

1 *\*Revision 2 for Manuscript 5783\**

2 *A Review and Update of Mantle Thermobarometry for Primitive Arc Magmas*

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6 **Abstract**

7 Erupted lavas and tephra remain among the best tools we have to ascertain the  
8 mantle processes that give rise to the compositional diversity and spatial distribution of  
9 near-primary magmas at volcanic arcs. A compilation of mantle-melt thermobarometry  
10 for natural, primitive arc magmas to date reveals published estimates vary between  
11 ~1000-1600°C at ~6-50 kbar. In addition to the variability of mantle melting processes  
12 within and between different arcs, this range of conditions is the result of different  
13 methodology, such as the nature of reverse fractional crystallization calculations, the  
14 choice of thermobarometer, how magmatic H<sub>2</sub>O was quantified and its calculated effect  
15 on pressure and temperature, and choices about mantle lithology and oxygen fugacity.  
16 New and internally-consistent reverse fractionation calculations and thermobarometry for  
17 a representative subset of the primitive arc samples with adequate published petrography,  
18 measured mineral and melt compositions, and constraints on pre-eruptive H<sub>2</sub>O content  
19 suggest a smaller range of global mantle-melt equilibration conditions (~1075-1450°C at  
20 ~8-19 kbar) than the literature compilation. The new pressure and temperature estimates  
21 and major element modeling are consistent with a model whereby several types of  
22 primitive arc magmas, specifically hydrous calc-alkaline basalt, primitive andesite and  
23 hydrous high-MgO liquid such as boninite, first form at the location of the water-  
24 saturated mantle solidus at pressures of ~20-35 kbar and rise into the hot core of the

25 mantle wedge reacting with the mantle en route. Due to their re-equilibration during  
26 ascent, these hydrous magmas ultimately record the conditions in the hot, shallow nose of  
27 the mantle wedge at the end of their mantle ascent path rather than the conditions at their  
28 point of origin as often interpreted. When the mantle residue for this process is lherzolite,  
29 calc-alkaline basalt is generated. When the mantle residue is harzburgite to dunite, either  
30 high-Mg primitive andesite or high-MgO liquid is generated, depending on the H<sub>2</sub>O  
31 content. A different type of primitive arc magma, specifically nominally anhydrous arc  
32 tholeiite, is generated by near-fractional decompression melting at or near the anhydrous  
33 lherzolite solidus in the upwelling back limb of corner flow at ~25-10 kbar and is focused  
34 into the same region of the shallow mantle wedge as the hydrous melts. The similarity in  
35 the terminus of the mantle ascent paths for both wet and dry primitive arc magmas likely  
36 explains their eruption in close spatial and temporal proximity at many arcs. The  
37 conditions of last mantle equilibration for primitive arc tholeiites generated by  
38 decompression melting also imply that the convecting mantle extends to 10 kbar (~30  
39 km) or less below most arcs. The range of mantle-melt equilibration conditions calculated  
40 here agrees well with the range of temperatures predicted for the shallow mantle wedge  
41 beneath arcs by geodynamic models, although it suggests some subduction zones may  
42 have higher maximum temperatures at shallower depths in the wedge than originally  
43 predicted. Primitive hydrous arc magmas also constrain natural variation on the order of  
44 200-250°C in the maximum temperature in the hot shallow nose of the mantle wedge  
45 between arcs. Thus the new primitive magma thermobarometry presented here is useful  
46 for understanding melt migration processes and the temperature structure in the

47 uppermost part of the mantle wedge, as well as the origin of different primitive magma  
48 types at arcs.

## 49 **Introduction**

50 Substantial work has advanced our knowledge of the underlying processes that  
51 give rise to volcanic arcs since the advent of plate tectonic theory. This includes an  
52 understanding of the first order processes that produce arc magmas such as models of the  
53 volatile flux from the subducting plate into the overlying mantle (e.g., Poli and Schmidt,  
54 1995, 2002; Hacker 2008; van Keken et al. 2011) and its effect on mantle melting  
55 behavior (Kushiro et al. 1968; Green, 1973; Mysen and Boettcher 1975; Kawamoto and  
56 Holloway 1997; Grove et al. 2006; Till et al. 2012b). Many different types of mantle-  
57 derived arc magmas have been observed, including high-Mg andesites, calc-alkaline  
58 basalts, high alumina olivine tholeiites, boninites and sanukitoids. But questions remain  
59 as to what is ultimately responsible for producing each variety of primitive arc magma  
60 and why different arcs have different abundances of these magmas. Thermobarometry of  
61 the reconstructed primary parental magmas for these primitive liquids provides a  
62 powerful means to answer these questions, as well as to determine where in the mantle  
63 these primitive liquids are sourced. In addition, thermobarometry of primary arc liquids  
64 provides observational constraints on the temperature at a given pressure in the mantle  
65 that can be used in conjunction with dynamical models of mantle flow (e.g., Kelemen et  
66 al. 2003). Outstanding questions about melt flow in the mantle wedge (e.g., reactive  
67 porous flow vs. diapiric or channelized flow: Navon and Stolper 1987; Grove et al. 2002)  
68 can also for example be addressed through the study of primitive magmas and the  
69 pressures and temperatures they record.

70           The opportunity to answer these questions on a global-scale requires a  
71 compilation of existing thermobarometry of primitive arc magmas. However, the  
72 methodology and assumptions vary between past studies. For example, the process of  
73 determining a primitive magma's liquid line of descent in order that the primary liquid  
74 composition can be estimated and used with thermobarometers remains somewhat of an  
75 art form and thus the methodology and assumptions vary between past studies (e.g.,  
76 Leeman et al. 2005; Lee et al. 2009; Till et al. 2012a; Kimura et al. 2014). Similarly, the  
77 different thermobarometers used in past studies incorporate different assumptions about  
78 the mantle residue composition (e.g., harzburgite: Mitchell and Grove 2015 vs. lherzolite:  
79 Till et al. 2012a vs. olivine + orthopyroxene in residue: Lee et al. 2009). In addition, there  
80 are a multitude of methods for reconstructing the volatile content of primary arc liquids,  
81 specifically the H<sub>2</sub>O content (e.g., Sisson and Grove 1993; Baker et al., 1994; Wade et al.  
82 2008; Kelley et al. 2010; Ruscitto et al. 2010; Waters and Lange, 2015; Mitchell and  
83 Grove 2015), which has a significant effect on the pressure and temperature returned by  
84 thermobarometry. As a result, a direct comparison of existing thermobarometric  
85 estimates is problematic.

86           In order to provide a global-scale comparison, this paper compiles the results of  
87 published studies of mantle-melt thermobarometry conducted on erupted natural  
88 primitive arc lavas, tephra, matrix glass compositions, and melt inclusions. The methods  
89 used in these studies are reviewed, such that the effect of the methodology on the  
90 calculated pressure and temperature can be quantified and potential pitfalls identified.  
91 These results are then used to recommend a series of best practices for calculating  
92 primary liquid compositions from erupted primitive magmas and conducting the

93 associated thermobarometry. These best practices are subsequently applied to a subset of  
94 the published primitive arc rock and melt inclusion compositions where there is adequate  
95 information in the source publication to carry out the recommended methods. These  
96 recalculated pressures and temperatures are then used to address overarching questions in  
97 arc magma genesis, such as the processes that govern the production of the most common  
98 types of primitive arc magmas, as well as provide observational constraints on the  
99 thermal structure and melt flow in the mantle wedge below arcs.

## 100 **Literature Review**

101 A literature review of primitive arc liquid thermobarometry is presented here and  
102 restricted to thermobarometry that provides constraints on the mantle origin and  
103 evolution of arc magmas. Primary magmas are melts that have not been chemically  
104 modified in any manner since they segregated from their source region. In reality, all  
105 magmas experience some processing en route to the surface, which consists of crystal  
106 growth (fractional crystallization) and/or mixing of the magma with new materials  
107 (assimilation) or other magmas (magma mixing or recharge), such that they are instead  
108 called primitive magmas. The P-T constraints reviewed here are from natural primitive  
109 magmas or melt inclusions generated in the mantle wedge in the range between arc fronts  
110 and back-arcs.

111 Two methods of constraining the pressures and temperatures using natural  
112 primitive arc magmas are included in this literature review of mantle-melt  
113 thermobarometry (Fig. 1). The first method is thermometric and barometric calculations  
114 for primitive arc-related magmatic liquids, where bulk rock, matrix glass or melt

115 inclusion compositions are used with thermobarometers such as Mitchell and Grove  
116 (2015), Till et al. (2012a), Lee et al. (2009), or Putirka (2007, 2008) following  
117 calculations to reverse fractional crystallization, post-entrapment crystallization etc.  
118 These studies are designed to calculate the temperature and pressure at which the liquid  
119 was in equilibrium with a peridotitic mantle (rather than the pressure or temperature of  
120 crystal fractionation, for example). The second method of constraining primitive liquid  
121 pressure and temperature in the literature compilation is experimental location of the  
122 multiple saturation points for primitive arc magmas. For these cases, a primitive magma  
123 or a synthetic oxide mixture of the same composition is used as the starting composition  
124 to determine the phase relationships for this sample over the portion of pressure-  
125 temperature space relevant to the upper mantle below volcanic arcs. The mineral phase  
126 boundaries are thus located, such that the point in pressure-temperature space where a  
127 melt is in equilibrium with a peridotitic mineral assemblage at given H<sub>2</sub>O content, or the  
128 *multiple saturation point*, can be determined. These experiments are also used to  
129 calibrate many of the thermobarometers used in the first method. For the types of  
130 experiments covered in this review, the peridotitic assemblages at the multiple saturation  
131 point are either lherzolitic (olivine + clinopyroxene + orthopyroxene + aluminous phase  
132 (plagioclase, spinel, garnet)) or harzburgitic (olivine + orthopyroxene).

133 Thermobarometric studies in the literature were filtered for inclusion in this  
134 compilation with the following requirements: 1) that the samples used for  
135 thermobarometry were natural rock compositions erupted in an arc setting past or present,  
136 2) that the samples were “primitive” as identified by the authors, and 3) that their  
137 pressure and temperature of melting or melt segregation from the mantle (or melt

138 entrapment in the case of melt inclusions) were estimated with thermobarometry or  
139 experimentation (Table 1). The samples used for mantle-melt thermobarometry in these  
140 studies have a wide compositional variation, wider than what is usually considered  
141 primitive (Fig. 2) as no filters based on composition were applied for inclusion in the  
142 literature compilation in Figure 1. The source publications for melt inclusion with <57  
143 wt% SiO<sub>2</sub>, Mg# > 0.5 and locations from arc settings in the GEOROC database were also  
144 queried for studies that met the criteria listed above. This review only includes melt  
145 inclusion pressure-temperature studies where the author identified the melt inclusion  
146 composition as reflecting a primitive liquid composition and both a temperature and  
147 pressure of mantle melt equilibration were determined. A few of the samples in the  
148 Cascades have been utilized for pressure-temperature determinations by multiple studies,  
149 and are represented as distinct points for each study in the literature compilation in Figure  
150 1, such that not every plotted point is a unique sample. In total the literature compilation  
151 includes 638 independent estimates of the temperature and/or pressure of melt  
152 segregation for natural primitive arc magmas from 35 references (Table 1; electronic  
153 supplement Table S1).

154 Published thermobarometric estimates for primitive arc magmas and melt  
155 inclusions compiled directly from the literature vary between ~6-50 kbar and ~1000-  
156 1600°C (n=638) (Figure 1; electronic supplement Table S1). The Cascades (n=410) and  
157 Izu-Bonin-Marianas (IBM) (n=131) arcs have the largest number of samples investigated  
158 to date and span the complete range of pressures and temperatures in the literature  
159 compilation with the exception of several experimental samples from Japan that suggest  
160 lower temperatures of mantle equilibration (<1150°C).

161 **Review of the Methods for Mantle-Melt Thermobarometry in the Literature**

162 **Compilation**

163 Here the methods employed to arrive at the pressure-temperature estimates in  
164 Figure 1 are reviewed in order to quantify the effect of different methodologies and  
165 identify best practices for an internally consistent set of new pressure-temperature  
166 calculations (presented in “Recalculation of Pressures & Temperatures for Common Arc  
167 Magma Types” section below).

168 **Calculating the Primary Liquid Composition through Reverse Fractional**  
169 **Crystallization**

170 To obtain the P-T conditions of mantle partial melting, a melt inclusion, bulk rock  
171 or matrix glass composition first must be adjusted for crystal fractionation, until it is in  
172 equilibrium with an assumed mantle olivine composition and/or mantle mineral  
173 assemblage (i.e., lherzolite, harzburgite or dunite). In addition, calculations to adjust for  
174 post-entrapment crystallization and/or diffusion may be necessary to return the  
175 composition of primitive melt inclusions to their original primary composition.

176 The fractional crystallization paths of mid-ocean ridge basalts (MORB) have been  
177 well established through experimental and petrologic studies (e.g., Tormey et al. 1987;  
178 Grove et al. 1992; Yang et al. 1996). MORBs tend to fractionate olivine and plagioclase  
179 and the critical variable in reconstructing fractionation paths is pressure. Calculations to  
180 adjust for fractional crystallization become more complex for primitive arc magmas and  
181 other primitive magmas erupted in continental settings, as their phase assemblages and  
182 sequences of crystallization are dependent on other variables besides pressure. The key is



183 to have a set of lavas related by fractional crystallization that can be used to identify 1)  
184 the proportion of the phases that crystallized, 2) the degree of crystallization of the  
185 magma with a given phase assemblage, and if applicable 3) the switching point between  
186 sets of co-crystallizing phase assemblages (i.e., when the magma leaves a cotectic) (see  
187 full review of reverse fractionation methods in the supplementary materials). An  
188 alternative approach is to restrict thermometry and barometry to primitive samples that  
189 have experienced a minimal amount of crystal fractionation, such that they have only  
190 experienced olivine crystallization, which is more straightforward to adjust for. For  
191 example, for MORB, FeO\* increases and CaO drops sharply when plagioclase joins  
192 olivine and a plot of FeO\* or CaO vs. MgO can reveal samples that fall on an olivine  
193 control line vs. those that experienced multiphase fractionation.

194 Failure to adequately approximate the fractionation path, and in particular  
195 ignoring the requirement of the final liquid plotting on a mantle multiple saturation point,  
196 can have a significant effect on the adjusted liquid composition and thus the calculated  
197 source pressure and temperature. For example, if a polybaric, near fractional MORB  
198 primary melt experienced multiphase fractionation (olivine, followed by  
199 olivine+plagioclase) but is then adjusted for olivine-only fractionation, the calculated  
200 “primary melt” has artificially high MgO + FeO\* and low Al<sub>2</sub>O<sub>3</sub> contents and thus the  
201 calculated mantle conditions are 100-150°C hotter and up to 13 kilobars higher than the  
202 actual pressure and temperature of generation for the parental MORB melt (see Fig. 6 of  
203 Till et al. 2012a for a worked example). A variety of approaches to reverse fractionational  
204 crystallization have been used for the primitive liquids with thermobarometry in the

205 literature collected in Figure 1, with the dominant approach being the addition of only  
206 olivine back to the liquid composition.

207 H<sub>2</sub>O also plays an important role in calculations to reverse fractionational  
208 crystallization as it affects the order and composition of the fractionating phases. The  
209 body of work on arc magma fractionation paths suggests that the onset of plagioclase  
210 crystallization is the most important variable controlling the liquid line of descent of arc  
211 magmas. Experimental studies of the liquid line of descent illustrate that increasing the  
212 water contents at a constant pressure will cause the temperature of plagioclase  
213 crystallization to go down relative to the liquidus, thereby reducing the proportion of  
214 plagioclase crystallized compared to the ferromagnesian silicates and increasing the SiO<sub>2</sub>  
215 content of the residual liquid, as well as the relative temperature of magnetite or FeTi  
216 oxide crystallization (e.g., Sisson and Grove 1993; Grove et al. 2003; Hamada and Fuji  
217 2008; Tatsumi and Suzuki 2009; Parman et al 2011; Blatter et al. 2013). Although H<sub>2</sub>O  
218 suppresses plagioclase crystallization at any oxygen fugacity, the amount of H<sub>2</sub>O required  
219 to evolve the liquid to a calc-alkaline composition increases as oxygen fugacity  
220 decreases. Thus increasing the H<sub>2</sub>O content at a given  $fO_2$  drives the liquid more directly  
221 to the calc-alkaline field, essentially decreasing the concavity of the fractionation path as  
222 demonstrated in experimental studies such as Hamada and Fuji (2008) and summarized in  
223 Figure 3. Sulfur degassing can also cause a liquid to become more reduced during ascent  
224 (Anderson and Wright, 1972; Kelley and Cottrell 2012; Moussallam et al. 2014), which  
225 alters the Fe<sup>2+</sup> content appropriate for the primary melt temperature and pressure  
226 calculations (Brounce et al. 2014). The composition of the minerals that crystallize from  
227 hydrous magmas also change, for example the Ca/Na of the feldspar varies as a function

228 of melt H<sub>2</sub>O content (e.g., Sisson and Grove, 1993), which will affect the  
229 thermobarometers that consider Ca and Na contents.

230         Although the theory for reverse fractional crystallization calculations for MORB  
231 and nominally anhydrous arc basalts discussed above still applies to wetter primitive arc  
232 magmas, there is not a well-accepted parameterization for the cumulative changes H<sub>2</sub>O  
233 causes in the liquid line of descent. The cutoff H<sub>2</sub>O content above which MORB-like  
234 fractionation paths no longer apply is not clear, but MORB-like fractionation schemes are  
235 likely most applicable over the range of H<sub>2</sub>O contents relevant for MORB genesis and the  
236 higher the magmatic H<sub>2</sub>O content, the more fractionation behavior will deviate from  
237 MORB-like behavior. Kimura et al. (2014) and Kimura and Araskin (2014) are the only  
238 studies in the literature review in addition to the experimental studies on primitive arc  
239 magma pressures and temperatures that adjust the composition of the fractionating phases  
240 according to H<sub>2</sub>O content. Therefore, future work is required to parameterize the discrete  
241 effects of H<sub>2</sub>O during fractionation, such that we can ultimately calculate hydrous  
242 primary arc magma compositions accurately.

#### 243             **Calculating Pressure and Temperature Using Primary Magma** 244 **Compositions.**

245         Many experiments have demonstrated that the composition of the melt in  
246 equilibrium with a mantle peridotite (lherzolite or harzburgite) varies as a function of  
247 pressure, temperature, mantle source composition, and volatile content (e.g., Tatsumi et  
248 al. 1981; Takahashi and Kushiro, 1983; Kushiro 1990; Kinzler and Grove 1992a; Parman  
249 and Grove 1998; Gaetani and Grove 1998; Till et al. 2012a; Grove et al. 2013; Mitchell

250 and Grove 2015). Thus primary liquids composition can be used as a purely empirical  
251 geothermometer as long as the appropriate restrictions in bulk composition and saturating  
252 phases are made (Helz & Thonber 1987; Grove and Juster 1989). It follows that the  
253 temperatures and pressures reported in the literature (Fig. 1) are a function of the models  
254 that were used to calculate them. A full review and evaluation of the different  
255 thermometers and barometers that have been applied to calculated primary arc magmas is  
256 beyond the scope of this study (the reader is referred to existing reviews of thermometers  
257 for volcanic rocks in Putirka 2008 and for melts in equilibrium with a harzburgite in  
258 Mitchell and Grove 2015). Instead here the focus is to determine the spread of  
259 temperatures and pressure in the literature compilation attributable to the use of different  
260 thermobarometers, as well as make recommendations regarding the most reliable  
261 thermobarometers for primitive arc liquids.

262         The spread of temperatures that can be attributed to the choice of thermometer  
263 alone is on the order of  $\leq 75^{\circ}\text{C}$  overall, and more likely to be  $\leq 35\text{-}40^{\circ}\text{C}$  in most cases (see  
264 electronic supplement). Recently published thermometers calibrated on the largest and  
265 most robust databases of experiments such as Putirka et al. (2008) eqn. 4, Lee et al.  
266 (2009), and Till et al. (2012a) tend to agree to within  $35^{\circ}\text{C}$  on average, which is within  
267 the error of these thermometers (SEE Putirka= $52^{\circ}\text{C}$ ; Lee= $\sim 40^{\circ}\text{C}$  (3%) and Till= $11^{\circ}\text{C}$ ).  
268 These three thermometers also include a term to consider the effect of  $\text{H}_2\text{O}$ , which makes  
269 them the most reliable and practical for the application to the continuum of dry to wet arc  
270 magmas at present. However, Lee et al. (2009) explicitly states that their melt barometer  
271 is “not intended for hydrous, unusually fertile or depleted mantle compositions that might  
272 characterize subduction-modified mantles” because it is based on the activity of  $\text{SiO}_2$  in

273 the melt, which varies with source mineralogy and water content, as well as pressure.  
274 Therefore although calibration of Lee et al (2009) utilized a wide range of ultramafic melt  
275 equilibria experiments where olivine and orthopyroxene were stable in the residue, it is  
276 not well suited to melt generated in the garnet stability field, as the relationship between  
277 melt SiO<sub>2</sub> and pressure diminishes above ~2.5 GPa when garnet is present in the residue  
278 (T. Plank, personal communication, 2014), nor water-saturated systems, which also alter  
279 the silica activity of the melt. Till et al. (2012a) and Grove et al. (2013) are updated  
280 calibrations using the methodology of Kinzler and Grove (1992b), which require a  
281 lherzolite residue (plagioclase or spinel lherzolite for Till et al. (2012a), and garnet  
282 lherzolite for Grove et al. (2013)) but have the additional advantage over Kinzler and  
283 Grove (1992a) of being calibrated to consider metasomatized as well as variably depleted  
284 lherzolite. These lherzolite thermometers reproduce experimental liquids with the  
285 smallest average absolute errors of all the thermometers examined, only 11°C for Till et  
286 al. (2012a) and 24°C for Grove et al. (2013), and are thus extremely well suited to  
287 application in arc environments, provided the liquid appears to be in equilibrium with a  
288 lherzolite residue.

289 In the case where primary arc liquids are in equilibrium with Fo90-91 olivine but  
290 are not in equilibrium with a lherzolite residue (e.g., Fig. 4b,c), the liquids may instead be  
291 saturated with a harzburgite or dunite residue, natural examples of which are found in  
292 exhumed sub-arc mantle sections and xenoliths (e.g., Kelemen et al., 1995; Pearce and  
293 Parkinson 1993; Morishita et al. 2011; Pirard et al. 2013). How to identify liquids in  
294 equilibrium with each of these potential residues is discussed in the supplementary  
295 material (see electronic supplement Fig. S1 & S2). Mitchell and Grove (2015) developed

296 a thermobarometer similar to Till et al (2012a) and Grove et al. (2013) but specifically for  
297 primitive liquids in equilibrium with harzburgite residues. The Lee et al (2009) and  
298 Putirka et al. (2007) thermometers significantly under predict the temperatures of  
299 experimental melts in equilibrium with harzburgite compared to Mitchell and Grove  
300 (2015) and Till et al. (2012a), which are within error. With the addition of water to the  
301 melt, the thermometers of Till et al (2012a) and Mitchell and Grove (2015) continue to be  
302 within error of the experimental temperature, whereas the Lee et al. (2009) and Putirka et  
303 al. (2007) are  $\sim 100^\circ\text{C}$  hotter. A number of thermometers based on olivine-liquid  
304 equilibria exist, including a new model that includes the effect of oxygen fugacity by  
305 Putirka (2016), which can be used for liquids in equilibrium with dunite.

306 Differences in the assumed mantle  $f\text{O}_2$  and thus the appropriate  $\text{Fe}^{2+}$  content of  
307 the primary melt will also affect the temperatures calculated. Although a range of  
308 approximately QFM-3 to QFM+2 has been estimated for the upper mantle (Frost and  
309 McCammon 2008 and references therein), and QFM to NNO for oceanic basalts (Putirka,  
310 2016), work on primitive arc magmas suggests a more oxidized range of oxygen  
311 fugacities ( $\sim$ QFM+1 to QFM+2 or even MH) is appropriate for the mantle in subduction  
312 zones (Brounce et al. 2014; Putirka 2016). The lower oxygen fugacities are thought to be  
313 found in drier/back-arc regions and the higher fugacities in the hydrated mantle due to the  
314 role of the subduction fluids/melts in oxidizing mantle wedge environments (e.g., Kelley  
315 and Cottrell 2009; Brounce et al. 2014).

316 The  $\text{H}_2\text{O}$  contents for samples included in the literature compilation in Figure 1  
317 have been estimated using a range of techniques and this is likely the variable for which  
318 the quality of the constraints is the most heterogeneous. For example, some studies have

319 carefully determined the H<sub>2</sub>O content of each individual sample through ion probe or  
320 FTIR analyses of melt inclusions (e.g., Kelley et al. 2010; Ruscitto et al. 2010), where  
321 others utilized mineral chemistry and hygrometry (e.g., Mullen & McCallum 2014), or  
322 made comparison to experimental liquid lines of descent (e.g., Leeman et al. 2005, 2009;  
323 Kimura et al. 2006), and others choose to assign all samples from a given subduction  
324 zone the same water content (e.g., Lee et al. 2009). Even if the H<sub>2</sub>O content of a primary  
325 melt has been effectively estimated, the calculated effect of this H<sub>2</sub>O on mantle  
326 equilibration temperature and pressures differs between models and may vary  
327 systematically with melt compositions. The thermobarometers of Putirka et al. (2007),  
328 Lee et al. (2009) and Till et al. (2012a) include a calibration for the effect of H<sub>2</sub>O on the  
329 calculated liquid temperature for lherzolite melts. The Till et al. (2012a) calibration  
330 results in the largest effect of H<sub>2</sub>O on the liquid temperature, followed by Putirka et al.  
331 (2007) and then Lee et al. (2009). The temperature difference predicted by these models  
332 can be up to 67°C at 5 wt% H<sub>2</sub>O for a calc-alkaline basalt, which is greater than the  
333 uncertainty of these thermometers (further discussed in the electronic supplement). The  
334 effect of H<sub>2</sub>O on the liquid temperature can therefore introduce an equivalent or often  
335 larger spread in temperatures in the literature compilation than the choice of which  
336 thermometer was used (see electronic supplement). The effects of H<sub>2</sub>O on pressure are  
337 compared for the Lee et al. (2009) and Till et al. (2012) barometers in the electronic  
338 supplement. The Lee et al. (2009) barometer has a larger model dependence on H<sub>2</sub>O than  
339 Till et al. (2012a) and the calculated pressure of equilibration is 2.5 kbar (or ~8.5 km)  
340 higher with Lee et al. (2009) than Till et al. (2012a) for a calc-alkaline basalt with 5 wt%  
341 H<sub>2</sub>O. This variability in the pressure calculations as a function of H<sub>2</sub>O content is

342 equivalent to or smaller than the range of pressures produced by using different  
343 barometers or types of reverse fractionation calculations on the same sample.

344 Thus large variations in pressure and temperature in Figure 1 may be attributed to  
345 different assumptions about H<sub>2</sub>O content. And it follows that our ability to calculate the  
346 pressures and temperatures at which primitive arc magmas are sourced in the mantle and  
347 thus interpret mantle wedge processes is the most limited by the consideration of H<sub>2</sub>O,  
348 specifically by differences in how the primary magmatic H<sub>2</sub>O-contents are estimated (or  
349 not), the lack of consideration of H<sub>2</sub>O's effects on the reverse fractionation crystallization  
350 calculations in existing studies, and the differences between models for the effects of H<sub>2</sub>O  
351 on mantle equilibration pressure and temperature.

## 352 **Recalculation of Pressures & Temperatures for Common Primitive Arc Magma** 353 **Types**

### 354 **Methods**

355 A representative subset of the primitive arc samples with thermobarometry in the  
356 literature review in Figure 1 and 2 (n=208 of 638 in literature review) were selected for a  
357 reassessment of their reverse fractional crystallization calculations and a recalculation of  
358 their pressures and temperatures of mantle equilibrium using an internally consistent set  
359 of methods and the latest thermobarometric tools that consider H<sub>2</sub>O (Table 2). Samples  
360 were chosen whose source literature provided substantial information about the sample's  
361 (or suite of samples') petrography and mineral compositions, oxygen fugacity and where  
362 possible H<sub>2</sub>O content. A wholesale recalculation for all samples used in the literature  
363 compilation is not possible because many source publications contain insufficient



364 information to conduct the reverse fractionation calculations and/or estimate H<sub>2</sub>O  
365 content. However, the samples included in the recalculation are representative of the full  
366 range of sample compositions in Figure 2 and calculated pressures and temperatures in  
367 the literature compilation in Figure 1. Once investigated the samples fall into three  
368 categories: 1) calc-alkaline basalts and low-K tholeiites, 2) primitive andesites, and 3)  
369 primitive boninites, picrites and other high-MgO liquids (Fig. 4, 5), and the methods for  
370 the recalculation of each category is discussed below (also see the worked example in the  
371 supplementary material). Here we distinguish high-MgO liquids with <52 wt. % SiO<sub>2</sub>  
372 and >15 wt% MgO from primitive andesite with >52 wt% SiO<sub>2</sub> and <15 wt% MgO (av.  
373 9-10 wt% MgO). In addition, three samples appear to have formed in the presence of  
374 significant amounts of CO<sub>2</sub> or be the result of melting pyroxenite as demonstrated by  
375 their major element compositions projected onto pseudo-ternary (see diagrams Figures 9  
376 and 11, respectively and associated text in Grove et al., 2013) and are excluded from the  
377 pressure-temperature calculations.

378         The subset of calc-alkaline and tholeiitic basaltic lavas or melt inclusions used for  
379 the recalculations are from the Cascade (Leeman et al. 2005; Rowe et al. 2009; Till et al.  
380 2013), Lesser Antilles (Pichavant, et al. 2010) and Mariana arcs (Kelley et al. 2010) and  
381 are similar to the majority of the rock types in the literature with pressure-temperature  
382 estimates. These samples tend to have experienced olivine, olivine +plagioclase,  
383 olivine+clinopyroxene or olivine+plagioclase+clinopyroxene fractionation based on the  
384 mineralogy of the samples and/or the liquid compositions and required calculations to  
385 reverse between 4 to 26% crystallization (Fig. 6). These minerals were added back to the  
386 whole rock composition (usually in proportions reflecting the modal proportions in the

387 sample), treating all Fe as FeO\* and using partition coefficients appropriate for the H<sub>2</sub>O  
388 contents of the sample (e.g., varying the Ca-Na plagioclase-liquid K<sub>D</sub> as a function of  
389 H<sub>2</sub>O) (see worked example in electronic supplement). The H<sub>2</sub>O content of these samples  
390 were determined via SIMS or FTIR on melt inclusion or matrix glass by several studies  
391 and estimated using the methods listed in Table 2 for the remaining samples. The major  
392 element compositions of these liquids are consistent with forming from a lherzolite  
393 residue, such that the reverse fractionation calculations aims at returning them to a  
394 lherzolite multiple saturation point and equilibrium with Fo90 mantle olivine (Fig. 4a).  
395 These adjusted primary liquids were used with the lherzolite thermometers and  
396 barometers of Till et al. (2012a) and Grove et al. (2013), which includes the effect of  
397 H<sub>2</sub>O.

398         The subset of primitive andesites used for the recalculations are those studied in  
399 Mitchell and Grove (2015) and are from the Setouchi volcanic belt (Tatsumi & Ishizaka  
400 1982; Tatsumi et al. 1983), the Cascades (Baker et al. 1994; Grove et al. 2002, Mitchell  
401 & Grove, 2015), Kamchatka (Bryant et al. 2010), and the Trans-Mexico volcanic belt  
402 (Weaver et al. 2011, Weber et al., 2011). These samples have high Mg#’s (0.71-0.76)  
403 and their compositions are consistent with liquids in equilibrium with a harzburgite  
404 residue as predicted by the model of Mitchell and Grove (2015) without any reverse  
405 fractionation calculations (Fig. 4b, 5). Given the degrees of freedom, two of the three  
406 variables of pressure, temperature and H<sub>2</sub>O contents can be calculated for these liquids  
407 using the thermometer, barometer and/or hygrometer for liquids in equilibrium with  
408 harzburgite from Mitchell and Grove (2015). Here the thermometer and hygrometer were

409 employed and pressure was assumed based on the thickness of modern crust in these  
410 locations, which is on average 30 km (~10 kbar).

411         The subset of boninites, picrites and other high MgO magmas (>13.5 wt% MgO)  
412 used for the recalculations are dredge samples from the Bonin forearc (Li et al. 2013) and  
413 Mariana (Bloomer and Hawkins 1987), subaerial samples from the Marianas (Dietrich et  
414 al., 1978) and the New Britain arc (Cameron et al., 1983) and melt inclusions from the  
415 Tonga trench (Sobolev and Danyushevsky 1994) and eastern Kamchatka (Kamenstky et  
416 al. 1995). They represent the samples with the highest Mg#’s and high MgO contents in  
417 the literature compilation (Fig. 2), as well as the samples that record the highest  
418 temperatures and pressures of mantle equilibration in the literature compilation (Fig. 1).  
419 Their high Mg#’s of 0.74-0.82 suggest these liquids were in equilibrium with Fo90-94  
420 olivine with a Fe-Mg  $K_D$  of 0.3 or that  $K_D$  values were higher than 0.3 to be in  
421 equilibrium with Fo90 olivine. As such, it was not necessary to adjust the liquids for  
422 fractionation in order to return these samples to equilibrium with the mantle. When  
423 plotted in pseudoternary space, these liquids exhibit lower plagioclase and clinopyroxene  
424 components than the mantle lherzolite multiple saturation points suggesting they may be  
425 in equilibrium with either a harzburgite or dunite residue instead (Fig. 4c, 5, S2). As the  
426 liquids fall along the olivine-orthopyroxene saturation boundaries experimentally  
427 determined by Wagner and Grove (1998), they may be the product of either harzburgite  
428 melting or lherzolite melts that re-equilibrated with harzburgite in the lithosphere as they  
429 ascended (Grove et al. 2013; Wagner and Grove 1998). A few of the samples with the  
430 lowest clinopyroxene mineral component values plot in regions of liquids in equilibrium  
431 with a dunite (see Fig. S1, S2) produced experimentally at very low melt-rock ratios (5 to

432 20% melt) at high temperatures 1220-1260°C found in the hot core of the wedge  
433 (Mitchell and Grove, 2016). Given the similarity of the majority of the high-Mg liquids  
434 to those in equilibrium with harzburgite, the Mitchell and Grove (2015) harzburgite  
435 thermometer and hygrometer were applied to all of them. For samples with H<sub>2</sub>O contents  
436 measured via ion probe in melt inclusions or matrix glass, the measured values agree with  
437 those estimated via the Mitchell and Grove (2015) hygrometer.

### 438 **Results**

439         The results of the recalculations show that the calc-alkaline and low-K tholeiitic  
440 basaltic samples were last in equilibrium with a lherzolite residue at intermediate  
441 pressures and temperatures of arc magma genesis between ~1130-1390°C at 8.5-19 kbar  
442 at 0-6 wt% H<sub>2</sub>O (Fig. 7). The primitive andesites that were last in equilibrium with a  
443 harzburgite residue at intermediate to high H<sub>2</sub>O contents and represent the lowest  
444 temperatures and intermediate to low pressures of last equilibration between ~1075-  
445 1260°C with H<sub>2</sub>O contents of 3.2-7.2 wt% H<sub>2</sub>O at 10 kbar. If pressures of last  
446 equilibration were in fact slightly higher at ~15 kbar, the liquids represent mantle  
447 equilibration temperatures of 1090-1270°C at 6-10 wt% H<sub>2</sub>O. The primitive boninites,  
448 picrites and other high-MgO liquids were last in equilibrium with a harzburgite residue  
449 on average and represent the highest temperatures over the entire range of pressures. Four  
450 of these samples are olivine-hosted melt inclusions (Kamenetsky et al. 1995; Sobolev and  
451 Danyushevsky 1994) and record temperatures of 1400-1450°C at 18 to 19 kbar using the  
452 H<sub>2</sub>O content of the melt inclusions determined by ion probe (0.60-1.4 wt% H<sub>2</sub>O). The  
453 other seven high MgO liquids, including boninite from the IBM arc (Bloomer and

454 Hawkins 1987; Dietrich et al. 1978; Li et al. 2013), record shallower conditions of last  
455 mantle equilibration of 1310-1385°C at 14-10 kbar at 1.0-1.6 wt% H<sub>2</sub>O.

456 Overall the recalculated fractionation paths and thermobarometry yielded lower  
457 temperatures ( $\Delta T = -1-198^\circ\text{C}$ ,  $n=166$ ) than the published literature estimates with only a  
458 few samples from the Cascades yielding higher temperatures ( $\Delta T = +22-327^\circ\text{C}$ ,  $n=7$ )  
459 (Table 2). The recalculated pressures also tend to be lower than the literature values  
460 ( $\Delta P = -1-21$  kbar,  $n=168$ ) with a few being higher ( $\Delta P = +0.5-19$  kbar,  $n=5$ ). These lower  
461 temperatures and pressures largely result from using multiple phases that reflect the  
462 sample's mineralogy to adjust for fractional crystallization, as well as the use of modern  
463 thermobarometers for lherzolite and harzburgite residues (Till et al. 2012a; Grove et al.  
464 2013; Mitchell and Grove 2015). This exercise reinforces the large effect of a reverse  
465 fractionational crystallization calculation scheme consistent with the rock mineralogy and  
466 H<sub>2</sub>O content, as well as imposing the criteria that the major element composition of the  
467 fractionation-adjusted liquid match the composition of experimentally-determined liquids  
468 in equilibrium with the appropriate mantle residue (e.g., lherzolite vs. harzburgite), in  
469 addition to the appropriate mantle olivine forsterite content. Because the recalculated  
470 samples included those with the maximum and minimum pressures and temperatures  
471 reported in the literature, these recalculations suggest the range of pressures and  
472 temperatures recorded by primitive arc magmas is in fact much smaller than suggested in  
473 Figure 1. Instead arc primitive arc magmas likely only record last pressures and  
474 temperatures of equilibration between 1050-1450°C at 8-19 kbar, rather than up to  
475 1600°C at 50 kbar as reported in the literature (Fig. 7).

476

## Discussion

477           Now that an assessment of the variability in the literature compilation due to  
478 methodology has been made and a subset of the primary arc magma compositions have  
479 been used to recalculate their conditions of mantle equilibration using internally  
480 consistent methodology (hence forward referred to as the ‘recalculated compilation’),  
481 there is the opportunity to interrogate the new P-T calculations for what they reveal about  
482 the underlying mantle processes.

### 483 **Mantle Melting Processes**

484           In part, the pressure and temperature variations in the recalculated compilation are  
485 the result of the multiple mantle melting processes. The tholeiitic arc basalts are thought  
486 to be generated by adiabatic decompression melting of nominally anhydrous, hot mantle  
487 being advected into the mantle wedge during corner flow (e.g., Grove et al. 2002; Sisson  
488 and Bronto 1998). The calc-alkaline lavas on the other hand likely result from hydrous  
489 flux melting, where a slab-derived H<sub>2</sub>O-rich component initiates melting at the vapor-  
490 saturated lherzolite solidus at the base of the mantle wedge and the buoyant melt ascends  
491 into the hot core of the mantle wedge (e.g., Grove et al. 2003; Till et al. 2012b). As it  
492 rises, this melt equilibrates with the hotter mantle, dissolving mantle minerals to increase  
493 the melt fraction and lower the melt H<sub>2</sub>O-content. Based on the calculations of the likely  
494 mantle residue composition here and in previous studies, the high-MgO arc primitive  
495 magmas and primitive arc andesites are likely the result of these same processes causing  
496 melting of harzburgite rather than lherzolite.

497           Once the first melt is formed, the continuation of mantle melting can be  
498 represented by two end-member categories; that where there is equilibration between the

499 melt and solid at all times so that the bulk composition is fixed (i.e., equilibrium or batch  
500 melting) and that where the liquids are extracted as soon as they form so that the bulk  
501 composition of the residual solid changes (i.e., fractional melting). The major and trace  
502 element composition of MORBs reveal that they are the product of polybaric near-  
503 fractional melting (e.g., Johnson et al. 1990; Langmuir et al. 1992) and record the  
504 *average pressure and temperature of the mantle melting column* (e.g., Kinzler and Grove  
505 1992b). In contrast, a number of detailed studies suggest that anhydrous to damp  
506 primitive magmas erupted in arc settings appear to be the product of batch melting (e.g.,  
507 Bartels et al. 1991; Bacon et al. 1997; Kent and Elliott 2002; Kelley et al. 2010; Till et al.  
508 2012a), such that they only record *the last pressure and temperature of equilibration with*  
509 *the mantle* rather than the average pressure and temperature as in near-fractional melting.  
510 This hypothesis is further tested here using the forward mantle melting model of Behn  
511 and Grove (2015), which is built on the formulation of Kinzler and Grove (1992a, 1992b,  
512 1993) and Kinzler (1997) for MOR-melting and incorporates new experiments from Till  
513 et al. (2012a) on metasomatized and depleted mantle melting so as to make the model  
514 appropriate for melting beneath arcs. ~1-10% isobaric batch melting of a depleted Hart  
515 and Zindler (1986) mantle (HZ-Dep1 in Table 1a of Kinzler and Grove (1992b)) in the  
516 spinel lherzolite field at 10-20 kbar overall reproduces the major element composition of  
517 the calc-alkaline basalts used for the recalculations (Fig. 8b). The tholeiitic basalts with  
518 recalculated pressures and temperatures can be fit by incremental batch melting of the  
519 same mantle composition with 90% melt extraction at each step (i.e., near fractional  
520 melting) between 20-9 kilobars, dF/dP of 1% per kilobar and an adiabatic gradient of  
521 1.5°C per kilobar over a range of mantle potential temperatures between ~1450-1300°C.

522 They can also be fit by batch melting curves like those that fit the calc-alkaline basalts  
523 (Fig. 8a). Therefore the calc-alkaline basalts reviewed here, and perhaps also the  
524 tholeiitic basalts, record their last pressure and temperature of mantle equilibration (i.e.,  
525 the conditions of melt extraction), not the initiation of melting. These equilibration  
526 conditions are commonly misinterpreted as indicating shallow and hot melting beneath  
527 arcs. Instead this interpretation reinforces prior observations by studies such as Kelley et  
528 al. (2010), Weaver et al. (2011), and Till et al. (2013) that primitive arc magmas tend to  
529 re-equilibrate near Moho depths as they rise from their deeper points of origin. This is  
530 further illustrated when the recalculated compilation is compared to geodynamics models  
531 of the temperature distribution within the mantle at modern subduction zones in the  
532 following section.

533 In the case of melt inclusions, the recorded temperatures and pressures reveal the  
534 conditions at which the primitive melt was trapped by the host mineral. For the majority  
535 of cases in this study the host mineral is olivine, with the remainder being clinopyroxene.  
536 Therefore, they record the pressures and temperatures during olivine or clinopyroxene  
537 crystallization. In the literature compilation and the recalculated compilation, the  
538 temperatures and pressures of melt inclusion formation overall appear to be similar to  
539 those where primitive magmas are extracted from the mantle.

#### 540 **Geodynamic Models**

541 Geodynamic models with increasing complexity have been applied to solid-state  
542 mantle convection in the mantle wedge. Vertical paths through a suite of modern models  
543 are compared to the recalculated magma thermobarometry in Figure 9. The recalculated



544 pressures and temperatures for damp to wet magmas tend to match the thermal structure  
545 of the Kelemen et al. (2003) models, while those from the nominally anhydrous magmas  
546 reflect higher temperatures at a given pressure than predicted by any model. Kelemen et  
547 al. (2003) compared the much more limited set of petrologic constraints on the pressure-  
548 temperature conditions for arc magmas and sub-arc crust available at the time to existing  
549 geodynamic models, and geared their modeling efforts toward reproducing the natural  
550 observations.

551         The comparison of the recalculated magmatic pressure-temperature compilation  
552 to the thermal structures predicted by dynamic models suggest that the magmas  
553 experience thermal equilibration in the hottest shallowest nose of the mantle wedge  
554 before they are extracted (Fig. 10). Syracuse et al. (2011) predict maximum temperatures  
555 in the hot core of the wedge that vary between 1200°C or 1275°C (depending on the  
556 location of full coupling between the mantle and slab) to 1459°C at different subduction  
557 zones with an average of  $\sim 1400 \pm 54$ °C. This suggests re-equilibration in the hot shallow  
558 nose of the mantle wedge at different arcs could lead to a natural variation in magmatic  
559 temperatures of  $\sim 200$ -250°C. While the range of recalculated pressures and temperatures  
560 broadly match Syracuse et al. (2011), in some cases the magmas are warmer than the  
561 model predictions at specific arcs. For example, magmatic temperatures are as warm as  
562 1400°C below the Cascades and 1450°C below the Kamchatka & Tonga arcs, while the  
563 model predicts maximum temperatures beneath Cascadia of 1285-1312°C and 1300°C  
564 below the Kamchatka & Tonga arcs. This may be in part due to the limitations of  
565 modeling mantle wedge thermal structures in two dimensions.

566           Shown for comparison in Figure 9 are the maximum pressure-temperature  
567 conditions for subduction zone blueschists and eclogites and thermal models for the  
568 subducting slab (Penniston-Dorland et al. 2015). The peak thermobarometric conditions  
569 recorded in exhumed metamorphic rocks are on average 100-300°C warmer than the  
570 models, and the greatest discrepancies occur at <2 GPa. Penniston-Dorland et al. (2015)  
571 argue that the omission of significant shear heating (up to 250°C at 35 km depth) and the  
572 exothermic hydration reactions within the overlying mantle just above the slab-wedge  
573 interface (<200° at 1 GPa for a flux of ~0.1 kg H<sub>2</sub>O/m<sup>2</sup>/yr from slab) are two of the most  
574 significant potential causes of this discrepancy. While the physics of heating up a slab  
575 are simpler than predicting the temperature of convecting mantle in the wedge, these  
576 features could also account for some of the discrepancy between the hottest primitive arc  
577 magma samples and the dynamic models. However the dimensionalization of  
578 temperature in the dynamic models and the prescribed boundary conditions are likely  
579 more significant factors controlling the discrepancies between the petrologic estimates  
580 and geodynamic models. For example, geodynamic models may underestimate the  
581 temperatures possible at the shallowest depths because of the prescribed lithospheric  
582 thickness in the models (e.g., 45-55 km for van Keken et al. (2002) and Kincaid and  
583 Sacks (1997)). Results from Till et al (2013) for the southern Cascadia subduction zone  
584 suggest the continental lithosphere must be ≤35 km thick. The observation that the  
585 warmer, driest arc basalts in the recalculated compilation require adiabatic  
586 decompression melting of asthenospheric mantle supports the interpretation that the  
587 convecting mantle extends to an average depth of ~30 km or less (~10 kbar) at arcs, even  
588 at arcs with an overriding continental plate.

589           In addition, strong focusing mechanisms that direct fluids and melts to hot and  
590 shallow regions beneath the arc may help explain the abundance of shallow, hot arc  
591 magmatic temperatures. Wilson et al. (2014) develop models that incorporate strong  
592 temperature-dependent rheologies in the slab and the wedge, and a physically reasonable  
593 model of fluid flow that includes the interaction of fluid transport with solid rheology in  
594 the form of compaction pressure. Similarly, Wada and Behn (2015) examine the effects  
595 of grain size on fluid flow in the mantle wedge. These models are able to reproduce the  
596 localization of fluids and melts to the subarc region with this more realistic permeability  
597 and solid viscosity structure. Although these models do not predict temperatures as warm  
598 as many of the magmatic temperatures in the recalculated compilation, they suggest a  
599 mechanism to explain the clustering of the P-T points at the shallowest pressures. These  
600 focusing mechanisms combined with the petrologic observations of shallow last  
601 conditions of mantle equilibration also provide an explanation for why wet and dry arc  
602 magmas are erupted in close spatial and temporal proximity at many arcs such as the  
603 Cascades (e.g., Till et al. 2013; Carlson et al. submitted).

#### 604 **Melt Flow Mechanisms**

605           In addition to the various melting mechanisms for primitive arc magmas, the  
606 rising melt flow behavior also controls the ultimate pressure and temperature recorded.  
607 The maintenance of equilibrium between the melt and the mantle requires reactive porous  
608 flow as a mechanism for transporting the melts rather than diapiric or channelized flow  
609 (e.g., Navon and Stolper 1987; Grove et al. 2002). Reactive porous flow can be  
610 approximated as Darcy flow where permeability exerts the main control on the melt  
611 ascent rate and whether or not the melts can achieve thermal and chemical equilibrium.

612 Provided permeability is sufficient for the fluids to outpace subduction, small degree  
613 batch melts will re-equilibrate with the hotter overlying mantle, dissolving silicate  
614 minerals and diluting the H<sub>2</sub>O content as they rise (Grove et al. 2002). Alternatively, if  
615 melt flow occurs as diapiric or channelized flow, it can be approximated by Stoke's flow  
616 and the size of diapirs is the main control on whether thermal and chemical equilibration  
617 with the surrounding mantle will occur. Modeling suggests that for diapirs large enough  
618 to escape subduction flow, the ascent rate is too rapid for thermal equilibration with the  
619 surrounding mantle to occur (Grove et al. 2002).

620 Thermal gradients in the mantle wedge can be up to 30-40°C/km based on  
621 geodynamic models (Cagnioncle et al. 2007; Syracuse et al. 2010). Therefore in the  
622 reactive porous flow model required for batch melting (Fig. 8), a difference in the  
623 pressure of last equilibration of 10 vs. 15 kbar (~15 km) equates to a difference in the  
624 temperature of last equilibration of up to 450°C (Fig. 10). This difference in last  
625 equilibration conditions is similar to the difference between the coolest primitive  
626 andesites and the hottest boninites, including notably within the Kamchatka arc where  
627 these conditions are recorded within the same arc. Geochemical and isotopic modeling  
628 suggests >90% of the major element abundances in primitive hydrous arc magmas can be  
629 explained as a product of flux melting and ascent via reactive porous flow (e.g., Grove et  
630 al. 2002), which is also supported by the composition of mantle xenoliths and field  
631 observations from the roots of arcs (e.g., Kelemen et al., 1992; Bouihol et al., 2009).  
632 Therefore, a likely explanation for the calc-alkaline basalts and primitive andesites with  
633 temperatures lower than the anhydrous peridotite solidus is that these magmas re-  
634 equilibrate as they rise, and record the decrease in temperature during ascent out of the

635 hot nose of the wedge (dashed teal ascent path in Fig. 10). Variability within the  
636 pressures and temperatures recorded by these hydrous magmas can be attributed to  
637 variations in subduction zone thermal structure through time, along strike, or between  
638 arcs (e.g., Carlson et al. submitted).

639         Alternatively, if channelized flow and a fluid adiabat of 1°C/km are assumed  
640 (Nisbet 1982), a 5 kbar difference in a magma's last pressure of equilibration equates to  
641 only a ~15°C difference in the temperature. There is evidence that the incompatible trace  
642 element budget of hydrous arc magmas is contributed from a fluid and/or melt  
643 component present in the mantle that rises via adiabatic diapiric or channelized flow and  
644 does not re-equilibrate (e.g., Grove et al. 2002; Pirard and Hermann 2015). However, if a  
645 hydrous magma forms at or near the water-saturated solidus at 30 kbar, adiabatic ascent  
646 to 10 kbar would lower magmatic temperatures on the order of 60°C and induce  
647 crystallization (see Grove et al. (2011) Fig. 2). As no magmas in the recalculated  
648 compilation record temperatures of  $\leq 1000^\circ\text{C}$  at any pressure, these magmas either  
649 crystallize before they reach the surface, or water-rich magmas do not rise via diapiric  
650 flow. Instead the recalculated compilation suggests adiabatic ascent may only be possible  
651 for the nominally anhydrous tholeiitic magmas (Fig. 8).

652         Models that include compaction pressure such as Wilson et al. (2014) represent an  
653 intermediate melt/fluid flow mechanism on the continuum between reactive porous and  
654 channelized flow models, which could also be responsible for intermediate temperature  
655 magma types. Alternatively, reactive porous flow may operate until there is a change in  
656 mantle permeability that causes a transition to channelized flow (e.g., Kelemen et al.  
657 1997, Aharonov et al. 1997). Future work is required to determine if these hypotheses

658 about melt flow are robust. The recalculated compilation provides a powerful set of  
659 pressure, temperature and compositional observations to test any proposed model.

660 **Summary of Thermobarometry and Mantle Origins for Four Types of Primitive**  
661 **Arc Magmas**

662 Low-K tholeiitic arc basalts represent nominally anhydrous lherzolite melts and  
663 record high average temperatures (~1300-1390°C) between 10-20 kbar, which are  
664 generated by adiabatic decompression melting in the back limb of corner flow (Fig. 10).  
665 These magmas tend to follow more tholeiitic liquid lines of descent in the crust similar to  
666 MORB's due to their low H<sub>2</sub>O and more reducing  $fO_2$ . Thus the appropriate reverse  
667 fractionation adjustment for these samples are the easiest to predict. These samples are  
668 the best suited to modern lherzolite thermobarometers (e.g., Till et al. 2012a; Lee et al.  
669 2009; Putirka et al. 2008) which yield temperatures of origin within 30°C on average,  
670 making their pressures and temperatures of mantle equilibration the most reliable.

671 Calc-alkaline arc basalts record comparatively lower average temperatures (1100-  
672 1300°C) over the same pressure interval due to melting lherzolite in the presence of  
673 higher H<sub>2</sub>O contents (>1 wt%). The lower temperature samples at a given pressure likely  
674 represent melts generated at or near the H<sub>2</sub>O-saturated solidus, which rise through the  
675 mantle via reactive porous flow (Fig. 10). Higher temperature calc-alkaline basalts (1250-  
676 1300°C) may be the result of the same process or adiabatic ascent from an H<sub>2</sub>O-  
677 undersaturated solidus due to lower H<sub>2</sub>O contents. The higher H<sub>2</sub>O and  $fO_2$  of calc-  
678 alkaline basalts result in their more complex and variable fractionation paths in the crust.  
679 Thus caution is required when reverse-fractionating these samples and the more

680 information about the suite of samples, their mineral contents, mineral compositions and  
681 H<sub>2</sub>O contents, the better the chance of an accurate fractionation adjusted composition.  
682 These samples are also appropriate for use with the lherzolite thermobarometers but will  
683 yield different results depending on the thermobarometer chosen because of the different  
684 calibrations for the effect of H<sub>2</sub>O on their mantle equilibration pressure and temperature.

685         Primitive high-Mg andesites record the lowest temperatures at a given pressure in  
686 the recalculated compilation and are generated by 20-30% melting of harzburgite residue  
687 that has been enriched by alkalis during metasomatism over a range of H<sub>2</sub>O contents (0-7  
688 wt%). The primitive nature of the samples in the recalculated compilation is such that  
689 they do not require any reverse fractionation calculations to be in equilibrium with the  
690 mantle, although liquid lines of descent for these primitive rock types have been studied  
691 by Grove et al (2003) and can be used to restore these samples to liquids in equilibrium  
692 with the harzburgite. The composition of harzburgite-derived mantle melts and their  
693 associated pressures, temperatures and H<sub>2</sub>O contents have been experimentally calibrated  
694 by Mitchell and Grove (2015). If these liquids are used with lherzolite thermometers or  
695 similar, they will yield higher temperatures, in error by up to 250°C.

696         High-MgO arc magmas, such as boninites and picrites, record the highest  
697 temperatures for a given pressure in the recalculated compilation and their major element  
698 compositions are consistent with either harzburgite melting or lherzolite melts that re-  
699 equilibrated with harzburgite or dunite as they ascended (Grove et al. 2013; Wagner and  
700 Grove 1998; Mitchell and Grove, 2016) at relatively low H<sub>2</sub>O contents. Their pressures  
701 and temperatures are consistent with thermal re-equilibration in the hottest nose of the  
702 mantle wedge and in some cases reactive porous flow to somewhat shallower conditions.

703 These samples also tend to be so primitive that no reverse fractionation calculations are  
704 required to be in equilibrium with the mantle. Little to no experimental work has been  
705 done to constrain their fractionation paths. These samples will also yield a wide range of  
706 temperatures when used with lherzolite thermometers, which vary by almost 200°C. The  
707 harzburgite thermobarometer of Mitchell and Grove (2015) appears to be the most  
708 appropriate given the composition of the liquids examined here, and yields temperatures  
709 at the lower end of the range.

## 710 **Implications**

711 The collection of published mantle pressure-temperature constraints from  
712 primitive arc magmas and the recalculations presented here provides observational  
713 constraints for shallow mantle processes at subduction zones relevant to a variety of  
714 disciplines. For example, in addition to the petrologic and geochemical perspective on  
715 how much of the range of calculated magmatic pressures and temperatures at arcs is  
716 “real” and likely melt generation models, the recalculated compilation provides  
717 observational constraints for geodynamic models of the thermal structure and melt flow  
718 at subduction zones. The magmatic pressures and temperatures also provide the  
719 opportunity to further quantify the effect of melt on seismic velocity, attenuation, and  
720 electrical conductivity in the upper mantle below arcs and to continue to evolve three  
721 dimensional maps of melt distribution at subduction zones.

722 A number of opportunities for future petrologic and geochemical study also arise.  
723 This paper focuses on the what can be learned from the major element composition of arc  
724 magmas and a logical next step is to interrogate the trace element and isotopic



725 compositions of the magmas in the literature and recalculated compilation to further  
726 interrogate and differentiate between magmas formed by decompression melting and flux  
727 melting. As discussed in the review of reverse fractional crystallization calculations  
728 above, there is a need to develop robust parameterizations for the compositional effects of  
729 variable H<sub>2</sub>O contents on the liquid line of descent for primitive arc magmas over the  
730 range of pressures and oxygen fugacities at which they crystallize in the arc lithosphere.  
731 In addition, the recalculated magmatic pressure-temperature compilation can ideally be  
732 used to understand the extent to which variations in the conditions of mantle equilibration  
733 can be attributed to variations between arcs with different subduction parameters (slab  
734 dip, convergence rate etc.), as well as variations along strike within an arc.

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#### 741 **Acknowledgements**

742 Deep thanks are extended to K. Putirka for the invitation to participate in American  
743 Mineralogist's 100<sup>th</sup> anniversary which precipitated this work, to T. Grove, A. Mitchell  
744 and the EPIC group at ASU for many stimulating conversations along the way, and to T.

745 Sisson, K. Kelley and K. Putirka for their constructive and insightful reviews of the  
746 manuscript.

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1159

1160 **Figure & Table Captions**

1161 **Figure 1. Compilation of primitive arc magma thermobarometry in the literature.**

1162 The pressure and temperatures compiled here were calculated for primitive arc liquids by  
1163 the studies listed in Table 1. The points are color-coded based on the technique used by  
1164 each study to calculate the temperature and pressure of origin in the mantle and the water  
1165 content. The anhydrous peridotite solidus is from Hirschman (2000) and the H<sub>2</sub>O-  
1166 saturated peridotite solidi from Till et al. (2012b). Inset is same plot color coded  
1167 according to subduction zone where each sample is found. The bulk of the data is from  
1168 three subduction zones: 410 are from the Cascades, 131 are from the Izu-Bonin-Marianas  
1169 and 21 are from Japan (n=638 total).

1170 **Figure 2. Harker diagrams.** Compositions of primitive arc samples taken directly from  
1171 studies in Table 1 and Figure 1, all of which are reported prior to reverse fractional  
1172 crystallization calculations or any post entrapment crystallization corrections in the case  
1173 of melt inclusions. Samples with red, blue, green and pink colored symbols were used to  
1174 for the new pressure and temperature calculations.

1175 **Figure 3. Summary of the liquid line of descent for a hydrous calc-alkaline basalt.**  
1176 Arrows represent the liquid lines of descent for high MgO basalt following olivine  
1177 fractionation at different conditions based on the experiments of Hamada and Fuji (2008).  
1178 The bottom two plots represent experiments conducted at 2 kbar, and the top two  
1179 illustrate experimentally-determined liquid evolution at 7 kbar. Dark blue arrow  
1180 represents experiments with the higher H<sub>2</sub>O content in each plot. Comparison amongst  
1181 the four plots illustrates differences in the liquid line of descent due to changes in oxygen  
1182 fugacity, H<sub>2</sub>O content and pressure.

1183 **Figure 4. Pseudo-ternary projections for representative arc calc-alkaline and**  
1184 **tholeiitic arc basalts, primitive andesites and high MgO liquids. a)** Pseudo-ternary  
1185 projections depicting the compositions of representative tholeiitic and calc-alkaline arc  
1186 basalts prior to reverse fractional crystallization calculations. These samples are shown  
1187 along with the location of a melt in equilibrium with plagioclase (blue y's), spinel (green  
1188 y's) and garnet (red y's) lherzolite, also known as the lherzolite "multiple saturation  
1189 points", over a range of pressures from Till et al. (2012a) and Grove et al. (2013), which  
1190 are plotted in all three diagrams. These liquids in a) are relatively silica-understaturated  
1191 and plot towards the plagioclase apex because they originated from a lherzolite residue.  
1192 **b)** Pseudo-ternary projections depicting the compositions of representative primitive arc  
1193 andesites and **c)** high MgO arc magmas such as boninites and picrites illustrated prior to  
1194 any reverse fractional crystallization calculations. Overall both the liquid types in b) & c)  
1195 are relatively silica-saturated and have a comparatively lower plagioclase component  
1196 relative to the more typical arc basalts because they are in equilibrium with a more  
1197 depleted mantle residue (i.e., harzburgite or in the case of a few high-MgO liquids  
1198 dunite), rather than lherzolite. Samples plotted in all three figures are those used in the  
1199 new calculations of pressures and temperatures with the exception of the black circles in  
1200 c) that included to illustrate the range of high MgO primitive arc magma compositions in  
1201 the literature.

1202 **Figure 5. Recalculated Primitive Arc Magma Compositions.** Composition of samples  
1203 included in the new pressure and temperature calculations compared to the calc-alkaline  
1204 vs. tholeiitic fields of Miyashiro (1974). Arrow indicates progressive depletion of the  
1205 mantle residue that sources the primitive magmas (lherzolite>harzburgite>dunite).

1206 **Figure 6.** Comparative amount of crystal fractionation to be reversed prior to the new  
1207 pressure and temperature calculations for the tholeiitic and calc-alkaline primitive basalts.  
1208 Black curves represent the composition of 1-20% isobaric batch melts for a depleted Hart  
1209 and Zindler (1986) mantle composition at 10, 15, 20 kbar as predicted by the forward  
1210 lherzolite melting model of Till et al. (2012a) as modified by Behn and Grove (2015).  
1211 These curves illustrate the composition of primary nominally anhydrous melts prior to  
1212 crystal fractionation. Crystal fractionation shifts the composition of these melts to the  
1213 right along a vector whose direction is determined by the combination of olivine ±  
1214 plagioclase ± clinopyroxene crystallization appropriate for that liquid. Samples on the  
1215 right side of the plot have experienced more crystal fractionation than those on the left.

1216 **Figure 7. Recalculated temperatures and pressures with subset of the literature**  
1217 **compilation.** a) Pressure-temperature plot color coded by primitive arc magma type. The  
1218 new pressures and temperatures were calculated following internally consistent methods  
1219 as described in the Methods section. The anhydrous peridotite solidus in a) is from  
1220 Hirschman (2000) and the H<sub>2</sub>O-saturated peridotite solidi from Till et al. (2012b).  
1221 Pressures for the high-Mg andesites are all the same because the pressure was assumed to  
1222 be that of the base of the av. arc crust (30 km, ~10 kbar on average) in order to accurately  
1223 assess their temperatures of mantle equilibration using the Mitchell and Grove (2015)  
1224 harzburgite-liquid hygrometer and thermometer. b) Recalculated pressure and  
1225 temperature contoured (by color and bubble size) for the H<sub>2</sub>O content used in the  
1226 recalculation. Samples in the recalculation are limited amongst other criteria to a range of  
1227 representative compositions and to those with H<sub>2</sub>O contents were measured via SIMS or  
1228 FTIR or adequate information to estimate H<sub>2</sub>O via hygrometry with the exception of 4  
1229 tholeiites which are similar in composition to other nominally anhydrous tholeiitic  
1230 magmas with H<sub>2</sub>O estimates (see details in methods for recalculations in Table 2).  
1231 Symbols with bold outlines and arrow illustrates the shift in P-T that results from  
1232 estimating the P and T of the sample with 0 wt% H<sub>2</sub>O (left) vs. 4.6 wt% H<sub>2</sub>O (on the right  
1233 at end of arrow).

1234 **Figure 8. Comparison of arc basalts to forward modeling of batch vs. near-**  
1235 **fractional mantle melting.** a) Comparison of tholeiitic basalts used for the pressure and  
1236 temperature recalculations to incremental batch melts of a depleted Hart and Zindler  
1237 mantle composition with 90% melt extraction and  $dF/dP = 1\%$  per kilobar and an  
1238 adiabatic gradient of 1.5°C per kilobar using the forward mantle model of Till et al.  
1239 (2012a) as modified by Behn and Grove (2015) Gray batch melting curves shown for  
1240 comparison as described in B. b) Comparison of the calc-alkaline basalts used for  
1241 pressure and temperature recalculations to isobaric batch melting curves for a depleted  
1242 Hart and Zindler (1986) mantle composition at 10, 15 and 20 kbar as predicted by the  
1243 forward lherzolite melting model of Till et. al (2012a) as modified by Behn and Grove  
1244 (2015). c) Comparison of all rock types to the batch melting and near-fractional melts of  
1245 spinel lherzolite. The calc-alkaline basalts are consistent with 1-10% batch melts of a



1246 depleted mantle at 10-20 kbar. The tholeiites can be modeled by either batch melting at  
1247 average higher pressures and extents of melting or by near-fractional melting between 20-  
1248 9 kbar.

1249 **Figure 9. Comparison to Geodynamic Models.** P-T paths from a selection of modern  
1250 thermal models of subduction zones are compared to the thermobarometry dataset.  
1251 Colored lines represent the temperature conditions at vertical slices through the mantle  
1252 wedge. The Kincaid and Sacks (1997) curve is from their model for fast subduction of a  
1253 thin plate assuming a mantle potential temperature of 1400°C. The van Keken et al.  
1254 (2002) curve is from their models with a non-linear mantle viscosity and compares the  
1255 structure of a “warm” (Cascadia) vs. “cold” (Japan) subduction zone. The Kelemen et al.  
1256 (2003) curves compare slices through the model at two different distances from the  
1257 trench, one closer to the trench where the slab is at 100 km depth (representing the hottest  
1258 conditions at the shallowest depth from the models) and one further from the trench with  
1259 the slab at depths of 150 km. Black solid and dashed lines are temperature conditions for  
1260 the slab surface from a suite of relevant models compared to the gray field of  
1261 thermobarometry constraints for the slab from exhumed metamorphic rocks as  
1262 summarized in Penniston-Dorland et al. (2015). In both the magmatic thermobarometry  
1263 reviewed here and the slab thermobarometry, the models tend to only reproduce the  
1264 cooler petrologic observations.

1265 **Figure 10. Summary of mantle processes that form primitive arc magmas reviewed**  
1266 **in this paper.** a) 2D schematic cross section of subduction zone with isotherm locations  
1267 from Kelemen et al. (2003). b) Pressure-temperature diagram with the recalculated  
1268 pressure and temperatures for primitive arc magma in Table 2 shown in colored squares  
1269 (which all fall within the gray field in panel a). The anhydrous peridotite solidus is from  
1270 Hirschmann (2000) and the H<sub>2</sub>O-saturated peridotite solidus from Till et al. (2012b).  
1271 Hydrous arc magmas are first formed at the locations of the water-saturated mantle  
1272 solidus just above the subducting lithosphere at pressures of ~20-30 kbar and then rise via  
1273 reactive porous flow (teal dashed arrows) into the hot core of the mantle wedge where  
1274 their melting extent increases and the water content decreases due to continued re-  
1275 equilibration with the mantle. As they continue to rise into the cooler top portion of the  
1276 mantle wedge via reactive porous flow their melt fraction decreases. The recalculated  
1277 pressures and temperatures (gray field in a. and b.) reflect the conditions during their re-  
1278 equilibration in the top half of the mantle wedge immediately prior to their extraction  
1279 from the mantle. If hydrous magmas rise via channelized flow, they would record much  
1280 lower temperatures at a given pressure than any magma in the recalculations done here or  
1281 the literature compilation in Figure 1. When the mantle residue for this process is  
1282 lherzolite, calc-alkaline basalts are generated. Alternatively, when the mantle residue is  
1283 harzburgite, depending on the H<sub>2</sub>O content either high-Mg andesites (higher av. H<sub>2</sub>O  
1284 content, lower av. temperatures) or high-Mg liquids (lower av. H<sub>2</sub>O content, higher av.  
1285 temperatures) are generated. Nominally anhydrous arc tholeiites are generated by near-  
1286 fractional decompression melting at or near the anhydrous lherzolite solidus in the  
1287 upwelling back limb of corner flow at ~20-10 kbar. These melts are focused into the  
1288 same region of last mantle equilibration as the hydrous melts. Adiabatic ascent of these  
1289 magmas (black dashed arrows) preserves the higher temperatures of their formation  
1290 rather than the lower temperatures in the top half of the wedge. Some relatively dry high-

1291 Mg liquids may also be generated via this process when the mantle residue is  
1292 harzburgitic.

1293 **Table 1. Published studies that include arc mantle-melt thermobarometry compiled**  
1294 **in Figure 1.**

1295 **Table 2. Studies and methods used for the recalculation of primitive arc magma**  
1296 **pressures and temperatures in “Recalculation of Pressure and Temperature for**  
1297 **Common Arc Magma Types” section and Figure. 7.**