1   Revision 1

2   # **Parameterized lattice strain models for REE**

3   # **partitioning between amphibole and silicate melt**

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21   **Abstract**

22   The distribution of rare earth elements (REEs) between amphibole and silicate melt is

23   important for understanding a wide variety of igneous and metamorphic processes in the

24   lithosphere. In this study, we used published experimental REE and Y partitioning data

25   between amphibole and silicate melt, the lattice strain model, and non-linear least squares

26   regression method to parameterize key partitioning parameters in the lattice strain model

27   (D_0, r_0, and E) as a function of pressure, temperature, and both amphibole and melt

28   compositions. Two models, which give nearly identical results, are obtained in this study.

29   In the first model, D_0 depends on temperature and amphibole composition: it positively

30   correlates with Ti content, and negative correlates with temperature and Mg, Na, and K

31   contents in the amphibole. In the second model, D_0 depends solely on the melt

32   composition: it positively correlates with Si content, and negatively correlates with Ti

33   and Ca contents in the melt. In both the mineral and melt composition models, r_0

34   negatively correlates with the ferromagnesian content in the M4 site of the amphibole and

35   E is a constant. The very similar coefficients in the equations for r_0 and best-fit values for

36   E in the two models allow us to connect the two models through amphibole-melt phase

37   equilibria. An application of our model to amphiboles in mantle xenoliths shows that

38   observed major element compositional variations in amphibole alone can give rise to

39   order of magnitude variations in amphibole-melt REE partition coefficients. Together

40   with experimental data simulating fractional crystallization of arc magmas, out models

41   suggest that (1) REE partition coefficients between amphibole and melt can vary by an

42   order of magnitude during arc magma crystallization due to variation in the temperature

43   and composition of the amphibole and melt, and that (2) amphibole fractional

44 crystallization plays a key role in depleting the middle REEs relative to heavy REEs and

45 light REEs in arc magmas.

46

47 **Keywords**

48 REE and Y partition coefficients; amphibole; amphibole melting in the mantle;

49 amphibole fractional crystallization

50

51 **1. Introduction**

52   Amphibole is ubiquitous in the Earth's lithosphere, occurring in a wide variety of

53 igneous and metamorphic rocks. As an inosilicate, amphibole has three main structural

54 sites (A, M4, and M1-M3) that can accommodate cations of a range of size and charge.

55 The general chemical formula of amphiboles may be described by the expression

56 $$A\ B_2\ C_5\ T_8\ O_{22}\ (OH, F, Cl)_2$$
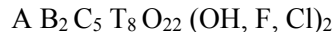
57 where A = Na, K, or vacant ($\square$) in A site; B = Ca, Na, Mn, Fe^{2+}, Mg in M4 site; C =

58 Fe^{2+}, Fe^{3+}, Mg, Al, Mn, Ti, Cr, in M1, M2, and M3 sites; T = Si, Al in tetrahedral site

59 (Hawthorne, 1983). The smaller M1-M3 sites are in 6-fold coordination, while the larger

60 M4 site is in 8-fold coordination. The latter can accommodate larger cations such as the

61 trivalent rare earth elements (REE) and Y (ionic radii 0.977–1.16 Å, 8-fold coordination,

62 Shannon (1976)), while the smaller M1-M3 sites can accommodate smaller cations such

63 as high-field strength elements.

64   The subject of the present study is REE partitioning between amphibole and

65 silicate melt, which is important to understand the generation and differentiation of

66 hydrous magmas. According to the lattice strain model (Blundy and Wood, 1994; Brice,

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67   1975; Wood and Blundy, 1997), the partition coefficients of trivalent REEs between

68   amphibole and silicate melt vary systematically with their ionic radii:

69    $$D_j^{\text{amph-melt}} = D_0 \exp\left[-\frac{4\rho E N_A}{RT}\left(\frac{r_0}{2}\left(r_0 - r_j\right)^2 - \frac{1}{3}\left(r_0 - r_j\right)^3 \right) \right],$$ (1)

70   where D_0 is the amphibole-melt partition coefficient for the strain-free substitution; r_0 is

71   the radius of a hypothetical cation that substitutes into the site with zero strain; r_j is the

72   ionic radius of the element of interest; E is the effective Young's modulus for the lattice

73   site; N_A is Avogadro's number; R (= 8.3145 J mol^{-1} K^{-1}) is the gas constant; and T is

74   temperature in Kelvin. The lattice strain parameters (D_0, r_0, E) are, in general, a function

75   of pressure (P), temperature (T), and composition (X).

76   Amphibole-melt REE partition coefficients have been shown to negatively

77   correlate with T (Green and Pearson, 1985; Klein et al., 1997; Nandedkar et al., 2016;

78   Nicholls and Harris, 1980) and P (Adam and Green, 1994; Adam and Green, 2003; Dalpé

79   and Baker, 2000; Green and Pearson, 1985), and positively correlate with the degree of

80   melt polymerization (Brophy, 2008; Green and Pearson, 1985; Klein et al., 1997;

81   Nandedkar et al., 2016; Nicholls and Harris, 1980; Tiepolo et al., 2007; Tiepolo et al.,

82   2000). The effect of amphibole crystal chemistry on amphibole-melt REE partition

83   coefficients has also been observed in previous studies. For example, greater occupancy

84   of the A site by Na and K were shown to decrease the partition coefficients, presumably

85   suggesting substitution of REEs in place of Na and Ca in the M4 site charge compensated

86   by a vacancy in the A site (e.g., $Ca_{M4}^{2+}K_A^{+1} \Leftrightarrow REE_{M4}^{3+}\square_A$) (Brenan et al., 1995; Green and

87   Pearson, 1985; Nicholls and Harris, 1980). Also, amphibole-melt REE partition

88   coefficients have been demonstrated to correlate with the amphibole-melt partition

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89   coefficient of Ca (Hilyard et al., 2000; Klein et al., 1997; Sisson, 1994). These

90   correlations have been used to build empirical models of amphibole-melt REE partition

91   coefficients (Sisson, 1994; Tiepolo et al., 2007; Tiepolo et al., 2000). These previous

92   models are useful for predicting the REE and Y partition coefficients when the

93   equilibrium melt composition (Sisson, 1994; Tiepolo et al., 2007; Tiepolo et al., 2000) or

94   amphibole-melt major element partition coefficients (Hilyard et al., 2000) are available.

95   These models are difficult to implement, however, for natural amphiboles such as those

96   found in cumulates and xenoliths where melt composition is not available. Further,

97   previous models parameterized partition coefficients for individual elements

98   independently, so each element requires a different set of model coefficients. This makes

99   it difficult to understand the general behavior of REE partitioning in amphibole and to

100   develop accurate models for elements with sparse partitioning data (such as Gd and Tm).

101   In addition these empirical models require a large number of coefficients to describe the

102   partitioning of all the REEs and Y.

103   In this study, we present the first parameterized lattice strain models for REE and

104   Y partitioning between amphibole and silicate melt for a range of P, T, melt and

105   amphibole compositions. These models are developed following a new protocol that has

106   been successfully used to develop parameterized lattice strain models for REE and Y

107   partitioning between major rock-forming minerals (clinopyroxene, orthopyroxene, garnet,

108   olivine, and plagioclase) and basaltic melts (Dygert et al., 2014; Sun et al., 2017; Sun and

109   Liang, 2012; Sun and Liang, 2013a; Sun and Liang, 2013b; Yao et al., 2012). We

110   develop two parameterized lattice strain models, one of which is described by T and

111   mineral composition, and the other is fully captured by melt composition. We reconcile

112   the two models through amphibole-melt equilibria, and, as a byproduct, develop a new

113   thermometer for calculating the amphibole liquidus. As geochemical applications of our

114   models, we (1) evaluate the ranges of amphibole-melt REE partition coefficients in

115   mantle amphiboles using observed amphibole compositions in mantle xenoliths, and (2)

116   calculate the REE concentration in experimental melts that simulate fractional

117   crystallization of arc magmas to evaluate the effect of amphibole fractional crystallization

118   on the REE concentration in arc magmas.

119

120   **2. Method**

121   **2.1. Data compilation**

122   REE and Y partitioning data for amphibole and silicate melts were compiled from

123   published experimental studies. The data were filtered on the basis of attainment of

124   equilibrium (e.g., absence of core to rim variation, sector zoning in major elements,

125   absence of melt inclusions in the analyzed volume, and run duration), misfits or outliers

126   with reference to the lattice strain model (e.g., Eu anomaly), following the procedure

127   established in the previous studies (Dygert et al., 2014; Sun and Liang, 2012; Sun and

128   Liang, 2013b; Yao et al., 2012). Experimental data that were analyzed using an ion probe

129   and laser ablation inductively coupled mass spectrometry (LA-ICP-MS) were inspected

130   for their quality by plotting the partition coefficients of similarly incompatible element

131   pairs (e.g., La-Ce, Eu-Nd, and Lu-Yb, example shown in supplementary Fig. S1). In

132   these plots, most partitioning data follow a well-defined correlation suggesting high

133   quality and internally consistent analysis while some partitioning data significantly

134   deviate off the trend. The off-trend partitioning data were excluded as they suggest either

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135   presence of Eu anomalies, poorly equilibrated experiments, or low quality analysis. This

136   method could not be used to inspect the quality of highly doped experiments analyzed

137   using an electron microprobe (EMP) as they often contain fewer than 3 elements that are

138   far from each other in incompatibility. Furthermore, the studies of Adam and Green

139   (1994) and Klein et al. (1997) showed evidence of Henry's law behavior of REEs in their

140   doped experiments by running an undoped experiment at the same *P-T-X* conditions,

141   while the study of Hilyard et al. (2000) did not show any evidence for this. As shown

142   later in this study, however, the partitioning data of Hilyard et al. (2000) follow our

143   partitioning models in the same manner as other partitioning data, suggesting the Henry's

144   law behavior of REEs in their experiments. Hence, we included the partitioning data from

145   Hilyard et al. (2000) in our dataset.

146   Following the data selection procedure outlined above, we obtained 556

147   partitioning data from 100 experiments reported in 9 studies (Adam and Green, 1994;

148   Adam and Green, 2003; Adam and Green, 2006; Dalpé and Baker, 2000; Hilyard et al.,

149   2000; Klein et al., 1997; LaTourrette et al., 1995; Nandedkar et al., 2016; Tiepolo et al.,

150   2000). Table 1 summarizes the selected partitioning studies that were used to calibrate the

151   model described below. The selected 100 experiments were conducted at 780–1100ºC

152   and 0.2–2.5 GPa. These experiments produced calcic amphiboles and melts with large

153   variations in composition (e.g., Si = 5.74–7.27 a.p.f.u. in amphibole, Mg# = 36.5–100 in

154   amphibole, Mg# = 1.9–100 in melt, SiO_2 = 34.14–68.7 wt% in melt; see Fig. 1 and Table

155   1 for details) and partition coefficients (e.g., D_{La} = 0.03–0.59, D_{Sm} = 0.27–5.56, D_{Lu} =

156   0.28–6.77) (Fig. 2). The compositional variations in the experimental amphiboles and

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157   melts cover a large portion of those in natural samples from arc and intraplate settings

158   and mantle xenoliths (Figs. 1a–f).

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160   **2.2. Parameterization method**

161   To develop a parameterized model for trivalent REE and Y partitioning between

162   amphibole and silicate melt, we conducted a multivariable nonlinear least squares

163   analysis. Following the procedure of recent studies on mineral-melt REE partitioning

164   (Dygert et al., 2014; Sun and Liang, 2012; Sun and Liang, 2013a; Yao et al., 2012), we

165   conduct the least squares analysis in two steps: (1) identification of key variables that

166   affect D_0, r_0, and E in the lattice strain model through least squares analysis of individual

167   experiments, and (2) simultaneous inversion of all the filtered experimental data using the

168   primary variables identified in step (1). An important advantage of step (2) is that it

169   allows us to include experiments that reported only one or two trace elements and hence

170   they can be used to calibrate the three-parameter lattice strain model in step (1) (see

171   supplementary Fig. S2 and S3 for experiments from Hilyard et al. (2000) and Klein et al.

172   (1997)). We assume that REEs and Y enter the M4 site in amphibole, and use eightfold

173   coordinated ionic radii from Shannon (1976). We did not distinguish between the M4 and

174   M4' sites (Bottazzi et al., 1999) given the lack of evidence of the two-site occupancy of

175   the REEs in amphibole in our data. We assumed that D_0 in the lattice strain model has the

176   simple form

177     $$\ln D_0 = a_0 + \frac{a_1}{RT} + f\left(X, \frac{P}{T} \right),$$ (2)

178   where a_0 and a_1 are constants to be determined, and f is a function of mineral and melt

179   composition and P/T. The r_0 is assumed to be a function of mineral composition as it

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180   correlates well with the amphibole composition. We explored the composition and r_0

181   dependence of E observed for other minerals (Sun and Liang, 2012; Sun and Liang,

182   2013b; Yao et al., 2012), but it shows only small variation for amphibole and does not

183   correlate well with amphibole composition or r_0. Hence, E was assumed to be a constant.

184   Through an extensive search of various permutations of the composition

185   variables, we found that D_0 can be described as a function of melt Si, Ti and Ca contents

186   or as a function of T and Ti, Mg, Na and K contents in amphibole. For convenience of

187   description, we refer to the latter as the mineral composition model and the former as the

188   melt composition model. In both models, ferromagnesian (sum of Mg, Fe^{2+}, and Mn^{2+},

189   designated as Fm hereafter) content in the M4 site of the amphibole is the main factor

190   affecting r_0, while E is a constant. For the melt composition model, the lattice strain

191   parameters D_0, r_0, and E take on the following expressions:

192    $$\ln D_0^{\text{amph}} = a_0 + a_1 \ln\left(X_{\text{Si}}^{\text{melt}}\right) + a_2 \ln\left(X_{\text{Ti}}^{\text{melt}}\right) + a_3 \ln\left(X_{\text{Ca}}^{\text{melt}}\right), \tag{3}$$

193    $$r_0^{\text{amph}} = a_4 + a_5 X_{\text{Fm}}^{\text{amph-M4}}, \tag{4}$$

194    $$E^{\text{amph}} = a_6. \tag{5}$$

195   For the mineral composition model, we have

196    $$\ln D_0^{\text{amph}} = b_0 + \frac{b_1}{RT} + b_2 X_{\text{Ti}}^{\text{amph}} + b_3 X_{\text{Mg}}^{\text{amph}} + b_4 X_{\text{Na}}^{\text{amph}} + b_5 X_{\text{K}}^{\text{amph}}, \tag{6}$$

197    $$r_0^{\text{amph}} = b_6 + b_7 X_{\text{Fm}}^{\text{amph-M4}}, \tag{7}$$

198    $$E^{\text{amph}} = b_8, \tag{8}$$

199   where $a_0, a_1, \ldots, a_6$ and $b_0, b_1, \ldots, b_8$ in Eqs. (3)–(8) are constants determined by stepwise

200   multiple linear regression analyses of the lattice strain parameters (D_0, r_0, and E); $X_{\text{Ti}}^{\text{amph}}$,

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201   X_{Mg}^{amph} , X_{Na}^{amph} , and X_{K}^{amph} are cation numbers (per 23 oxygen) and $X_{Fm}^{amph\text{-}M4}$ is the Fe^{2+}

202   + Mn^{2+} + Mg content in the M4 site assuming all iron is present as ferrous iron; and X_{Si}^{melt}

203   , X_{Ti}^{melt} , and X_{Ca}^{melt} are mole fractions of cations in the melt calculated on an anhydrous

204   basis assuming all iron is present as ferrous iron. The experiments used to parameterize

205   our model were performed at oxygen fugacities between QFM-2 to QFM+3.2 (where

206   QFM is the quartz-fayalite-magnetite buffer), which covers a large range of those found

207   in natural magmatic systems (Ballhaus, 1993; Kelley and Cottrell, 2009; Parkinson and

208   Arculus, 1999). Hence, our assumption of all iron in amphibole and melt being present as

209   ferrous iron is incorrect. Nevertheless, this simplification allows us to develop

210   parameterized lattice strain models for amphibole-melt REE partitioning without making

211   complicated assumptions with regard to the ferric iron content in the amphibole and melt.

212   Also, Na occupies both the M4 and A sites in amphibole, but we use the total Na content

213   for the mineral composition model. We attempted to use Na in the M4 and A sites as

214   separate variables, but the coefficients for the two variables are nearly identical, leading

215   us to use total Na content instead. Finally, we used the anhydrous basis for the melt as

216   another simplification because in some studies, H$_2$O contents in the melt are calculated

217   according to mass balance, which may introduce large uncertainties. These more

218   complicated but realistic treatment of amphibole and melt compositions should be

219   considered in future studies when knowledge of redox state, site occupancy and water

220   content becomes available.

221   To further improve the fit to the measured partitioning data and better assess the

222   uncertainties for the fitting coefficients, we performed global least squares analyses for

223   the melt composition and mineral composition models by substituting equations (3)–(5)

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224   and (6)–(8) into Eq. (1), respectively. For the melt composition model (Eqs. (1), (3)–(5)),

225   we inverted the 6 coefficients (a_0, a_1,…, a_6) simultaneously through a global inversion of

226   the 556 filtered partitioning data. For the mineral composition model (Eqs. (1), (6)–(8)),

227   we inverted the 8 coefficients (b_0, b_1,…, b_8) simultaneously through a global inversion of

228   the same data used for the melt composition model. To carry out the global inversions,

229   we used the coefficients from the stepwise multiple linear regression as initial values in

230   the nonlinear least squares analysis and minimize the Chi-square as defined below:

231
$$C_p^2 = \sum_{j=1}^{N} \left(\ln D_j - \ln D_j^m \right)^2 , \qquad\qquad (9)$$

232   where D_j is defined by Eq. (1) for element j, D_j^m is the measured amphibole-melt

233   partition coefficient for element j, and N (= 556) is the total number of measured

234   partitioning data used in this study. Since it is difficult to assess inter-laboratory

235   uncertainties arising from different experimental procedures and analytical methods in

236   the selected partitioning studies (Table 1), we did not weight the Chi-square using

237   reported uncertainties of measured partition coefficients. The latter are based solely on

238   chemical analysis of REE and Y in individual charges. Uncertainties due to temperature

239   gradient, oxidation state, water content and water loss, experimental reproducibility,

240   among others, maybe larger than the reported uncertainty. Hence Eq. (9) assumes equal

241   uncertainty for all the experimental data included in this study. This is an obvious

242   simplification, but can be judged by the quality of our best fit models for individual

243   samples (see supplementary Figs. S2 and S3).

244   Although convenient in nonlinear regression analysis, the absolute values of the

245   Chi-square defined by Eq. (9) depend on the number of data used in the inversion. To

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246   assess the goodness of fit in a simple way, we calculated the Pearson's Chi-square (C_p^2)

247   after the inversion using the expression

248     $$C_p^2 = \sum_{j=1}^{N} \frac{\left(D_j - D_j^m\right)^2}{D_j} .$$ (10)

249   A better predictive model should provide partition coefficients closer to measured values

250   and hence has a smaller C_p^2 . The results are shown in Fig. 3 and discussed below.

251

252   **3. Results**

253   The global fit to the 556 partitioning data from the 100 experiments produces two sets of

254   expressions for the lattice strain parameters for REE and Y partitioning in amphibole. For

255   the melt composition model, we have:

256     $$\ln D_0^{amph} = -3.08\left(\pm 0.52\right) + 0.74\left(\pm 0.34\right)\ln\left(X_{Si}^{melt}\right) - 0.33\left(\pm 0.05\right)\ln\left(X_{Ti}^{melt}\right)$$
$$- 0.84\left(\pm 0.07\right)\ln\left(X_{Ca}^{melt}\right),$$ (11)

257     $$r_0^{amph} = 1.045\left(\pm 0.003\right) - 0.048\left(\pm 0.009\right) X_{Fm}^{amph\text{-}M4},$$ (12)

258     $$E^{amph} = 341\left(\pm 18\right),$$ (13)

259   where r_0 is in Å; and E is in GPa; and numbers in parentheses are 2σ uncertainties

260   estimated directly from the simultaneous inversion. As D_0 defines the peak value of the

261   parabola in the lattice strain model (Eq. (1)), the melt composition model indicates REE

262   partition coefficients in amphibole increase with the increase of Si content in the melt and

263   decrease with the increase of Ti and Ca content in the melt. Figs. 4a–c show that the

264   amphibole-melt Sm partition coefficient positively correlates with Si and negatively

265   correlates with Ti and Ca contents in the melt. The Si, Ti, and Ca contents in the

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266   experimental melts are comparable to those in the natural melts saturated in amphibole

267   (SiO_2 = 34.14–68.7 wt%, TiO_2 = 0.09–5.39 wt%, CaO = 1.6–12.89 wt%; data sources in

268   Fig. 1).

269   For the mineral composition model, we have

270
$$\ln D_0^{amph} = -4.21(\pm1.20) + \frac{7.27(\pm0.88) \times 10^4}{RT} + 1.52(\pm0.24) X_{Ti}^{amph} - 0.35(\pm0.06) X_{Mg}^{amph}$$
$$- 1.83(\pm0.34) X_{Na}^{amph} - 2.95(\pm0.34) X_{K}^{amph}, \quad (14)$$

271    $$r_0^{amph} = 1.043(\pm0.004) - 0.039(\pm0.012) X_{Fm}^{amph\text{-}M4}, \quad (15)$$

272    $$E^{amph} = 337(\pm23). \quad (16)$$

273   The mineral composition model indicates REE partition coefficients in amphibole

274   increase with the increase of Ti content and decrease with the increase of T and Mg, Na,

275   and K contents in the amphibole. Fig. 4d shows a negative correlation between

276   amphibole-melt Sm partition coefficient and T that is consistent with the expression for

277   D_0 in the mineral composition model (Eq. (14)). In order to highlight the effect of

278   amphibole composition, we subtract the effect of T on the amphibole-melt Sm partition

279   coefficient using the following expression

280    $$\overline{D_{Sm}^{amph\text{-}melt}} = D_{Sm}^{amph\text{-}melt} \exp\left[\frac{4\rho E N_A}{RT}\left(\frac{r_0}{2}(r_0 - r_{Sm})^2 - \frac{1}{3}(r_0 - r_{Sm})^3\right) - \frac{7.27 \times 10^4}{RT}\right], \quad (17)$$

281   where $\overline{D_{Sm}^{amph\text{-}melt}}$ is the normalized amphibole-melt Sm partition coefficient; r_0 is

282   calculated using Eq. (15) and E is that in Eq. (16). Figs. 4e, 4f, and supplementary Fig. S4

283   show that, to the first order, normalized amphibole-melt Sm partition coefficient

284   positively correlates with Ti content, and negatively correlates with Mg and K contents in

285   the amphibole, consistent with Eq. (14). The negative correlation with Na contents in

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286 amphibole is less clear (Fig. S4a), but it is clearer when other compositional effects are

287 subtracted from the normalized amphibole-melt Sm partition coefficient (not shown). The

288 Ti, Mg, Na, and K contents in the experimental amphiboles are comparable to those in

289 natural amphiboles (TiO_2 = 0.73–6.35, MgO = 6.35–18.5, Na_2O = 1.20–4.04 and K_2O =

290 0.03–2.77; data sources in Fig. 1).

291   In both the mineral and melt composition models, r_0 decreases with increasing Fm

292 content of the M4 site in the amphibole. We interpret this to indicate that the ideal radius

293 of the M4 site decreases with increasing occupancy by elements with relatively small

294 ionic radius such as Mg, Fe^{2+}, and Mn^{2+}. The range in Fm content of the M4 site in the

295 experimental amphibole is 0–0.58, which exceeds the 0–0.47 observed in the compilation

296 of natural amphiboles (data source in Fig. 1). This range in Fm content of the M4 site in

297 the compilation of natural amphiboles translates to a small range in r_0 of 1.02–1.045 Å

298 which is consistent with the subparallel parabola defined by the REE + Y partitioning

299 data (Fig. 2). Further, the proximity of r_0 to MREE such as Dy (1.027 Å) and Tb (1.04

300 Å) also explains why fractional crystallization of amphibole can produce depletion in

301 MREEs relative to HREEs and LREEs in the magma (Davidson et al., 2007; Davidson et

302 al., 2013).

303

304   **4. Discussion**

305   Our mineral composition and melt composition models reproduce the 556

306 partitioning data from the 100 partitioning experiments (fits to the individual experiments

307 are shown in Supplementary Figs. S2 and S3). The partition coefficients predicted by the

308 melt composition model (Fig. 3a) and the mineral composition model (Fig. 3b) both

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309   follow the 1:1 correlation line when plotted against the measured values and generally

310   fall between the 1:2 and 2:1 correlation lines. Hence to the first approximation, both

311   models equally describe the variability of partition coefficients. In detail, the melt

312   composition model (C_p^2 = 41.3) performs slightly better than the mineral composition

313   model (C_p^2 = 93.7), especially for cases when measured D > 1.

314

315   **4.1. Comparison with the empirical model of Tiepolo et al. (2007)**

316   Our new melt composition model has 4 variables and 7 coefficients for the 15

317   elements (REE+Y), whereas the melt composition model of Tiepolo et al. (2007), which

318   is a linear fit to one composition variable, has 8 coefficients for 4 elements (La, Dy, Y,

319   and Yb). In terms of reproducing measured partitioning data for these 4 elements, the

320   Pearson's Chi-square for the original model of Tiepolo et al. (2007) (26.0) is larger than

321   our melt model (11.6 for a fit using La, Dy, Y, and Yb only). To further compare with the

322   model of Tiepolo et al. (2007), we recalibrated their equations for the 15 elements

323   (REE+Y) using our compiled database (Table S1 provides the new coefficients). The

324   updated model has a C_p^2 value of 54.6, which is still larger than that for our melt model

325   (41.3). Therefore, our melt composition model has a better reproducibility and a smaller

326   number of coefficients to describe the REE partitioning between amphibole and silicate

327   melt. This further underscores the advantage and importance of the lattice strain model in

328   quantifying REE partitioning in amphibole. In addition, as shown later in this study, our

329   mineral composition model provides an understanding of the REE substitution

330   mechanism in amphibole, and has the advantage of being applicable to natural samples

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331   without the knowledge of the melt composition.

332

333   **4.2. Relation between the mineral composition and melt composition models**

334   The connection between the mineral composition and melt composition models

335   can be understood in terms of amphibole-melt phase equilibria. To within estimated

336   uncertainties, the coefficients in the equations for r_0 and best-fit values for E are identical

337   between the melt composition and mineral composition models (Eqs. (12) vs. (15); Eqs.

338   (13) vs. (16)). This implies that D_0 values between the two models are the same, given

339   the two models are equivalent in terms of reproducing measured REE partitioning data

340   (Figs. 3a and 3b). Equating Eqs. (11) and (14), we have the following expression relating

341   amphibole composition to coexisting melt composition,

342    $$-3.08 + 0.74\ln\left(X_{\text{Si}}^{\text{melt}}\right) - 0.33\ln\left(X_{\text{Ti}}^{\text{melt}}\right) - 0.84\ln\left(X_{\text{Ca}}^{\text{melt}}\right) = -4.21 + \frac{7.27 \times 10^4}{RT} + 1.52 X_{\text{Ti}}^{\text{amph}} - 0.35 X_{\text{Mg}}^{\text{amph}} - 1.83 X_{\text{Na}}^{\text{amph}} - 2.95 X_{\text{K}}^{\text{amph}}.$$

343   (18)

344   Eq. (18), in effect, describes the liquidus of amphibole, and hence can be taken as a

345   thermometer for amphibole-melt equilibria, viz.,

346    $$T = \frac{8.74 \times 10^3}{1.13 - 1.52 X_{\text{Ti}}^{\text{amph}} + 0.35 X_{\text{Mg}}^{\text{amph}} + 1.83 X_{\text{Na}}^{\text{amph}} + 2.95 X_{\text{K}}^{\text{amph}} + 0.74\ln\left(X_{\text{Si}}^{\text{melt}}\right) - 0.33\ln\left(X_{\text{Ti}}^{\text{melt}}\right) - 0.84\ln\left(X_{\text{Ca}}^{\text{melt}}\right)}.$$

347   (19)

348   This thermometer provides an opportunity to independently test our melt composition

349   model (Eqs. (1) and (11)–(13)) and mineral composition model (Eqs. (1) and (14)–(16))

350   as discussed below.

351   There are a large number of amphibole-melt phase equilibria studies reported in

352   the literature. Here we use Eq. (19) to calculate the temperatures of 185 amphibole-melt

16

353   phase equilibrium experiments from 16 studies (Alonso-Perez et al., 2009; Blatter et al.,

354   2013; Costa et al., 2004; Foden and Green, 1992; Gardner et al., 1995; Grove et al., 1997;

355   Grove et al., 2003; Holtz et al., 2004; Kawamoto, 1996; Moore and Carmichael, 1998;

356   Nandedkar et al., 2014; Nekvasil et al., 2004; Pichavant et al., 2002; Pilet et al., 2010;

357   Prouteau and Scaillet, 2003; Sato et al., 2005). These experiments were conducted at

358   730–1130ºC and 0.1–1.5 GPa, generally at lower *P-T* conditions compared to the REE

359   partitioning experiments. Despite some overlap in composition, these experiments

360   produced calcic amphiboles generally higher in Si and lower in alkalis, and melt with

361   higher SiO_2 content compared to those in the REE partitioning experiments (Fig. 1). The

362   temperatures of these experiments calculated using our thermometer (Eq. (19)) and the

363   measured temperatures generally follow the 1:1 correlation line to within 100ºC of the

364   measured temperature with a precision of 66ºC (RMSE) (Fig. 5), which is an independent

365   verification of our amphibole-melt thermometer (Eq. 19) and hence our mineral

366   composition and melt composition models. Furthermore, the validity of our thermometer

367   to lower *P-T* conditions and more evolved amphibole and melt composition compared to

368   the REE partitioning experiments suggests the applicability of our models at these

369   conditions.

370   Our thermometer for amphibole-melt equilibria (Eq. 19) shows similarities to a

371   recent amphibole-melt thermometer of Putirka (2016) that has the expression

372
$$T\left(^{\circ}C\right)=\frac{8037.85}{3.69+2.62X_{H_2O}^{melt}+0.66Fe_{total}^{amph}-0.416\ln\left(X_{TiO_2}^{melt}\right)-0.37\ln\left(X_{MgO}^{melt}\right)-1.05\ln\left(X_{FmO}^{melt}X_{Al_2O_3}^{melt}\right)-0.462\ln\left(D_{Ti}\right)},$$
(20)
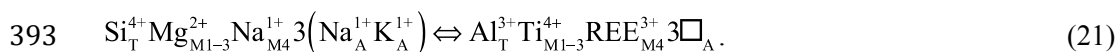
373   where X_i^{melt} are hydrous mole fractions of oxides in the melt, Fe_{total}^{amph} is the total Fe cation

374   number in amphibole (per 23 oxygen), and D_{Ti} is the ratio of the Ti cation number in

17

375   amphibole (per 23 oxygen) divided by the hydrous mole fraction of Ti in the melt. This

376   thermometer and our thermometer both involve the temperature dependence of Ti

377   partitioning between the amphibole and melt. The thermometer of Putirka (2016) has

378   better precision (38ºC) than our thermometer (66ºC) based on the same data set as in Fig.

379   5, but the two thermometers are surprisingly comparable, especially given that our

380   models are calibrated to predict REE partitioning between amphibole and melt and not

381   temperatures. Therefore, our thermometer captures the essential parameters required in a

382   thermometer for amphibole-melt equilibria.

383

384   **4.3. Substitution mechanism**

385   The mineral composition model may provide insights to the REE substitution

386   mechanism in amphibole. According to the mineral composition model, D_0 positively

387   correlates with Ti and negatively with Mg. Hence REE substitution is related to the Ti–

388   Al^{iv} substitution in the M1,2,3 and tetrahedral sites. Furthermore, the model may suggest

389   that REE substitution for Na in the M4 site is charge compensated by vacancies in the A

390   site, given the negative correlation between Na and K contests in amphibole and D_0.

391   Taken together, the mineral composition model suggests the following substitution

392   mechanism of REE in amphibole,

393    $$Si_T^{4+}Mg_{M1-3}^{2+}Na_{M4}^{1+}3\left(Na_A^{1+}K_A^{1+}\right) \Leftrightarrow Al_T^{3+}Ti_{M1-3}^{4+}REE_{M4}^{3+}3\square_A . \tag{21}$$

394   According to this substitution mechanism, REE partition coefficients should positively

395   correlate with Al^T similar to that observed in clinopyroxene (e.g Cascio et al., 2008;

396   Gaetani and Grove, 1995; Hill et al., 2000; Lundstrom et al., 1998; Wood and Blundy,

397   1997). There is a weak positive correlation between Al^T and normalized amphibole-melt

18

398 Sm partition coefficient (Fig. S4c), and its scatter may be due to the effect of variation in

399 other mineral compositions (e.g. Ti, Mg, Na, and K) similar to that observed for Na

400 content in the mineral composition model (Fig. S4a). A mineral composition model with

401 Al^T, Mg, Na, and K contents in the amphibole as compositional variables for D_0 has a

402 Pearson's Chi-square of 117, which is higher than our preferred mineral composition

403 model (93.7). Although Al^T plays an important role in REE substitution in amphibole, in

404 practice our mineral composition model performs slightly better when we use Ti rather

405 than Al^T as a compositional variable.

406

407 **5. Applications**

408 **5.1. Melting of amphiboles in the mantle**

409   Amphibole is often observed in mantle xenoliths brought to the surface by basalt

410 volcanism, suggesting the presence of hydrated and metasomatized mantle lithosphere

411 (e.g. Boettcher and O'Neil, 1980; Chazot et al., 1996; Ionov and Hofmann, 1995). Partial

412 melting of such mantle can give rise to melts with a range of compositions (e.g., alkali

413 basalts to nephelinites) (e.g. Médard et al., 2006; Pilet et al., 2008; Sorbadere et al.,

414 2013). In general, major element compositions in mantle amphiboles vary considerably

415 (Figs. 1d–f). According to the data compiled from 10 studies shown in Fig. 1, TiO_2 in

416 amphiboles found in mantle xenoliths varies from 0.15 to 5.94 wt%, MgO from 9.82 to

417 19.43 wt%, Na_2O from 2.31 to 4.3 wt%, and K from 0 to 2.05 wt%. Based on our mineral

418 model, we expect considerable variability in amphibole-melt REE partition coefficients.

419 For purpose of demonstration, we calculated the amphibole-melt REE partition

420 coefficients in amphiboles found in mantle xenoliths from the 10 studies listed in table 1

19

421   using the mineral composition model for a temperature of 1000ºC. As shown in Fig. 6,

422   amphibole-melt REE partition coefficients in amphiboles found in xenoliths vary by

423   nearly an order of magnitude, purely due to their compositional variation. Further, the

424   REE partition coefficients decrease more than 20% when the temperature is increased to

425   1100ºC (cf. heavy blue and red lines in Fig. 6). Despite the large range in REE partition

426   coefficient, its pattern does not noticeably change due to the small range in Fm content in

427   the M4 site of the amphiboles. This simple example demonstrates the importance of

428   composition- and temperature- dependent amphibole-melt REE partition coefficients to

429   geochemical modeling of melting of an amphibole-bearing lithology in the mantle. For

430   convenience, we list in Table 2 the average, maximum, and minimum REE partition

431   coefficients between amphiboles in mantle xenoliths and melt calculated using the

432   mineral composition model at four selected temperatures.

433

434   **5.2. Fractional crystallization of arc magmas**

435   Fractional crystallization of amphibole and clinopyroxene in arc magmas has been

436   postulated to decrease Dy/Yb and Dy/Dy* $\left(Dy_N \middle/ \left(La_N^{4/13} Yb_N^{9/13} \right) \right)$ ratios (i.e. depletion in

437   MREEs relative to HREEs and LREEs) with increasing SiO_2 content, as observed in rock

438   samples from single arc volcanoes (Davidson et al., 2007; Davidson et al., 2013).

439   However, given the large range in published mineral-melt partition coefficients, the

440   relative importance of amphibole and clinopyroxene in producing low Dy/Yb and

441   Dy/Dy* ratios in arc magmas is not clear. In order to better understand this, we use REE

442   partitioning models and mass balance calculations to estimate and compare the effects of

443   amphibole and clinopyroxene fractional crystallization on the REE patterns of

444 experimental melts compositionally similar to arc magmas (Nandedkar, 2014; Nandedkar

445 et al., 2014). The experiments of Nandedkar et al. (2014) and Nandedkar (2014) simulate

446 fractional crystallization of the same initial starting material at pressures of 0.7 GPa and

447 0.4 GPa, respectively. (Hereafter we refer to the experiments of Nandedkar et al. (2014)

448 as the 0.7 GPa experiments and those of Nandedkar (2014) as the 0.4 GPa experiments.)

449 The initial starting material in these experiments is an olivine-tholeiite with an Mg# of 73

450 and H_2O content of 3 wt%, and both experiments were run at an oxygen fugacity of Ni-

451 NiO. The experimental temperatures of the 0.7 GPa and 0.4 GPa experiments range from

452 1170 to 700ºC and 1110 to 920ºC, respectively. The final amounts of fractional

453 crystallization are 85 wt% for the 0.7 GPa experiments and 76 wt% for the 0.4 GPa

454 experiments. Both experiments crystallized clinopyroxene, olivine, plagioclase, and

455 magnetite, but the 0.7 GPa experiment also crystallized amphibole with less plagioclase.

456 This may be due to the greater stability of amphibole and the lesser stability of

457 plagioclase at high pressure (Allen and Boettcher, 1983; Nandedkar, 2014; Spulber and

458 Rutherford, 1983). Hence, the comparison between the model REE patterns and

459 abundances in the melts of these experiments using REE partitioning models and mass

460 balance calculations provide an insight into the effect of fractional crystallization on the

461 REE pattern of arc magmas under different *P-T* conditions and crystallizing phases.

462 Particularly interesting is the effect of amphibole fractional crystallization, which may

463 play a key role in the depletion of MREEs relative to HREEs in arc magmas (Davidson et

464 al., 2007; Davidson et al., 2013).

465   We used the temperature, mineral and melt composition in the 0.7 GPa and 0.4

466 GPa experiments to calculate the amphibole-melt and clinopyroxene-melt REE partition

21

467   coefficients using the melt composition model of this study and the model of Sun and

468   Liang (2012). The amphibole-melt REE partition coefficients in the 0.7 GPa experiments

469   were measured by Nandedkar et al. (2016), and they are part of the partitioning data used

470   for our model calibration. However, we chose to use our models to calculate the

471   amphibole-melt REE partition coefficients to understand what parameters cause changes

472   in the partition coefficients between different experimental runs. The calculated

473   amphibole-melt MREE and HREE partition coefficients in the 0.7 GPa experiments

474   increase by approximately an order of magnitude from the highest to lowest temperature

475   experiment due to the increase in Si, and decrease in Ti and Ca content in the melt (Fig.

476   7a). In contrast to the MREE and HREE, the LREE partition coefficients do not vary

477   significantly because elements with larger ionic radius relative to r_0 become more

478   incompatible with decreasing temperature (Eq. 1), and this counteracts the increase in D_0.

479   A calculation using the mineral composition model from this study also predicts an

480   increase in MREE and HREE partition coefficients with progressive fractional

481   crystallization largely due to the decrease in temperature, but also due to the decrease in

482   Na and K content in the amphibole. However, the increase of partition coefficients is a

483   factor of 2 smaller than that predicted by the melt composition model at 730°C. The

484   disagreement between the models is likely due to the low crystallization temperature

485   (730°C), which is below the model calibration range (780–1100ºC). (The amphibole

486   formed at 730ºC is cummingtonite unlike the magnesio-hornblende formed at slightly

487   higher temperature of 780ºC, which may give rise to a different REE substitution

488   mechanism than those described in section 4.3. We suspect kinetics may also play a role

489   in controlling major element compositions in amphiboles at lower temperatures). Hence

490   caution should be exercised when extrapolating our models to *T-X* conditions outside the

491   calibration range (Table 1). At temperatures higher than 730ºC, the differences between

492   the amphibole-melt REE partition coefficients predicted by the two models are all within

493   34%, and the results discussed in the rest of this section are not model dependent. The

494   range in clinopyroxene-melt REE partition coefficients in the 0.7 GPa and 0.4 GPa

495   experiments are similar to each other except for the high Al clinopyroxene found in the

496   0.7 GPa experiment at 1040ºC. The olivine-melt, opx-melt, and plagioclase-melt REE

497   partition coefficients are calculated using the models of Sun and Liang (2013b), Yao et al.

498   (2012), and Sun et al. (2017) respectively. The spinel-melt REE partition coefficients are

499   from Kelemen et al. (2003). The other phases such as apatite and magnetite were not

500   considered for simplicity.

501   The partition coefficients and the phase proportions in the 0.7 GPa and 0.4 GPa

502   experiments (Nandedkar, 2014; Nandedkar et al., 2014) were used to model the REE

503   abundances in the melts during fractional crystallization. The model results are shown in

504   in Figs. 7b, c, and d. The Dy/Dy* and Dy/Yb ratios of the 0.7 GPa melt decrease

505   significantly more than those of the 0.4 GPa melt during fractional crystallization (Fig.

506   7b). Furthermore, the 0.7 GPa melts are more depleted in MREEs and HREEs compared

507   to the 0.4 GPa melts for a given degree of fractional crystallization (Figs. 7c and d).

508   These differences are due to fractional crystallization of amphibole in the 0.7 GPa melts.

509   As shown in the results section, amphibole fractional crystallization decreases the

510   Dy/Dy* and Dy/Yb ratios in the melt due to the affinity of amphibole for MREEs over

511   HREEs and LREEs (i.e. similarity between r_0 of the amphibole and ionic radius of

512   MREEs) (Figs. 2 and 7a). In addition, amphibole fractional crystallization moderates the

23

513   MREE and HREE concentration in the melt since they behave compatibly in amphiboles,

514   especially in those crystallizing from more evolved melts (i.e., high Si) at lower

515   temperatures (Fig. 7a). In contrast, the Dy/Dy* and Dy/Yb ratios do not decrease as much

516   and the MREE and HREE concentrations are significantly higher in the 0.4 GPa melts

517   than the 0.7 GPa melts since they do not crystallize amphibole (Fig. 7b). To some extent,

518   the Dy/Dy* and Dy/Yb ratios in the 0.4 GPa melts decrease due to clinopyroxene

519   fractional crystallization (Fig. 7b), but by much less than the 0.7 GPa melts, since REEs

520   are incompatible in the crystallizing clinopyroxenes especially at high temperatures (Fig.

521   7a). In contrast, amphibole can significantly fractionate the REE pattern of the 0.7 GPa

522   melts due to the lower crystallization temperatures in the 0.7 GPa melts compared to the

523   0.4 GPa melts for a given degree of fractional crystallization, perhaps due to the larger

524   temperature difference between the solidus and liquidus at higher pressure.

525   Applying the present REE partitioning model (melt composition model) to the 0.7

526   GPa experiments by Nandedkar et al. (2014) suggests that the amphibole-melt REE

527   partition coefficient can vary by an order of magnitude during fractional crystallization of

528   an arc magma due to changes in T, and the melt and amphibole compositions. This range

529   of values demonstrates the importance of composition- and temperature-dependent REE

530   partition coefficients in geochemical modeling of amphibole-melt fractionation. For

531   convenience, we list the amphibole-melt REE partition coefficients for amphiboles in the

532   0.7 GPa experiments calculated using the melt composition model (Table 3). Our

533   modeling results suggest that fractional crystallization of amphibole plays a key role in

534   decreasing the Dy/Yb and Dy/Dy* ratios and also in moderating the MREE and HREE

535   concentrations in arc magmas. Fractional crystallization of clinopyroxene can also

536   decrease the Dy/Yb and Dy/Dy* ratios in the arc magmas, although much less efficiently.

537   The pressure of fractional crystallization affects the crystallization temperature of the

538   melt and stability of amphibole (Allen and Boettcher, 1983; Nandedkar, 2014; Spulber

539   and Rutherford, 1983), so it is also a key factor that controls the behavior of REE in

540   solidifying magmas.

541   Our model results suggest that arc magmas that crystallize amphibole should have

542   a fairly restricted range in MREE and HREE concentrations and low Dy/Yb and Dy/Dy*

543   ratios compared to those that do not crystallize amphibole (Fig. 7). As an example of

544   geological application, we compare two sets of samples from single arc volcanoes, one in

545   which these characteristics are present and another in which they are not. Samples from

546   Mt. Pelée in the Lesser Antilles Arc (Davidson and Wilson, 2011) (Fig. 8a) show the

547   effects of fractional crystallization of amphibole, while those from Anatahan Island in the

548   Mariana Arc (Wade et al., 2005) (Fig. 8b) do not. The samples from Mt. Pelée have a

549   fairly restricted range in MREE and HREE concentrations compared to those from

550   Anatahan Island despite the similar range in bulk SiO_2 content (51–63 wt% for Mt. Pelée

551   and 49–66 wt% for Anatahan Island) and other major element contents (Fig. S5)

552   suggesting similar range in degrees of fractional crystallization between the two sets of

553   samples. To the first order, REE and Y concentrations in the samples from Mt. Pelée and

554   Anatahan Island can be fairly well reproduced using the model REE and Y

555   concentrations in subsets of the 0.7 GPa experiments (Nandedkar et al., 2014) and 0.4

556   GPa experiments (Nandedkar, 2014) that have the most similar major element

557   concentrations to those in the samples (Fig. S5) and assuming the REE and Y

558   concentrations in the initial melts are those in the samples with lowest SiO_2 contents. The

25

559   model REE and Y concentrations also reproduce the greater decrease in Dy/Dy* and

560   Dy/Yb ratios in the samples from Mt. Pelée compared to those from Anatahan Island

561   (Figs. 8c and d). Although scatter in the data (Fig. 8c and d) and variation in the isotopic

562   composition may suggest some amount of source variation and/or crustal contamination

563   (Davidson and Wilson, 2011), the model results suggest amphibole fractional

564   crystallization associated with Mt. Pelée samples but not the Anatahan Island samples.

565   The *P-T-X* conditions of the equilibrium crystallization experiments designed for

566   studying the Mt. Pelée samples (Martel et al., 1998; Martel et al., 1999; Pichavant et al.,

567   2002) are a more accurate representation of those in the Mt. Pelée magma chamber, but

568   we chose to use the 0.7 GPa experiments (Nandedkar et al., 2014) as they are fractional

569   crystallization experiments that allows continuous modeling of the effects of changing

570   temperature and melt/mineral composition on the REE concentration in a crystallizing

571   melt. A combination of fractional crystallization experiments ran at relevant *P-T-X*

572   conditions and the REE partitioning models for amphibole and other mineral phases

573   (Dygert et al., 2014; Sun et al., 2017; Sun and Liang, 2012; Sun and Liang, 2013b; Yao et

574   al., 2012) may be useful for unraveling the *P-T* conditions and variations in major and

575   REE abundance of sets of samples from single arc volcanoes.

576

577   **6. Conclusions**

578   The partitioning of rare earth elements between amphibole and silicate melt

579   depends on temperature, and amphibole and melt compositions. We developed two

580   parameterized lattice strain models for REE and Y partitioning between amphibole and

581   silicate melt over a large range of *P-T-X* using published partitioning data between

582   amphibole and silicate melt and non-linear least squares regression method. The melt

583   composition model suggests that REE and Y partition coefficients in amphibole

584   positively correlate with Si content, and negatively correlate with Ti and Ca contents in

585   the melt. The mineral composition model suggests that REE and Y partition coefficients

586   in amphibole negatively correlate with T and Mg, Na, and K contents and positively

587   correlate with Ti content in amphibole. In both the mineral and melt composition models,

588   r_0 negatively correlates with the Fm content in the M4 site of amphibole and E is a

589   constant. The very similar coefficients of the equations for r_0 and best-fit values for E in

590   the two models suggest that the D_0 in the two models are equivalent. Hence there are

591   considerable trade-offs between major element compositions of coexisting amphibole and

592   melt in the parameterized lattice strain models for REE partitioning in amphibole. The

593   connection is the liquidus surface of amphibole. To further demonstrate this point, we

594   developed a hybrid model for amphibole-melt REE partitioning using a combination of

595   amphibole and melt compositions and the results are summarized in Appendix A. The

596   hybrid model, which performs slightly better than the melt composition model and the

597   mineral composition model, can be used to predict REE partition coefficients if major

598   element compositions of both amphibole and melt are available.

599   Application of our mineral composition model to amphiboles found in mantle

600   xenoliths suggests an order of magnitude variation in the amphibole-melt REE partition

601   coefficients purely due to compositional variation. Application of our melt composition

602   model to fractional crystallization experiments of arc magma (Nandedkar, 2014;

603   Nandedkar et al., 2014) suggests that REE partition coefficients between amphibole and

604   melt can increase by an order of magnitude due to a combined effect of decreasing T and

605   varying amphibole (e.g. decrease in Na and K) and melt compositions (e.g. increase in Si)

606   within this environment. In contrast, r_0 of the crystallizing amphiboles does not change

607   significantly and remains similar to the ionic radius of MREE such as Dy and Tb.

608   Therefore, fractional crystallization of amphibole can play a key role in buffering the

609   REE concentrations in arc magmas, and also in depleting its MREEs relative to HREEs

610   and LREEs.

611

612   **7. Implications**

613   Our new mineral composition model is a useful tool to estimate the REE and Y

614   concentration in silicate melt that is in equilibrium with amphibole. Previous models of

615   amphibole-melt REE partition coefficients (Hilyard et al., 2000; Sisson, 1994; Tiepolo et

616   al., 2007; Tiepolo et al., 2000) require the major element composition of the melt that is

617   in equilibrium with amphibole, which is not always available for natural samples such as

618   cumulates. Studies on amphibole-bearing rocks (e.g. Davidson and Wilson, 2011; Peters

619   et al., 2017) had to choose a set of amphibole-melt trace element partition coefficients

620   from the literature to estimate the trace element concentration in the equilibrium melt.

621   The new mineral composition model developed in the present study is useful in such

622   instances as it only requires the amphibole composition (i.e. Ti, Mg, Na, and K contents)

623   and temperature. Here temperature can be estimated using the amphibole composition-

624   dependent thermometer of Putirka (2016). The application of the mineral composition

625   model on amphibole-bearing cumulates would allow estimation of the REE concentration

626   in the melt that is in equilibrium with the amphibole-bearing cumulate, which is a useful

627   information for understanding the origin of the cumulates and the effect of its

28

628   crystallization on evolution of the trace element concentration in the melt. It can also be

629   used to model processes such as formation of amphibole by reaction-replacement of

630   clinopyroxene observed in cumulates (Smith, 2014), which may be an important process

631   for explaining the rarity of amphibole phenocrysts in arc lavas i.e. amphibole being a

632   'cryptic' fractionating phase (Davidson et al., 2007).

633   Applications of the new amphibole-melt REE partitioning models demonstrate the

634   significantly stronger effect of amphibole fractional crystallization, relative to

635   clinopyroxene fractional crystallization, on buffering the MREE and HREE

636   concentrations and decreasing Dy/Yb and Dy/Dy* ratios in arc magmas (Davidson et al.,

637   2007; Davidson et al., 2013). The magnitude of decrease in Dy/Yb and Dy/Dy* ratios

638   found in the samples from Mt. Pelée consistent with amphibole fractional crystallization,

639   is also observed in many other sets of samples from single arc volcanoes (Fig. 7 in

640   Davidson et al., 2013). This suggests that fractional crystallization of amphibole in arc

641   magmas is a common process, which is consistent with its common observation in arc

642   cumulates (e.g. Beard, 1986; DeBari and Coleman, 1989; Jagoutz et al., 2009; Lapierre et

643   al., 1992; Larocque and Canil, 2010). Our study implies that REEs are especially

644   enriched in amphibole-rich cumulates that crystallize from the most differentiated arc

645   magmas, since amphibole-melt REE partition coefficient increases with increasing

646   differentiation of arc magmas.

647

648   **Appendix A.** A Hybrid Model for Amphibole-Melt REE Partitioning

649   Following the same procedure outlined in the parameterization method, we found a

650   hybrid model in which parameters D_0, r_0, and E take on the following expressions:

29

651
$$\ln D_0^{amph} = -3.17(\pm0.71) - 0.61(\pm0.10)X_{Si}^{amph} - 2.19(\pm0.20)X_{Na}^{amph} - 1.95(\pm0.32)X_{K}^{amph}$$
$$+ 0.89(\pm0.29)\ln\left(X_{Si}^{melt}\right) - 1.21(\pm0.07)\ln\left(X_{Ca}^{melt}\right), \qquad (A1)$$

652
$$r_0^{amph} = 1.044(\pm0.002) - 0.050(\pm0.008)X_{Fm}^{amph-M4}, \qquad (A2)$$

653
$$E^{amph} = 332(\pm15), \qquad (A3)$$

654   where r_0 is in Å; and E is in GPa; and numbers in parentheses are 2σ uncertainties

655   estimated directly from the simultaneous inversion. The hybrid model has 9 fitting

656   parameters and provides an improved fit ($C_p^2 = 31.5$) over the melt (7 fitting parameters)

657   and mineral composition (9 fitting parameters) models presented in the main text. It can

658   be used to predict REE partition coefficients if major element compositions of both

659   amphibole and melt composition are available.

660

661   **Acknowledgements**

667

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1015   **Figure captions**

1016   Figure 1. Compositions of melt and amphibole in phase equilibrium experiments (gray

1017   dots) and partitioning experiments (yellow dots). Also shown are compositions of lavas

1018   and amphiboles in intraplate and arc settings (orange crosses) and xenoliths (red plus

1019   signs). The structural formula of amphiboles in panels d and e were calculated using the

1020   method of 13 cations excluding Ca, Na, and K described by Leake et al. (1997) for

1021   amphibole classification purpose, but for the parameterization procedure, all iron in the

1022   amphibole was assumed to be ferrous iron for reasons given in section 2.2. The

1023   partitioning data are from the compiled experiments in Table 1. Phase equilibrium data

1024   from 16 studies (Alonso-Perez et al., 2009; Blatter et al., 2013; Costa et al., 2004; Foden

1025   and Green, 1992; Gardner et al., 1995; Grove et al., 1997; Grove et al., 2003; Holtz et al.,

1026   2004; Kawamoto, 1996; Moore and Carmichael, 1998; Nandedkar et al., 2014; Nekvasil

1027   et al., 2004; Pichavant et al., 2002; Pilet et al., 2010; Prouteau and Scaillet, 2003; Sato et

1028   al., 2005). Lavas and amphiboles in intraplate and arc settings from 20 studies (Bernard

1029   et al., 1996; Buckley et al., 2006; Costa and Chakraborty, 2004; Demény et al., 2004;

1030   Gourgaud et al., 1989; Grove et al., 2005; Heliker, 1995; Mayer et al., 2013; Mortazavi

1031   and Sparks, 2004; Neumann et al., 1999; Nye and Turner, 1990; Pallister et al., 1996;

1032   Pallister et al., 2008; Pichavant et al., 2002; Reubi and Nicholls, 2004; Ridolfi et al.,

1033   2008; Samaniego et al., 2005; Shane et al., 2005; Tappe et al., 2007; Toya et al., 2005)

1034   and xenoliths from 10 studies (Chazot et al., 2005; Chazot et al., 1996; Grégoire et al.,

1035   2000; Ionov and Hofmann, 1995; Moine et al., 2001; Vannucci et al., 1995; Vaselli et al.,

1036   1995; Witt-Eickschen et al., 2003; Wulff-Pedersen et al., 1996; Zanetti et al., 1996).

1037

1038   Figure 2. Onuma diagram showing the REE and Y partition coefficients between

1039   amphibole and silicate melt measured in the partitioning studies listed in Table 1 (yellow

1040   dots). The orange lines are the best-fit parabolas to the trivalent REE and Y using the

1041   lattice strain model (Blundy and Wood, 1994; Brice, 1975; Wood and Blundy, 1997) for

1042   experiments in which there are more than 3 partitioning data.

1043

1044   Figure 3. Comparison between the experimentally measured partition coefficients to

1045   those predicted using (a) the melt composition model (Eqs. (1), (11)–(13)) and (b) the

1046   mineral composition model (Eqs. (1), (14)–(16)). Observed values are from partitioning

1047   studies listed in Table 1. The solid line represents 1:1 ratio, and dashed lines represent 2:1

1048   and 1:2 ratios, respectively. C_p^2 is the Pearson's Chi-square calculated according to Eq.

1049   (10).

1050

1051   Figure 4. Plots of amphibole-melt Sm partition coefficient against mole fractions of (a)

1052   Si, (b) Ti, and (c) Ca in the melt and (d) T, (e) Ti, and (f) Mg content in the amphibole.

1053   The partition coefficients of Sm in (e) and (f) are normalized using Eq. (17). The

1054   partitioning data are from the compiled experiments in Table 1.

1055

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1056   Figure 5. Comparison between observed temperatures in phase equilibrium experiments

1057   to those predicted using the thermometer for amphibole-melt equilibria (Eq. 19). Open

1058   symbols are experiments containing melts with composition beyond the calibration range

1059   of our melt and mineral composition models (SiO_2 higher than 68.7 wt%). Sources of

1060   data: (1) Alonso-Perez et al. (2009), (2) Blatter et al. (2013), (3) Costa et al. (2004), (4)

1061   Foden and Green (1992), (5) Gardner et al. (1995), (6) Grove et al. (1997), (7) Grove et

1062   al. (2003), (8) Holtz et al. (2004), (9) Kawamoto (1996), (10) Moore and Carmichael

1063   (1998), (11) Nandedkar et al. (2014), (12) Pilet et al. (2010), (13) Pichavant et al. (2002),

1064   (14) Nekvasil et al. (2004), (15) Sato et al. (2005), and (16) Prouteau and Scaillet (2003).

1065

1066   Figure 6. Amphibole-melt REE partition coefficients calculated using the mineral

1067   composition model (Eqs. (1), (14)–(16)) and compositions of for amphiboles found in

1068   mantle xenoliths. All except the red curve labeled 1100°C were calculated assuming a

1069   temperature of 1000ºC. The general effects of *T* and amphibole and melt composition on

1070   the amphibole-melt REE partition coefficients are also shown. Data source is the same as

1071   those in Fig. 1.

1072

1073   Figure 7. (a) Predicted amphibole-melt (blue lines) and clinopyroxene-melt (red and

1074   green lines) REE partition coefficients for mineral and melt compositions reported in the

1075   studies of Nandedkar et al. (2014) (0.7 GPa experiments, blue and red lines) and

1076   Nandedkar (2014) (0.4 GPa experiments, green lines), calculated using the melt

1077   composition model for amphibole-melt and the model of Sun and Liang (2012) for the

1078   clinopyroxene-melt. The dotted red line is the clinopyroxene-melt REE partition

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1079   coefficient for a high Al clinopyroxene found in the 0.7 GPa experiment at 1040ºC.

1080   Numbers on the right of each line are the experimental temperatures in ºC. (b) Dy/Dy*

1081   vs. Dy/Yb ratios (Davidson et al., 2013) and (c)-(d) REE concentrations in the 0.7 GPa

1082   and 0.4 GPa melts normalized to those in the initial melt calculated using the predicted

1083   mineral-melt partition coefficients (melt composition model, Eqs. (1), (11)–(13) for

1084   amphibole) and consideration of mass balance. Subsets of the experiments are shown for

1085   clarity. In (b), red circles are 0.7 GPa melts saturated in clinopyroxene, blue circles are

1086   those saturated in amphibole, and the green circles are the 0.4 GPa melts with the

1087   experimental temperatures in ºC. For (c) and (d) the numbers on the right of each line are

1088   the experimental temperatures in ºC, and the cumulative percentage of the melt that has

1089   not been crystallized.

1090

1091   Figure 8. Primitive mantle normalized REE concentrations and Dy/Dy* vs. Dy/Yb ratios

1092   in samples from (a, c) Mt. Pelée in the Lesser Antilles Arc (Davidson and Wilson, 2011)

1093   and (b, d) Anatahan Island in the Mariana Arc (Wade et al., 2005). Also plotted are those

1094   in the (a, c) 0.7 GPa melts (Nandedkar et al., 2014) and the (b, d) 0.4 GPa melts

1095   (Nandedkar, 2014) calculated using the predicted mineral-melt partition coefficients

1096   (melt composition model, Eqs. (1), (11)–(13) for amphibole), consideration of mass

1097   balance, and assuming the REE concentration in the initial melts of those in the samples

1098   with lowest SiO_2 contents. Subsets of experiments with similar major element

1099   concentrations to those in the samples (Fig. S5) were used for the calculation. For (a) and

1100   (b) the numbers associated with each circles correspond to experimental temperatures in

1101   ºC, and the SiO_2 content in the experimental melts. For (c), red circles are 0.7 GPa melts

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1102   saturated in clinopyroxene, blue circles are those saturated in amphibole, and in (d) the

1103   green circles are the 0.4 GPa melts with the experimental temperatures in ºC. Primitive

1104   mantle values are from McDonough and Sun (1995).

1105

1106   **Table Headings**

1107   Table 1. Data sources and experimental run conditions.

1108

1109   Table 2. List of recommended amphibole-melt REE and Y partition coefficients for

1110   amphiboles found in xenoliths.

1111

1112   Table 3. List of recommended amphibole-melt REE and Y partition coefficients for arc

1113   magma environment.

1114

1115   **Table footnotes**

1116   Table 1. [a]n represents the number of experiments. [b]m represents the number of

1117   partitioning data. [c]Melt H_2O content shown when reported in the study. It was measured

1118   using SIMS by Tiepolo et al. (2000) and LaTourrette et al. (1995), and using micro

1119   Raman spectroscopy by Nandedkar et al. (2016), and calculated using mass balance by

1120   Adam and Green (2003) and Adam and Green (2006).

1121

1122   Table 2. Note: Calculated at different temperatures using the mineral composition model

1123   of this study and compositions of for amphiboles found in mantle xenoliths (Data source

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1124   in Fig. 1). The composition of amphiboles is kept constant for the calculation at different

1125   temperatures.

1126

1127   Table 3. Note: Calculated using the melt composition model and the composition of

1128   amphiboles in the 0.7 GPa experiments of Nandedkar et al. (2014). *The set of partition

1129   coefficient at 730ºC should be used with caution since the temperature is below the

1130   calibration range of our model.

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Table 1. Data sources and experimental run conditions.

Study	n^a	m^b	P (GPa)	T (ºC)	Dur (h)	Amph Mg#	Melt Mg#	Melt SiO$_2$ (wt%)	Melt H$_2$O (wt%)^c
Ion probe analysis									
LaTourrette et al., (1995)	1	10	1.5	1092	17.5	79.3	63.2	44.6	4.27
Tiepolo et al., (2000)	24	222	1.4	950–1075	36	36.5–100	15.1–100	41.5–54.6	2.4–6.15
LA-ICP-MS analysis									
Dalphe and Baker (2000)	7	88	1.5–2.5	1000–1100	24–100	67.0–93.0	46.4–87.3	34.1–47.1	
Adam and Green (2003)	4	27	0.5–2	1000–1050	24	73.0–78.5	48.1–54.3	39.9–46.0	6.2–13.0
Adam and Green (2006)	2	20	1.0–2.0	1050	48	78.9–80.0	51.2–56.5	39.1–41.4	10.3–14.1
Nandedkar et al., (2016)	8	98	0.7	780–1010	4–168	66.3–77.1	42.2–58.8	51.1–65.9	6.2–9.9
EMP analysis									
Adam and Green (1994)	2	8	2	1000	24	78.3–78.5	60.4–72.0	41.6–43.3	
Klein et al., (1997)	18	27	1	800–900	58–85	55.5–69.0	21.6–45.1	60.5–68.7	
Hilyard et al., (2000)	34	56	0.2–0.5	900–945	70–100	59.3–75.5	1.9–40.2	55.8–67.0	
Total range	100	556	0.2–2.5	780–1100	4–168	36.5–100	1.9–100	34.1–68.7	2.4–14.1

[a]n represents the number of experiments.

[b]m represents the number of partitioning data.

[c]Melt H$_2$O content shown when reported in the study. It was measured using SIMS by Tiepolo et al. (2000) and LaTourrette et al. (1995), and using micro Raman spectroscopy by Nandedkar et al. (2016), and calculated using mass balance by Adam and Green (2003) and Adam and Green (2006).

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Table 2. List of recommended amphibole-melt REE and Y partition coefficients for amphiboles found in xenoliths.

Temperature (°C)	1100			1000			900			800		
	Min	Average	Max	Min	Average	Max	Min	Average	Max	Min	Average	Max
La	0.030	0.078	0.235	0.042	0.112	0.339	0.064	0.170	0.520	0.104	0.280	0.863
Ce	0.049	0.127	0.379	0.073	0.189	0.566	0.115	0.302	0.907	0.197	0.523	1.586
Pr	0.075	0.192	0.563	0.115	0.294	0.868	0.189	0.486	1.442	0.339	0.881	2.631
Nd	0.106	0.266	0.773	0.167	0.420	1.223	0.282	0.715	2.091	0.527	1.343	3.951
Sm	0.162	0.397	1.127	0.263	0.645	1.836	0.463	1.138	3.250	0.906	2.235	6.400
Eu	0.182	0.439	1.237	0.297	0.720	2.030	0.529	1.283	3.624	1.047	2.547	7.209
Gd	0.195	0.467	1.303	0.321	0.769	2.147	0.575	1.378	3.851	1.147	2.753	7.704
Tb	0.201	0.477	1.318	0.332	0.786	2.174	0.596	1.411	3.905	1.194	2.827	7.821
Dy	0.200	0.468	1.283	0.329	0.770	2.111	0.590	1.381	3.782	1.181	2.761	7.552
Y	0.195	0.454	1.238	0.321	0.746	2.031	0.574	1.333	3.626	1.145	2.656	7.214
Ho	0.192	0.445	1.209	0.315	0.729	1.981	0.562	1.301	3.529	1.120	2.587	7.002
Er	0.179	0.413	1.114	0.293	0.673	1.813	0.520	1.193	3.206	1.029	2.352	6.304
Tm	0.165	0.377	1.011	0.268	0.610	1.632	0.472	1.073	2.860	0.925	2.095	5.566
Yb	0.150	0.341	0.909	0.242	0.548	1.456	0.423	0.955	2.528	0.821	1.844	4.862
Lu	0.136	0.308	0.816	0.218	0.491	1.296	0.378	0.847	2.228	0.726	1.617	4.235

Note: Calculated at different temperatures using the mineral composition model of this study and compositions of for amphiboles found in mantle xenoliths (Data source in Fig. 1). The compositions of amphiboles are kept constant for the calculation at different temperatures.

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Table 3. List of recommended amphibole-melt REE and Y partition coefficients for arc magma environment.

Temperature (ºC)	1010	950	920	890	860	830	780	730*
La	0.14	0.17	0.19	0.25	0.24	0.34	0.39	0.13
Ce	0.26	0.32	0.36	0.49	0.48	0.69	0.85	0.36
Pr	0.42	0.54	0.61	0.86	0.86	1.26	1.67	0.87
Nd	0.63	0.83	0.96	1.37	1.4	2.1	2.93	1.88
Sm	1.07	1.45	1.69	2.5	2.66	4.06	6.18	5.6
Eu	1.24	1.7	1.98	2.97	3.21	4.95	7.77	8.13
Gd	1.37	1.9	2.22	3.37	3.68	5.71	9.23	11.1
Tb	1.46	2.03	2.38	3.63	4.02	6.26	10.4	14.3
Dy	1.48	2.08	2.43	3.74	4.18	6.53	11.11	17.39
Y	1.47	2.06	2.4	3.72	4.18	6.54	11.27	19.09
Ho	1.45	2.04	2.38	3.68	4.15	6.5	11.28	19.84
Er	1.38	1.94	2.26	3.51	3.98	6.24	11.01	21.48
Tm	1.28	1.8	2.09	3.27	3.73	5.85	10.44	22.34
Yb	1.18	1.65	1.92	3	3.44	5.38	9.72	22.53
Lu	1.08	1.51	1.74	2.73	3.14	4.91	8.95	22.24

Note: Calculated using the melt composition model and the composition of amphiboles in the 0.7 GPa experiments of Nandedkar et al. (2014). *The set of partition coefficient at 730ºC should be used with caution since the temperature is below the calibration range of our model.
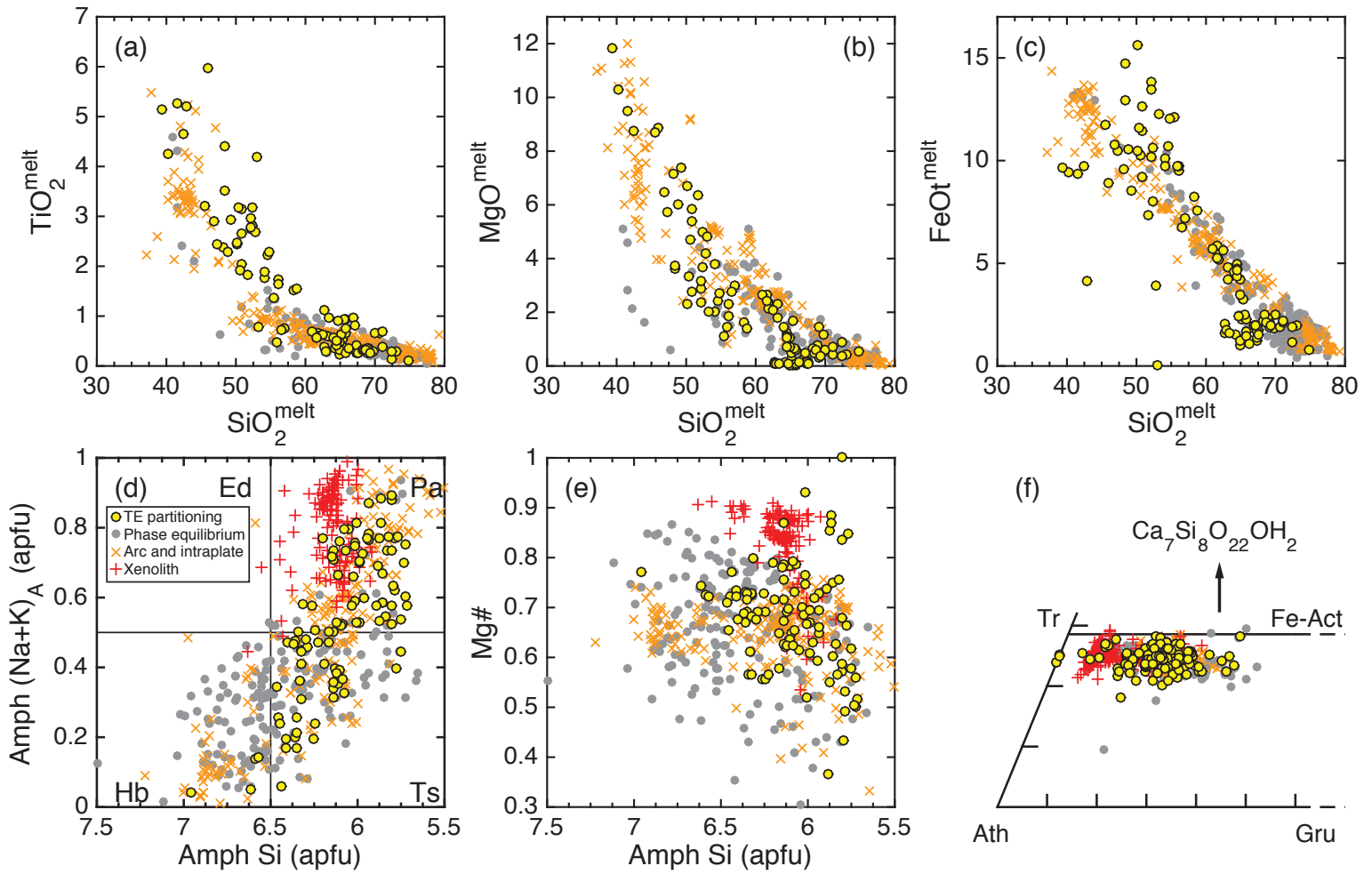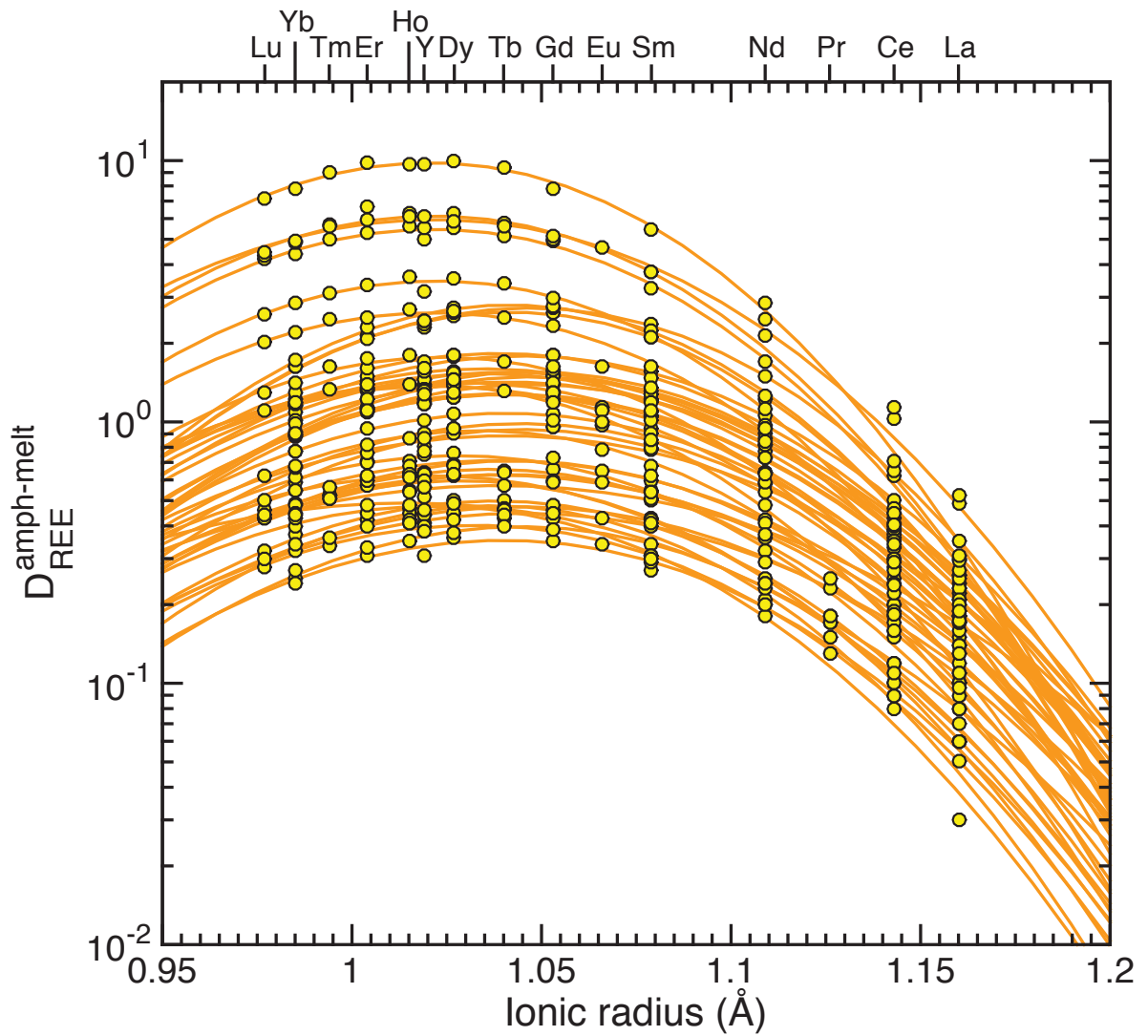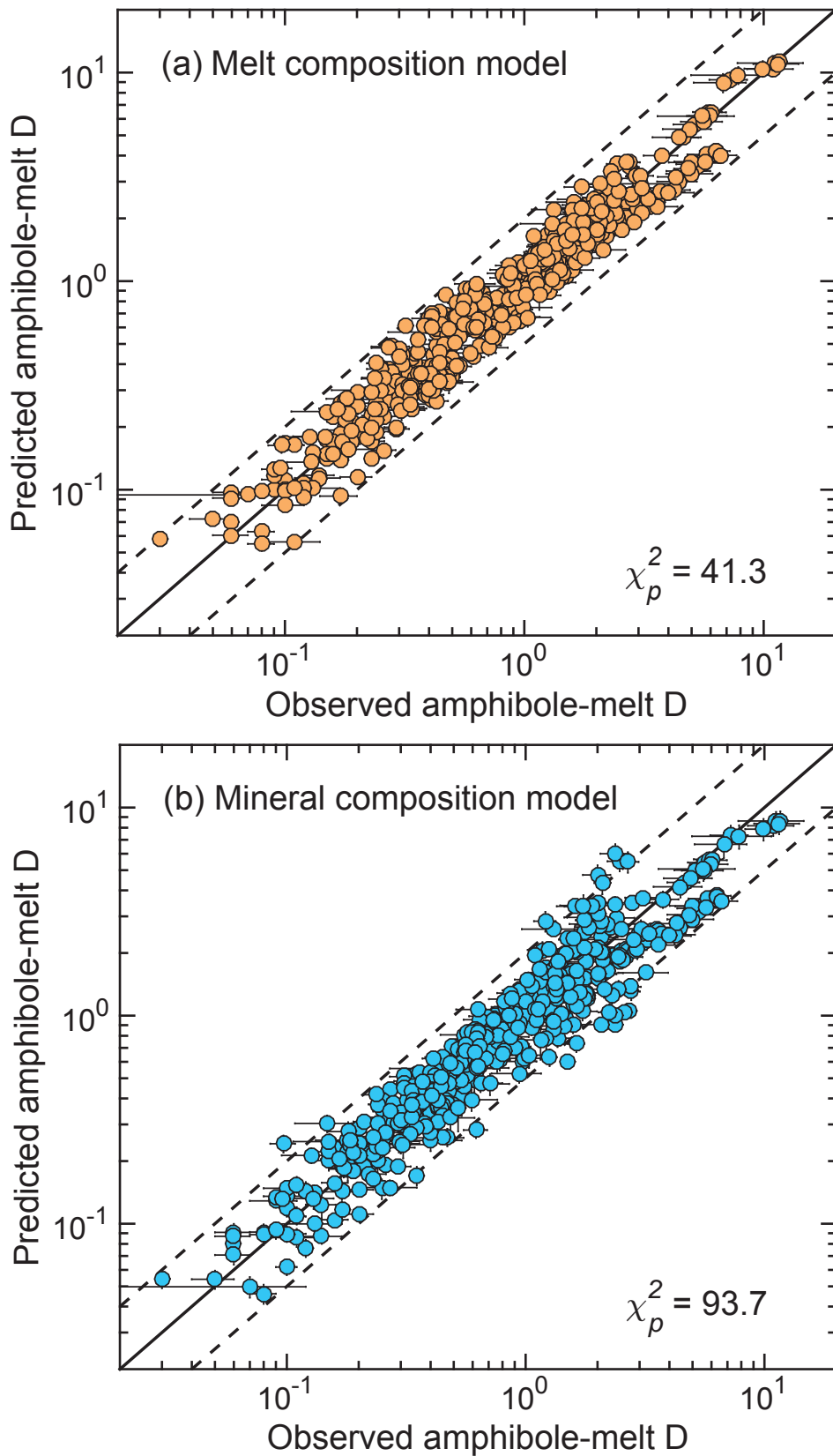
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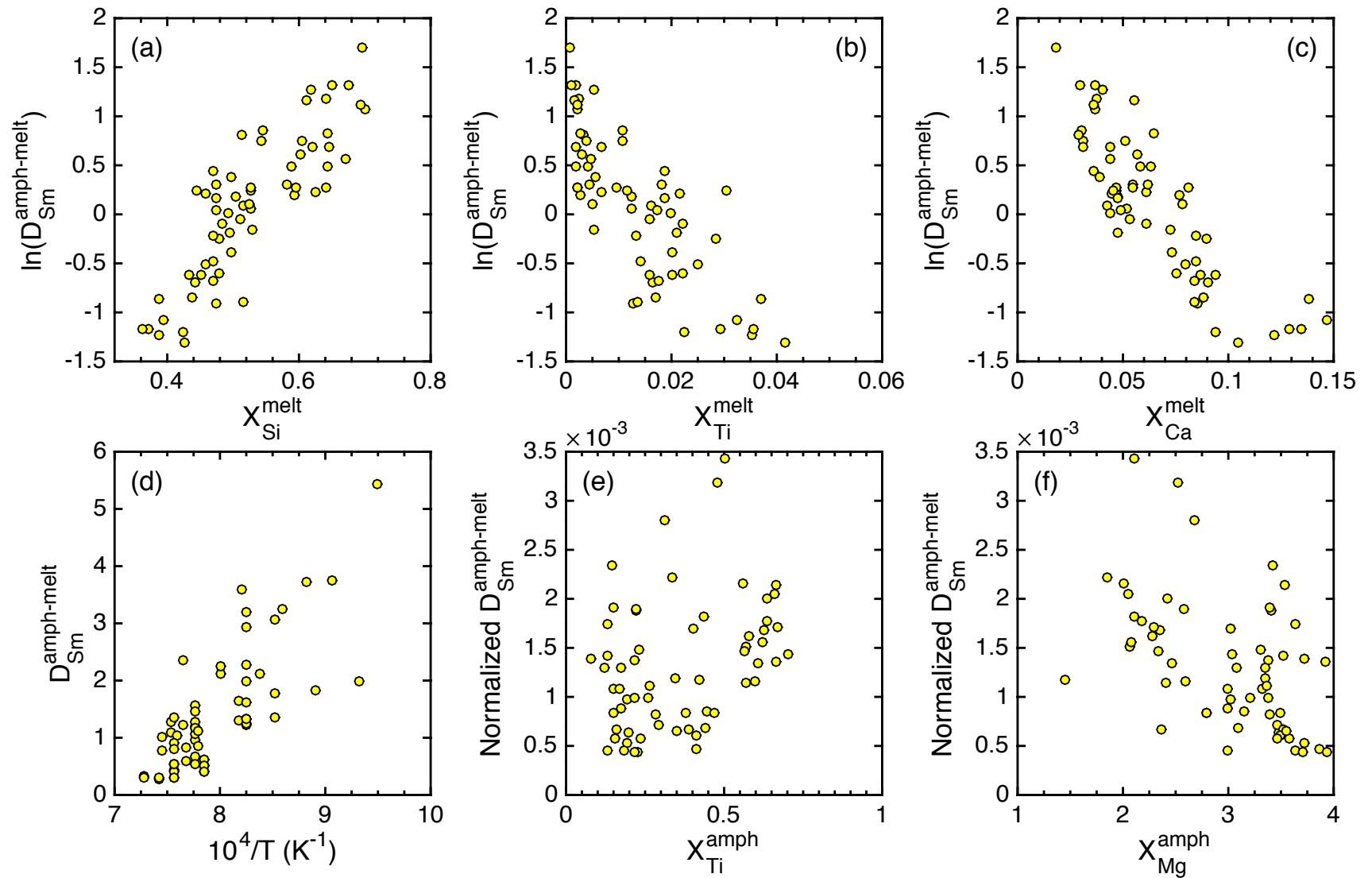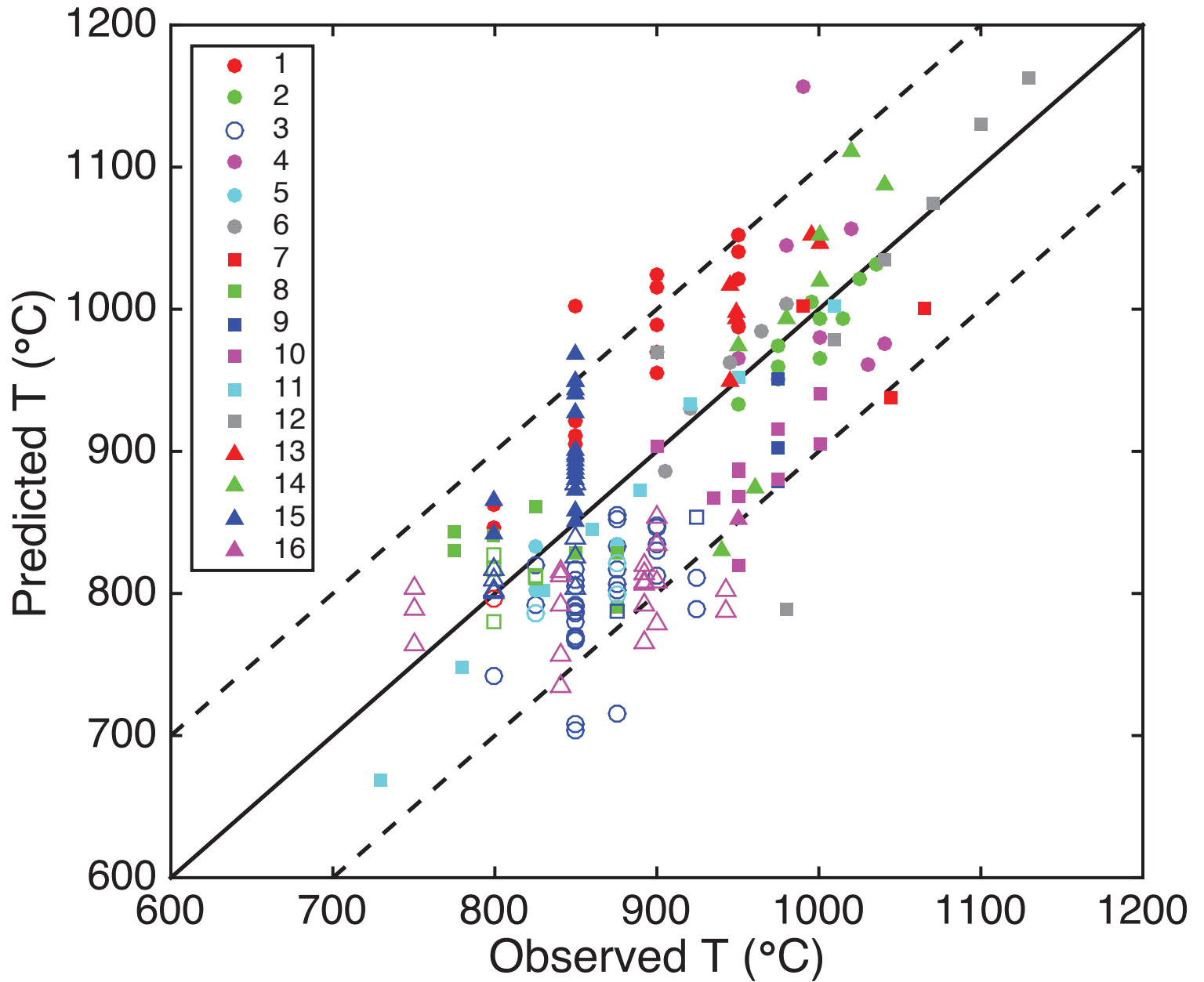1138
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Figure 1

Figure 2

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