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 tephras 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_2O 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_2O 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

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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_2O

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

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47   uppermost part of the mantle wedge, as well as the origin of different primitive magma

48   types at arcs.

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. diapric 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.

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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_2O 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, tephras, 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

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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

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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_2O 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

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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_2, 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).

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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

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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_2O_3 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

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205   literature collected in Figure 1, with the dominant approach being the addition of only

206   olivine back to the liquid composition.

207   H_2O 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_2

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_2O

218   suppresses plagioclase crystallization at any oxygen fugacity, the amount of H_2O required

219   to evolve the liquid to a calc-alkaline composition increases as oxygen fugacity

220   decreases. Thus increasing the H_2O 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^{2+} 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_2O 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_2O

233   causes in the liquid line of descent. The cutoff H_2O 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_2O contents relevant for MORB genesis and the

236   higher the magmatic H_2O 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_2O content. Therefore, future work is required to parameterize the discrete

241   effects of H_2O 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

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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 $\leq 75°C$ overall, and more likely to be ≤ 35-$40°C$ 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 $35°C$ on average, which is within

267   the error of these thermometers (SEE Putirka=$52°C$; Lee=~$40°C$ (3%) and Till=$11°C$).

268   These three thermometers also include a term to consider the effect of H_2O, 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 SiO_2 in

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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_2 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

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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 ~100°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 fO_2 and thus the appropriate 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 (~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 H_2O 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

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319   carefully determined the H_2O 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_2O content of a primary

325   melt has been effectively estimated, the calculated effect of this H_2O 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_2O on the

329   calculated liquid temperature for lherzolite melts. The Till et al. (2012a) calibration

330   results in the largest effect of H_2O 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_2O 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_2O 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_2O 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_2O than

339   Till et al. (2012a) and the calculated pressure of equilibration is 2.5 kbar (or ~8.5 km)

340   higher with Lee at. (2009) than Till et al. (2012a) for a calc-alkaline basalt with 5 wt%

341   H_2O. This variability in the pressure calculations as a function of H_2O content is

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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_2O 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_2O,

348   specifically by differences in how the primary magmatic H_2O-contents are estimated (or

349   not), the lack of consideration of H_2O's effects on the reverse fractionation crystallization

350   calculations in existing studies, and the differences between models for the effects of H_2O

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_2O (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_2O content. A wholesale recalculation for all samples used in the literature

363   compilation is not possible because many source publications contain insufficient

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364   information to conduct the reverse fractionation calculations and/or estimate H_2O

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_2

372   and >15 wt% MgO from primitive andesite with >52 wt% SiO_2 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_2 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

17

387   sample), treating all Fe as FeO* and using partition coefficients appropriate for the H_2O

388   contents of the sample (e.g., varying the Ca-Na plagioclase-liquid K_D as a function of

389   H_2O) (see worked example in electronic supplement). The H_2O 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_2O.

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_2O 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

19

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_2O 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_2O (Fig. 7). The primitive andesites that were last in equilibrium with a

443   harzburgite residue at intermediate to high H_2O contents and represent the lowest

444   temperatures and intermediate to low pressures of last equilibration between ~1075-

445   1260°C with H_2O contents of 3.2-7.2 wt% H_2O 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_2O. 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_2O content of the melt inclusions determined by ion probe (0.60-1.4 wt% H_2O). The

453   other seven high MgO liquids, including boninite from the IBM arc (Bloomer and

20

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_2O.

456   Overall the recalculated fractionation paths and thermobarometry yielded lower

457   temperatures ($\Delta T= -1-198$°C, n=166) than the published literature estimates with only a

458   few samples from the Cascades yielding higher temperatures ($\Delta T= +22-327$°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_2O 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 mininum 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**

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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_2O-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_2O-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

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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.

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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

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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 ~1400±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 ~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 $H_2O/m^2/yr$ 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.

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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.

27

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_2O 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

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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 ≤1000°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 thoeliitic 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

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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_2O 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_2O contents (>1 wt%). The lower temperature samples at a given pressure likely

674 represent melts generated at or near the H_2O-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_2O-

677 undersaturated solidus due to lower H_2O contents. The higher H_2O 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

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680   information about the suite of samples, their mineral contents, mineral compositions and

681   H_2O 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_2O 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_2O 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_2O 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_2O 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

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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_2O 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**

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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_2O-
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_2O 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_2O 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 arcmagma compositions in
1201 the literature.

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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 depletionof 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_2O-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_2O 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_2O contents were measured via SIMS or
1228 FTIR or adequate information to estimate H_2O via hygrometry with the exception of 4
1229 tholeiites which are similar in composition to other nominally anhydrous tholeiitic
1230 magmas with H_2O 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_2O (left) vs. 4.6 wt% H_2O (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

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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_2O-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_2O content either high-Mg andesites (higher av. H_2O
1284   content, lower av. temperatures) or high-Mg liquids (lower av. H_2O 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.**