1   Revision 2

# A method to estimate the pre-eruptive water content of basalts: application to the Wudalianchi–Erkeshan–Keluo volcanic field, Northeastern China

Yankun Di[1,a], Wei Tian[1,*], Mimi Chen[1], Zefeng Li[2,b], Zhuyin Chu[3], Ju Liang[1]

[1]School of Earth and Space Sciences, Peking University, Beijing 100871, China

[2]School of Physics, Peking University, Beijing 100871, China

[3]State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

[a]Present address: Research School of Earth Sciences, Australian National University, Acton, ACT 2601, Australia

[b]Present address: Research School of Astronomy & Astrophysics, Australian National University, Weston Creek, ACT 2611, Australia

[*]Corresponding author, email: davidtian@pku.edu.cn

**Abstract**

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19    Water plays an important role in the generation and evolution of volcanic systems.

20   However, the direct measurement of the pre-eruption water content of subaerial volcanic

21   rocks is difficult, because of the degassing during magma ascent. In this study, we

22   developed a method to calculate the pre-eruption water content of the basalts from the

23   Cenozoic Wudalianchi─Erkeshan─Keluo (WEK) potassic volcanic field, Northeastern

24   China, and investigated their mantle source. A water-insensitive clinopyroxene–melt

25   thermobarometer and a water-sensitive silica activity thermobarometer were applied to

26   these basalts. Two pressure─temperature ($P$–$T$) paths of the ascending magma were

27   calculated using these two independent thermobarometers, with a similar $P$–$T$ slope but

28   clear offset. By adjusting the water content used in the calculation, the difference between

29   the two $P$–$T$ paths was minimized, and the water content of the WEK melts was estimated

30   to be 4.5 ± 1.2 wt% at a pressure range of 10.1─13.5 kbar, corresponding to depths of 37–

31   47 km. Degassing modeling shows that during the magma ascent from below the Moho to

32   near the surface, $CO_2$ was predominantly degassed, while the melt $H_2O$ content kept

33   stable. Significant $H_2O$ degassing occurred until the magma ascended to 5─2 kbar. The

34   silica activity $P$–$T$ estimates of the most primary WEK samples suggest that the magmas

35   were generated by the melting of convective mantle, which was probably facilitated by a

36   wet upwelling plume from the mantle transition zone. The high water content found in

37   the WEK basalts is similar to the recent reports on Phanerozoic intraplate large igneous

38   provinces (LIPs), and supports the presence of hydrated deep mantle reservoirs as one

39    possible source of the LIPs.

40

41    **Keywords:** water content, potassic basalt, degas, thermobarometer, Northeastern

42    China, Wudalianchi−Erkeshan−Keluo

43

## Introduction

45    Water plays an important role in terrestrial and planetary magmatic processes

46    (Hirschmann 2006; O'Neill et al. 2007; Wilson 2009; Ni et al. 2016; Peslier et al. 2017).

47    In the source mantle, water controls the two most important factors constraining the

48    primary melt composition: the depth and degree of melting (Katz et al. 2003; Asimow

49    and Langmuir 2003). During magma ascent, the exsolution of water can trigger

50    vesiculation and change the fluid dynamics of the volcanic system (Gonnerman and

51    Manga 2007). During the eruption, water can control the explosiveness and flow regime

52    (Wilson 1980, 2009; Kieffer 1995). Thus, the water contents of magmas, especially the

53    water contents of primary melts, have long been investigated.

54    For magmas erupted on the deep seafloor, the primary water content can be

55    acquired by direct analysis of glass (e.g., Michael 1995; Dixon et al. 1997; Hauri et al.

56    2002). For subaerially erupted volcanic rocks, however, the estimation of the primary

57    water content is difficult due to the ubiquitous escape of volatiles during the eruption.

58    Primary melt inclusions are believed to be a good indicator of the pre-eruption water

59    content (e.g., Hauri 2002; Dixon and Clague 2001); however, these inclusions are very

60  rare and easily altered by the interaction with the host minerals (Chen et al. 2011; Gaetani

61  et al. 2012). Another method is to measure the water content of clinopyroxene

62  phenocrysts and calculate the melt water content using a partitioning coefficient

63  $[K_D(H_2O)^{cpx-melt}]$ (e.g., Wade et al. 2008; O'Leary et al. 2010), which, however, is not

64  applicable at all times as the water content of clinopyroxene decreases owing to the

65  diffusive re-equilibration with the melt during ascent-driven degassing (Cashman 2004;

66  Lloyd et al. 2016; Turner et al. 2017). Due to the diffusive water loss, both the melt

67  inclusion and phenocryst methods provide a minimal estimation of the pre-eruption water

68  content of the melt. Therefore, an ideal method of water content estimation for melts that

69  have experienced water exsolution is still required.

70      In this study, we develop a new method to determine the pre-eruption water

71  contents of melts by combining a water-insensitive and a water-sensitive

72  thermobarometer. The water-insensitive thermobarometer is based on the clinopyroxene–

73  melt equilibrium (Putirka et al. 2003) and has been widely applied for the pressure–

74  temperature (*P–T*) estimation of magmas with variable water contents (e.g., Putirka 1997,

75  2008; Putirka et al. 2009, 2012; Wang et al. 2012; Armienti et al. 2013). Another popular

76  thermobarometer, first established by Carmichael et al. (1970) and recalibrated by Lee et

77  al. (2009), is based on the Si activity in the olivine–melt–orthopyroxene equilibrium

78  system and is water-sensitive. Theoretically, these two thermobarometers should give

79  identical *P–T* estimates, i.e., they should plot onto a common *P–T* trajectory when

80  applied to the same volcanic field. Thus, we can obtain the water content of the melt by

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81    fitting these two suites of $P$–$T$ estimates into a common $P$–$T$ trajectory. The water content

82    fitted by the thermobarometers can represent the actual quantity of water in the melt prior

83    to degassing.

84        Recently, the Cenozoic continental flood basalt (CFB) province in Central-East

85    Asia has been of interest to many researchers, owing to the arguments over whether it is

86    the product of dry melting of the hot upwelling mantle or of wet melting of the

87    transition-zone mantle hydrated by slab stagnation (Wang et al. 2015). The Wudalianchi–

88    Erkeshan–Keluo (WEK) potassic volcanic field, NE China, is the youngest representative

89    of this CFB province. Some researchers suggest that the WEK potassic basalts have a

90    relatively low water content (Chen et al. 2015), while others argue that the basalts were

91    derived from the melting of the highly hydrous transition-zone mantle (Kuritani et al.

92    2013). Here we apply the clinopyroxene–melt thermobarometer (Putirka et al. 2003) and

93    the Si activity thermobarometer (Lee et al. 2009) to the WEK volcanic rocks, with the

94    aims of estimating the water content of the WEK melts prior to degassing and

95    constraining their source mantle.

96

## Geological setting

98        Cenozoic intraplate volcanic activity has occurred widely in Northeastern China

99    (Fig. 1). These eruptions began in the Late Cretaceous and have continued until recent

100    human history (Liu et al. 2001). Over 590 volcanic edifices and ~50,000 km$^2$ of surface

101    lava flows are distributed along the NNE/NE trending rift-graben systems (Zhou et al.

102    1988; Basu et al. 1991; Liu et al. 2001). Their compositions range from tholeiitic to

103    alkaline basalts, with more evolved trachybasalts, trachytes, and phonolites. These

104    volcanic rocks have been regarded either as a result of the replacement of the ancient

105    lithosphere by new, oceanic mantle (Xu et al. 2005, 2012; Tang et al. 2006) or related to

106    the stagnation of the Pacific slab in the mantle transition zone (Sakuyama et al. 2013;

107    Kuritani et al. 2011, 2013; Wang et al. 2015).

108        As one of the major alkaline volcanic rock fields in Northeastern China, the

109    Wudalianchi–Erkeshan–Keluo (WEK) volcanic field (Basu et al. 1991; #5 in Fig. 1) has

110    drawn special attention because of its highly potassic magma compositions (Zhang 1984;

111    Qiu 1991; Basu et al. 1991; Zhang et al. 1995, 1998; Zou et al. 2003; Chen et al. 2007;

112    Kuritani et al. 2013; Chu et al. 2013; Sun et al. 2014, 2015, 2017; Zhao et al. 2014a,

113    2014b; Liu et al. 2016; Tian et al. 2016; Wang et al. 2017). Recent studies also

114    demonstrated that this potassic volcanic field may extend to the adjacent Xiaogulihe site

115    (Shao et al. 2009; Sun et al. 2014). The WEK volcanoes erupted potassic magmas

116    including olivine leucitite, leucite basanite, and trachybasalt, at three episodes during

117    Miocene (9.6–7.0 Ma), middle Pleistocene (0.56–0.13 Ma), and recent human history

118    (1719–1721 A.D.; Zhang et al. 1995).

119        The WEK volcanic field contains substantial scoria cones with height/base

120    diameter ratios of ~0.2 (Zhao et al. 2014b). The lava flows are characterized by abundant

121    elongated vesicles as well as volcanic bombs on the flow surfaces (Fig. 2c). These field

122    characteristics indicate that the eruption styles of the WEK volcanoes were mainly

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123    Strombolian type. Many mantle xenoliths are enclosed in the WEK basalts (Zhang et al.

124    2000, 2011; Chen et al. 2007).

125

126    **Sample description**

127    Twenty-six lava flow samples (Table S1 in the Supplemental Materials) were

128    collected from the flow fields of Yaoquanshan volcano (acronym in Table S1: YQ; same

129    as below), the proximal area of Laoheishan volcano (LHS), the distal area of Laoheishan

130    volcano (SC), Huoshaoshan volcano (HSS), the distal area of Jiaodebu volcano (GST),

131    Erkeshan volcano (KD), and Dayishan volcano (KL). We present major- and

132    trace-element results and Sr–Nd isotope data for all the 26 samples in Tables S1 and S2.

133    Eight samples were analyzed in this study; the remaining 18 were reported in Chu et al.

134    (2013). Mineral chemistry of clinopyroxene for six representative samples are listed in

135    Table S3. The detailed methodology is described in Appendix A in the Supplemental

136    Materials.

137    Photographs of representative samples are provided in Fig. 2. Based on mineral

138    mode compositions, the WEK potassic volcanic rocks are classified as olivine leucitites,

139    leucite basanites, and trachybasalts. The volcanic rocks are aphyric and glassy, containing

140    a small proportion of phenocrysts (<5%). These phenocrysts are less than 0.5 mm in

141    diameter and consist of olivine, clinopyroxene, and leucite. The presence of euhedral

142    olivine and clinopyroxene phenocrysts, together with melt inclusions, suggests a

143    magmatic rather than xenocrystic origin (Chu et al. 2013). Most clinopyroxene

144 phenocrysts do not show detectable zoning; some occasional oscillatory zoning (Fig. 2a)

145 observed indicates the normal pattern of crystal growth (Shore and Fowler 1996). The

146 embayment structure of olivine (Fig. 2d) indicates rapid decompression (Kuritani et al.

147 2013). The matrix mainly consists of quenched glass, olivine, clinopyroxene, K-feldspar,

148 and minor oxide minerals. Elongated bubbles, a typical gas-rich eruption feature,

149 ubiquitously occur in our samples (Figs. 2b, 2c). Mantle-derived peridotite xenoliths and

150 xenocrysts are present at each volcanic site.

151    On the total alkali–silica (TAS) diagram (Fig. S1), the WEK volcanic rock samples

152 plot in the areas of potassic phonotephrite, tephriphonolite, basaltic trachyandesite, and

153 trachyandesite. Although chemical classification shows that the WEK volcanic rocks are

154 not basalts, they have been consistently referred to as "potassic basalts" since Basu et al.

155 (1991). For consistency and simplicity, we adopt "potassic basalt" as a generalized name

156 for the WEK volcanic rocks.

157

158                          **Thermobarometric methods**

159 **Clinopyroxene–melt thermobarometer**

160    The thermobarometer of Putirka et al. (2003) was applied to our WEK samples.

161 This thermobarometer was calibrated based on the jadeite–melt and jadeite–diopside +

162 hedenbergite exchange equilibrium thermodynamics, and the calibration dataset covers a

163 wide range of pressure (up to 35 kbar), temperature (850–1300 °C), and composition

164 (including Si-rich, alkali-rich, and hydrous melts). In our $P$–$T$ calculations, the

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165  clinopyroxene compositions were paired with their corresponding bulk-rock

166  compositions. For large clinopyroxene phenocrysts, multiple analytical spots were treated

167  individually. The standard estimate error (SEE) is 33 °C for temperature and 1.7 kbar for

168  pressure (Putirka et al. 2003).

169      There are several ways to test the equilibrium between clinopyroxene and melt (see

170  Appendix B in the Supplemental Materials for details); herein the Fe–Mg exchange test

171  was used before $P$–$T$ calculation. The Fe─Mg exchange coefficient between

172  clinopyroxene and the equilibrated melt $[K_D(Fe–Mg)^{cpx–melt} = (Fe/Mg)^{cpx}/(Fe/Mg)^{melt}$,

173  where Fe and Mg are in molar fraction] derived from 1,245 experimental observations

174  yields a roughly normal distribution ranging from 0.04 to 0.68, with a mean value of 0.28

175  and standard deviation (σ) of 0.08 (Putirka 2008). Using this criterion at 2σ level, 78 (out

176  of 122) equilibrated clinopyroxene–melt pairs with $K_D(Fe–Mg)^{cpx–melt}$ between 0.12 and

177  0.44 were selected. All these clinopyroxene grains have Mg# > 75 [Mg# =

178  100×Mg/(Mg+Fe), where Fe and Mg are in molar fraction]. We plot the clinopyroxene

179  and bulk-rock Mg# values in the Rhodes' diagram (Rhodes et al. 1979) (Fig. 3a) to

180  illustrate this equilibrium test. Nearly all the phenocrysts (including multi-spot analyses

181  on zoned phenocrysts) are in equilibrium with their host rocks. However, most

182  groundmass clinopyroxene grains exhibit disequilibrium features, suggesting that they

183  formed after significant magma crystallization, perhaps during the surface lava evolution.

184  Clinopyroxene grains that are not in equilibrium with their host rocks were excluded in

185  the $P$–$T$ estimation.

186    The host bulk-rock composition of each clinopyroxene crystal was assumed as the

187    melt composition in our calculation, because the compositional evolution of the melt due

188    to crystallization is found to be negligible. The area analysis of thin-sections indicates

189    that phenocrysts (diameter ≤ 0.5 mm) occupy less than 5% of the thin-section area,

190    making their contribution to the modification of the melt composition insignificant. In

191    addition, the Mg# values of low-pressure clinopyroxene grains do not show a marked

192    decrease when compared to the higher-pressure ones (Fig. 3b). The groundmass

193    clinopyroxene grains have lower Mg# (Fig. 3a), but their crystallization occurred after the

194    crystallization of the high-Mg# phenocrysts. Therefore, the crystallization of groundmass

195    clinopyroxene grains could not have influenced the composition of the melt at deeper

196    depths. Finally, the melt-equilibrated clinopyroxene compositions simulated using the

197    models of Putirka (1999) at the *P–T* conditions obtained from thermobarometry are

198    identical to the measured clinopyroxene compositions within the prediction errors (Fig.

199    3c).

200

201    **Si activity thermobarometer**

202    The Si activity thermobarometer of Lee et al. (2009), which was calibrated based

203    on the thermodynamics of $SiO_2$(melt)–$Mg_2SiO_4$(olivine)–$MgSiO_3$(orthopyroxene)

204    equilibrium, was applied to our samples. This thermobarometer was calibrated over a

205    wide range of pressure (up to 7 GPa), temperature (1100–1800 °C), and composition

206    (including Si-rich, alkali-rich, low-Mg#, and hydrous melts). The application of this

207   thermobarometer requires a melt water content input. Currently, no direct $H_2O$ content

208   measurement for the WEK basalts is available, thus two $H_2O$ contents were assumed in

209   our *P–T* calculation: 0.50 wt% (Chen et al. 2015) and 1.4 wt% (Kuritani et al. 2013). The

210   uncertainty is 2.0 kbar for pressure estimation and is 3% for temperature estimation (Lee

211   et al. 2009).

212        A major prerequisite for using the Si activity thermobarometer is that the melts are

213   in equilibrium with both olivine and orthopyroxene. The source mantle lithology of the

214   WEK basalts is dominated by peridotite rather than pyroxenite, based on the low Fe/Mn

215   ratios of olivine phenocrysts (Sun et al. 2014 and our unpublished data). In addition, the

216   mantle xenoliths recovered in the WEK lava consist of lherzolites and harzburgites

217   (Zhang et al. 2011). Therefore, the Si activity of the WEK melts tend to be consecutively

218   buffered by olivine and orthopyroxene during the mantle-level evolutions, such as partial

219   melting (polybaric or monobaric) and re-equilibration at shallower depths (Lee et al. 2009;

220   Plank and Forsyth 2016). Crustal assimilation and fractional crystallization, however, can

221   alter the equilibrated melt composition and cause underestimations of pressure and

222   temperature (Putirka et al. 2012; Plank and Forsyth 2016). The WEK basalts have not

223   experienced significant crustal assimilation, as evidenced by the rapid magma ascending

224   rates indicated by the occurrence of mantle xenoliths and significant $^{230}$Th excesses (Zou

225   et al. 2003), the uncontaminated mantle Os isotope and platinum group element

226   signatures (Chu et al. 2013; Sun et al. 2014), and the limited interactions between crust

227   xenoliths and the host lava (McGee et al. 2015). Fractional crystallization of olivine may

228   have occurred, but the degree is restricted to have negligible effects in generating the

229   observed magma composition variations (Zhang et al. 1995; Kuritani et al. 2013; Wang et

230   al. 2017). Thus, in principle, these basalts should have nearly mantle-equilibrated

231   signatures as exemplified by their high Mg#. We compiled 127 reliable WEK basalt

232   compositions with ferrous/ferric ratios from the literature (Qiu 1991; Zhang 1984). The

233   $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ ratio shows a logarithmic normal distribution, with an expected value of

234   0.28. Using this $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ ratio, we got better constrained Mg# values of 67–74

235   for our WEK samples. Combined with Tamura et al. (2000)'s composition-dependent

236   $K_D(Fe–Mg)^{ol–melt}$, the olivine crystals in equilibrium with most WEK basalts (except

237   sample YQ4) have Fo values [Fo = 100×Mg/(Mg+Fe), where Fe and Mg are in molar

238   fraction] ranging from 87 to 90, falling into the range of mantle xenolith olivine grains

239   discovered in this area (Zhang et al. 2000). Therefore, our WEK samples are likely to be

240   in equilibrium with the olivine and orthopyroxene in the proximal mantle, and the

241   crust-level evolutions should be negligible.

242          Another Si activity barometer, calibrated by Putirka (2008) based on the same

243   thermodynamic equilibrium but with a different Si activity expression and experimental

244   dataset (in similar $P$, $T$, melt composition, and $H_2O$ ranges), was used to cross-check the

245   pressure estimates. With the same temperature inputs, the two independent barometers

246   yielded identical pressure estimates for our WEK basalts (Fig. 3d). This agreement

247   provides additional confidence for our $P$–$T$ estimates.

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# Results

## Clinopyroxene–melt thermobarometer

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251     The $P$–$T$ results of the clinopyroxene–melt thermobarometer are listed in Table S3

252 (in the Supplemental Materials) and plotted as blue circles in Fig. 4a. The clinopyroxene

253 and the melt equilibrated at a pressure range of 0.8–13.5 kbar and a temperature range of

254 1051–1162 °C. The $P$–$T$ results exhibit a linear trend of $P$/kbar $= -118.0 + 0.113\ T$/°C ($R^2$

255 $= 0.85$).

256

## Si activity thermobarometer

257

258     The $P$–$T$ results of the Si activity thermobarometer are illustrated in Fig. 4a. The

259 $H_2O$ content of 0.50 wt% yields pressures between 8.8 and 15.5 kbar (corresponding to

260 depths of 33–54 km) and temperatures between 1129 and 1260 °C, and the $H_2O$ content

261 of 1.4 wt% yields pressures between 9.1 and 15.6 kbar (corresponding to depths of 34–54

262 km) and temperatures between 1124 and 1247 °C. The $P$–$T$ estimates from this

263 thermobarometer also exhibit linear trends, with a slope similar to that of the

264 clinopyroxene–melt thermobarometer. However, the intercepts with the $T$-axis of both Si

265 activity $P$–$T$ arrays are different from that of the clinopyroxene–melt array.

266

## Melt water content estimation

267

268     The plot of $P$–$T$ results is generally divided into three pressure ranges (Fig. 4a): the

269 lower-pressure range determined only by the clinopyroxene–melt thermobarometer; the

270 higher-pressure range determined only by the Si activity thermobarometer; and the

271 overlapping pressure range in which both thermobarometers yielded $P$–$T$ results. The

272 overlapping pressure range of two thermobarometers are from 8.8 to 13.5 kbar when the

273 0.50 wt% $H_2O$ content is used, and from 9.1 to 13.5 kbar when the 1.4 wt% $H_2O$ content

274 is used. At the overlapping pressure ranges, the temperatures estimated by the

275 clinopyroxene–melt thermobarometer tend to be systematically lower than those of the Si

276 activity thermobarometer.

277     There is only one real $P$–$T$ path for the magmas, and both the thermobarometers

278 should reproduce this real $P$–$T$ path. The clinopyroxene–melt thermobarometer (Putirka

279 et al. 2003) is independent of $H_2O$ content, and hence the $P$–$T$ path calculated by this

280 thermobarometer would represent the real $P$–$T$ path within its SEE. However, the Si

281 activity thermobarometer of Lee et al. (2009) is water-sensitive. A higher $H_2O$ content

282 used in the calculation can effectively increase the pressure but decrease the temperature,

283 as demonstrated by the contrast between the $P$–$T$ paths calculated using the 1.4 wt% and

284 the 0.50 wt% $H_2O$ content (Fig. 4a). When the actual melt $H_2O$ content is used in the

285 calculation, the Si activity thermobarometer should generate a $P$–$T$ path consistent with

286 the clinopyroxene–melt thermobarometer, i.e., both thermobarometers should generate

287 identical temperature estimates at the same pressure range. The observed offsets between

288 the $P$–$T$ paths of the two thermobarometers in the overlapping pressure ranges (Fig. 4a)

289 therefore indicate that the $H_2O$ contents used in the Si activity thermobarometer (0.50 wt%

290 and 1.4 wt%) may not represent the actual melt $H_2O$ content. In contrast, the $H_2O$ content

291   that minimizes the difference between the two $P$–$T$ paths should be close to the actual

292   amount of water dissolved in the melt at the overlapping pressure range.

293        The temperature difference at the same pressure ($|\Delta T|$) between the $P$–$T$ results of

294   the two thermobarometers varies with the $H_2O$ content used in the calculation of the Lee

295   et al. (2009) thermobarometer (Table 1). We note that $|\Delta T|$ is minimized when the $H_2O$

296   content approaches ~5 wt%. Therefore, it is reasonable to suppose ~5 wt% as the actual

297   melt $H_2O$ content in the overlapping pressure range of 10.3–13.5 kbar (Table 1). However,

298   this temperature difference is only a qualitative indicator based on the arbitrary judgment

299   of scattered data points. For most of the cases, due to the lack of a perfect match in

300   pressure, this arbitrary point-fitting method may not work well.

301        We instead propose to use a single parameter, "buffer overlapping area (BOA)", to

302   evaluate the offset of the two $P$–$T$ paths as a function of $H_2O$ content. To construct a

303   buffer for a thermobarometer, the error ellipse of each $P$–$T$ point estimated by this

304   thermobarometer was drawn on the $P$–$T$ plot. The fields covered by these ellipses were

305   then outlined to form one (or more) closed shape(s), which is called a buffer. We

306   constructed buffers for the clinopyroxene–melt thermobarometer and the Si activity

307   thermobarometer (Fig. 4a) following this procedure. The overlapping "area" of the two

308   buffers in the $P$–$T$ space, BOA, can be calculated when the $H_2O$ content used in the Si

309   activity thermobarometer is known (details of the BOA calculation are given in Appendix

310   C in the Supplemental Materials). It is clear that, the smaller is the difference of the two

311   $P$–$T$ paths, the larger is the BOA. Thus, when the BOA is maximized, the difference of

312    the two $P$–$T$ paths is minimized. We calculated BOA values at $H_2O$ contents from 0 wt%

313    to 9 wt% with increment of 0.1 wt%. The maximal BOA (BOAmax) was obtained for an

314    $H_2O$ content of 4.5 wt%. In Fig. 4b, we plot the BOA/BOAmax ratio against the melt

315    $H_2O$ content used in the Si activity thermobarometer. This ratio reaches unity

316    (BOA/BOAmax = 1) when $H_2O$ = 4.5 wt%, as expected. When the $H_2O$ content is below

317    or above this value, BOA/BOAmax decreases gradually. Therefore, 4.5 wt% is taken as

318    our best estimate for the pre-eruptive WEK melt $H_2O$ content at the overlapping pressure

319    range of 10.1–13.5 kbar (corresponding to depths of 37–47 km).

320        Quantifying the uncertainty of our estimate of the $H_2O$ content, however, is not

321    explicit, because it has no direct error propagation relationship from the uncertainties of

322    the thermobarometers. Moreover, the systematic error in our estimation has not been

323    examined. Evaluation of the reliability and accuracy of our $H_2O$ content estimation

324    method can be done with an experimentally-derived dataset of hydrous compositions. We

325    compiled twenty-one sets of experimental data with equilibrium phase assemblages of

326    melt + olivine + clinopyroxene + orthopyroxene ± other phases and $1 \leq H_2O^{melt} \leq 7$ wt%

327    from the Library of Experimental Phase Relations database (LEPR, Hirshmann et al.

328    2008) and summarize them in Table 2. For each set of equilibrium phases, we estimated

329    the $P$–$T$ conditions using the two thermobarometers, and then calculated BOAs with $H_2O$

330    content changing from 0 to 9 wt% with 0.1 wt% increment. In this case, a buffer is simply

331    an error ellipse instead of a closed shape formed by multiple ellipses. The melt $H_2O$

332    content was estimated as the $H_2O$ content that maximizes the BOA, i.e., when the $P$–$T$

333  estimates of the two thermobarometers are the closest. Fig. 5a shows estimated versus

334  measured melt $H_2O$ contents for the experimental equilibria. The $H_2O$ content estimates

335  scatter near the 1:1 line, indicating no significant systematic error in our estimation. Our

336  method reproduces the experimental melt $H_2O$ contents with standard estimate error

337  [standard estimate error (SEE) = $\sqrt{\sum(X_{est} - X_{true})^2/N}$, where $X_{est}$ is the estimated value,

338  $X_{true}$ is the true value, $N$ is the number of data] of 1.2 wt%. Using the estimated $H_2O$

339  contents, the Si activity thermobarometer also reproduces the experimental $P–T$

340  conditions (Fig. 5b and 5c), confirming the inter-consistency of the models. Therefore,

341  we take the SEE of 1.2 wt% as an indicative uncertainty for our $H_2O$ content estimate of

342  the WEK melts. This SEE may be further justified with larger testing datasets, and be

343  improved with better calibrations of thermobarometers.

344       The saturation temperature of clinopyroxene is controlled by the melt $H_2O$ content

345  at a given pressure. All the WEK basalts are nearly aphyric with trace amount (<5 % area

346  in thin section) of clinopyroxene microphenocrysts, suggesting that the clinopyroxene

347  grains had crystallized when the magma temperatures were close to the clinopyroxene

348  saturation temperatures. By using the equation (34) of Putirka (2008), we calculated the

349  clinopyroxene saturation surfaces of a typical WEK potassic basalt sample, HSS5, at

350  different $H_2O$ contents. The $P–T$ path of the WEK magmas is roughly parallel to the

351  clinopyroxene saturation surfaces. At >5 kbar, nearly all the clinopyroxene–melt $P–T$

352  estimates are located between the clinopyroxene saturation surfaces with 4 and 5 wt%

353  $H_2O$ (Fig. 4a). Such high $H_2O$ contents are notably consistent with our estimate acquired

17

354  from the dual-thermobarometer method. This result also indicates that, nearly no decrease

355  of the melt $H_2O$ content occurred during the magma decompression from 13.5 to 5 kbar.

356

357  **Discussion**

358  **Elevated d$T$/d$P$ of the magma and $H_2O$–$CO_2$ degassing**

359  The linear regression of the $P$–$T$ array of the WEK magma yielded a d$T$/d$P$ value

360  of 8.8 °C/kbar (Fig. 4a). However, a basaltic magma isentropically (i.e., reversibly and

361  adiabatically) ascending through the lithosphere follows a $P$–$T$ trajectory with $(\partial T/\partial P)_S \approx$

362  3.3 °C/kbar [or $(\partial T/\partial z)_S \approx 1.0$ °C/km, McKenzie and Bickle 1988; $(\partial T/\partial P)_S$: d$T$/d$P$ when

363  the entropy is constant; $(\partial T/\partial z)_S$: d$T$/d$z$ when the entropy is constant]. When the magma

364  ascends adiabatically but irreversibly (e.g., rapid ascending process), the $(\partial T/\partial P)_{Q,ir}$ value

365  [$(\partial T/\partial P)_{Q,ir}$: d$T$/d$P$ when the heat is zero and the process is irreversible] decreases owing

366  to the generation of entropy (Ganguly 2008; Armienti et al. 2013). The isentropical

367  decompression slope $(\partial T/\partial P)_S$ is controlled by the thermal expansion coefficient (α),

368  specific heat capacity ($c_p$), and density (ρ) of the system (McKenzie and Bickle 1988).

369  Using the α, $c_p$, and ρ data listed in Table 3, our calculated $(\partial T/\partial P)_S$ for the volatile-free

370  HSS5 melt is 2.5 °C/kbar, close to the recommended value for basaltic melt (McKenzie

371  and Bickle 1988) but far lower than the regressed d$T$/d$P$ value of 8.8 °C/kbar.

372  The heat loss through magma–wall rock interaction during the magma ascending

373  can increase the d$T$/d$P$ value. However, the exceptionally hot eruption temperature

374  (~1250 ºC) of the WEK magmas estimated by Kuritani et al. (2013) and the rapid ascent

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375    constrained by significant [230]Th excesses (Zou et al. 2003) are consistent with extensive

376    magma–wall rock thermal interaction being unlikely. An alternative explanation of this

377    high $dT/dP$ is the exsolution of volatiles, such as $H_2O$ and $CO_2$. Significant expansion of

378    fluid during adiabatic decompression can facilitate the cooling of the magma system,

379    leading to a high $dT/dP$ value. As shown in Table 3, to produce such a high adiabatic

380    $dT/dP$ value of 8.8 °C/kbar, the existence of fluid with high α and low ρ is required for

381    the WEK magma system.

382         The existence of a fluid phase indicates that the magma ascent is accompanied by

383    degassing. The pressure of volatile saturation depends on the contents of major volatile

384    species in the melt, i.e., $H_2O$ and $CO_2$. We have no direct constraint on the volatile

385    saturation pressure of the WEK magmas, because the melt $CO_2$ contents are unknown.

386    However, the ubiquitous occurrence of mantle xenoliths in the lava (Zhang et al. 2000)

387    strongly implies that the WEK magmas started degassing at mantle depths, as the

388    entrapment of xenoliths and the high magma transport rate essential for preserving the

389    xenoliths ($10^{-1}$ to several m/s, Spera 1984) require rapid brittle failure (i.e., explosion) of

390    the mantle wall rock, which is most likely triggered by the formation of bubbles (Lensky

391    et al. 2006). Therefore, we assume that the melt dissolving 4.5 wt% $H_2O$ is

392    volatile-saturated at 13.5 kbar and 1438 K (the deepest point on the clinopyroxene–melt

393    $P$–$T$ array). At this state, the melt $CO_2$ content is predicted to be 2.0 wt% using the

394    solubility model of Duan (2014). If the pre-degassing melt $CO_2$ content was lower (or

395    higher) than 2.0 wt%, the degassing would start from a lower (or higher) pressure. As

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396    shown in Fig. 6, the $H_2O$–$CO_2$ degassing along the $P$–$T$ path of the WEK magmas in both

397    closed and open systems were simulated using the model of Duan (2014). From the

398    degassing curves, $CO_2$ was substantially removed from the melt when the pressure drops

399    from 13.5 kbar to 5 kbar, while the loss of $H_2O$ was insignificant. At $P < 5$ kbar, the

400    degassing behavior of $H_2O$ is distinct between closed and open systems: the onset of $H_2O$

401    exsolution from the melt was earlier in the closed system but later in the open system

402    until ~2 kbar. It is clear that the melt $H_2O$ content of the ascending magma stayed

403    unchanged during high pressure degassing, which is in good agreement with the

404    clinopyroxene saturation surface calculation results above (Fig. 4a).

405

**Constraints on the source mantle**

407    The most unique geochemical characteristics of the WEK basalts are their

408    EM1-like Sr–Nd–Hf isotopes, low $\delta^{26}Mg$ values, and extremely unradiogenic Pb isotopes

409    (Zhang et al. 1995; Chu et al. 2013; Sun et al. 2014, 2017; Wang et al. 2017). The

410    correlations of these features indicate a recycled, isotopically "enriched" component in

411    the source mantle. However, the interpretation of this enriched component, coupled with

412    the issue of the ultimate source of the WEK magmas, is being debated. Several competing

413    theories concerning this problem have been put forward: (1) potassium-rich

414    sub-continental lithospheric mantle (SCLM) metasomatized by melt/fluid from ancient

415    asthenosphere (Zhang et al. 1995, 1998, 2000; Zou et al. 2003), delaminated Precambrian

416    lower crust fragments (Chu et al. 2013), or ancient subducted oceanic crust (Sun et al.

20

417    2014, 2015, 2017); (2) sub-lithospheric (or transition zone) mantle metasomatized by (or

418    mixed with) sediment fluid from an ancient stagnant slab (Kuritani et al. 2013), carbonate

419    melt from the modern Pacific slab (Tian et al. 2016), or remnants of an ancient

420    carbonate-bearing slab upwelled from the mantle transition zone (MTZ) (Wang et al.

421    2017). These conflicting models cannot provide a clear prospect about the real magma

422    source, thus evidence external to geochemical data are needed to constrain the origin of

423    the WEK volcanic rocks.

424        The source of the magmas can be located by determining the depths of melt

425    generation and transportation. We calculated the pressures and temperatures for six

426    low-SiO$_2$ melts from Zhang et al. (1995) using the Lee et al. (2009) Si activity

427    thermobarometer. Compared to our WEK dataset, these complimentary samples have

428    higher MgO contents (up to 14.40 wt%) and equilibrium Fo values (up to 92.0), thus

429    representing the compositions of more primary melts. They plot on the extrapolation of

430    our regressed $P$–$T$ path and extend to higher $P$ and $T$ (Fig. 7a), suggesting that the WEK

431    melts originated from a deeper mantle. The deepest melt–olivine–orthopyroxene

432    equilibria occurred at 80–110 km (translated from $P$ = 23–33 kbar). These depths

433    coincide with the low-velocity asthenosphere underlying the 70–80 km thick

434    high-velocity lithosphere lid from seismological constraints (e.g., Zheng et al. 2011; Li et

435    al. 2012, 2013; Guo et al. 2014), thus clearly indicating that the parental WEK melts were

436    generated beneath the SCLM. These $P$–$T$ estimates lie closely along a hydrous peridotite

437    solidus with $X_{H_2O}^{bulk}$ = 450 ppm (calculated using the model of Katz et al. 2003, with

438    $X_{H2O}^{melt}$ = 4.5 wt% from our estimation and a partitioning coefficient of 0.01), implying

439    that the melts can be generated by small-degree wet melting at these depths. If $CO_2$ has

440    further lowered the peridotite solidus (e.g., Dasgupta et al. 2007), melting may begin at a

441    greater depth, and the observed melt–mantle equilibrium depths may reflect the ponding

442    of melts at the base of the lithosphere. The stalled melts may thermally and chemically

443    erode the overlying lithosphere and cause its degradation (Plank and Forsyth 2016;

444    Putirka et al. 2012). Overall, our inferred melting depths support the geochemical models

445    with a sub-lithospheric mantle origin of the WEK magmas.

446        The melting of the sub-lithospheric mantle may be related to the mantle upwelling

447    initiated from the MTZ. Recent high-resolution mantle tomography studies have revealed

448    large-scale (deep to ~400 km), vertically continuous low-velocity anomalies beneath

449    WEK and other NE China Cenozoic volcanos (Wei et al. 2019; Ma et al. 2018; Zhao et al.

450    2009). The nature of this deep mantle upwelling, however, is debated. The upwelling of

451    wet mantle materials from the MTZ (Kuritani et al. 2011, 2013, 2019; Zhao et al. 2009)

452    or a hot mantle plume through a hole at the edge of the stagnant Pacific slab (Tang et al.

453    2014) have both been proposed for the origin of the deep back-arc volcanisms in NE

454    China. To examine whether excess heat contributed to the mantle upwelling beneath

455    WEK, we calculated the mantle potential temperature ($T_p$) using the Putirka (2016) model.

456    The most primary WEK melt compositions passed all the essential equilibrium tests of

457    this model, and yielded an average $T_p$ of 1372 ± 30 °C. This $T_p$ is significantly lower than

458    those of the intraplate volcanic hotspots (e.g., Hawaii and Samoa $T_p$ = 1722 °C, Putirka et

459  al. 2007; Emeishan $T_p$ = 1740–1810 °C, Tao et al. 2015; Siberian Trap $T_p$ = 1600 °C,

460  Sobolev et al. 2011), but is similar to the ambient upper mantle temperature represented

461  by the average mid-ocean ridge ($T_p$ = 1454 ± 78 °C, Putirka et al. 2007) and the $T_p$ of wet

462  arc or back-arc mantle in subduction zones (e.g., Mariana arc and trough $T_p$ = 1350 °C,

463  Kelly et al. 2010; Yamato Basin, Japan Sea $T_p$ = 1200–1320 °C, Hirahara et al. 2015;

464  Changbaishan, NE China $T_p$ = 1314–1357 °C, Kuritani et al. 2019). This low-$T_p$

465  characteristic suggests that the mantle upwelling beneath the WEK area is not an active

466  plume driven by thermal buoyancy, but rather, facilitated by fluids released from the

467  stagnated Pacific slab in the MTZ (Kuritani et al. 2019; Richard and Bercovici 2009;

468  Richard and Iwamori 2010). The "wet plumes" (Iwamori 1991, 1992) may carry water

469  and other fluids from the MTZ to the upper mantle, and lead to wet melting in the

470  asthenosphere (Fig. 7b). This volatile-rich mantle source is consistent with our inferred

471  high $H_2O$ (and $CO_2$) contents of the WEK magmas.

472

473  **Comparison with Xiaogulihe volcanic rocks: implication of mantle $H_2O$**

474  **heterogeneity**

475  The WEK potassic basalts and the Pleistocene ultrapotassic volcanic rocks from

476  Xiaogulihe (Fig. 1) are closely related in petrogenesis, owing to their similar geochemical

477  features, including high $K_2O$ contents (4–9 wt%), strong enrichment of incompatible

478  elements (Fig. S3) compared to other Cenozoic basalts in eastern China and ocean island

479  basalts, and EM1-like Sr–Nd–Hf isotopic signatures (Zhang et al. 1998; Sun et al. 2014;

23

480    Wang et al. 2017). The melt $H_2O$ contents of the Xiaogulihe volcanic rocks have been

481    estimated to be 0.36–0.50 wt%, based on Fourier transform infrared spectrometry

482    analyses of $H_2O$ contents in clinopyroxene phenocrysts (Chen et al. 2015). Our 4.5 ± 1.2

483    wt% $H_2O$ content estimation of the WEK melts is markedly higher than that of the

484    Xiaogulihe melts. We propose two possible explanations for this difference: (1) the

485    clinopyroxene phenocrysts analyzed by Chen et al. (2015) crystallized after significant

486    degassing; (2) the difference in melt $H_2O$ content was inherited from the heterogeneous

487    $H_2O$ abundance in the source mantle.

488        Analyzing the $H_2O$ content of clinopyroxene can be a reliable method to retrieve

489    the primary (i.e., pre-eruption) melt $H_2O$ content (e.g., Wade et al. 2008; Xia et al. 2013).

490    Application of this method, however, requires that: (1) clinopyroxene had crystallized

491    before significant $H_2O$ degassing; and (2) clinopyroxene had not experienced

492    degassing-associated H diffusion. By showing the invariant $H_2O$ contents along profiles

493    within clinopyroxene crystals, Chen et al. (2015) demonstrated that the requirement (2)

494    was attained, while the requirement (1) was not fully verified. If the clinopyroxene grains

495    had crystallized during/after magma degassing at shallow depths (e.g., $P < 5$ kbar), they

496    may record reduced melt $H_2O$ contents. To test this possibility, we calculated

497    crystallization pressures for the clinopyroxene grains analyzed by Chen et al. using the

498    Putirka et al. (2003) thermobarometer, and plotted pressure against the corresponding

499    melt $H_2O$ content in Fig. 8. The $H_2O$ content of the Xiaogulihe melts remains constantly

500    low (~0.3 wt%) as the magma decompressed from 10 kbar to 3 kbar, but shows a notable

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501    rise at $P < 3$ kbar. Considering the high clinopyroxene crystallization pressures (up to 10

502    kbar), as well as the low and constant melt $H_2O$ content during the magma ascending, it is

503    unlikely that degassing occurred prior to the earliest clinopyroxene crystallization.

504    Therefore, we confirm that the clinopyroxene phenocrysts analyzed by Chen et al. (2015)

505    crystallized from undegassed melts, and the low $H_2O$ content signature of the Xiaogulihe

506    melts is primary. The absence of deep degassing of the Xiaogulihe magmas is also

507    evidenced by the absence of mantle xenoliths at this volcanic site (Zhang et al. 1998), as

508    the generation and transport of xenoliths is highly dependent on volatile exsolution and

509    bubble nucleation (Lensky et al. 2006). The enhancement of melt $H_2O$ content at $P < 3$

510    kbar can be explained by substantial shallow-level isobaric crystallization under

511    $H_2O$-undersaturated condition (Blundy and Cashman 2008), which is supported by the

512    observed high crystallinity (~40%) in the Xiaogulihe volcanic rocks (Shao et al. 2009).

513        Alternatively, the difference in $H_2O$ content between the Xiaogulihe and WEK

514    volcanic rocks can be explained by a heterogeneous distribution of $H_2O$ in the source

515    mantle, considering the >200 km distance between the two volcanic sites. Although

516    similar in geochemistry, the Xiaogulihe volcanic rocks exhibit more extreme

517    characteristics compared to the WEK basalts, such as the "ultra-high" $K_2O$ contents (up

518    to 9.29 wt%, cf. 6.09 wt% for WEK), more enriched large-ion lithophile elements, more

519    fractionated rare earth elements, less radiogenic Pb isotope compositions, and lower

520    $^{143}Nd/^{144}Nd$ and higher $^{87}Sr/^{86}Sr$ ratios (Zhang et al. 1998; Sun et al. 2014; Wang et al.

521    2017). These features indicate a lower melting degree and an isotopically more enriched

522    source. If the source mantle of the Xiaogulihe volcanic rocks is less hydrous than that of

523    the WEK basalts, it is reasonable for these rocks to have a lower mantle melting degree at

524    given $T_p$, and therefore higher $K_2O$ and incompatible element concentrations than the

525    WEK basalts.

526        A regional-scale mantle $H_2O$ heterogeneity in eastern China has been recently

527    revealed; from southeast (close to Pacific subduction zone) to northwest (away from

528    Pacific subduction zone), the source mantle $H_2O$ contents of the eastern China Cenozoic

529    basalts tend to decrease from 4700 ppm to 150 ppm (Chen et al. 2017; Xia et al. 2019).

530    The geochemical characteristics of these basalts are also influenced by increasing

531    subduction-related fluid activities with decreasing distance to the Pacific plate boundary

532    (Zhao et al. 2019). This spatial variation of mantle and magma hydration can be most

533    easily understood as the time-integrated contributions of the wet upwelling fluxes arising

534    from the MTZ during the subduction and stagnation of the Pacific slab. The Xiaogulihe

535    volcano is among the westernmost volcanisms in eastern China, ~200 km farther away

536    from the Pacific trench than WEK, and located far beyond the western edge of the

537    present-day stagnant Pacific slab (Fig. 1). Therefore, the water content contrast between

538    the WEK and Xiaogulihe volcanic rocks is consistent with the regional-scale variation

539    trend. We infer that the source mantle of the WEK and Xiaogulihe potassic volcanic rocks

540    is heterogeneously hydrated, and the Xiaogulihe volcanic rocks were derived from a less

541    hydrous domain.

542

## Implications

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544     In most subaerially erupted volcanic rocks, $H_2O$ dissolved in the melt at depths

545     escapes when the magma ascends to shallower depths and flows towards the surface.

546     Traditionally, melt inclusion analyses and direct measurements of nominally anhydrous

547     minerals (NAMs) can help to constrain the $H_2O$ content of the melt before eruption.

548     However, melt inclusions that preserve primitive $H_2O$ contents are not easy to find, and H

549     in nominally anhydrous minerals is also susceptible to diffusive loss. The method

550     reported in this paper provides a new approach to estimate the primary $H_2O$ contents of

551     subaerially erupted volcanic rocks despite their having experienced extensive degassing

552     before eruption. This quantitative $H_2O$ content estimation is useful especially when no

553     direct $H_2O$ analysis is available.

554     The Wudalianchi–Erkeshan–Keluo magma is an intraplate magma, which has long

555     been believed to have originated by the dry melting of a lithospheric mantle source.

556     However, our estimation of water contents shows that the WEK magmas with ~4.5 wt%

557     $H_2O$ have as much water as some arc magmas. This finding is similar to the recent reports

558     on Phanerozoic intraplate large igneous provinces (LIPs) (Xia et al. 2016; Liu et al. 2017;

559     Ivanov et al. 2018), and supports the presence of hydrated deep mantle reservoirs as the

560     sources of these LIPs.

561     Our method is not restricted to primary melt inclusions or primary NAMs, and

562     therefore, it may be also applicable to some evolved magmatic samples, such as the

563     Martian nakhlite (e.g., Peslier et al. 2019) and chassignite meteorites.

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564

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579

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935

936                                    **Figure captions**

937    **Figure 1.** Schematic map of the late Cenozoic intraplate volcanic province in

938    Central-East Asia, modified after Wang et al. (2015). The dark gray fields and numbers

939    indicate the locations of the late Cenozoic volcanic fields in Central–East Asia. The thick

940    solid white curves represent plate boundaries. The red dashed curve indicates the western

941    edge of the present-day stagnant Pacific slab (Zhao et al. 2011). Digital topography of

942    Central-East Asia is from National Oceanic and Atmospheric Administration/National

943    Geophysical Data Center (http://www.ngdc.noaa.gov/mgg/image/).

944

945    **Figure 2.** Representative photographs of the WEK basalt samples. **(a)** Back-scattered

946    electron (BSE) image of a euhedral, zoned clinopyroxene phenocryst from sample HSS5.

947    **(b)** Microphotograph of sample HSS5, showing glassy features. Clinopyroxene

948    phenocrysts are distributed in the groundmass, which is composed of glass with

949    subordinate clinopyroxene, olivine, and K-feldspar microcrystals. Note the substantial

950    bubbles present in the rock. Cpx denotes clinopyroxene. **(c)** Field photograph of a surface

951    lava flow of Laoheishan volcano, showing rope-like features, a volcanic bomb, and

952    elongated bubbles. **(d)** Microphotograph of sample HSS8 showing a euhedral olivine

953    crystal with embayment structure. Ol denotes olivine.

954

955    **Figure 3.** Tests for the thermobarometers. **(a)** Rhodes' diagram (Rhodes et al. 1979) for

956    clinopyroxene in the WEK potassic basalts. $Mg\# = 100 \times Mg/(Mg+Fe^{2+})$, where Mg and

957    $Fe^{2+}$ are in molar fraction. Here the proportion of $Fe^{2+}$ is set to be 100%, following the

958    treatment in experimental calibration (Putirka, 2008). Solid curve: the mean value of the

959    experimental $K_D(Fe–Mg)^{cpx–melt}$; two dashed curves: 2σ range of the mean experimental

960    $K_D(Fe–Mg)^{cpx–melt}$; grey field: the range of all experimental $K_D(Fe–Mg)^{cpx–melt}$ (Putirka

961    2008). **(b)** Mg# of clinopyroxene vs. crystallization pressure (*P*) calculated using the

962    clinopyroxene–melt barometer of Putirka et al. (2003). The Mg# value of clinopyroxene

46

963   has a normal distribution and yields an average of 81.9 ± 4.8 (2σ), without a decreasing

964   trend as the crystallization pressure decreases. **(c)** Measured vs. predicted clinopyroxene

965   composition using equations (3.1a), (3.2) and (3.5) of Putirka (1999). All the

966   clinopyroxene grains in equilibrium with their melts are plotted on the 1:1 line within

967   prediction error. DiHd denotes the diopside–hedenbergite component in pyroxene; EnFs

968   denotes the enstatite–ferrosilite component in pyroxene; Jd denotes the jadeite component

969   in pyroxene. **(d)** Comparison of pressure ($P$) estimates using the Lee et al. (2009) and

970   Putirka (2008) Si activity barometers for the WEK basalts. Input temperatures are the

971   same in both barometers, which are calculated using the Lee et al. (2009) thermometer

972   with a melt $H_2O$ content of 4.5 wt%. The two barometers yield identical pressure

973   estimates within error.

974

975   **Figure 4. (a)** Pressure–temperature calculation results of the clinopyroxene–melt

976   thermobarometer (Putirka et al. 2003) and the Si activity thermobarometer (Lee et al.

977   2009) for the WEK basalts. The results of the clinopyroxene–melt thermobarometer (blue

978   circles and the blue field) are linearly fitted and yield d$T$/d$P$ = 8.8 °C/kbar. The Si activity

979   pressures and temperatures are calculated based on different $H_2O$ concentration estimates,

980   which are 0.50 wt% (Chen et al. 2015; red field), 1.4 wt% (Kuritani et al. 2013; green

981   field) and 4.5 wt% (our best estimation value; gray field). Error bars and ellipses are

982   drawn according to Putirka et al. (2003) and Lee et al. (2009). Buffers are constructed for

983   the clinopyroxene–melt thermobarometer and the Si activity thermobarometer by

984  outlining the corresponding $P–T$ points with their error ellipses; see the text for details.

985  Black dashed curves represent clinopyroxene saturation surfaces of the HSS5 melt with

986  $H_2O$ contents of 4 and 5 wt%, calculated using the equation (34) of Putirka (2008). **(b)**

987  Relationship between the buffer overlapping area/maximal buffer overlapping area

988  (BOA/BOAmax) ratio and the melt $H_2O$ content used in the Si activity thermobarometer

989  calculation. The upright dashed line shows the best estimation of the melt $H_2O$ content,

990  which is 4.5 wt%.

991

992  **Figure 5.** Estimated vs. experimental **(a)** melt $H_2O$ content, **(b)** pressure, and **(c)**

993  temperature, using the experimental data listed in Table 2. Melt $H_2O$ contents are

994  estimated using the same method as used for the WEK basalts. Pressures and

995  temperatures are calculated using the Si activity thermobarometer (Lee et al. 2009) with

996  the estimated $H_2O$ contents in **(a)**. Red lines show linear fittings of the data points. SEE

997  (standard estimate error) = $\sqrt{\sum(X_{est} - X_{true})^2/N}$, where $X_{est}$ is the estimated value, $X_{true}$

998  is the true value, $N$ is the number of data.

999

1000  **Figure 6.** Modeled $H_2O-CO_2$ degassing curves of the WEK magma. Degassing curves

1001  are calculated using the model of Duan (2014) and the HSS5 melt composition. The

1002  initial state is $H_2O$ = 4.5 wt% and $CO_2$ = 2.0 wt% at 13.5 kbar and 1438 K. The red and

1003  black curves represent degassing in closed and open system, respectively. The gray

1004  curves are $H_2O-CO_2$ solubility isobars. The temperature of each isobar is the same as that

1005   of the magma, i.e., determined by $P/\text{kbar} = -118.0 + 0.113 \, T/°C$. The blue curves are

1006   curves of identical vapor composition. The numbers on these curves represent the molar

1007   fraction of $H_2O$ in the vapor phase.

1008

1009   **Figure 7. (a)** *P–T* path of the WEK magmas extending to higher pressures. Compositions

1010   of the low-$SiO_2$ samples are from Zhang et al. (1995) (DZ–6, DZ–3, H–1, MH–4, A–2,

1011   H–38); other data points are the same as in Fig. 4a. Silica activity pressures and

1012   temperatures are calculated using the estimated 4.5 wt% melt $H_2O$ content. Dry and wet

1013   $(X_{H2O}^{bulk} = 450 \text{ ppm})$ peridotite solidi are plotted using the parameterization of Katz et al.

1014   (2003). Mantle potential temperature $(T_p)$ is calculated using the model of Putirka (2016),

1015   with composition and pressure inputs from the most primary WEK samples. **(b)**

1016   Schematic illustration of the origin of the WEK magmas. Hydrated mantle materials

1017   originating from the mantle transition zone (MTZ) crossed the solidus during their

1018   upwelling in the convective mantle, and generated small-degree partial melts. The melts

1019   stalled at the base of the lithosphere, followed by extraction and rapid magma ascent to

1020   the surface. The local Moho depth of 31.3 ± 0.6 km is from Tao et al. (2014); the

1021   lithosphere–asthenosphere boundary (LAB) depth of 70–80 km is from Zheng et al.

1022   (2011), Li et al. (2012, 2013), and Guo et al. (2014). Depth and pressure are translated

1023   assuming a crust average density of 2.7 $g/cm^3$ and a lithospheric mantle average density

1024   of 3.3 $g/cm^3$, following Tao et al. (2014).

1025

1026 **Figure 8.** Pressure–$H_2O$ content relation of the Xiaogulihe melts recorded by

1027 clinopyroxene crystals. Pressures are calculated using the Putirka et al. (2003)

1028 thermobarometer with clinopyroxene and bulk-rock compositions from Chen et al. (2015).

1029 Only the clinopyroxene crystals with $K_D(\text{Fe–Mg})^{\text{cpx–melt}}$ between 0.12 and 0.44 were used

1030 for $P$ estimation. The melt $H_2O$ contents corresponding to the clinopyroxene phenocrysts

1031 are from Chen et al. (2015).

1032  **Table 1.** Example temperature differences at similar pressures calculated using the two

1033  thermobarometers.

| $H_2O$ (wt%) | Overlapping pressure (kbar) | $P$ (cpx–melt)[a] (kbar) | $T$ (cpx–melt)[a] (°C) | $P$ (Si activity)[b] (kbar) | $T$ (Si activity)[b] (°C) | $|\Delta T|$[c] (°C) |
|---|---|---|---|---|---|---|
| 0 | 8.6–13.5 | 8.8 | 1120 | 8.8 | 1164 | 44 |
| | | 9.1 | 1121 | 9.0 | 1163 | 42 |
| | | 9.6 | 1127 | 9.6 | 1171 | 44 |
| | | 10.2 | 1131 | 10.2 | 1175 | 44 |
| | | 11.3 | 1140 | 11.4 | 1207 | 67 |
| 0.5 | 8.8–13.5 | 8.8 | 1120 | 8.8 | 1170 | 50 |
| | | 9.5 | 1125 | 9.5 | 1166 | 41 |
| | | 10.3 | 1134 | 10.3 | 1182 | 48 |
| | | 10.6 | 1137 | 10.6 | 1184 | 47 |
| | | 11.6 | 1140 | 11.6 | 1201 | 61 |
| 1.4 | 9.1–13.5 | 9.1 | 1151 | 9.1 | 1121 | 30 |
| | | 9.3 | 1104 | 9.3 | 1124 | 20 |
| | | 10.0 | 1129 | 10.0 | 1159 | 30 |
| | | 10.8 | 1135 | 10.8 | 1175 | 40 |
| | | 11.8 | 1192 | 11.9 | 1146 | 46 |
| 3 | 9.6–13.5 | 9.6 | 1127 | 9.6 | 1139 | 12 |
| | | 10.0 | 1141 | 10.0 | 1129 | 12 |
| | | 10.5 | 1147 | 10.5 | 1135 | 12 |
| | | 11.3 | 1161 | 11.3 | 1140 | 21 |
| | | 12.3 | 1176 | 12.3 | 1149 | 27 |
| 5 | 10.3–13.5 | 10.3 | 1134 | 10.3 | 1134 | 0 |
| | | 10.6 | 1137 | 10.6 | 1128 | 9 |
| | | 11.0 | 1137 | 11.0 | 1132 | 5 |
| | | 11.9 | 1146 | 11.9 | 1145 | 1 |
| | | 12.8 | 1154 | 12.8 | 1158 | 4 |
| 7 | 10.9–13.5 | 10.9 | 1136 | 10.9 | 1114 | 22 |
| | | 11.3 | 1140 | 11.2 | 1116 | 24 |
| | | 11.6 | 1140 | 11.6 | 1120 | 20 |
| | | 12.4 | 1149 | 12.4 | 1125 | 24 |
| | | 13.5 | 1162 | 13.3 | 1143 | 19 |
| 9 | 11.5–13.5 | 11.6 | 1140 | 11.5 | 1105 | 35 |
| | | 11.9 | 1146 | 11.9 | 1107 | 39 |
| | | 12.3 | 1149 | 12.2 | 1110 | 39 |
| | | 12.4 | 1149 | 12.4 | 1111 | 38 |

|  |  | 12.7 | 1154 | 12.8 | 1119 | 35 |
|---|---|---|---|---|---|---|

1034  [a] Pressures and temperatures are calculated using the clinopyroxene–melt

1035  thermobarometer of Putirka et al. (2003).

1036  [b] Pressures and temperatures are calculated using the Si activity thermobarometer of Lee

1037  et al. (2009).

1038  [c] $|\Delta T| = |T(\text{cpx–melt}) - T(\text{Si activity})|$. Note $|\Delta T|$ is minimized at $H_2O$ content of 5 wt%.

1039

1040

1041 **Table 2.** Summary of the experimental data used for testing the water content estimation method.

| LEPR Index | Reference | $P$ (kbar) | $T$ (°C) | Phases[a] | $H_2O^{melt}$ (wt%) | $H_2O^{melt}$ error [b] (wt%) | Estimated $H_2O^c$ (wt%) | Estimated $P^d$ (kbar) | Estimated $T^d$ (°C) |
|---|---|---|---|---|---|---|---|---|---|
| 2269 | Müntener et al. (2001) | 12 | 1230 | liq+ol+cpx+opx | 5.80 | 0.02 | 4.4 | 9.2 | 1175 |
| 2440 | Hesse and Grove (2003) | 16 | 1380 | liq+ol+opx+cpx | 2.8 | n.r. | 1.3 | 14.8 | 1280 |
| 3227 | Takagi et al. (2005) | 2 | 1030 | liq+ol+plag+cpx+opx+spn | 4.5 | n.r. | 3.4 | -0.4 | 1082 |
| 4573 | Gaetani and Grove (1998) | 12 | 1245 | liq+cpx+opx+ol+spn | 3.3 | 0.3 | 3.8 | 14.3 | 1263 |
| 4575 | Gaetani and Grove (1998) | 12 | 1215 | liq+cpx+opx+ol+spn | 5.99 | 0.05 | 4.6 | 14.6 | 1241 |
| 4576 | Gaetani and Grove (1998) | 12 | 1200 | liq+cpx+opx+ol+spn | 5.06 | 0.04 | 4.9 | 13.3 | 1223 |
| 4577 | Gaetani and Grove (1998) | 12 | 1185 | liq+cpx+opx+ol+spn | 6.3 | 0.1 | 5.0 | 12.6 | 1207 |
| 4583 | Gaetani and Grove (1998) | 16 | 1260 | liq+cpx+opx+ol+spn+gt | 4.9 | 1.1 | 4.7 | 17.5 | 1268 |
| 4584 | Gaetani and Grove (1998) | 16 | 1255 | liq+cpx+opx+ol+spn+gt | 5.0 | 0.6 | 4.9 | 17.3 | 1267 |
| 4585 | Gaetani and Grove (1998) | 16 | 1245 | liq+cpx+opx+ol+spn | 5.3 | 0.5 | 4.8 | 17.4 | 1267 |

53

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 4586 | Gaetani and Grove (1998) | 16 | 1230 | liq+cpx+opx+ol+gt | 4.8 | 0.6 | 5.4 | 16.4 | 1245 |
| 4589 | Gaetani and Grove (1998) | 20 | 1290 | liq+cpx+opx+ol+gt | 5.3 | 0.6 | 5.7 | 19.6 | 1280 |
| 4590 | Gaetani and Grove (1998) | 20 | 1275 | liq+cpx+opx+ol+gt | 6.8 | 0.4 | 4.6 | 18.6 | 1290 |
| 4595 | Gaetani and Grove (1998) | 12 | 1185 | liq+cpx+opx+ol+spn | 6.2 | 0.4 | 5.0 | 13.5 | 1196 |
| 5063 | Kelemen et al. (1990) | 4.985 | 1052 | liq+ol+cpx+opx+amph+ilm | 4.3 | 0.4 | 5.4 | 7.7 | 1134 |
| 20068 | Grove et al. (2013) | 22 | 1410 | liq+cpx+opx+ol+spn | 3.0 | 0.2 | 1.0 | 21.6 | 1352 |
| 20074 | Grove et al. (2013) | 24 | 1410 | liq+cpx+opx+ol+gt | 2.95 | 0.25 | 3.5 | 23.6 | 1294 |
| 55001 | Gaetani et al. (2003) | 12 | 1315 | liq+cpx+opx+ol+spn | 0.98 | 0.24 | 3.0 | 14.8 | 1275 |
| 55002 | Gaetani et al. (2003) | 12 | 1185 | liq+cpx+opx+ol+spn | 6.3 | 0.1 | 5.0 | 12.6 | 1207 |
| 55003 | Gaetani et al. (2003) | 16 | 1370 | liq+cpx+opx+ol+spn | 1.70 | 0.17 | 2.1 | 17.4 | 1333 |
| 55004 | Gaetani et al. (2003) | 16 | 1230 | liq+cpx+opx+ol+gt | 4.8 | 0.6 | 5.4 | 16.4 | 1245 |

1042 [a] liq = liquid, ol = olivine, cpx = clinopyroxene, opx = orthopyroxene, plag = plagioclase, spn = spinel, grt = garnet, amph =

1043 amphibole, ilm = ilmenite.

1044 [b] n.r., not reported.

54

1045  [c] $H_2O$ content when BOA is maximized.

1046  [d] Pressures and temperatures are calculated using the Si activity thermobarometer (Lee et al. 2009) with the estimated melt $H_2O$

1047  contents.

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55

1050    **Table 3.** Thermal expansion coefficient ($\alpha$), specific heat capacity ($c_p$), and density ($\rho$)

1051    data of basaltic melts, water, and carbon dioxide at 1400 K and 10 kbar.

|  | $\alpha$ | $c_p$ | $\rho$ | $(\partial T/\partial P)_S$[e] |
|---|---|---|---|---|
|  | ($10^{-4}$ K$^{-1}$) | [$10^3$ J/(kg·K)] | ($10^3$ kg/m$^3$) | (°C/kbar) |
| Volatile-free HSS5 melt[a] | 0.72 | 1.4 | 2.8 | 2.5 |
| Basaltic melt[b] | 0.68 | 1.0 | 2.8 | 3.4 |
| $H_2O$[c] | 4.1 | 3.4 | 0.8 | 22 |
| $CO_2$[d] | 3.2 | 1.5 | 1.1 | 28 |

1052    [a] Calculated using the partial molar thermodynamic properties from Lesher and Spera

1053    (2015); the melt composition is from Chu et al. (2013).

1054    [b] From McKenzie and Bickle (1988).

1055    [c] Calculated using the model of Verma (2003).

1056    [d] From Bottinga and Richet (1981).

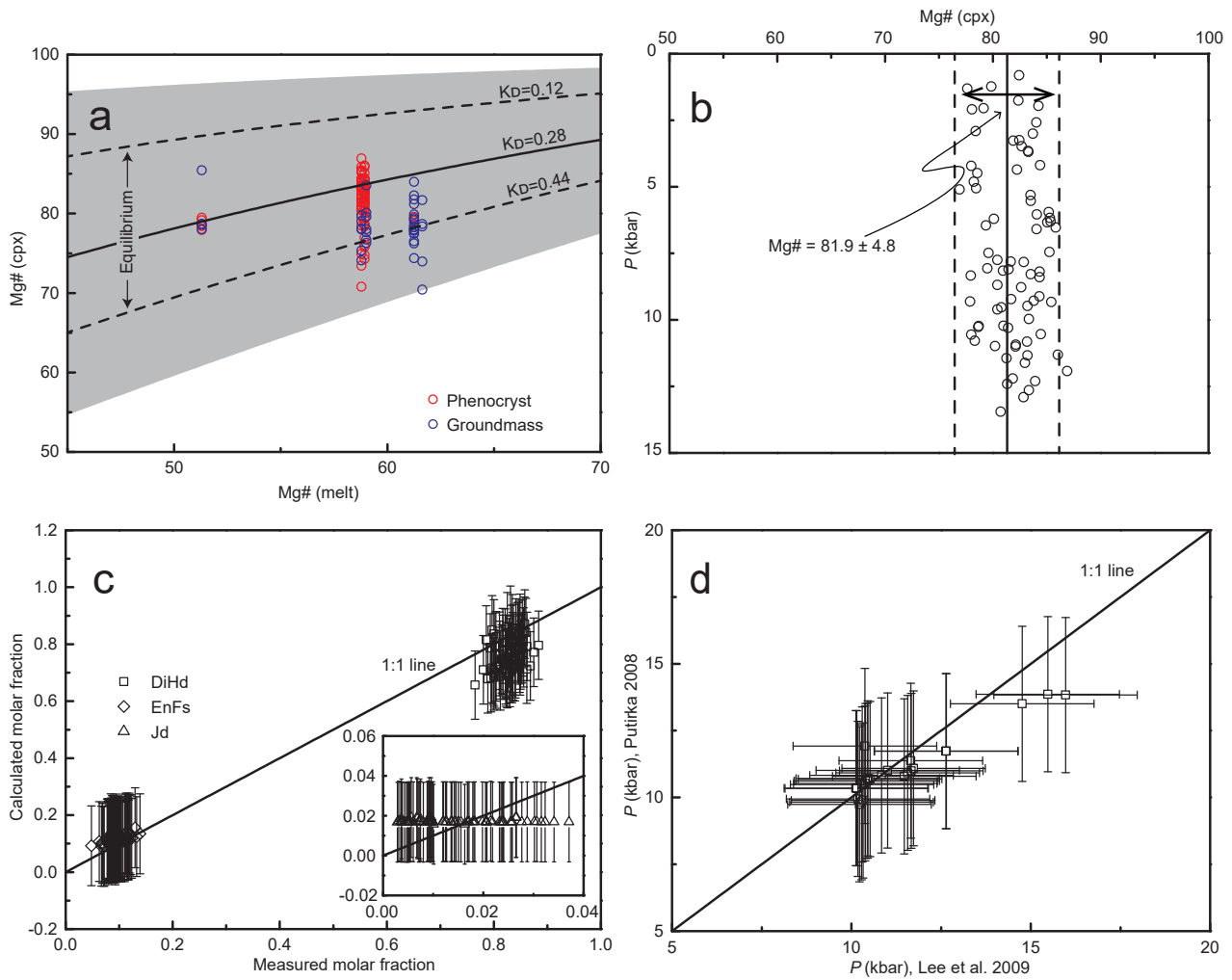1057    [e] $(\partial T/\partial P)_S = T\alpha/(\rho c_p)$, where $T$ is the temperature (1400 K).
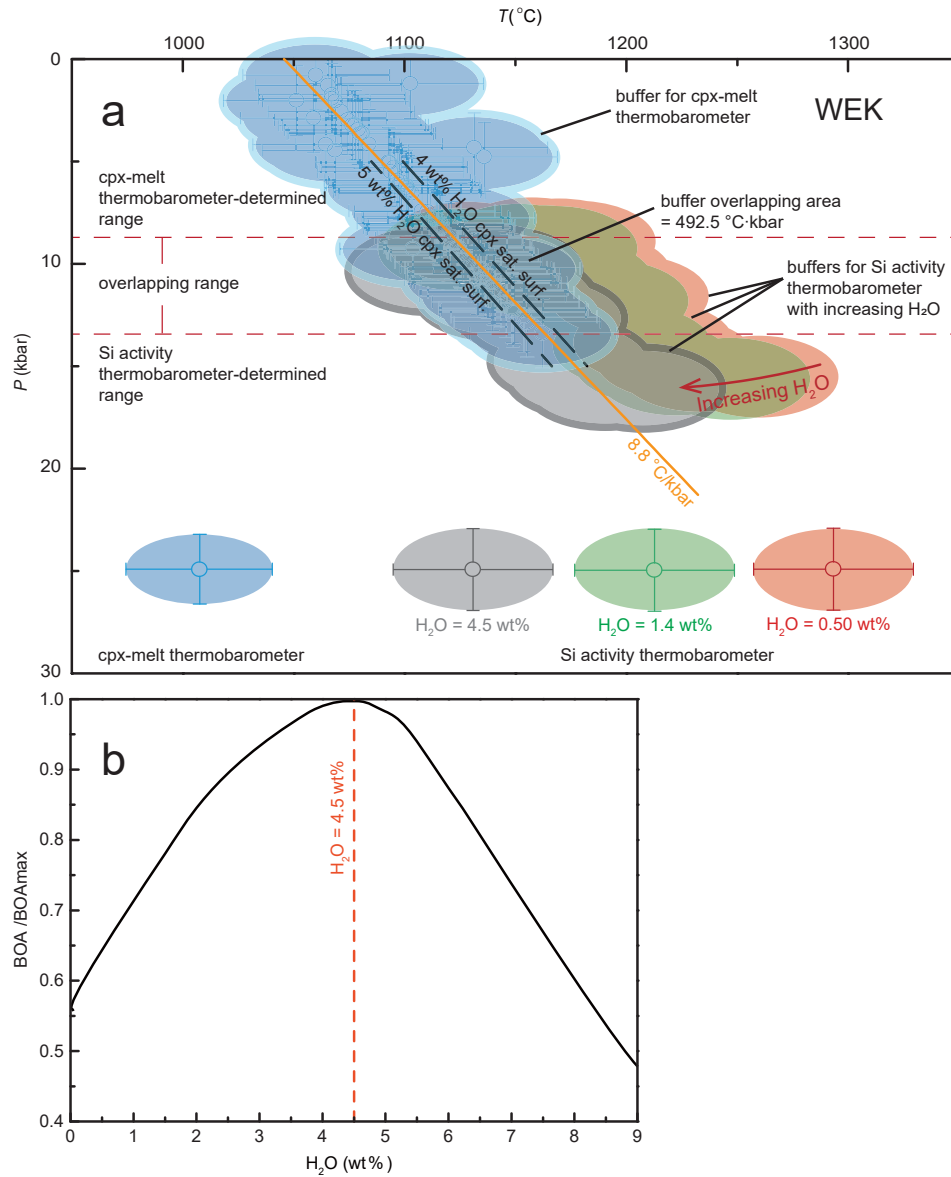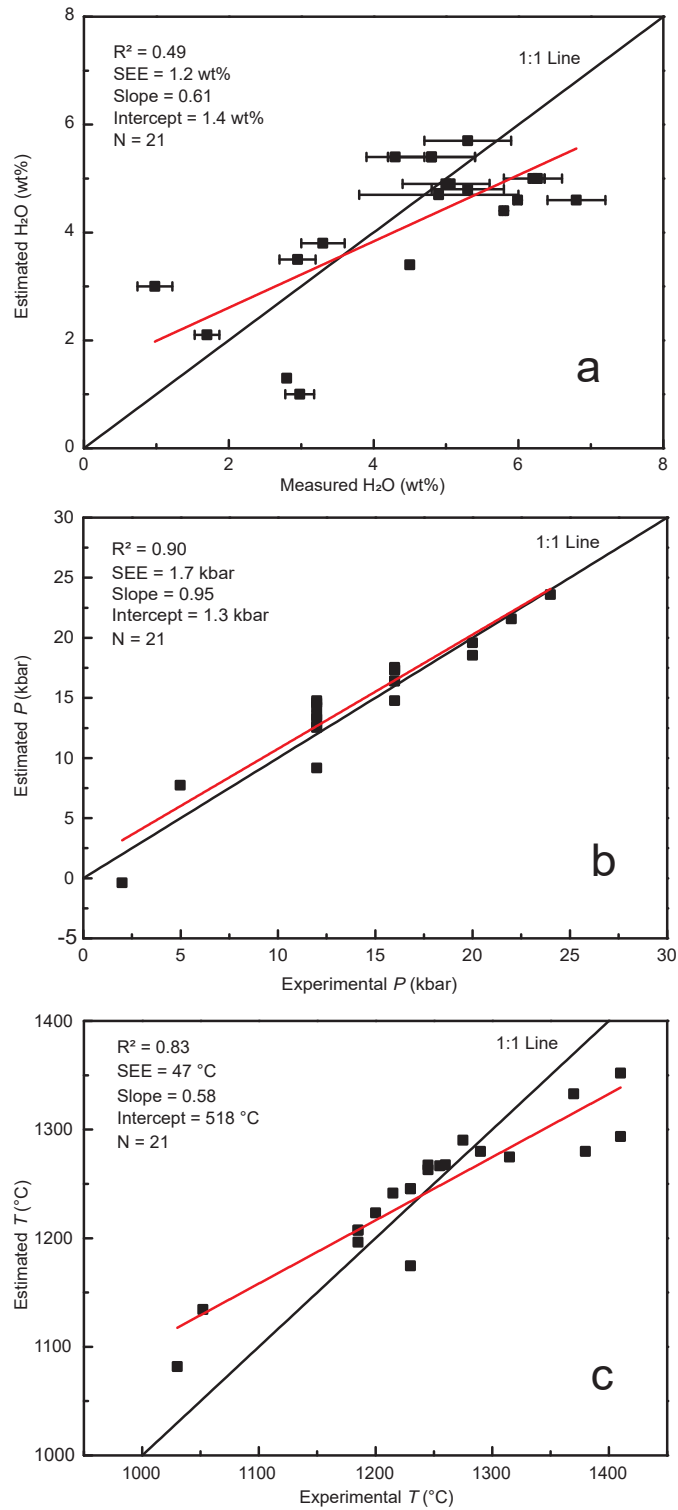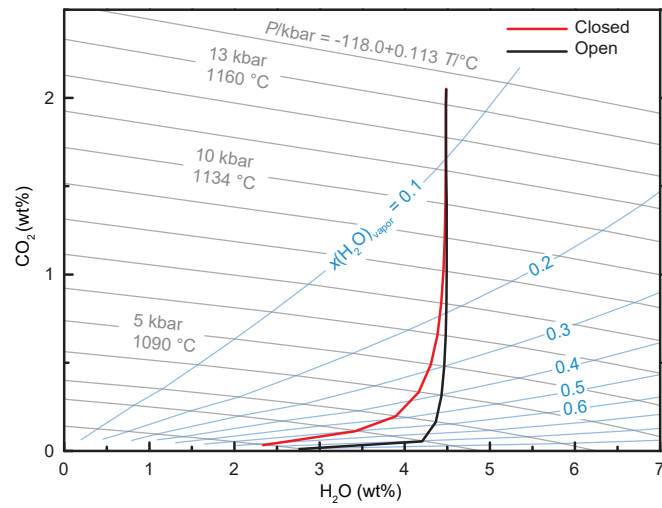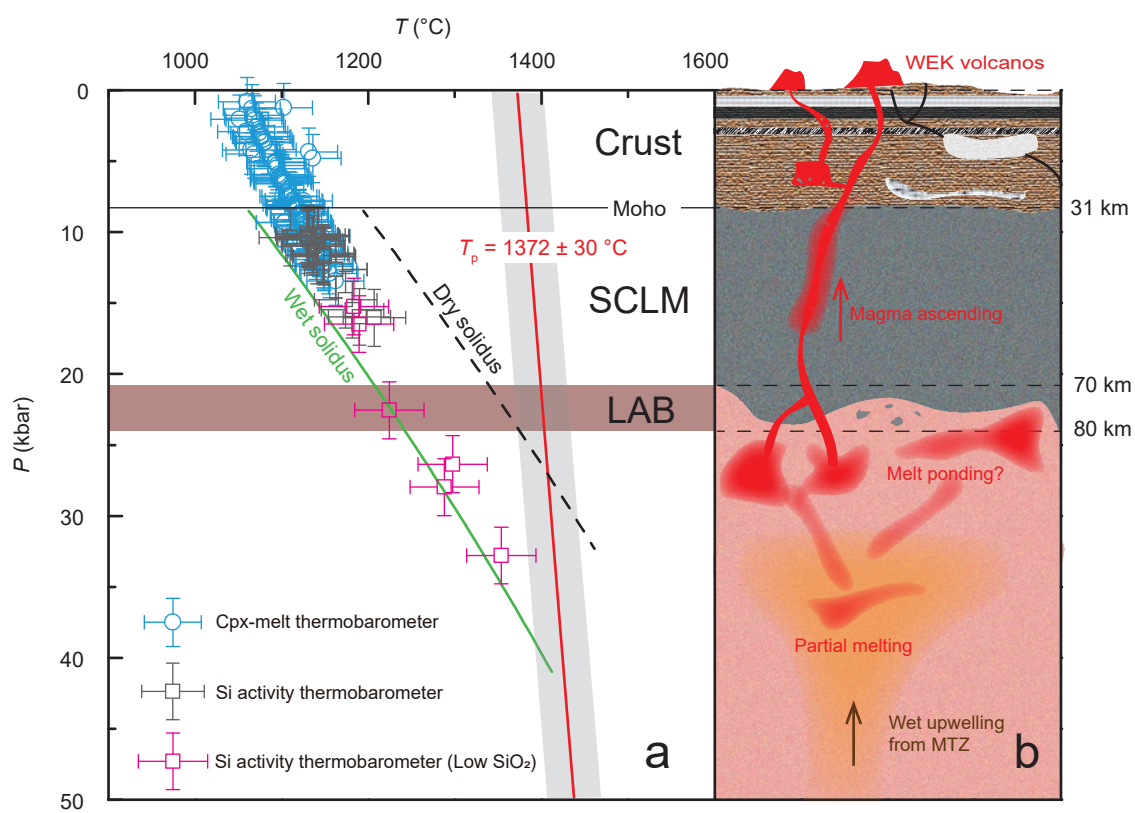
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8