiolite (Bailey et al., 1991), and Guam (Reagan and Meijer, 1984) exhibit  
621 chemical zonation consistent with pre-eruptive oxidation, as chromite rim-mantle zone  
622 analyses return more ferric compositions than analyses of their cores. Such features are  
623 unique to the pre-eruptive regime but may be confused with compositional trends that are  
624 attributable to chemical weathering. Thus, it is important to discern here oxidation of  
625 chromite that occurs in this scenario and oxidation that occurs post-eruption (i.e. chemical  
626 weathering or metamorphism of chromite). In the literature on the zoned chromites described  
627 above, there is no mention of textures consistent with porous-chromite oxidation (Gervilla et  
628 al., 2019; Hodel et al., 2020). The volcanic rocks sampled by the studies cited above were  
629 observed to be fresh with little to no evidence of alteration, which is not consistent with a  
630 weathering environment capable of significantly modifying chromite compositions in either  
631 hydrothermal (Hodel et al., 2020) or metamorphic (Gervilla et al., 2019) regimes. Instead,  
632 since the chromite FeO and Al<sub>2</sub>O<sub>3</sub> concentrations are observed to increase from core to rim  
633 (which is a geochemical signature of magmatic oxidation in our model, i.e. reaction 2 of  
634 Figure 7), we maintain that these zonation patterns are of magmatic rather than secondary  
635 origin. With this in mind, the next sections assess natural chromite and glass compositions  
636 recovered from the extrusive suite of the Troodos ophiolite in a similar manner as our  
637 experimental products, and data available from the literature are used to constrain ascent rates  
638 for these lavas.

639 5.3. *Experimental observations vs. natural processing in the crustal column*

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

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

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

667 SPINMELT-2.0 output was treated in a similar way as the experimental data (Supplemental  
668 Text 4). When  $fO_2$  is provided, melt  $Fe^{2+}/Fe^{3+}$  is calculated internally and used to model  
669 chromite composition. Since temperature is not provided to the program, it must be predicted  
670 by the algorithm to provide a chromite composition estimate for each input melt composition.  
671 For these lavas, liquid temperatures have been inferred to vary between *c.* 1030-1130°C  
672 (Golowin et al., 2017). These temperatures are consistent with temperatures inferred from  
673 viscosity models (Schouten and Kelemen, 2002) generated for lavas on the North side of the  
674 extrusive sequence and with independent thermometry (inferred to provide a quantification of  
675 closure temperature) performed by Dare et al. (2009) for the Kalavassos Mine locality.

676 SPINMELT-2.0 output was observed to lie within 25°C of this temperature range for a  
677 majority of the glass samples (Table S6) for each  $fO_2$  condition. Thus, we inferred that our  
678 models faithfully replicated equilibrium conditions for chromite-melt at the time of eruption.

679 Figure 8 illustrates the relationships between modelled and observed chromite compositions  
680 of the Troodos (cf. Figure 5). Sample glass recovered from the Kalavassos Mine produced  
681 one major cluster for each  $fO_2$  condition and one Al-rich glass sample displaced modelled  
682 chromite compositions to higher Al and lower Cr. All glass samples were determined to be  
683 “tholeiitic” by Woelki et al. (2020). All of the matrix chromite compositions observed for this  
684 locality are similar to olivine-hosted chromite inclusions observed in these same lavas  
685 (Golowin et al., 2017). A single natural chromite composition is displaced to higher Al  
686 compared with the others. However, according to our models, all of these chromite

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

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

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



710 Regarding  $\text{Fe}^{2+}$ , slowly cooled chromites lose Mg to coexisting ferromagnesian silicates  
711 (Ozawa, 1984), while rapidly quenched mineral pairs preserve high-temperature  
712 compositions (e.g. Scowen et al., 1991). Since the glasses sampled from the Troodos rapidly  
713 quenched upon eruption (e.g. Robinson et al., 1983), chromite Mg# may have been  
714 preserved. By focusing on a single locality where glass, opx, and chromite data exist, we may  
715 treat natural samples in the same way as the experimental products above and test for system  
716  $\text{Fe}^{2+}$ -Mg equilibrium. To this end, we refocus on the Kapilio locality. Glass data from this site  
717 (Woelki et al., 2020) were processed to predict  $K_D(\text{Fe-Mg})^{\text{opx-liq}}$  values using equation 1.  
718 Mineral data from this locality are from Flower and Levine (1987). In total, two opx and  
719 three chromite compositions were used (their sample AM-4, Table 5). Unfortunately, there is  
720 no way of determining if these materials come from the same outcrops as the glass, which is  
721 why all glass data were used in modelling. Based on model physiochemical constraints  
722 outlined above, the opx sampled by Flower and Levine (1987) is in equilibrium with residual  
723 melts (within  $1\sigma$  of the mean model  $K_D(\text{Fe-Mg})^{\text{opx-liq}}$  value). Using a median  $Y_{\text{Cr}}^{\text{chrom}}$  for the  
724 matrix chromites (0.70), model  $K_D(\text{Fe-Mg})^{\text{chrom-opx}}$  values (calculated using equation 2) are  
725 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  
726 0.5 kbar (Table 5). Varying  $Y_{\text{Cr}}^{\text{chrom}}$  by 0.1 (the actual variation observed among the sample  
727 chromites) causes these model  $K_D$  values to vary by  $\pm 0.07$  (*c.*  $\pm 3\%$ ), which is roughly one  
728 half of the magnitude of the uncertainty associated with the model parameters. Observed  
729  $K_D(\text{Fe-Mg})^{\text{chrom-opx}}$  values are found to vary between 4.8 and 7.3 depending on which  
730 chromite-opx pair is used. Two of the three chromite grains are seen to be in equilibrium with  
731 at least one of the opx grains based on these  $K_D$  models. One other chromite grain in this  
732 sample returned high observed  $K_D$  values for both opx grains, reflecting low MgO  
733 concentrations. This chromite also has a low total EPMA composition (94.79) compared to  
734 the other analyses (*c.* 98). Regardless, it is remarkable, given the dearth of mineral data

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

739 The effects of natural quench crystallization and syn-eruptive microlite growth on modelling  
740 equilibrium chromite composition also needs to be considered. Depending on the Fe-Mg ratio  
741 of the minerals that crystallize,  $\text{Fe}^{2+}$  may be enriched or depleted in the residual melt. Using  
742 equilibrium exchange coefficients (e.g. Putirka, 2008), the crystallization of ferromagnesian  
743 silicates like olivine and opx are expected to enrich melts in FeO relative to MgO, and the  
744 differentiation of melt by these minerals should modestly enrich  $\text{Fe}^{3+}$  over  $\text{Fe}^{2+}$  (Birner et al.,  
745 2018; Kelley and Cottrell, 2012; O'Neill et al., 2018; Shorttle et al., 2015). Melt  $\text{Al}_2\text{O}_3$  is  
746 expected to increase with the equilibrium crystallization of ferromagnesian silicates. Based  
747 on observations of the experimental products made at 1200°C, melt  $\text{Al}_2\text{O}_3$  concentrations  
748 were not significantly affected by quench crystallization (Table 3). Although this effect will  
749 depend on the volume of crystallization produced during quenching, which was not  
750 constrained, we do not expect minor degrees of quench crystallization to significantly affect  
751 melt  $\text{Al}_2\text{O}_3$  unless an aluminous phase crystallizes. In some relatively differentiated Troodos  
752 lavas, plagioclase feldspar is observed (Flower and Levine, 1987; Schmincke et al., 1983).  
753 Feldspar crystallization is expected to reduce melt  $\text{Al}_2\text{O}_3$  and thus modelled chromite  $\text{Al}_2\text{O}_3$   
754 concentrations, which would cause observed chromite compositions to appear closer to  
755 equilibrium. Instead, we propose that (i) the higher chromite Al concentrations predicted by  
756 our modelling (Figure 8) reflect  $\text{Al}_2\text{O}_3$  enrichment in the magmas (and thus the absence of  
757 plagioclase in glasses sampled by Woelki et al., 2020) that comprise the Troodos extrusive  
758 sequence, which is consistent with the predominate silicate mineral assemblages observed  
759 therein; namely olivine, olivine+cpx, or olivine+opx+cpx (Flower and Levine, 1987; Malpas

760 and Langdon, 1984; Schmincke et al., 1983), and that (ii) quench crystallization does not  
761 significantly affect these data. Since the most primitive glasses sampled by Woelki et al.  
762 (2018) were observed to classify as boninite liquids, we infer that the most Cr-rich  
763 equilibrium chromite compositions in our models (Figure 8), which correspond to these  
764 relatively primitive melt compositions, represent chromite compositions that genuinely reflect  
765 the equilibrium composition of chromite in melts unaffected by quench/syn-eruptive  
766 crystallization.

#### 767 5.4. *Estimation of maximum/minimum ascent time through diffusion modelling*

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

777 Based on chromite-melt behaviour modelled above and observed in the mafic lavas of the  
778 extrusive suite of the Troodos ophiolite, we estimated the maximum and minimum ascent  
779 times by calculating the time (t) it would take to equilibrate a hypothetical groundmass  
780 chromite microphenocryst [30-60  $\mu\text{m}$  diameter with a composition similar to those of  
781 primitive chromite microphenocryst cores and mineral inclusions from the Kalavassos Mine  
782 locality (Figure 8, Golowin et al., 2017; Sobolev et al., 1993)] with residual melt under the  
783 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,  $\tau$  is non-dimensional time, and  $D$  is the interdiffusion  
786 coefficient.

787  $D_{\text{Cr-Al}}$ , 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  $D_{\text{Cr-Al}}$  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  $\log D_{\text{Cr-Al}}$  as a function of temperature (Supplemental Text 5). The  
793 following equation was recovered:

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

795 Using this equation, we estimate  $\log D_{\text{Cr-Al}}$  ( $\text{cm}^2/\text{s}$ ) 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  $\log D_{\text{Fe-Mg}}$  at the same conditions as  $\log D_{\text{Cr-Al}}$ . 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,  $\log D_{\text{Fe-Mg}}$ . For this calculation, we used the following  
801 linear equations recovered from their Arrhenius plots:

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

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

828 2002). Golowin et al. (2017) used olivine-melt compositional data and the equilibrium  
829 relationships given by Ford et al. (1983) and Almeev et al. (2007) to quantify minimum  
830 crystallization temperatures, which they interpreted as eruption temperatures. Schouten and  
831 Kelemen (2002) used the geothermometer of Sisson and Grove (1993) to estimate  
832 temperature for their viscosity models. Finally, Dare et al. (2009) calculated temperature  
833 using the olivine-spinel thermometer of Ballhaus et al. (1991) and inferred this temperature as  
834 a closure temperature for chromite. Taken together, since the present discussion is focused on  
835 the kinetics of chromite-melt re-equilibration at pre-eruptive conditions, the estimates of  
836 Golowin et al. (2017) represent our preferred liquid temperatures because they are most likely  
837 to constrain melt temperatures prior to significant syn-eruptive crystallization of microlitic  
838 pyroxene. Granted, when significant pyroxene crystallization occurs, melt water  
839 concentrations assumed by Golowin et al. (2017) for Troodos glasses (*c.* 3 wt%) represent  
840 maxima and their temperatures minima following the liquidus depression relationships given  
841 by Almeev et al. (2007). Woelki et al. (2020) quantified water concentrations in boninite  
842 glasses to be 1.7-2.7 wt%, which is slightly below the value provided by Golowin et al.  
843 (2017). This means our models may use temperatures that are slightly underestimated. The  
844 consequence of this is that our model ascent rates may be minima under high-temperature  
845 conditions and that ascent times for the Troodos extrusive sequence may be higher than  
846 modelled here. The likelihood of lower liquid temperatures are low due to the high closure  
847 temperature of 1100°C inferred by Dare et al. (2009).

848 Additional complexity is added when considering the effect of changing Cr# during  
849 oxidation. Since  $\log D_{\text{Cr-Al}}$  becomes lower as chromite loses Cr (Suzuki et al., 2008), since we  
850 elected to regress data provided for the highest Cr# chromites in the study of Suzuki et al.  
851 (2008) in order to estimate maximum ascent rate, and since natural chromites have slightly

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

854 Because primitive compositional characteristics of the oxide mineral cargo are retained in  
855 several chromite crystals in the matrices of lavas of the Troodos ophiolite extrusive sequence  
856 and because, in some cases, mineral textures relating to diffusive equilibration seem to be  
857 preserved, we propose that chromites in such boninitic-tholeiitic lavas are products of either  
858 (i) crystallization from primary magmas or the incongruent melting reaction that is known to  
859 produce olivine + chromite in the shallow sub-arc mantle, or (ii) crystallization in complex  
860 fluid-melt or melt-melt mixtures in the same part of the magmatic system. In either case,  
861 chromite is likely precipitated prior to extensive pyroxene crystallization, as melt  
862 fractionation by pyroxene tends to compromise chromite stability in some igneous systems  
863 (e.g. layered mafic intrusions or ocean island basalts, Irvine, 1967; Roeder, 1994). Such  
864 behaviour appears to be absent in boninites and tholeiites associated with ophiolitic terranes  
865 such as the Troodos or the forearc regions of intra-oceanic arc systems (e.g. Whattam et al.,  
866 2020). In these rocks, matrix chromite appears with stable pyroxene minerals as euhedral-  
867 subhedral mineral grains with no signs of resorption or breakdown. Thus, chromite is most  
868 likely a primitive component of the boninite-tholeiite petrogenetic system that perseveres  
869 through differentiation in arc systems and likely records compositional traits that reflect the  
870 full range of physiochemical states these magmas undergo prior to eruption (Figure 9).

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

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

## 885 6. CONCLUSIONS

886 1) The experiments presented here enabled us to infer the kinetic behaviour of chromite  
887 in boninitic melt. Pyroxene is a ubiquitous component of the experimentally  
888 synthesized boninites, and residual melts are andesitic in composition. Matrix glasses  
889 preserved in natural boninites (Coulthard Jr et al., 2021; Woelki et al., 2020)  
890 demonstrate that olivine  $\pm$  pyroxene crystallization commonly generates residual  
891 melts that are basaltic andesitic to andesitic in composition, similar to the products of  
892 these crystallization experiments.

893 2) The fact that these same natural glasses are enriched in  $\text{Fe}^{3+}$  upon eruption (Brounce  
894 et al., 2019; Rautenschlein et al., 1985) suggests that primitive boninitic melts (i)  
895 crystallize chromite under less oxidizing conditions than those characteristic of the  
896 pre-eruptive crustal column and within what are likely complex melt-fluid/melt-melt  
897 mixtures present in the sub-arc or back-arc mantle, (ii) crystallize olivine/pyroxene  
898 phenocrysts under magmatic conditions without significant chromite crystallization in  
899 the crust, and (iii) entrain most of their chromite crystal cargo prior to microlitic



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

902 3) If chromite, including microlitic matrix chromite, were to crystallize from these  
903 residual liquids, then they would incorporate more  $\text{Fe}^{3+}$  and Al than observed, as  
904 shown by the natural samples taken from the extrusive sequence of the Troodos  
905 Ophiolite. Thus, most chromites are products of primitive melt crystallization in the  
906 crustal domain or of the incongruent melting of orthopyroxene in the mantle domain.  
907 When entrained in an evolving magma, melt oxidation perturbs the equilibrium  
908 chromite composition to higher  $\text{Fe}^{3+}$ . If sufficiently oxidizing conditions are achieved,  
909  $\text{Fe}^{3+}$  replaces Al efficiently such that  $\text{Fe}^{2+}/\text{Fe}^{3+} + \text{Fe}^{3+}/\text{Al}$  chromite-melt equilibrium is  
910 approached. The disequilibrium textures and compositions preserved in some  
911 phenocrystic-microphenocrystic chromites should be examined closely to ascertain  
912 ascent rates using  $\text{Fe}^{3+}$  diffusivity.

913 4) In chromite, Cr-Al/ $\text{Fe}^{3+}$  equilibrium is achieved over much longer timescales. If  
914 considered the limiting factor of chromite-melt equilibration, natural  
915 microphenocrystic chromite observed in the extrusive suite of the Troodos ophiolite  
916 would equilibrate with residual melts in less than *c.* 170 years. Diffusion may be  
917 much more rapid, and future work on the diffusive equilibration of both experimental  
918 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 H<sub>2</sub>O 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 fO<sub>2</sub> 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.

- 964 Brandon, A.D. and Draper, D.S. (1996) Constraints on the origin of the oxidation state of  
965 mantle overlying subduction zones: An example from Simcoe, Washington, USA.  
966 *Geochimica et Cosmochimica Acta* 60, 1739-1749.
- 967 Brounce, M., Reagan, M.K., Coulthard Jr., D.A., Kelley, K.A. and Cottrell, E. (2019) The  
968 oxidation states of iron and volatile compositions of Expedition 352 glasses, Goldschmidt  
969 2019, Barcelona, Spain.
- 970 Burnham, C.W. (1979) The importance of volatile constituents, in: Yoder, H.S., Jr. (Ed.), *The*  
971 *evolution of the igneous rocks*. Princeton University Press, Princeton, New Jersey, pp. 439-  
972 482.
- 973 Cameron, W.E. (1985) Petrology and origin of primitive lavas from the Troodos ophiolite,  
974 Cyprus. *Contributions to Mineralogy and Petrology* 89, 239-255.
- 975 Cashman, K. and Blundy, J. (2000) Degassing and crystallization of ascending andesite and  
976 dacite. *Philosophical Transactions of the Royal Society of London. Series A: Mathematical,*  
977 *Physical and Engineering Sciences* 358, 1487-1513.
- 978 Chou, I.M., Eugster, H.P., Berens, P. and Weare, J.H. (1978) Diffusion of hydrogen through  
979 platinum membranes at high pressures and temperatures. *Geochimica et Cosmochimica Acta*  
980 42, 281-288.
- 981 Cottrell, E., Birner, S., Brounce, M., Davis, F.A., Waters, L.E. and Kelley, K.A. (2020)  
982 Oxygen Fugacity Across Tectonic Settings, in: Neuville, D.R., Moretti, R. (Eds.), *AGU*  
983 *Geophysical Monograph Redox variables and mechanisms in magmatism and volcanism*.  
984 Wiley.
- 985 Couch, S., Sparks, R.S.J. and Carroll, M.R. (2001) Mineral disequilibrium in lavas explained  
986 by convective self-mixing in open magma chambers. *Nature* 411, 1037-1039.
- 987 Coulthard Jr, D.A., Reagan, M.K., Shimizu, K., Bindeman, I.N., Brounce, M., Almeev, R.R.,  
988 Ryan, J., Chapman, T., Shervais, J. and Pearce, J.A. (2021) Magma Source Evolution  
989 Following Subduction Initiation: Evidence From the Element Concentrations, Stable Isotope  
990 Ratios, and Water Contents of Volcanic Glasses From the Bonin Forearc (IODP Expedition  
991 352). *Geochemistry, Geophysics, Geosystems* 22, doi: [10.1029/2020GC009054](https://doi.org/10.1029/2020GC009054).
- 992 Crank, J. (1975) *The Mathematics of Diffusion*. Oxford University Press, London.
- 993 Dare, S.A.S., Pearce, J.A., McDonald, I. and Styles, M.T. (2009) Tectonic discrimination of  
994 peridotites using  $fO_2$ -Cr# and Ga-Ti-Fe<sup>III</sup> systematics in chrome-spinel. *Chemical Geology*  
995 261, 199-216.
- 996 Davis, F.A. and Cottrell, E. (2018) Experimental investigation of basalt and peridotite  
997 oxybarometers: Implications for spinel thermodynamic models and Fe<sup>3+</sup> compatibility during  
998 generation of upper mantle melts. *American Mineralogist* 103, 1056-1067.
- 999 Dilek, Y. and Thy, P. (2009) Island arc tholeiite to boninitic melt evolution of the Cretaceous  
1000 Kizildag (Turkey) ophiolite: Model for multi-stage early arc-forearc magmatism in Tethyan  
1001 subduction factories. *Lithos* 113, 68-87.

- 1002 Droop, G.T.R. (1987) A general equation for estimating Fe<sup>3+</sup> 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<sup>2+</sup>, 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<sup>2+</sup> and Fe<sup>3+</sup> during the formation of ferrian chromite: a  $\mu$ XANES  
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<sup>3+</sup> and Cr<sup>2+</sup> 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., Rouse, 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<sub>2</sub>O<sub>3</sub> 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<sup>2+</sup> 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<sup>2+</sup>-Mg fractionation between orthopyroxene and  
1098 spinel: experimental calibration in the system FeO-MgO-Al<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, 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<sup>2+</sup>-Fe<sup>3+</sup> 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-Fe<sup>2+</sup>  
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 fH<sub>2</sub> 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 H<sub>2</sub>O 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) *Adiabat\_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 Catalonian 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 H<sub>2</sub>O 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

1288 **Figure Captions**

1289 **Figure 1:** A) BSE image of Bon1150U. This image is representative of the “general” texture  
1290 observed in the boninitic charges. This includes several examples of euhedral prismatic opx  
1291 (dark mineral grains) and platy elongated opx (same colour) set in a relatively homogeneous  
1292 glass with anhedral chromite (bright grains). The black orb-shaped parts are vapour bubbles.  
1293 B) Close up of an opx cut parallel to the (010) plane exhibiting a ghost core (red ellipse). The  
1294 core is likely related to crystallization occurring within the melt/glass phase before stable  
1295 thermal conditions were achieved within the IHPV. The arrow points to bright caps that form  
1296 at the apices of most if not all opx in this sample (from experiment Bon1200B). These caps  
1297 are thought to have grown during quench. The glass adjacent to these minerals is darker,  
1298 indicating the loss of iron to the quench-grown rim. C) Broad view of sample Bon1100U with  
1299 calcic pyroxene highlighted (red ellipses). Several opx are aligned here, with their c-axes sub-  
1300 perpendicular to the image plane. D) BSE image of chromite in Bon1150B after thresholding  
1301 brightness and contrast to isolate and amplify Fe enrichment textures.

1302 **Figure 2:** Cation proportion (O = 6) vs Mg# (calculated using  $Fe_{total}$ ) for opx core analyses.  
1303 Literature data are taken from sources listed in the text. Point uncertainties are within the  
1304 boundaries of the symbol.

1305 **Figure 3:** Chromite compositional data. A) A portion of a conventional ternary diagram  
1306 illustrating the relative proportions of octahedrally coordinated trivalent cations after  
1307 recalculation (dimensions of the ternary are illustrated on the inset). Literature data are taken  
1308 from sources listed in the text. B) Diagram that illustrates Fe incorporation into both  
1309 octahedral and tetrahedral sites using Mg# and the  $Fe^{3+}/(Fe^{3+}+Al+Cr)$  parameter. Symbols  
1310 same as Figure 2. Analytical uncertainties associated with each composition lie within the  
1311 symbol boundaries.

1312 **Figure 4:** A) Equilibrium exchange coefficients calculated for opx and residual melt. B)  
1313 Equilibrium exchange coefficients for opx and chromite. Symbols as in Figure 2.

1314 **Figure 5:** Results from MELTS and SPINMELT-2.0 modelling compared to experimental  
1315 data (the edge of the ternary diagram from Figure 3A is shown as a dashed line). Lines are  
1316 drawn in the direction of decreasing temperature from 1200°C to 1100°C. Solid symbols  
1317 represent model data that do not account for iron loss, while empty symbols represent data  
1318 generated using models with 30% imposed iron loss.

1319 **Figure 6:** Comparison between average chromite  $\text{Fe}^{2+}/\text{Fe}^{3+}$  observed in experimental charges  
1320 and modelled equilibrium glass values of the same ratio (grey lines). For equilibrium  
1321 conditions to be met, the symbols for each sample would need to lie below the grey lines.

1322 **Figure 7:** Graphical representation of the chemical evolution of chromites within the  
1323 compositional space of the spinel prism (inset). Hypothesized relationship: Fe-Mg  
1324 interdiffusivity > Fe-Al interdiffusivity > Cr-(Al, Fe) interdiffusivity. If Fe-Mg and Fe-Al  
1325 equilibrate chromite  $\text{Mg}^\#$ ,  $\text{Fe}^{2+}/\text{Fe}^{3+}$ , and  $\text{Fe}^{3+}/\text{Al}$ , with Cr equilibration following, then re-  
1326 equilibration is a process that may be approximated by reactions 1 and 2 in a multi-step  
1327 fashion. A) Reaction 1 displaces chromite compositions to higher  $\text{Fe}^{2+}/\text{Mg}$  and  $\text{Fe}^{3+}/\text{Al}$  as the  
1328 spinel (*s.s.*) component in chromite decreases. In ternary space, this reaction causes a shift to  
1329 higher  $\text{Fe}^{3+}$  concentrations along lines of equal Cr proportion (B). Reaction 2 proceeds along  
1330 lines of equal  $\text{Fe}^{3+}/\text{Al}$  (dashed grey line in B) as Cr is lost to the melt phase. Reaction 2  
1331 proceeds in a direction perpendicular to the page (up) in A.

1332 **Figure 8:** Partial ternary diagrams (see inset) generated to compare trivalent cation  
1333 proportions of natural chromite minerals from the Troodos ophiolite (green triangles) with  
1334 modelled chromite compositions generated using SPINMELT-2.0. The grey-bordered green  
1335 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  $\text{Fe}^{2+}$  and Mg. D) Silicate minerals grow and completely alter the surrounding melt. The  
1345 melt has acquired an evolved residual composition rich in  $\text{Fe}^{3+}$ . 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 <sub>2</sub>	56.74	0.05	57.92	55.51
TiO <sub>2</sub>	0.17	0.05	0.04	0.17
Cr <sub>2</sub> O <sub>3</sub>	***0.19	53.81	0.19	1.26
Al <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O	2.01	-	1.86	1.97
K <sub>2</sub> O	0.82	-	0.46	0.80
P <sub>2</sub> O <sub>5</sub>	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% Cr<sub>2</sub>O<sub>3</sub>

- = not quantified



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

Capsule ID	IHPV Lab	Initial Composition		Experimental Conditions			
		Seed Size ( $\mu\text{m}$ )	wt% D <sub>2</sub> O (1 $\sigma$ )	T ( $^{\circ}\text{C}$ )	P (kbar)	pH <sub>2</sub> <sup>added</sup> (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 $\sigma$ )			Activity Model		Oxygen Fugacity		
	Orthopyroxene	Chromite	Glass	Final wt% <sup>2</sup> H <sub>2</sub> O (1 $\sigma$ )	aH <sub>2</sub> O (1 $\sigma$ )	Sensor X <sub>Ni</sub> (1 $\sigma$ )	log $f\text{O}_2$ (bars)	$\Delta\text{NNO}$ (1 $\sigma$ )
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 <sub>2</sub>	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	NiO	Total	Mg#	Cr#	*Fe <sup>2+</sup> /Fe <sup>3+</sup>
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><math>K_D(Fe-Mg)^{opx-liq} (1\sigma)</math></u>	<u><math>*K_D(Fe-Mg)^{chrm-opx}</math></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 $\sigma$  is a quantification of the distribution of modelled/observed values based on analytical precision and detected heterogeneity*

*\*Model uncertainty =  $c. \pm 0.157 (1\sigma)$  using error propagation*

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

<i>Opx data (norm.)</i>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MgO	Total				<i>Average <math>Y_{Cr}^{chrom}</math></i>
*AM-4 chrm-a	51.65	9.82	23.73	9.59	94.79		0.238	0.244	0.70
*AM-4 chrm-b	52.71	9.98	23.43	11.60	97.72		0.288	0.216	
*AM-4 chrm-c	53.80	10.18	23.46	11.25	98.69		0.279	0.228	
<i>Glass data and model <math>K_D</math></i>	<i>**Average Model <math>K_D(Fe-Mg)^{opx-liq}</math> (<math>1\sigma</math>)</i>			<i>**Average melt molar MgO (<math>1\sigma</math>)</i>			<i>**Average melt molar FeO (<math>1\sigma</math>)</i>		
	0.292 (0.004)			0.232 (0.024)			0.108 (0.004)		
<i>Modelled <math>K_D(Fe-Mg)^{chrom-opx}</math></i>	opx-a	opx-b	<i>***(<math>1\sigma</math>)</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 <math>K_D</math> Values</i>	$K_D(Fe-Mg)$	<i>***(<math>1\sigma</math>)</i>		<i>Equilibrium?</i>		<i>*** Same model uncertainty as in previous table</i>			
opx-a and average melt	0.334	0.041		yes		<i>**** Calculated using error propagation methods applied to average melt composition</i>			
opx-b and average melt	0.300	^		yes		^ = Same as above			
chrm-a and opx-a	6.587	-		no		- = Cannot be calculated using available data			
chrm-a and opx-b	7.324	-		no					
chrm-b and opx-a	4.827	-		yes (1030°C)					
chrm-b and opx-b	5.367	-		yes (mod T)					
chrm-c and opx-a	5.238	-		yes (mod T)					
chrm-c and opx-b	5.824	-		yes (opx-b 1130°C)					

**Table 6: Ascent time calculations**

<i>Chromite Radius (<math>\mu\text{m}</math>)</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 (<math>\text{cm}^2/\text{sec}</math>)</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: