

 Open access • Journal Article • DOI:10.1007/S00410-018-1543-5

Unravelling the complexity of magma plumbing at Mount St. Helens: a new trace element partitioning scheme for amphibole — [Source link](#)

Madeleine C. S. Humphreys, [George F. Cooper](#), [J. Zhang](#), [J. Zhang](#) ...+5 more authors

Institutions: [Durham University](#), [Chinese Academy of Sciences](#), [United States Geological Survey](#), [Oregon State University](#)

Published on: 02 Jan 2019 - [Contributions to Mineralogy and Petrology](#) (Springer Berlin Heidelberg)

Topics: [Melt inclusions](#), [Magma](#), [Amphibole](#), [Phenocryst](#) and [Trace element](#)

Related papers:

- [Amphibole thermometers and barometers for igneous systems and some implications for eruption mechanisms of felsic magmas at arc volcanoes](#)
- [Stability and chemical equilibrium of amphibole in calc-alkaline magmas: an overview, new thermobarometric formulations and application to subduction-related volcanoes](#)
- [Chemical and isotopic systematics of oceanic basalts. Implications for Mantle Composition and Processes](#)
- [Calcic amphiboles in calc-alkaline and alkaline magmas: thermobarometric and chemometric empirical equations valid up to 1,130°C and 2.2 GPa](#)
- [Experimental investigations of the role of H₂O in calc-alkaline differentiation and subduction zone magmatism](#)

Share this paper:    

View more about this paper here: <https://typeset.io/papers/unravelling-the-complexity-of-magma-plumbing-at-mount-st-595h7kbatz>

Durham Research Online

Deposited in DRO:

08 February 2019

Version of attached file:

Accepted Version

Peer-review status of attached file:

Peer-reviewed

Citation for published item:

Humphreys, Madeleine C. S. and Cooper, George F. and Zhang, Jing and Loewen, Matthew and Kent, Adam J. R. and Macpherson, Colin G. and Davidson, Jon P. (2019) 'Unravelling the complexity of magma plumbing at Mount St. Helens : a new trace element partitioning scheme for amphibole.', *Contributions to mineralogy and petrology.*, 174 (1). p. 9.

Further information on publisher's website:

<https://doi.org/10.1007/s00410-018-1543-5>

Publisher's copyright statement:

This is a post-peer-review, pre-copyedit version of an article published in *Contributions to mineralogy and petrology*. The final authenticated version is available online at: <https://doi.org/10.1007/s00410-018-1543-5>

Additional information:

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a [link](#) is made to the metadata record in DRO
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the [full DRO policy](#) for further details.

1 **Unravelling the complexity of magma plumbing at Mount St Helens: a new trace element**
2 **partitioning scheme for amphibole**

3

4 Madeleine. C. S. Humphreys^{1*}, George. F. Cooper¹, Jing Zhang^{1,2}, Matthew Loewen^{3,4}, Adam. J. R.
5 Kent³, Colin. G. Macpherson¹ and Jon. P. Davidson^{1§}

6

7 ¹Department of Earth Sciences, University of Durham, Durham, DH1 3LE, UK

8 ²State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese
9 Academy of Sciences, Beijing, 100029, China

10 ³College of Earth, Ocean and Atmospheric Sciences, Oregon State University, Corvallis, OR 97330,
11 USA

12 ⁴ Alaska Volcano Observatory, U.S. Geological Survey, Anchorage, AK 99508, USA

13 *Corresponding author. E-mail: madeleine.humphreys@durham.ac.uk

14 § Deceased

15

16

17 **ABSTRACT**

18 Volcanoes at subduction zones reside above complex magma plumbing systems, where individual
19 magmatic components may originate and interact at a range of pressures. Because whole rock
20 compositions of subduction zone magmas are the integrated result of processes operating throughout
21 the entire plumbing system, processes such as mixing, homogenisation and magma assembly during
22 shallow storage can overprint the chemical signatures of deeper crustal processes. Whereas melt
23 inclusions provide an effective way to study the uppermost 10-15 km of the plumbing system,
24 challenges remain in understanding magma intrusion, fractionation and hybridisation processes in the
25 middle to lower crust (15-30 km depth), which commonly involves amphibole crystallisation. Here,
26 we present new insights into the mid-crustal plumbing system at Mount St Helens, USA, using
27 multiple regression methods to calculate trace element partition coefficients for amphibole

28 phenocrysts, and thus infer the trace element compositions of their equilibrium melts. The results
29 indicate vertically distributed crystal fractionation, dominated by amphibole at higher pressures and in
30 intermediate melts, and by plagioclase at lower pressures. Variations in Nb, Zr and REE
31 concentrations at intermediate SiO₂ contents suggest repeated scavenging of partially remelted
32 intrusive material in the mid-crust, and mixing with material from geochemically diverse sources.
33 Amphibole is an effective probe for deep crustal magmatism worldwide, and this approach offers a
34 new tool to explore the structure and chemistry of arc magmas, including those forming plutonic or
35 cumulate materials that offer no other constraints on melt composition.

36

37 **KEYWORDS**

38 Trace elements; partitioning; amphibole; subduction zones; Mount St Helens; magma plumbing

39

40 **INTRODUCTION**

41 Subduction zone volcanoes produce some of the most petrographically and geochemically complex
42 igneous rocks of any tectonic setting. This complexity arises from the diversity of processes operating
43 from melt generation, through crustal storage and differentiation, to magma transport and eruption.
44 An accurate understanding of these subterranean magmatic processes is essential for interpreting the
45 eruptive behaviour and hazards of volcanoes, as well as the formation and evolution of the continental
46 crust. Knowledge of the complexities of a volcanic plumbing region can also aid interpretation of
47 geophysical observations, as well as any temporal changes in eruptive products. Geophysical studies
48 commonly indicate the presence of low-seismic velocity or low resistivity regions in the middle to
49 deeper crust, that may be linked to the presence of fluids or melt (e.g. Pritchard and Gregg 2016).
50 Both geophysical and experimental studies also suggest that the lower crust at arcs may be dominated
51 by mafic minerals, including amphibole (Holbrook et al. 1992; Melekhova et al. 2015; Müntener and
52 Ulmer 2018), and this is corroborated by studies of exposed arc sections (e.g. DeBari and Greene
53 2011). However, this information can be hard to integrate with petrology, which tends to yield
54 information mainly about processes in the uppermost 10-15 km of the crust. We need, therefore, to

55 develop new petrological methods to interrogate processes operating within the deeper regions of the
56 crust at subduction zones.

57

58 Mount St Helens volcano, Washington, USA, is one of the most extensively studied and well
59 monitored subduction zone volcanoes in the world. It has been active for at least 272,000 years based
60 on K-Ar and Ar-Ar ages (Clynne et al. 2008; Clynne personal communication) but zircon ages >500
61 ka (Claiborne et al. 2010) suggest that the magmatic system in general has been active for
62 significantly longer. The explosive eruption of 1980 resulted in significant disruption to the regional
63 economy and infrastructure, as well as fatalities (Mason et al. 1980), and was followed by an
64 extended period of unrest and dome growth. The structure and form of the plumbing system
65 underneath the volcano is still debated. Several geophysical studies linked to the recent iMUSH
66 project (Witze 2014) have recognised broad regions of the deep crust (15-35 km) with seismic
67 velocity anomalies that have been interpreted as indicating the presence of melt (Hill et al. 2009;
68 Kiser et al. 2016; Flinders and Shen 2017), together with deep long-period earthquakes suggesting
69 movement of magma and/or magmatic fluids (Nichols et al. 2011). Petrological studies have shown
70 that the 1980-2006 dacites from Mount St Helens represent hybrid magmas with multiple crystal
71 populations from diverse sources (e.g. Berlo et al. 2007; Streck et al. 2008; Thornber et al. 2008;
72 Wanke et al. in press), inherited from different crustal sources and melting processes. This diversity of
73 petrologic products hints at a role for deep crustal processes, as seen in the geophysical imaging. In
74 contrast, melt inclusions show that the magmas were erupted from storage regions in the upper crust,
75 with recorded volatile saturation pressures of 120 to 240 MPa (Blundy and Cashman 2001, 2005;
76 Blundy et al. 2008) (5-10 km). This disconnect between geophysical and petrological investigations
77 implies a gap in our knowledge about the locations of melt differentiation, magma storage, and final
78 assembly and homogenisation.

79

80 Here, we present new details on processes operating throughout the arc crust beneath Mount St
81 Helens, using an innovative partitioning scheme that inverts the trace element chemistry of
82 amphiboles to yield equilibrium melt compositions. Amphibole is one of the most important mafic

83 minerals to form in the mid- and deep crust at arcs: it occurs early in the fractionation sequence of
84 many arc magmas and crystallises at moderate to high pressures (Nandedkar et al. 2016). Our
85 approach is to build multiple-regression relationships from a database of existing experimental
86 amphiboles, to link the partition coefficients of commonly used trace elements to the major element
87 chemistry of the amphibole. This method enables us to develop new insights into processes operating
88 in less evolved (andesitic) melts at relatively high pressures (mid- to lower crust). We show that the
89 magmatic system under Mount St Helens is dominated by mafic minerals including amphibole (\pm
90 clinopyroxene \pm Fe-Ti oxides) in the mid-crust, and by plagioclase (\pm Mg-hornblende) at low
91 pressures (<300 MPa). The compositions of amphibole equilibrium melts allow us to identify the
92 signatures of mid-crustal assimilation of older intrusive magmatism, which are blended together
93 during final magma assembly. This approach enables us to build a picture of the vertical extent and
94 progressive geochemical homogenisation of diverse magmatic components within the deeper volcanic
95 plumbing system.

96

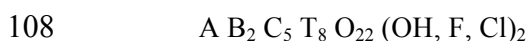
97 **METHODS**

98 **Amphibole structure and chemistry**

99 Amphibole is a common constituent of arc magmas and is particularly common in mafic to
100 intermediate magmas crystallising at high p_{H_2O} . This means it has the potential to record the evolving
101 chemical compositions of subduction zone magmas. The chemical composition of any magmatic
102 mineral depends on intrinsic parameters such as pressure, temperature and fO_2 , as well as the major-
103 and trace-element composition of its host melt. However, using this information to interpret magmatic
104 processes relies on a quantitative understanding of the partitioning behaviour of trace elements
105 between mineral and coexisting melt.

106

107 The double-chain crystal structure of amphibole can be described as:



109 and includes several crystallographic sites with different coordination and size (Leake et al. 1997),
110 that can accommodate a range of trace elements, including large ion lithophile elements (Rb, Sr, Ba),

111 Pb, U, Th, high field strength elements (Ti, Zr, Hf, Nb and Ta), rare earth elements (REE) and Y, and
112 transition metals (e.g. (Tiepolo et al. 2007). In terms of major element chemistry, Si and Al are the
113 dominant components of the tetrahedral (T) site; Mg, Fe (both Fe²⁺ and Fe³⁺), Ti, Mn and Al occupy
114 the small-medium octahedral (M1-3, 'C') sites; the larger octahedral (M4, 'B') site is dominated by
115 Ca and Na; and Na also sits in the partially filled 'A' site together with K. For the trace elements, Rb,
116 Ba and Pb have high ionic radius and are accommodated in the A site, while Sr can occur at either A
117 or M4 (Tiepolo et al. 2007). Tetravalent HFSE (Zr⁴⁺ and Hf⁴⁺) are incorporated onto M2 by
118 substitution for Ti (Oberti *et al.*, 2000) while Nb and Ta are incorporated preferentially into M1
119 (Tiepolo *et al.*, 2000b). REE and Y are thought to be partitioned into M4, substituting for either Ca
120 and/or Na (Brenan et al. 1995; Klein et al. 1997; Hilyard et al. 2000; Shimizu et al. 2017).

121
122 This strong crystal-chemical control on trace element partitioning means that variations in raw
123 amphibole trace element abundances can result either from real variations in the coexisting melt
124 composition during crystallisation, *and/or* from variations in amphibole major element chemistry at
125 fixed melt composition. Previous work shows that trace element partitioning in amphibole is related
126 to the degree of melt polymerization (Tiepolo et al. 2007; Nandedkar et al. 2016) but, in general, the
127 complexity of the amphibole crystallographic structure means that these controls are poorly
128 understood. Furthermore, for petrological studies a primary aim is typically to retrieve *unknown* melt
129 compositions from analyses of naturally occurring crystals; therefore the degree of melt
130 polymerization is generally not known. Instead we focus on the crystal-chemical controls on
131 partitioning outlined above, and use multiple regression (MR) methods on a large experimental
132 dataset drawn from the literature (table 1; Figure 1) to calculate trace element partition coefficients for
133 amphibole from the major element composition of the crystal. This enables us to predict the trace
134 element composition of its equilibrium host melt ("amphibole equilibrium melts", AEM). We used a
135 version of our earlier multiple regression study (see supplementary information; Zhang et al. 2017) to
136 find the corresponding major element chemistry of the AEM.

137

138 **Multiple regression analysis**

139 For the MR analysis, we used $^{Amph/L}D$ values reported in 13 experimental studies conducted over a
140 wide range of conditions (200-2,500 MPa, 780-1,100 °C, figure 1, table 1), using starting
141 compositions from basanite to rhyolite (Table 1; Figure 1). The experiments crystallised calcic
142 amphiboles in the range Pargasite – Edenite – Hastingsite - Magnesiohastingsite (MgHst) – Kaersutite
143 – Tschermakite (Tsch) – Magnesiohornblende (MgHbl). Obvious outliers were removed prior to
144 regression.

145
146 We carried out the MR analysis using the statistical software package R (R Core Team 2013), and
147 specifically the package ‘robustbase’ which includes routines to minimise the effects of outliers
148 during regression. Here we focus on temperature-independent regressions because temperature is
149 rarely known independently (or precisely) for petrological studies. Temperature undoubtedly can
150 affect partitioning (e.g. Green and Pearson 1985; Klein et al. 1997); therefore, we include
151 temperature-dependent regressions, for those elements where temperature was a statistically
152 significant parameter in the results (see supplementary information). We do not consider these further
153 but they are presented for completeness.

154
155 In the regression analysis, the natural logarithms of $^{Amph/L}D$ (lnD) were treated as dependent variables.
156 Amphibole stoichiometric formula components were considered as independent variables, including
157 tetrahedral Si (Si_T); M1-3 site Al (Al_{VI}), Ti, Fe^{3+} , and Fe^{2+} ; M4 site Ca (Ca_{M4}) and A-site Na (Na_A).
158 Tetrahedral-site Al (Al_T), Mg and Na_{M4} were excluded to avoid the issue of strong multi-collinearity
159 (following Zhang et al. 2017). Although some multi-collinearity between variables remains (most
160 commonly between Fe^{3+} and Fe^{2+}), this does not preclude successful application of the results, though
161 it does limit physical interpretation of trace element site occupancy (not a primary aim of our study).
162 We did not consider Cr and Mn (hosted in M1-3) or K (hosted in A site), due to their minor
163 abundances in amphibole and thus high relative analytical uncertainties. Because amphibole
164 stoichiometric formula calculations depend on ferric iron content, and the experiments cover a wide
165 range of fO_2 (e.g. from haematite-magnetite to magnetite-wüstite buffer, (Green and Pearson 1985)
166 we used the ‘average Fe^{3+} ’ approach (Leake et al. 1997) to calculate ferric and ferrous components,

167 following (Zhang et al. 2017). While this approach remains relatively inaccurate, it is better than
168 assuming $Fe_T = FeO$ (Schumacher 1991; Hawthorne and Oberti 2007; Locock 2014). Direct
169 measurement of $Fe^{3+}/\Sigma Fe$ in amphibole remains difficult, requiring Mössbauer or synchrotron
170 methods such as XANES (e.g. Dyar et al. 2016) and such measurements are rarely available. We
171 emphasise that replacing Fe^{3+} and Fe^{2+} with total Fe (Fe_T) in the regression does not significantly
172 affect the accuracy or precision of the regressions. All MR equations presented have residual standard
173 error (RSE) between 0.19-0.49 (Table 2). As a check of accuracy, the predicted partition coefficients
174 were plotted against the measured experimental partition coefficients, together with calculated 1σ and
175 2σ prediction intervals, and show good agreement (Figure 2; table 2; supplementary figures 1 and 2).

176

177 **Multiple regression equations**

178 Statistically significant MR results were retrieved for LILE (Rb and Sr), Pb, HFSE (Zr and Nb), REE
179 (La, Ce, Nd, Sm, Gd, Dy, Ho, Er, Yb, Lu) and Y. The output of each MR analysis is given as the
180 intercept and coefficients of the nominated independent variables, from which a multiple regression
181 equation can be derived (Table 2). For example, the equation for the prediction of $^{Amph/L}D_{Nb}$ (Eq. 5) is
182 expressed as:

$$183 \quad ^{Amph/L}D_{Nb} = \exp(-22.27 + 2.3241Si + 2.9786 Fe^{3+} + 1.44 Fe^{2+} + 3.7633 Ti + 1.8719 Ca)$$

184 This equation enables the Nb content of the amphibole equilibrium melt to be calculated, based on
185 knowledge of the amphibole major element composition (because this affects the structure and trace
186 element capacity of different crystallographic sites). The values of D_{REE} calculated using our MR
187 approach are similar to those derived by Shimizu et al. (2017) using a lattice strain model. Statistically
188 significant regressions could not be retrieved for several elements including Ba, Cs, Hf, Ta, and Sc,
189 typically because of low concentrations and a paucity of calibration data. A template for calculation of
190 partition coefficients using these methods is provided in the supplementary information.

191

192 **Electron microprobe analyses**

193 Amphiboles from the 1980-1986 eruption of Mount St Helens were analysed in polished 25 mm
194 epoxy rounds or standard polished thin sections. Major element analysis was carried out using a
195 Cameca SX-100 electron microprobe at Oregon State University. All analyses used a 1 μm beam
196 diameter, 30 nA beam current and 15 kV accelerating voltage. Count times were 60 seconds for Cl, 30
197 seconds for Mg, Ca, Ti, Mn, Fe, Al, and S, 20 seconds for F, K, and P, and 10 seconds for Na and Si.
198 Sodium, Si, and K were corrected to zero time intercepts. Background count times were half the peak
199 times. Kakanui hornblende (USNM 143965) was used as a secondary standard to check the accuracy
200 of the calibration.

201

202 **Laser ablation inductively coupled plasma mass spectrometry**

203 Trace element analysis of amphiboles was done by LA-ICP-MS at Oregon State University using an
204 ArF 193 nm Photon Machines G2 laser ablation system and a Thermo Scientific X-Series2
205 quadrupole ICP-MS following Loewen and Kent (2012). Amphiboles were analyzed using a 30 or 50
206 μm spot pulsed at 7 Hz for approximately 30 seconds. Standard reference material GSE-1G was used
207 as a calibration standard and GSD-1G, BHVO-2G, and BCR-2G were monitored as secondary
208 standards. Ca (from EPMA analyses) was used as the internal standard.

209

210 **RESULTS**

211 **Trace elements in Mount St Helens amphiboles and predicted melts**

212 We collected new major- and trace element analyses of amphiboles from Mount St. Helens dacites
213 erupted during May – August 1980 (including samples from Cashman and McConnell 2005), and also
214 processed published amphibole data from the 2004-2006 eruption (from Thornber et al. 2008). Most
215 amphiboles are MgHst-Tsch with a smaller population of MgHbl. MgHbl have Mg-numbers from
216 0.62 to 0.76 ($\text{Mg}/\text{Mg}+\text{Fe}^{2+}$) and $(\text{Na}+\text{K})_{\text{A}}$ of 0.32 to 0.58, whereas MgHst-Tsch have Mg-numbers
217 from 0.65 to 0.84 and $(\text{Na}+\text{K})_{\text{A}}$ of 0.39 to 0.61 (supplementary table). Trace element contents of the
218 amphiboles range from ~70-300 ppm Sr, 12-100 ppm Ba, ~20-150 ppm Zr, 1-30 ppm Nb and 15-80

219 ppm Y (supplementary table 2). Amphibole REE contents for the 1980 eruptions were analysed in the
220 same laboratory as those reported by (Thornber et al. 2008) and (Rowe et al. 2008), and their
221 compositions are consistent, typically in the range 1-10 ppm La and 2-15 ppm Sm.

222

223 The major element compositions of AEM were calculated following the approach of our previous MR
224 analysis results (see supplementary dataset for regression equations used; Zhang et al. 2017).

225 Compositions of AEM range from ~60 to 75 wt% SiO₂, and overlap with previously published
226 andesitic to dacitic whole rocks and with the less evolved (rhyodacite) end of the melt inclusion field
227 (Figure 3). SiO₂ contents are similar to those inferred using the approach of Ridolfi and Renzulli
228 (2012). MgHbl yield the most evolved AEM, with relatively high SiO₂, and these agree well with the
229 compositions of plagioclase-hosted melt inclusions (Blundy et al. 2008; 69-76 wt% SiO₂, 1.6-2.7 wt%
230 FeO, 2.3-3.2 wt% K₂O, 1.8-2.9 wt% CaO and 0.3- 0.65 wt% MgO, Figure 3). AEM for Tsch-MgHst
231 are more primitive (58-69 wt% SiO₂) and extend the melt inclusion trends backwards to overlap with
232 Mount St Helens whole rocks (Figure 3).

233

234 Trace element partition coefficients were calculated from equations constructed using the parameters
235 presented in table 2. These partition coefficients were then used to calculate the trace element
236 compositions of amphibole equilibrium melts. The calculated partition coefficients for Mount St
237 Helens amphiboles varied from 0.29 to 0.49 for Sr, from 0.14 to 1.0 for La, from 1.3 to 4.37 for Y and
238 from 0.3 to 2.4 for Nb (supplementary information). This variation is a result of the variable major
239 element chemistry of the crystals (or of zones within individual crystals) and emphasises the
240 importance of correcting for the effects of major element chemistry on trace element partitioning
241 (Figure 4). The majority of trace element analyses yield AEM compositions (supplementary table)
242 that fit very well with both melt inclusions and whole rocks (see Blundy et al. 2008 for melt
243 inclusions, and Blundy et al. 2008, Wanke et al. in press and Wanke et al. 2019 for sources of
244 compiled whole rock data for Mount St Helens). There are two exceptions. First, despite having a
245 statistically significant regression, calculated partition coefficients for Rb give very low predicted
246 melt concentrations (typically 2-10 ppm) that do not agree with melt inclusion compositions (~40-50

247 ppm); the reason for this is not clear. Second, a subset of analyses gives AEMs with trace element
248 concentrations up to 2-3 times higher than the main population (Figure 5), typically at intermediate
249 silica (59-68 wt% SiO₂); this will be discussed further below.

250

251 Dealing first with the main body of AEM compositions, Sr contents decrease continuously with
252 increasing SiO₂, projecting from the whole-rocks towards the plagioclase-hosted melt inclusions
253 (Figure 5), and suggesting compatible behaviour. The melt inclusions also show decreasing Sr
254 contents with increasing SiO₂, but with a steeper gradient than the AEMs (Figure 5). This is important
255 because it likely indicates a change in the crystallising assemblage (see below). The other trace
256 elements show variably incompatible behaviour. The rare earth element concentrations of AEM
257 overlap well with the more evolved whole rocks and the less evolved melt inclusions but are scattered
258 and typically show no significant variations with SiO₂, whereas the melt inclusions increase strongly
259 (Figure 5). In the 2004-2006 dataset (Thornber et al. 2008) MgHst-Tsch yield AEM similar to the
260 1980 eruptions, whereas MgHbl yield AEM with a similar range of LREE but slightly lower average
261 MREE and HREE concentrations (Figure 5). Similarly, Nb and Zr show little change with increasing
262 SiO₂ (perhaps increasing slightly) and correlate well with each other. Zircon concentrations in the
263 AEM are typically lower than those in the whole rocks (Figure 5), though there is some overlap as
264 well as considerable scatter. In contrast, the Nb and Zr concentrations of melt inclusions increase
265 more strongly with increasing differentiation (Figure 5).

266

267 Superimposed on these general patterns is considerable variability towards higher incompatible
268 element concentrations, mainly at intermediate silica (59-68 wt% SiO₂), as mentioned above. This is
269 most striking for Nb (up to 30 ppm), La (up to 37 ppm) and Zr (up to 306 ppm) but is also observed
270 for other REE and Y (Figure 5). These significantly higher melt trace element concentrations are
271 nonetheless similar to those of rare melt inclusions (Blundy et al. 2008) and some whole rocks
272 (Leeman et al. 1990; Wanke et al. in press; Wanke et al. 2019). We were not able to produce
273 statistically reliable AEM regressions for Ba, but the Ba concentrations of amphiboles correlate

274 strongly with Nb and Zr in the amphiboles. We would therefore also expect that Nb-rich AEM may
275 also have anomalous Ba contents.

276

277 Both Sm/Yb and La/Yb of AEM are essentially constant with increasing SiO₂, and again agree well
278 with both whole-rock and melt inclusions, in particular for La/Yb (Figure 6). In both cases, some
279 anomalous values are seen, in particular to high La/Yb at intermediate SiO₂. As with the HFSE, these
280 anomalous values are consistent with rare melt inclusion compositions (Figure 6).

281

282 **DISCUSSION**

283 **Upper crustal fractionation of dacites**

284 Amphibole equilibrium melts calculated from MgHbl are rhyodacitic, equivalent to the major element
285 compositions of less evolved melt inclusions, while MgHst-Tsch amphiboles are calculated to be in
286 equilibrium with andesite to dacite melts. The Sr concentrations of AEM from MgHbl coincide with
287 the Sr contents of melts in equilibrium with plagioclase phenocryst rims from the 1980s magmas
288 (150-300 ppm, Berlo et al. 2007), and with melt inclusion Sr concentrations. The Sr concentrations of
289 AEM decrease with increasing SiO₂, and AEM from MgHbl also have low Eu/Eu* (Figure 7),
290 indicating a strong negative Eu anomaly. Taken together, this is good evidence that the latest stages of
291 fractionation (phenocryst growth, but prior to crystallisation of the dacite groundmass) involve
292 rhyodacite melt crystallising abundant plagioclase and minor MgHbl at low to moderate pressures,
293 which would stabilise plagioclase (e.g. Rutherford et al. 1985; Moore and Carmichael 1998; Martel et
294 al. 1999; Blundy and Cashman 2001; Prouteau and Scaillet 2003). Fractionation dominated by
295 plagioclase ± hornblende is also consistent with the low bulk partition coefficients for Zr, Nb and Yb
296 that are required to generate significant enrichment during progressive crystallisation, as observed in
297 the melt inclusions. This general picture is consistent with existing understanding of the genesis of the
298 dacites (e.g. Pallister et al. 2008; Blundy et al. 2008) and therefore gives confidence that the
299 amphibole equilibrium melts are able to retrieve useful information about the magmatic system. We

300 note that the fractionation of minor orthopyroxene in the dacites probably has little effect on REE and
301 HFS concentrations, and our AEM calculations are therefore relatively insensitive to this.

302

303 **Generation of intermediate magmas**

304 The variation of Eu/Eu* in the AEM from MgHst-Tsch (Figure 7) indicates that plagioclase was also
305 crystallising actively at intermediate SiO₂, but the rate of Sr decrease with increasing SiO₂ is lower
306 than it is for the melt inclusions, suggesting that a lower proportion of plagioclase was fractionating
307 during crystallisation of the MgHst-Tsch than for the MgHbl. However, the whole rocks lack a Eu
308 anomaly (Figure 7), and some have higher Sr contents than MgHst-Tsch AEM, despite having similar
309 SiO₂ contents (Figure 5). This supports suggestions that the bulk rocks contain some feldspar ‘crystal
310 cargo’, in other words antecrystic material that is carried by the host melt (Blundy et al. 2008). The Sr
311 contents of intermediate AEM are consistent with those in equilibrium with most plagioclase cores
312 from the 1980s magmas (300-400 ppm), while the least evolved AEM have Sr concentrations similar
313 to those of unusually calcic, boxy-cellular plagioclase cores (An₆₇₋₈₂, 400-530 ppm Sr, Berlo et al.
314 2007). Similar plagioclase textures have been observed elsewhere including at Karymsky, Kamchatka
315 (Izbekov et al. 2002) and Colima, Mexico (Crummy et al. 2014) and have been variably attributed to
316 resorption during decompression (e.g. Nelson and Montana 1992); to resorption during mixing with
317 more primitive melts (Nakamura and Shimakita 1998; Izbekov et al. 2002); and to rapid skeletal
318 growth (for a summary see Streck 2008). For Mount St Helens, we interpret the overlap of MgHst-
319 Tsch AEM with plagioclase equilibrium melts (from Berlo et al. 2007) as an indication that these
320 cellular textures formed through mixing with more primitive (andesitic) melts within the volcanic
321 plumbing system, perhaps during mingling with more primitive hybrid basalts (Wanke et al. in press;
322 Wanke et al. 2019; see also below). Therefore the magmas arrive in the shallow system already
323 carrying a significant quantity of crystalline material, including both plagioclase crystals (which go on
324 to grow new rims in the shallow storage region) and amphibole. This is also consistent with U-series
325 ages for plagioclase which indicate mechanical mixing of older recycled crystals and younger
326 overgrowths (Cooper and Reid 2003).

327

328 The most primitive whole-rocks erupted from Mount St Helens (<55 wt% SiO₂) are geochemically
329 and isotopically heterogeneous, including an HFSE-enriched, intraplate-like component with elevated
330 TiO₂ and P₂O₅ and high La/Yb (Leeman et al. 1990; Smith and Leeman 1993; Bacon et al. 1997;
331 Leeman and Smith 2019; Wanke et al. 2019), as well as low-K olivine tholeiites with much lower
332 La/Yb (Wanke et al. 2019) and arc-type basaltic andesites with moderate La/Yb and depletion in
333 HFSE (Wanke et al. 2019). This diversity has been attributed to the result of decompression melting
334 of a heterogeneous, variably enriched mantle source region (Leeman & Smith 2019) with water-poor
335 margins producing HFSE-enriched magmas (Wanke et al. 2019). Domains that are either
336 metasomatised (Leeman et al. 2005) or experience greater contributions from slab-derived fluids
337 (Wanke et al. 2019) produce magmas with an arc-like geochemical signature. Similar conclusions
338 were drawn for the occurrence of Nb-rich basalts from Borneo (Macpherson et al. 2010). At Mount St
339 Helens, the degree of whole-rock trace element heterogeneity decreases with increasing SiO₂,
340 consistent with mixing and homogenisation of melts during the earliest stages of fractionation
341 (Leeman & Smith 2019; Wanke et al. 2019). From 55 to 70 wt% SiO₂, whole-rock concentrations of
342 trace elements such as Nb, Zr, La, Sm, Y and Yb are approximately constant or decrease slightly
343 whereas La/Yb increases slightly and Sm/Yb is flat (see Figure 6). These trace element patterns are
344 generally not consistent with generation of the more evolved rocks by low-pressure fractional
345 crystallisation from primitive parental magmas, which would result in incompatible behaviour for
346 these elements (Smith and Leeman 1987, 1993; Gardner et al. 1995; Blundy et al. 2008; Pallister et al.
347 2008; Sisson et al. 2014). Although the erupted magmas contain various cumulate gabbro inclusions
348 (Scarfe and Fujii 1987; Heliker 1995), U-Pb dates for zircons from these samples show that they are
349 not cognate to the Mount St Helens system but derive from an older (Miocene) intrusion (Pallister et
350 al. 2008, 2017). Amphibole equilibrium melts from MgHst-Tsch also show approximately constant
351 (though scattered) HFSE and HREE, concentrations, and slightly increasing La/Yb, constant Sm/Yb
352 and decreasing Dy/Yb from 55-70 wt% SiO₂ (Figure 6). In contrast, the melt inclusions show
353 increasing LREE, MREE and HFSE concentrations and decreasing La/Yb and Sm/Yb but nearly
354 constant Dy/Yb, consistent with low-pressure fractionation of plagioclase and MgHbl (Blundy et al.
355 2008). This suggests that the conditions for generation of intermediate melts (as sampled by MgHst-

356 Tsch) were different from the formation conditions of more evolved rhyodacite and rhyolite melts, as
357 sampled by the melt inclusions.

358

359 The trace element patterns of whole rocks have previously been ascribed to (i) melting in the presence
360 of garnet, which would retain HFS and HREE (Smith and Leeman 1987), (ii) mixing of replenishing
361 primitive melts with either highly evolved residual liquids or with low degree partial melts of older
362 crustal materials (Pallister et al. 2008; Claiborne et al. 2010; Sisson et al. 2014), and (iii) high
363 pressure fractionation in the presence of garnet, amphibole and/or ilmenite (Blundy et al. 2008).
364 Recent experiments show that the dacite is not in equilibrium with garnet at near-liquidus conditions
365 between 400 and 1200 MPa, indicating that amphibole \pm oxide is a better candidate to retain HFS and
366 MREE-HREE in evolved melts at high pressure (Blatter et al. 2017). The REE compositions of our
367 calculated AEMs show increasing La/Yb, constant Sm/Yb and decreasing Dy/Yb with increasing
368 SiO₂ (Figure 6). These patterns are consistent with fractionation of amphibole \pm clinopyroxene
369 (Davidson et al. 2007).

370

371 The MgHst-Tsch amphiboles themselves are similar to near-liquidus experimental amphiboles
372 produced from Mount St Helens dacite at 700-900 MPa (Blatter et al. 2017). Those experiments also
373 generated liquids similar to the more evolved end of our AEM array, and similar to the least evolved
374 melt inclusions reported by Blundy et al. (2008). Our AEM data therefore support suggestions that
375 while dacite magmas with a trace element signature depleted in HFS and HREE could be formed
376 through intermediate pressure fractionation involving amphibole, they could also be generated
377 through partial (re)-melting of amphibole-bearing gabbros (Blatter et al. 2017).

378

379 Our amphibole dataset contains crystals with normal zoning and those with reverse zoning, suggesting
380 that both mixing and fractionation are occurring. This is also consistent with some plagioclase zoning
381 profiles (Smith and Leeman 1987; Streck et al. 2008; Cashman and Blundy 2013) and with co-
382 variations between crystallinity, composition and inferred temperature of whole-rocks (Gardner et al.
383 1995). We suggest, therefore, that andesite and primitive dacite melts fractionate a mafic assemblage

384 including amphibole (MgHst-Tsch) \pm pyroxene \pm Fe-Ti oxide \pm plagioclase at moderately high
385 pressures (e.g. >400 MPa; (Alonso-Perez et al. 2009; Blatter et al. 2017). At these mid-crustal
386 pressures, plagioclase crystallisation is suppressed relative to other phases as a result of high water
387 concentrations (Eggler 1972; Blundy and Cashman 2001; Thornber et al. 2008; Melekhova et al.
388 2015; Blatter et al. 2017), consistent with the relatively shallow decrease of Sr with increasing SiO₂ in
389 the AEM (Figure 4). Mixing between multiple small aliquots of fractionating melt over time, as well
390 as with partial (re-)melts of older intrusive materials also contributes to the formation of a range of
391 dacite magmas. The magmas ascend to shallow pressures (<300 MPa) where crystallisation is
392 dominated by plagioclase \pm MgHbl, resulting in low bulk Ds for HFS and REE. Overall, our new
393 dataset gives a picture of a vertically extensive magma plumbing system, involving mid- to lower-
394 crustal pressure fractionation of a mafic assemblage including amphibole \pm pyroxene \pm Fe-Ti oxides;
395 and low-pressure fractionation dominated by plagioclase \pm MgHbl. It is notable that our calculated
396 AEM do not record any melts more primitive than andesite, and this is consistent with observations
397 that mingled basalts and basaltic andesites typically contain an assemblage of olivine + plagioclase +
398 clinopyroxene \pm orthopyroxene (Wanke et al. 2019; Pallister et al. 2017); and this may reflect
399 insufficiently high water concentrations to stabilise amphibole in these primitive melts (e.g. Leeman
400 & Smith 2019; Rea et al. 2012; Gardner et al. 1995).

401

402 **Partial remelting of older intrusives, or source heterogeneity?**

403 The trace element AEM data show significant scatter towards high Nb, Zr, and REE concentrations at
404 intermediate SiO₂ (Figure 5). These equilibrium melt compositions are supported by rare melt
405 inclusions with elevated Nb, Zr, La and La/Yb, which previously appeared to be conspicuous outliers
406 (Blundy et al. 2008), and are also similar to some Castle Creek dacite whole-rocks with elevated trace
407 element concentrations (Figure 5; data from Wanke et al. in press; Wanke et al. 2019). The absolute
408 Nb concentrations are similar to those of enriched, intraplate-like basaltic whole rocks from Mount St
409 Helens (Leeman et al. 1990), but their major element compositions are more evolved, similar to those
410 from neighbouring Mt Adams (Hildreth and Fierstein 1997; Jicha et al. 2009), which show unusually
411 strong geochemical enrichment with increasing SiO₂. These anomalously Nb-rich AEM compositions

412 were determined from both amphibole cores with non-enriched rims and from amphibole rims on
413 non-enriched cores, and texturally the crystals show no consistent features that might indicate a
414 distinctive origin. This indicates both mechanical incorporation of Nb-enriched amphibole cores into
415 more geochemically typical Mount St Helens melts; and interaction of geochemically typical
416 amphibole crystals with an incompatible-element enriched *melt*. Some of the Castle Creek era dacite
417 whole-rocks approach our trace-element enriched AEM in composition, albeit showing more muted
418 variations (Figure 5). During the Castle Creek period, intrusion and mixing of basalts and basaltic
419 andesites with the resident dacite occurred (Wanke et al. in press; Wanke et al. 2019), accompanying
420 a shift to hotter, more H₂O-poor dacites (Gardner et al. 1995). This suggests that the AEM may be
421 recording melts, generated during mixing, that are only transiently present in the magmatic plumbing
422 system. In general, however, the compositional variability of melts recorded by the AEM exceeds the
423 variability of the andesite-dacite whole rocks, which are relatively homogeneous. We infer that the
424 sub-surface storage and plumbing system can efficiently homogenise diverse melt components that
425 can now only be identified through the distinctive trace element signature that is captured within the
426 compositions of the mineral phases.

427

428 Solidification of evolved dacites at within the crust under Mount St. Helens would generate diorites
429 and granodiorites with low-temperature minerals such as biotite, zircon and apatite, as shown by the
430 presence of these as interstitial phases in plutonic inclusions in Mount St Helens magmas (Heliker
431 1995; Wanke et al. 2019). Although the plutonic inclusions typically have older (Tertiary) zircon ages
432 (Pallister et al. 2017), similar mineralogy is observed in the oldest (Ape Canyon) deposits from Mount
433 St Helens, which included low-temperature dacites and rhyodacites with quartz and biotite (Clynne et
434 al. 2008). Therefore, partial remelting of plutonic residua from earlier intrusive events or magmatic
435 stages would generate disequilibrium melts enriched in Zr and HREE (from zircon), LREE (from
436 apatite) and Ba, Rb and Nb (from biotite) (Villaros et al. 2009; McLeod et al. 2012). The scattered
437 trace element enrichments seen in the AEM could be generated by mixing with limited quantities of
438 such partial melts. This model is consistent with the presence of rare biotite inclusions in amphibole
439 phenocrysts from the 1980s magmas (this study, Loewen 2013) and in older tephros (Smith and

440 Leeman 1987); with the presence of zircons with significantly older ages in magmas from all eruptive
441 periods, indicating recycling of older components (Claiborne et al. 2010); and with the decoupling of
442 Ra-Th and U-Th ages of plagioclase crystals, which can also be explained by mechanical mixtures of
443 older recycled crystals and younger overgrowths (Cooper and Reid 2003). The higher Zr
444 concentrations of whole rocks than AEM (Figure 5) are also consistent with some mechanical
445 incorporation of zircon into the whole rocks, notwithstanding the scatter and uncertainty on the
446 calculated AEM. This finding emphasises the importance of repeated episodes of intrusion and
447 remobilisation during the formation of arc magmas, and the efficiency of the shallow magma storage
448 system in homogenising diverse inputs. We suggest that the extent of partial melting would be
449 controlled by the local heat flux, available volatile contents and the solid mineral assemblage of the
450 plutonic component, resulting in localised variations in the absolute concentrations of different trace
451 elements.

452

453 Finally, it is also possible that the trace elements of amphiboles are reflective of mantle source
454 heterogeneity. The concentrations of Nb in the most enriched AEM are similar to those of the high-
455 Nb basalts erupted at Mount St Helens, derived from an enriched source, even though the major
456 element compositions are more evolved. It is therefore plausible that some amphiboles (perhaps those
457 with ‘enriched’ cores) actually represent components of differentiating intraplate-like magmas within
458 the plumbing system at Mount St Helens. In principle this hypothesis could be tested using fluid-
459 mobile elements or other indicators of earlier metasomatism; in addition careful petrographic
460 observation of Cascades amphiboles is now required to examine any characteristic textural indications
461 of a distinct origin.

462

463 **Summary – extending the crystal record to the lower crust**

464 Our trace element regression analysis opens up the potential for using amphibole to interrogate the
465 nature of deep crustal melt evolution in arcs and other hydrous magmas. This gives a new way to

466 understand the complex nature of subterranean magma systems, and the interactions between multiple
467 batches of magma, and between magmas and solid residues from older intrusive events. Amphibole
468 may come early in the fractionation sequence for mafic magmas (Alonso-Perez et al. 2009;
469 Krawczynski et al. 2012; Melekhova et al. 2015), enabling investigation of earlier stages of magma
470 evolution. Unlike olivine and plagioclase, amphibole contains significant concentrations of a broad
471 range of trace elements, and this may permit quantitative modelling of petrogenetic processes. The
472 method is particularly sensitive to minor proportions of chemically distinct components that are
473 otherwise efficiently homogenised during mid- to low-pressure magma fractionation and ascent.
474 Amphibole is stable across a wide variety of magma compositions, and can specifically trace hydrous
475 magmas found in subduction zone systems. Our method is therefore applicable widely, including in
476 cumulate and plutonic rocks, and will help to construct and refine conceptual models of subvolcanic
477 plumbing systems in arcs.

478

479 **Acknowledgements**

480 Jing Zhang was supported by a Durham Doctoral Studentship (Durham University), China
481 Scholarship Council (201206170178) and National Natural Science Foundation of China (41702362).
482 Madeleine Humphreys was supported by a Royal Society University Research Fellowship. AJRK and
483 ML were supported by National Science Foundation grants 1425491 and 1028707. GFC was
484 supported by a NERC grant (NE/K010824/1). We thank Mark Allen and Ed Llewellyn for helpful
485 comments on an earlier version of the manuscript, and John Pallister and Mike Clynne for additional
486 internal reviews that significantly improved the text. We acknowledge Mike Krawczynski and an
487 anonymous reviewer for helpful reviews. We greatly appreciate helpful discussions with Maren
488 Wanke as well as early access to her whole-rock geochemical dataset. Any use of trade, firm, or
489 product names is for descriptive purposes only and does not imply endorsement by the U.S.
490 Government.

491

492 **Author contributions**

493 JZ, MCSH and AJRK conceived the project. JZ and GFC performed the multiple regression and ML
494 conducted the major and trace element analysis. MCSH and GFC drafted the text and all authors
495 contributed to discussion of the data and writing of the manuscript.

496

497 **References**

- 498 Adam J, Green T (2006) Trace element partitioning between mica- and amphibole-bearing
499 garnet lherzolite and hydrous basanitic melt: 1. Experimental results and the
500 investigation of controls on partitioning behaviour. *Contrib Mineral Petrol* 152:1–17
- 501 Adam J, Green TH (1994) The effects of pressure and temperature on the partitioning of Ti,
502 Sr and REE between amphibole, clinopyroxene and basanitic melts. *Chem Geol*
503 117:219–233
- 504 Adam J, Green TH, Sie SH (1993) Proton microprobe determined partitioning of Rb, Sr, Ba,
505 Y, Zr, Nb and Ta between experimentally produced amphiboles and silicate melts
506 with variable F content. *Chem Geol* 109:29–49
- 507 Alonso-Perez R, Müntener O, Ulmer P (2009) Igneous garnet and amphibole fractionation in
508 the roots of island arcs: experimental constraints on andesitic liquids. *Contrib Mineral*
509 *Petrol* 157:541. doi: DOI 10.1007/s00410-008-0351-8
- 510 Bacon CR, Bruggman PE, Christiansen RL, et al (1997) Primitive magmas at five Cascades
511 volcanic fields: melts from hot, heterogeneous sub-arc mantle. *Can Mineral* 35:397–
512 423
- 513 Berlo K, Blundy J, Turner S, Hawkesworth C (2007) Textural and chemical variation in
514 plagioclase phenocrysts from the 1980 eruptions of Mount St. Helens, USA. *Contrib*
515 *Mineral Petrol* 154:291–308. doi: 10.1007/s00410-007-0194-8
- 516 Blatter DL, Sisson TW, Hankins WB (2017) Voluminous arc dacites as amphibole reaction-
517 boundary liquids. *Contrib Mineral Petrol* 172:27:27. doi: 10.1007/s00410-017-1340-6
- 518 Blundy J, Cashman K (2001) Ascent-driven crystallisation of dacite magmas at Mount St
519 Helens, 1980–1986. *Contrib Mineral Petrol* 140:631–650. doi:
520 10.1007/s004100000219
- 521 Blundy J, Cashman K (2005) Rapid decompression-driven crystallization recorded by melt
522 inclusions from Mount St. Helens volcano. *Geology* 33:793–796
- 523 Blundy J, Cashman KV, Berlo K (2008) Evolving magma storage conditions beneath Mount
524 St. Helens inferred from chemical variations in melt inclusions from the 1980-1986
525 and current (2004-2005) eruptions. In: *A volcano rekindled: The renewed eruption of*

- 526 Mount St. Helens, 2004-2006. U.S. Geological Survey Professional Paper 1750, Ed:
527 David R. Sherrod, William E. Scott, and Peter H. Stauffer pp 755–790
- 528 Brenan JM, Shaw HF, Ryerson FJ, Phinney DL (1995) Experimental determination of trace-
529 element partitioning between pargasite and a synthetic hydrous andesitic melt. *Earth*
530 *Planet Sci Lett* 135:1–11
- 531 Cashman K, Blundy J (2013) Petrological cannibalism: the chemical and textural
532 consequences of incremental magma body growth. *Contrib Mineral Petrol* 166:703–
533 729. doi: 10.1007/s00410-013-0895-0
- 534 Cashman KV, McConnell S (2005) Multiple levels of magma storage during the 1980
535 summer eruptions of Mount St. Helens, WA. *Bull Volcanol* 68:57–75
- 536 Claiborne LL, Miller CF, Flanagan DM, et al (2010) Zircon reveals protracted magma
537 storage and recycling beneath Mount St. Helens. *Geology* 38:1011–1014
- 538 Clyne MA, Calvert AT, Wolfe EW, et al (2008) The Pleistocene eruptive history of Mount
539 St. Helens, Washington, from 300,000 to 12,800 years before present. In: *A volcano*
540 *rekindled: The renewed eruption of Mount St. Helens, 2004-2006*. U.S. Geological
541 Survey Professional Paper 1750, Ed: David R. Sherrod, William E. Scott, and Peter
542 H. Stauffer, pp 593-627
- 543 Cooper KM, Reid MR (2003) Re-examination of crystal ages in recent Mount St. Helens
544 lavas: implications for magma reservoir processes. *Earth Planet Sci Lett* 213:149–167
- 545 Crummy JM, Savov IP, Navarro-Ochoa C, et al (2014) High-K Mafic Plinian Eruptions of
546 Volcan de Colima, Mexico. *J Petrol* 55:2155–2192. doi: 10.1093/petrology/egu053
- 547 Dalpé C, Baker DR (2000) Experimental investigation of large-ion-lithophile-element-, high-
548 field-strength-element- and rare-earth-element-partitioning between calcic amphibole
549 and basaltic melt: the effects of pressure and oxygen fugacity. *Contrib Mineral Petrol*
550 140:233–250
- 551 Davidson J, Turner S, Handley H, et al (2007) Amphibole “sponge” in arc crust? *Geology*
552 35:787–790
- 553 DeBari SM, Greene AR (2011) Vertical stratification of composition, density, and inferred
554 magmatic processes in exposed arc crustal sections. In: *Arc-continent collision*.
555 Springer-Verlag, Berlin Heidelberg, pp 121–144. Ed: D. Brown and P. Ryan.
- 556 Dyar MD, Breves EA, Gunter ME, et al (2016) Use of multivariate analysis for synchrotron
557 micro-XANES analysis of iron valence state in amphiboles. *Am Mineral* 101:1171–
558 1189
- 559 Eggler DH (1972) Amphibole stability in H₂O-undersaturated calc-alkaline melts. *Earth*
560 *Planet Sci Lett* 15:28–34
- 561 Flinders AF, Shen Y (2017) Seismic evidence for a possible deep crustal hot zone beneath
562 Southwest Washington. *Sci Rep* 7:7400. doi: DOI:10.1038/s41598-017-07123-w

- 563 Gardner JE, Carey S, Rutherford MJ, Sigurdsson, Haraldur (1995) Petrologic diversity in
564 Mount St. Helens dacites during the last 4,000 years: implications for magma mixing.
565 *Contrib Mineral Petrol* 119:224–238
- 566 Green TH, Pearson NJ (1985) Experimental determination of REE partition coefficients
567 between amphibole and basaltic to andesitic liquids at high pressure. *Geochim*
568 *Cosmochim Acta* 49:1465–1468
- 569 Hawthorne FC, Oberti R (2007) Amphiboles: crystal chemistry. *Rev Mineral Geochem* 67:1–
570 54
- 571 Heliker C (1995) Inclusions in Mount St. Helens dacite erupted from 1980 through 1983. *J*
572 *Volcanol Geotherm Res* 66:115–135
- 573 Hildreth W, Fierstein J (1997) Recent eruptions of Mount Adams, Washington Cascades,
574 USA. *Bull Volcanol* 58:472–490
- 575 Hill GJ, Caldwell TG, Heise W, et al (2009) Distribution of melt beneath Mount St Helens
576 and Mount Adams inferred from magnetotelluric data. *Nat Geosci* 2:785–789
- 577 Hilyard M, Nielsen RL, Beard JS, et al (2000) Experimental determination of the partitioning
578 behaviour of rare earth and high field strength elements between pargasitic amphibole
579 and natural silicate melts. *Geochim Cosmochim Acta* 64:1103–1120
- 580 Holbrook SW, Mooney WD, Christensen NI (1992) The seismic velocity structure of the
581 deep continental crust. In: *Continental Lower Crust*. Elsevier, Amsterdam, Ed: D.M.
582 Fountain, R. Arculus, and R. Kay pp 1–43.
- 583 Izbekov PE, Eichelberger JC, Patino LC, et al (2002) Calcic cores of plagioclase phenocrysts
584 in andesite from Karymsky volcano: Evidence for rapid introduction by basaltic
585 replenishment. *Geology* 30:799–802
- 586 Jicha BR, Hart GL, Johnson CM, et al (2009) Isotopic and trace element constraints on the
587 petrogenesis of lavas from the Mount Adams volcanic field, Washington. *Contrib*
588 *Mineral Petrol* 157:189–207
- 589 Kiser E, Palomeras I, Levander A, et al (2016) Magma reservoirs from the upper crust to the
590 MOHO inferred from high-resolution V_p and V_s models beneath Mount St. Helens,
591 Washington State, USA. *Geology* 44:411–414. doi: doi:10.1130/G37591.1
- 592 Klein M, Stosch H-G, Seck HA (1997) Partitioning of high field-strength and rare-earth
593 elements between amphibole and quartz-dioritic to tonalitic melts: an experimental
594 study. *Chem Geol* 138:257–271
- 595 Krawczynski MJ, Grove TL, Behrens H (2012) Amphibole stability in primitive arc magmas:
596 effects of temperature, H₂O content, and oxygen fugacity. *Contrib Mineral Petrol*
597 164:317–339. doi: 10.1007/s00410-012-0740-x
- 598 LaTourrette T, Hervig RL, Holloway JR (1995) Trace element partitioning between
599 amphibole, phlogopite, and basanite melt. *Earth Planet Sci Lett* 135:13–30

- 600 Leake BE, Woolley AR, Arps CES, et al (1997) Nomenclature of amphiboles: report of the
601 subcommittee on amphiboles of the International Mineralogical Association,
602 Commission on New Minerals and Mineral Names. *Can Mineral* 35:219–246
- 603 Leeman WP, Lewis JF, Evarts RC, et al (2005) Petrologic constraints on the thermal structure
604 of the Cascades arc. *J Volcanol Geotherm Res* 140:67–105
- 605 Leeman WP, Smith DR (2018) The role of magma mixing, identification of mafic magma
606 inputs, and structure of the underlying magmatic system at Mount St. Helens. *Am*
607 *Mineral Press* 1925–1944
- 608 Leeman WP, Smith DR, Hildreth W, et al (1990) Compositional diversity of late Cenozoic
609 basalts in a transect across the southern Washington Cascades: Implications for
610 subduction zone magmatism. *J Geophys Res* 95:19561–19582
- 611 Li L, Xiong XL, Liu XC (2017) Nb/Ta fractionation by amphibole in hydrous basaltic
612 systems: Implications for arc magma evolution and continental crust formation. *J*
613 *Petrol* 58:3–28
- 614 Locock AJ (2014) An Excel spreadsheet to classify chemical analyses of amphiboles
615 following the IMA 2012 recommendations. *Comput Geosci* 62:1–11
- 616 Loewen MW (2013) Volatile mobility of trace metals in volcanic systems. PhD, Oregon State
617 University
- 618 Loewen MW, Kent AJR (2012) Sources of elemental fractionation and uncertainty during the
619 analysis of semi-volatile metals in silicate glasses using LA-ICP-MS. *J Anal At*
620 *Spectrom* 27:1502. doi: 10.1039/c2ja30075c
- 621 Macpherson CG, Chiang KK, Hall R, et al (2010) Plio-Pleistocene intra-plate magmatism
622 from the southern Sulu Arc, Semporna peninsula, Sabah, Borneo: Implications for
623 high-Nb basalt in subduction zones. *J Volcanol Geotherm Res* 190:25–38
- 624 Martel C, Pichavant M, Holtz F, et al (1999) Effects of fO_2 and H_2O on andesite phase
625 relations between 2 and 4 kbar. *J Geophys Res* 104:29453–29470
- 626 Mason KR, Grant L, Furlow E (1980) The economic effects of the eruptions of Mount St.
627 Helens. U.S. International Trade Commission publication 1096, 84 pp
- 628 McLeod CL, Davidson JP, Nowell GM, de Silva SL (2012) Disequilibrium melting during
629 crustal anatexis and implications for modeling open magmatic systems. *Geology*
630 40:435–438
- 631 Melekhova E, Blundy J, Robertson R, Humphreys MCS (2015) Experimental evidence for
632 polybaric differentiation of primitive arc basalt beneath St. Vincent, Lesser Antilles. *J*
633 *Petrol* 56:161–192
- 634 Moore G, Carmichael ISE (1998) The hydrous phase equilibria (to 3 kbar) of an andesite and
635 basaltic andesite from western Mexico: constraints on water content and conditions of
636 phenocryst growth. *Contrib Mineral Petrol* 130:304–319

- 637 Müntener O, Ulmer P (2018) Arc crust formation and differentiation constrained by
638 experimental petrology. *Am J Sci* 318:64–89
- 639 Nakamura M, Shimakita S (1998) Dissolution origin and syn-entrapment compositional
640 change of melt inclusion in plagioclase. *Earth Planet Sci Lett* 161:119–133
- 641 Nandedkar RH, Hürlimann N, Ulmer P, Müntener O (2016) Amphibole-melt trace element
642 partitioning of fractionating calc-alkaline magmas in the lower crust: an experimental
643 study. *Contrib Mineral Petrol* 171:71. doi: 10.1007/s00410-016-1278-0
- 644 Nelson ST, Montana A (1992) Sieve-textured plagioclase in volcanic rocks produced by
645 rapid decompression. *Am Mineral* 77:1242–1249
- 646 Nicholls IA, Harris KL (1980) Experimental rare earth element partition coefficients for
647 garnet, clinopyroxene and amphibole coexisting with andesitic and basaltic liquids.
648 *Geochim Cosmochim Acta* 44:287–308
- 649 Nichols ML, Malone SD, Moran SC, et al (2011) Deep long-period earthquakes beneath
650 Washington and Oregon volcanoes. *J Volcanol Geotherm Res* 200:116–128
- 651 Pallister JS, Clynne MA, Wright HM, et al (2017) Field-trip guide to Mount St. Helens,
652 Washington - An overview of the eruptive history and petrology, tephra deposits, 1980
653 pyroclastic density current deposits, and the crater. US Geol Surv Sci Investig Rep
654 2017–5022–D, 65 pp
- 655 Pallister JS, Thornber CR, Cashman KV, et al (2008) Petrology of the 2004-2005 Mount St.
656 Helens lava dome - implications for magmatic plumbing and eruption triggering. In:
657 A volcano rekindled: The renewed eruption of Mount St. Helens, 2004-2006. U.S.
658 Geological Survey Professional Paper 1750, Ed: David R. Sherrod, William E. Scott,
659 and Peter H. Stauffer pp 647–702
- 660 Pritchard ME, Gregg PM (2016) Geophysical evidence for silicic crustal melt in the
661 continents: Where, what kind, and how much? *Elements* 12:121–127. doi:
662 10.2113/gselements.12.2.121
- 663 Prouteau G, Scaillet B (2003) Experimental Constraints on the Origin of the 1991 Pinatubo
664 Dacite. *J Petrol* 44:2203–2241. doi: 10.1093/petrology/egg075
- 665 R Core Team (2013) R: A language and environment for statistical computing. R Foundation
666 for Statistical Computing, Vienna, Austria. URL <http://www.R-project.org/>
- 667 Rea J, Wallace PJ, Clynne MA (2012) Pre-eruptive volatile content of mafic magma from the
668 2.0-1.7 ka Castle Creek eruptive period, Mount St. Helens. p V53C–2853
- 669 Ridolfi F, Renzulli A (2012) Calcic amphiboles in calc-alkaline and alkaline magmas:
670 thermobarometric and chemometric empirical equations valid up to 1,130°C and 2.2
671 GPa. *Contrib Mineral Petrol* 163:877–895. doi: 10.1007/s00410-011-0704-6
- 672 Rowe MC, Kent AJR, Thornber CR (2008) Using amphibole phenocrysts to track vapor
673 transfer during magma crystallization and transport: An example from Mount St.
674 Helens, Washington. *J Volcanol Geotherm Res* 178:593–607. doi:
675 10.1016/j.jvolgeores.2008.01.012

- 676 Rutherford MJ, Sigurdsson, Haraldur, Carey S, Davis A (1985) The May 18, 1980, eruption
677 of Mount St. Helens 1. Melt composition and experimental phase equilibria. *J*
678 *Geophys Res* 90:2929–2947
- 679 Scarfe CM, Fujii T (1987) Petrology of crystal clots in the pumice of Mount St Helens’
680 March 19, 1982 eruption; significant role of Fe-Ti oxide crystallization. *J Volcanol*
681 *Geotherm Res* 34:1–14
- 682 Schumacher JC (1991) Empirical ferric iron corrections: necessity, assumptions, and effects
683 on selected geothermobarometers. *Mineral Mag* 55:3–18
- 684 Shimizu K, Liang Y, Sun C, et al (2017) Parameterized lattice strain models for REE
685 partitioning between amphibole and silicate melt. *Am Mineral* 102:2254–2267
- 686 Sisson TW (1994) Hornblende-melt trace-element partitioning measured by ion microprobe.
687 *Chem Geol* 117:331–344
- 688 Sisson TW, Salters VJM, Larson PB (2014) Petrogenesis of Mount Rainier andesite: Magma
689 flux and geologic controls on the contrasting differentiation styles at stratovolcanoes
690 of the southern Washington Cascades. *GSA Bull* 126:122–144
- 691 Smith DR, Leeman WP (1993) The origin of Mount St. Helens andesites. *J Volcanol*
692 *Geotherm Res* 55:271–303
- 693 Smith DR, Leeman WP (1987) Petrogenesis of Mount St. Helens dacitic magmas. *J Geophys*
694 *Res* 92:10313–10334
- 695 Streck MJ (2008) Mineral textures and zoning as evidence for open system processes. *Rev*
696 *Mineral Geochem* 69:595–622
- 697 Streck MJ, Broderick CA, Thornber CR, et al (2008) Plagioclase populations and zoning in
698 dacite of the 2004-2005 Mount St. Helens eruption: constraints for magma origin and
699 dynamics. In: *A volcano U.S. Geological Survey Professional Paper 1750*, Ed: David
700 R. Sherrod, William E. Scott, and Peter H. Stauffer dled: The renewed eruption of
701 Mount St. Helens, 2004-2006. pp 791–808
- 702 Taylor SR, McLennan SM (1981) The composition and evolution of the continental crust:
703 rare earth element evidence from sedimentary rocks. *Philos Trans R Soc Lond A*
704 301:381–399
- 705 Thornber CR, Pallister JS, Lowers HA, et al (2008) Chemistry, mineralogy, and petrology of
706 amphibole in Mount St. Helens 2004-2006 dacite. In: *A volcano rekindled: The*
707 *renewed eruption of Mount St. Helens, 2004-2006. U.S. Geological Survey*
708 *Professional Paper 1750*, Ed: David R. Sherrod, William E. Scott, and Peter H.
709 Stauffer pp 727–754
- 710 Tiepolo M, Bottazzi P, Foley SF, et al (2001) Fractionation of Nb and Ta from Zr and Hf at
711 mantle depths: the role of titanian pargasite and kaersutite. *J Petrol* 42:221–232
- 712 Tiepolo M, Oberti R, Zanetti A (2007) Trace-element partitioning between amphibole and
713 silicate melt. *Rev Mineral Geochem* 67:417–452

714 Tiepolo M, Vannucci R, Bottazzi P, et al (2000a) Partitioning of rare earth elements, Y, Th,
715 U, and Pb between pargasite, kaersutite, and basanite to trachyte melts: Implications
716 for percolated and veined mantle. *Geochem Geophys Geosystems* 1:n/a–n/a. doi:
717 10.1029/2000GC000064

718 Tiepolo M, Vannucci R, Oberti R, et al (2000b) Nb and Ta incorporation and fractionation in
719 titanian pargasite and kaersutite: crystal–chemical constraints and implications for
720 natural systems. *Earth Planet Sci Lett* 176:185–201. doi: 10.1016/S0012-
721 821X(00)00004-2

722 Villaros A, Stevens G, Moyen J-F, Buick IS (2009) The trace element compositions of S-type
723 granites: evidence for disequilibrium melting and accessory phase entrainment in the
724 source. *Contrib Mineral Petrol* 158:543–561

725 Wanke, M., Karakas, O., & Bachmann, O. (in press) The genesis of arc dacites: the case of
726 Mount St. Helens, WA. *Contributions to Mineralogy and Petrology* (in press)

727 Wanke M, Clynne MA, von Wykradt-Huchtenbruck A, et al (2019) Geochemical and
728 petrologic diversity of mafic magmas from Mount St. Helens. *Contrib Mineral Petrol*
729 in revision:

730 Witze A (2014) Survey probes volcano’s depths. *Nature* 511:136–137

731 Zhang J, Humphreys MCS, Cooper GF, et al (2017) Magma mush chemistry at subduction
732 zones, revealed by new melt major element inversion from calcic amphiboles. *Am*
733 *Mineral* 102:1353–1367

734

735

736 Figure 1.
737 Host melt composition, temperature and pressure range of the experimental amphiboles used for
738 regression. Data sources given in Table 1. Melt compositions are shown normalised to 100%
739 anhydrous.

740
741 Figure 2.
742 Comparison of measured partition coefficients *vs* those predicted from the multiple regression models
743 given in Table 2, for La, Nb, Yb and Sr. For equivalent plots for the whole suite of elements see
744 supplementary figure 1. Solid grey line is 1:1 relationship. Dashed lines are $\pm 90\%$ prediction interval.
745 Grey bars give $\pm 1\sigma$ and 2σ prediction intervals.

746
747 Figure 3.
748 Variation of major elements in Mount St Helens whole rocks (red triangles, sources reported in
749 Blundy et al. 2008; orange triangles, data and sources reported in Wanke et al. in press and Wanke et
750 al. 2019), melt inclusions (filled circles, from Blundy et al. 2008) and amphibole equilibrium melts
751 (AEM; diamonds). AEM are calculated following Zhang et al. (2017) (see supplementary
752 information). Amphiboles used to calculate the AEM are from the 1980 eruptions (this study) and
753 include MgHbl and MgHst-Tsch. AEM from MgHbl (black) agree well with the least evolved melt
754 inclusions. AEM from MgHst-Tsch (blue) extend the melt inclusion trends back towards the whole
755 rocks.

756
757 Figure 4.
758 Comparison of measured (raw) amphibole trace element concentrations (field with blue dashed
759 outline) with calculated amphibole equilibrium melts. Symbols as for figure 3.

760
761 Figure 5.
762 Trace element variations (ppm) for Mount St Helens whole rocks, melt inclusions and amphibole
763 equilibrium melts (AEM). Data sources and symbols as for figure 3, but yellow diamonds show AEM

764 for rocks erupted during 2004-2006 (data from Thornber et al. 2008). A subset of AEM show
765 significant variability in concentration at intermediate SiO₂, towards enriched compositions.
766 Representative errors bars indicating accuracy ($\pm 1\sigma$ confidence intervals) are shown for each element,
767 based on regression statistics (see table 2 and supplementary information). Grey bars indicate
768 equilibrium melts for plagioclase as calculated by Berlo et al. (2007).

769

770 Figure 6.

771 Variation of trace element ratios La/Yb, Sm/Yb and Dy/Yb with SiO₂ for amphibole equilibrium
772 melts, melt inclusions and whole rocks from Mount St. Helens. Symbols as for figure 5.

773

774 Figure 7.

775 Europium anomaly for amphibole equilibrium melts and a subset of whole rocks for which data are
776 available. Symbols as for Figure 5. $Eu/Eu^* = Eu_N / \sqrt{(Sm_N * Gd_N)}$ where subscript N indicates
777 normalisation to chondrite values (Taylor and McLennan 1981).

778

779

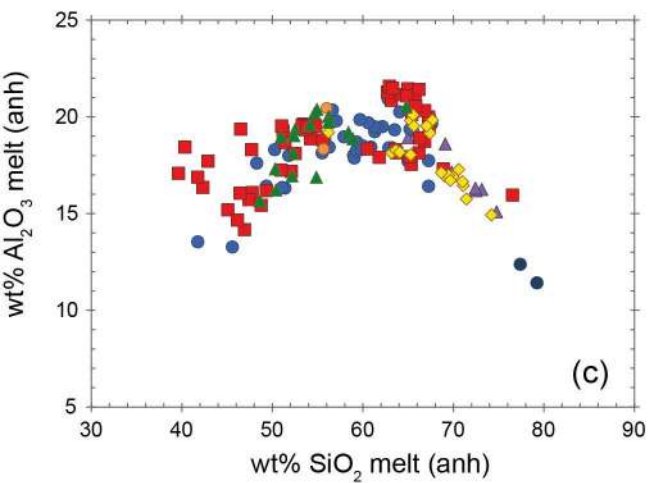
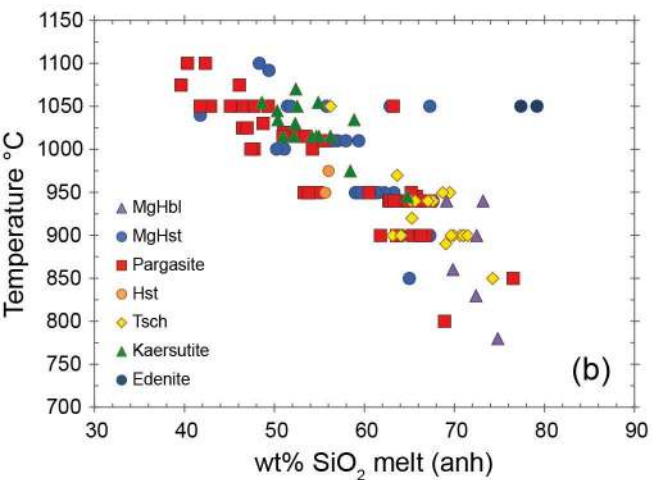
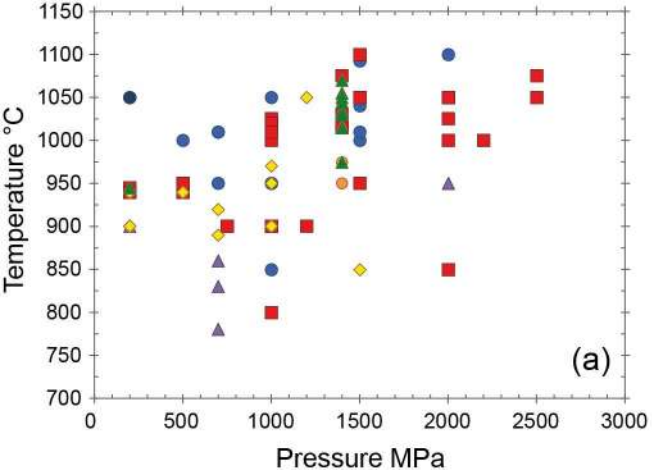
780 Table 1.

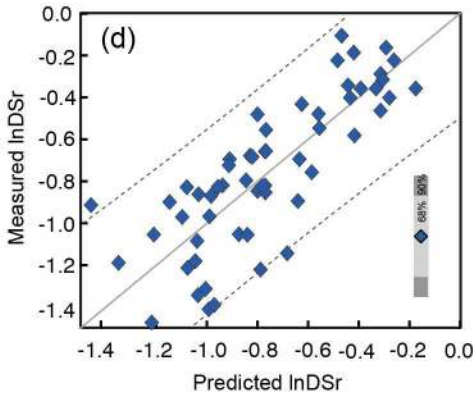
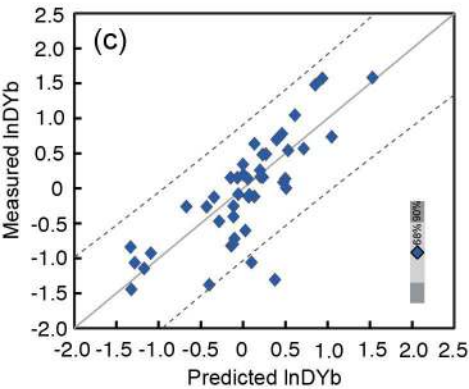
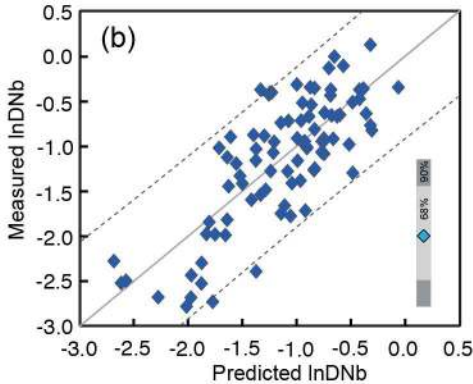
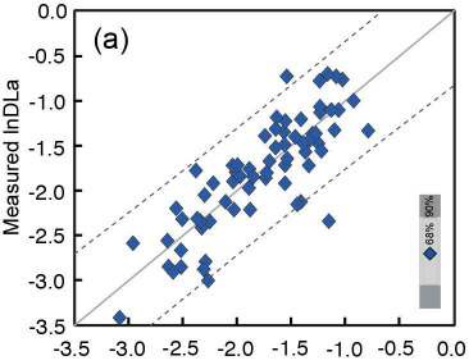
781 Run conditions and crystallisation products of published experimental studies used for multiple
782 regression analysis. References cited: Nicholls and Harris 1980; Green and Pearson 1985; Adam et al.
783 1993; Adam and Green 1994, 2006; Sisson 1994; LaTourrette et al. 1995; Klein et al. 1997; Dalpé
784 and Baker 2000; Hilyard et al. 2000; Tiepolo et al. 2000a; b, 2001, 2007; Nandedkar et al. 2016; Li et
785 al. 2017.

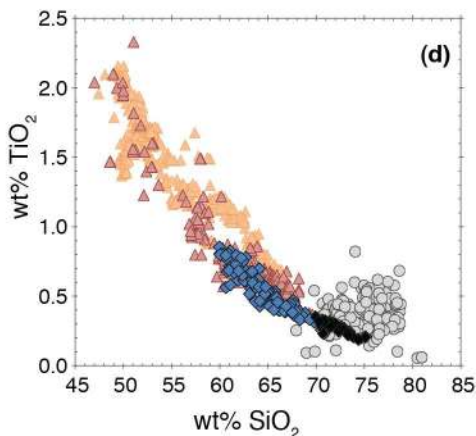
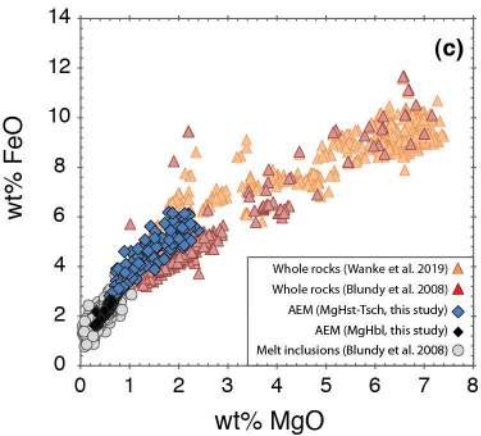
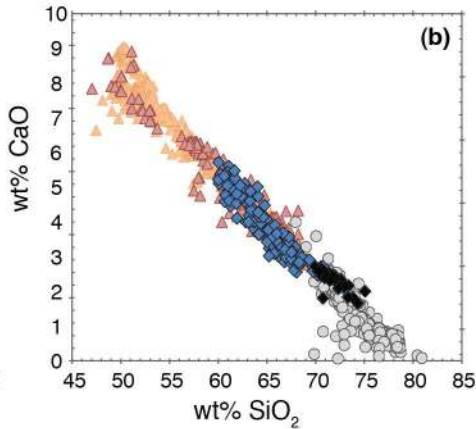
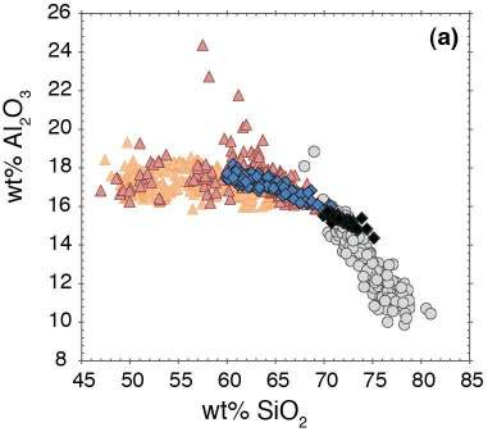
786

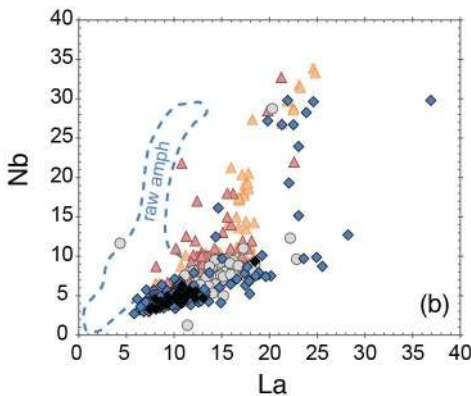
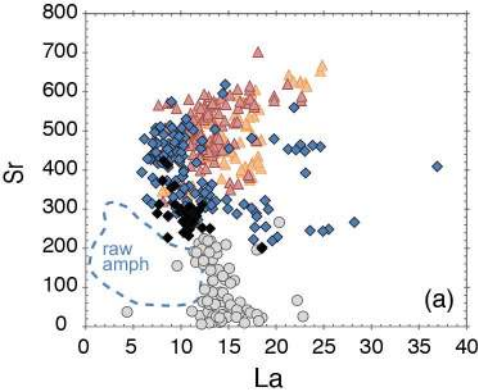
787 Table 2.

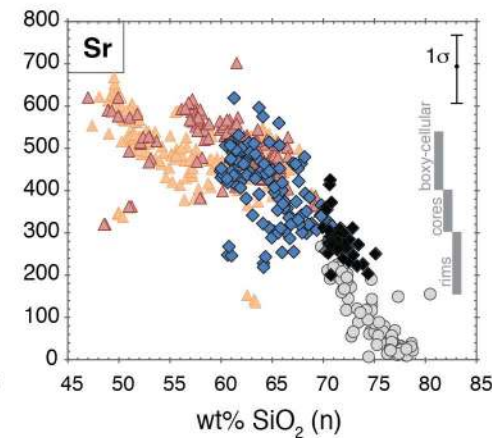
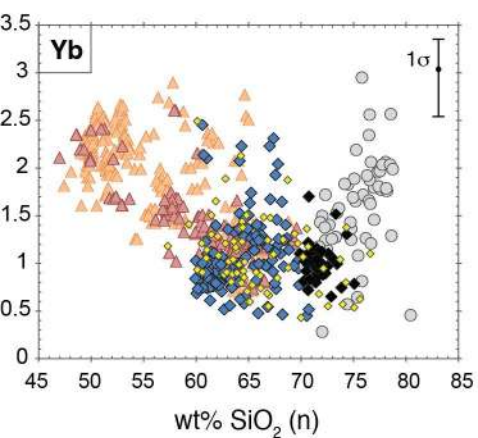
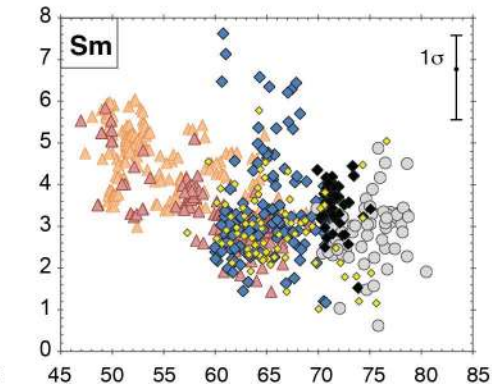
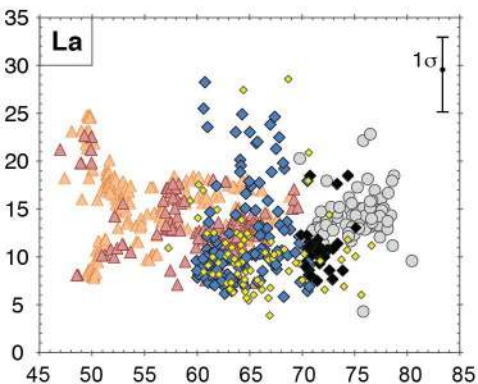
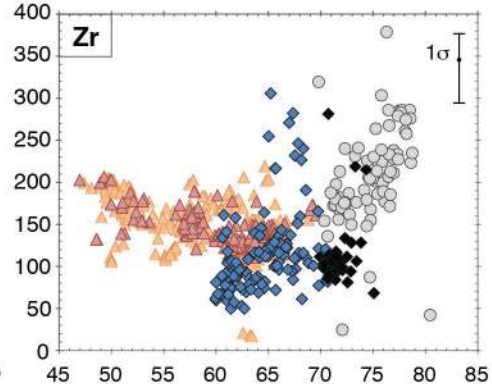
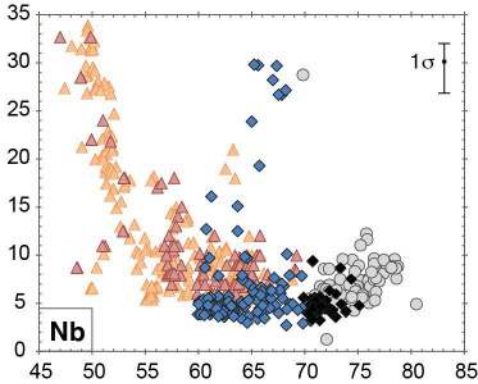
788 Results of multiple linear regression analysis. Compositional parameters are stoichiometric formula
789 components calculated following the "average ferric" approach of Leake et al. (1997). N, number of
790 measurements used. ^a Prediction intervals for the regression.

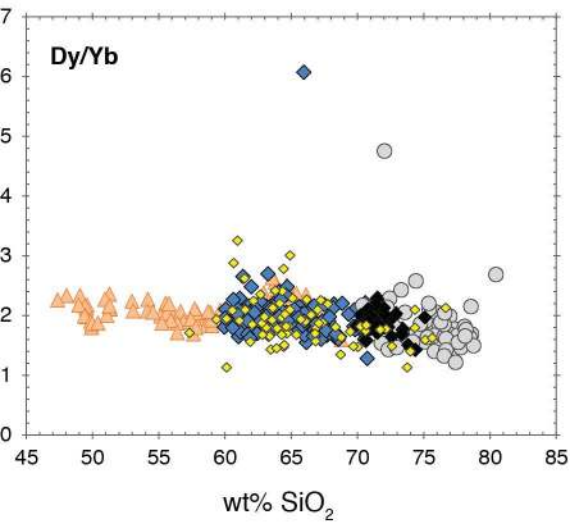
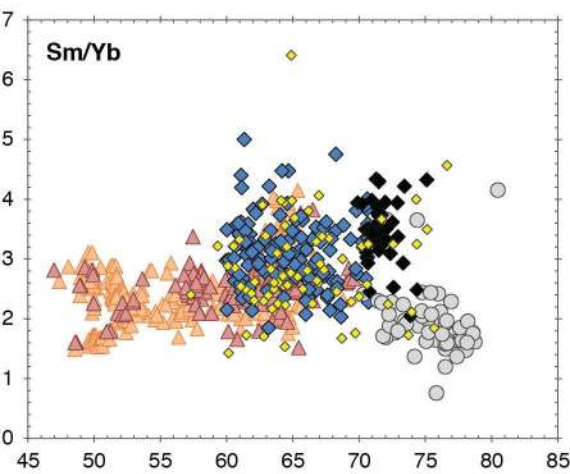
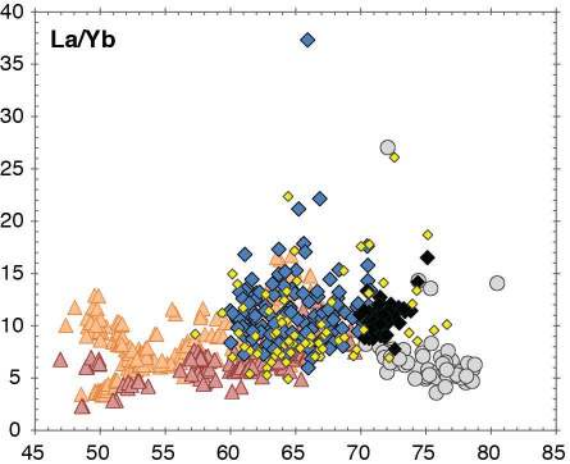












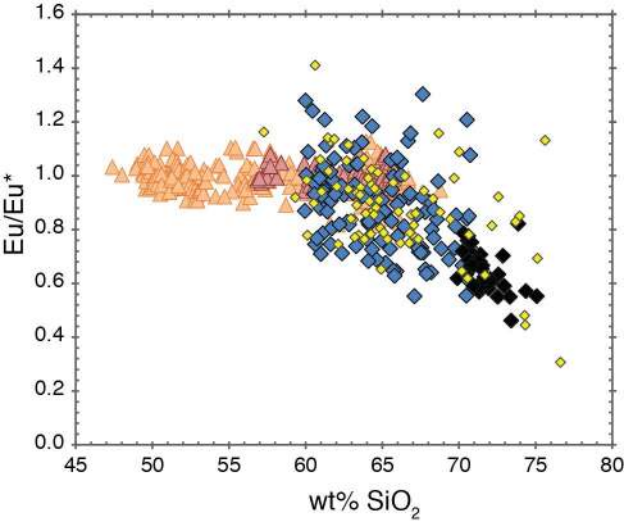


Table 1. Run conditions and crystallisation products of published experimental studies used for multiple regression analysis.

Experimental Study	Starting compositions	n	Pressure (MPa)	Temperature (°C)	Amphibole species
Adam et al. (1993)	basanite-basalt	6	1000-2000	925-1050	MgHbl, MgHst, Parg
Adam & Green (1994)	basanite	6	500-2000	1000-1100	MgHst
Adam & Green (2006)	basanite	2	1000-2000	1025-1050	MgHst
Dalpé & Baker (2000)	basanite-basalt	8	1500-2500	1000-1100	MgHst, Parg
Green & Pearson (1985)	andesite	5	750-2000	900-1050	Tsch, MgHst
Hilyard et al. (2000)	dacite-tonalite	35	200-500	900-945	Tsch, MgHst, MgHbl
Klein et al. (1997)	dacite	3	1000	800-900	Parg, Tsch
LaTourrette et al. (1995)	basanite	1	1500	1150	MgHst
Nicholls & Harris (1980)	basalt-andesite	9	1000	900-1020	Tsch, Parg, MgHst
Nandedkar et al. (2016)	basalt-andesite-rhyolite	8	700	780-1010	MgHst, Tsch, MgHbl
Sisson (1994)*	basalt-andesite-dacite-rhyolite	5	200	1050	MgHst, Edenite
Tiepolo et al. (2000a; 2000b; 2001; 2007)	basalt-andesite	25	1400	1070	MgHst, Kaer, Hastingsite
Li et al. (2017)	basalt	32	500-2000	850-1010	MgHst, Tsch

*This study is a natural material with the matrix rehomogenised at the stated conditions.

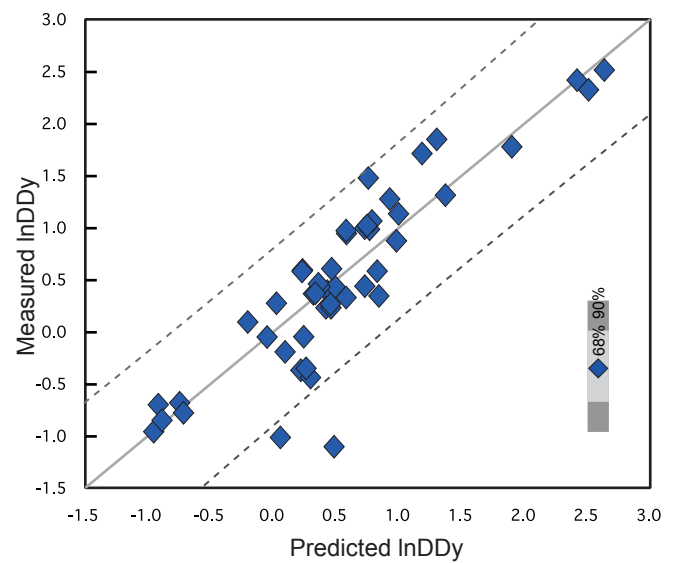
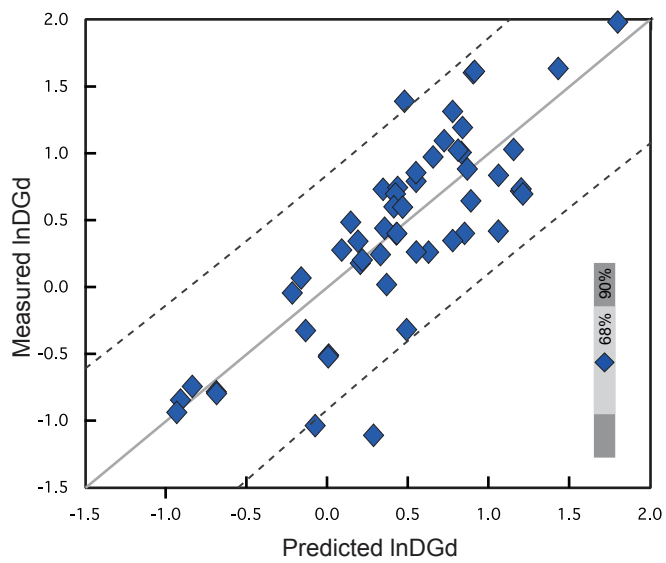
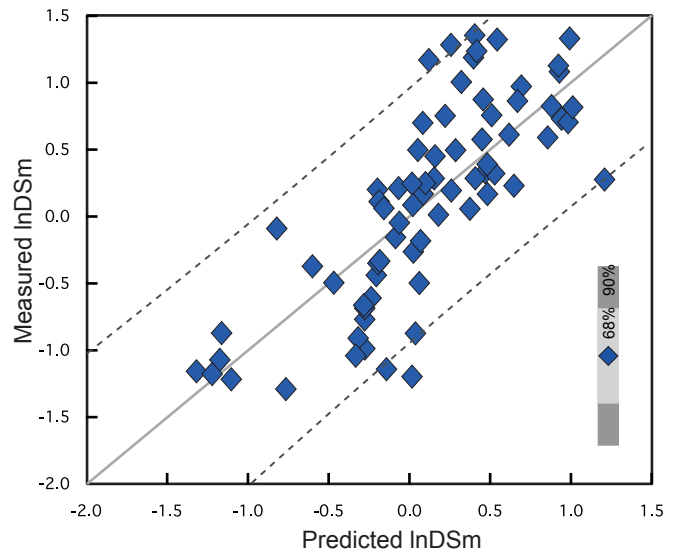
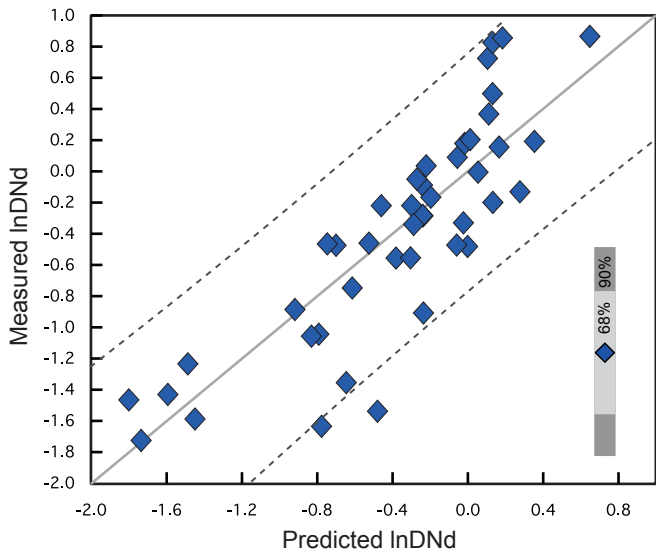
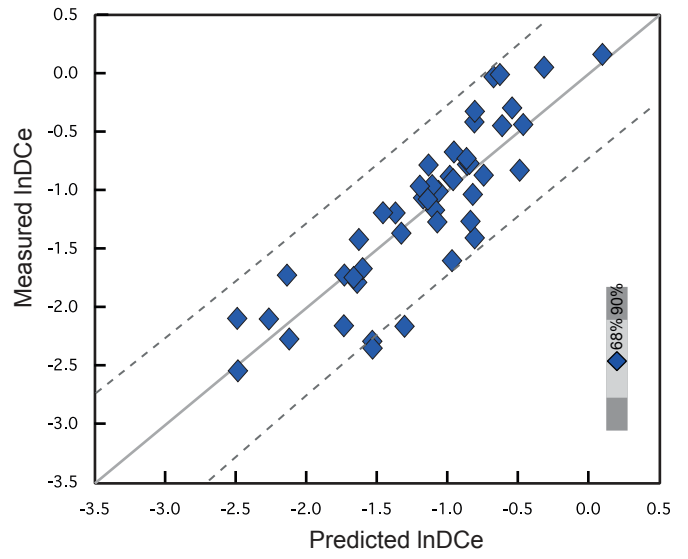
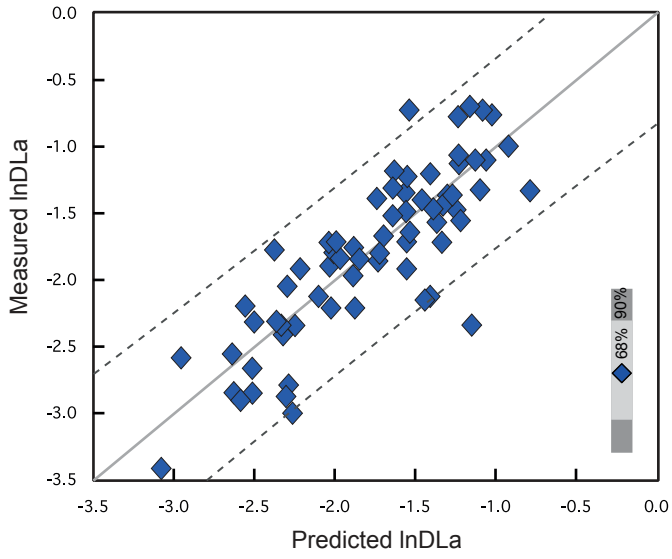
Table 2. Results of multiple linear regression analysis. Compositional parameters are stoichiometric formula components calculated following the "average ferric" approach of Leake et al. (1997). n, number of meas

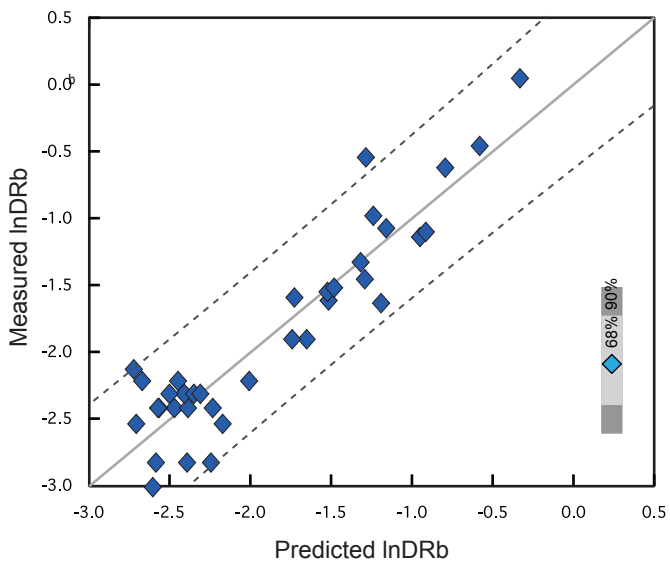
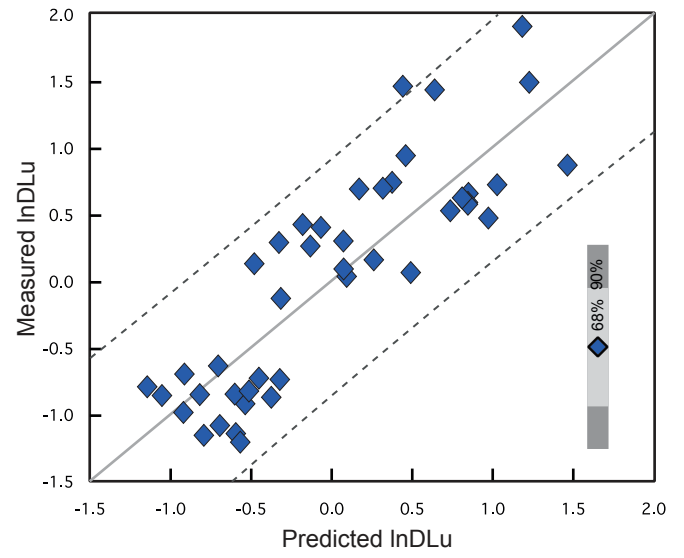
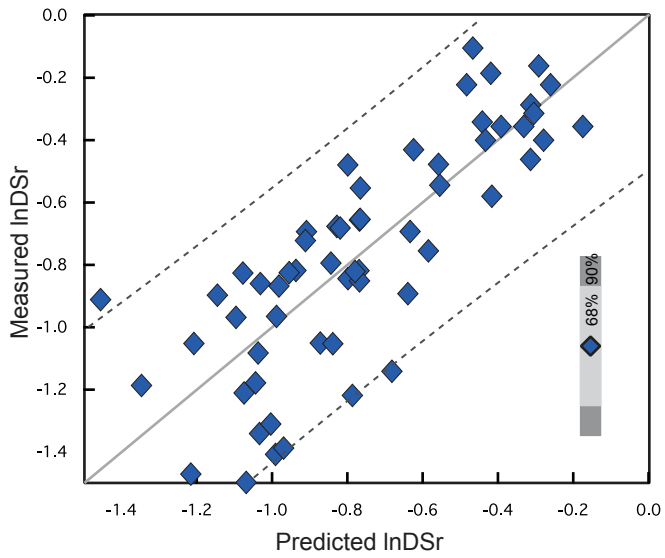
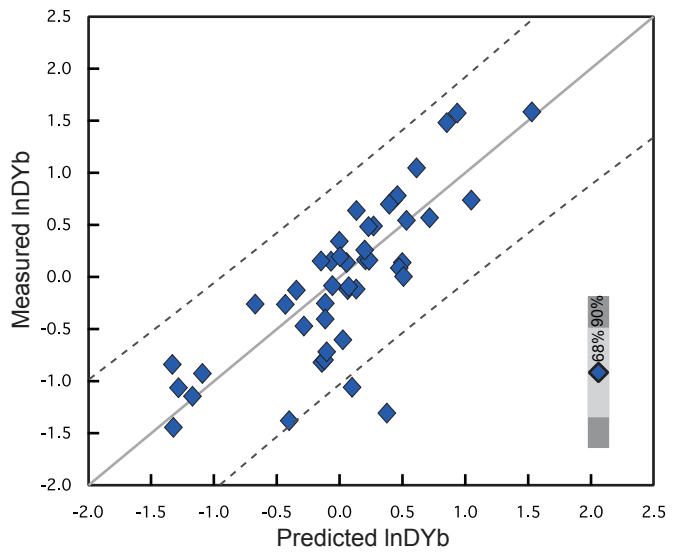
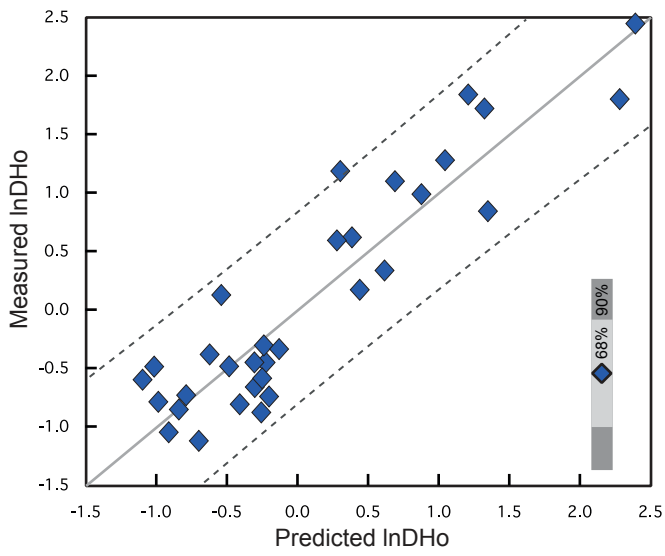
Equation	Dependent variable	D range	Constant	Si	Al ^{vi}	Ti	Fe ³⁺	Fe ²⁺	Ca	Na(A)	n	Adjusted R ²	Residual standard		
													error	± 90% §	± 68% §
1	ln DRb	0.05 - 1.04	9.1868	-1.3898		-3.6797	-1.5769	-0.6938			36	0.85	0.29	0.53	0.32
2	ln DSr	0.22 - 0.90	3.41585	-0.75281				0.36529			59	0.64	0.19	0.33	0.20
3	ln DPb	0.03 - 0.17	-4.2533		2.7155	1.69	0.7065			-1.0433	27	0.57	0.23	0.41	0.24
4	ln DZr	0.08 - 1.06	-25.6167	2.6183	2.6867	4.838	2.6591	0.6536	2.5248		60	0.46	0.49	0.80	0.49
5	ln DNb	0.06 - 1.14	-22.27	2.3241		3.7633	2.9786	1.44	1.8719		89	0.60	0.45	0.78	0.47
6	ln DLa	0.03 - 0.59	-20.0493	2.0732		2.5498	1.5317	1.117	2.2771	-1.4576	69	0.69	0.34	0.59	0.36
7	ln DCe	0.08 - 4.23	-21.1078	2.4749		2.4719	1.5722	0.952	1.5311		49	0.82	0.32	0.58	0.34
8	ln DNd	0.18 - 2.46	-20.3082	2.5162		2.5863	1.9459	0.9566	1.2763		45	0.71	0.36	0.64	0.38
9	ln DSm	0.27 - 3.85	-11.3625	1.602			1.2898	1.2376			72	0.60	0.43	0.73	0.44
10	ln DEu	0.28 - 5.8	-35.6604	4.1452	2.6886	6.4057	3.8508	0.7255	3.0679		39	0.77	0.37	0.70	0.42
11	ln DGd	0.33 - 7.22	-19.0583	2.4417		1.9786	1.8765	0.9943	1.3677		54	0.66	0.40	0.71	0.43
12	ln DDy	0.33 - 12.33	-16.0687	2.3858		1.8255	1.9741	0.6922			49	0.79	0.33	0.58	0.35
13	ln DHo	0.32 - 11.66	-20.4148	2.3654		2.484	3.2601	1.2922	3.1762	-4.9224	32	0.90	0.40	0.79	0.47
14	ln DYb	0.24 - 7.83	-15.8659	2.281		1.5905	2.1534	0.7867			48	0.66	0.43	0.45	0.45
15	ln DLu	0.30 - 6.76	-19.3462	2.1142		2.8478	2.7011	1.0402	2.9625	-3.2356	43	0.74	0.39	0.46	0.46
16	ln DY	0.31 - 5.24	-36.2514	3.6078	3.78	7.513	4.8366	0.814	4.6048		61	0.71	0.32	0.37	0.37

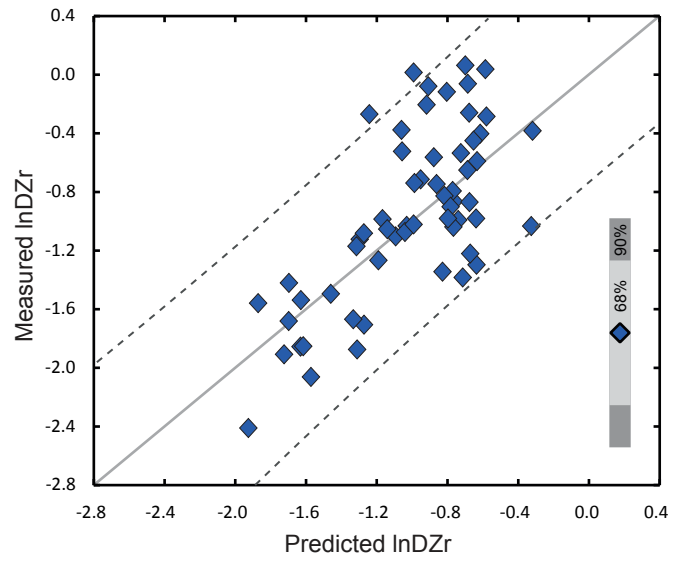
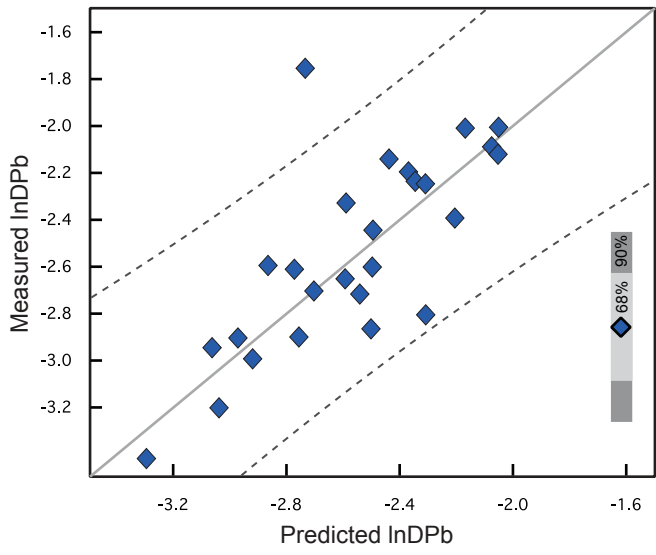
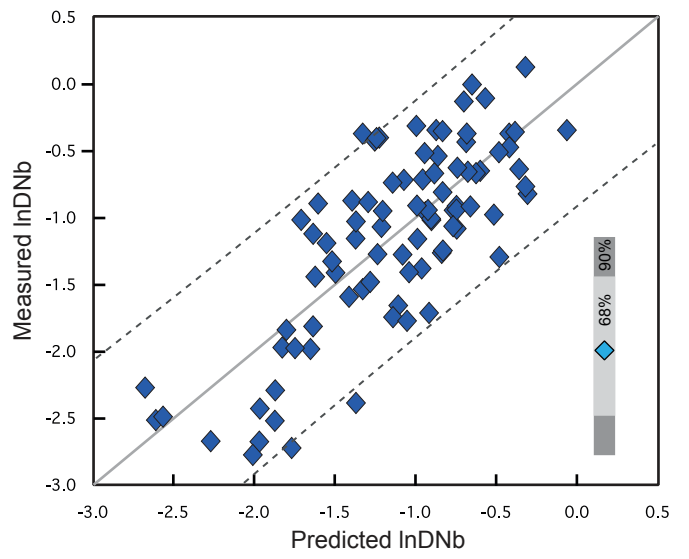
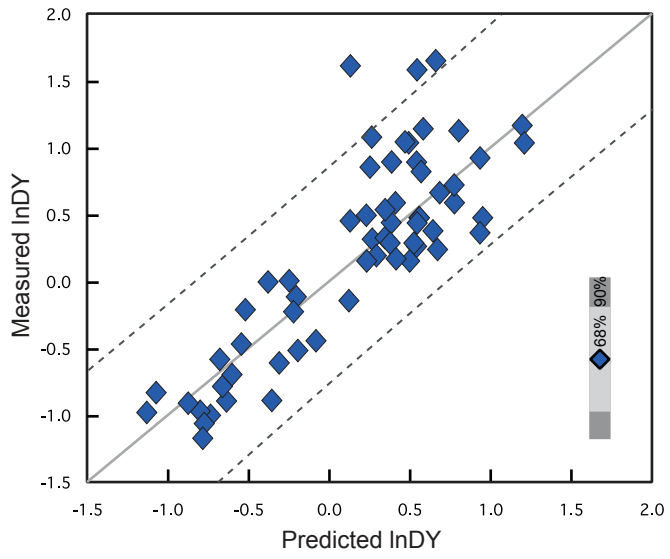
§ Prediction intervals for the regression.

Supplementary figure 1.

Comparison of measured partition coefficients with those predicted from regression analysis.







Supplementary figure 2.

Comparison of measured partition coefficients with those predicted from regression analysis.
(temperature-dependent regressions)

