

Redox evolution during arc magma differentiation revealed by mineral/melt Fe³⁺ and Fe²⁺ partitioning

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3 4 Abstract

5 The oxidizing capacity of volcanic gases relies on both the redox state of the
6 mantle and the redox evolution of mantle-derived magmas. Arc magmas transfer
7 abundant volatiles from the mantle and undergo extensive differentiation before
8 degassing. But how the magmatic redox state evolves during differentiation remains
9 enigmatic. The redox evolution of a magma depends on the mineral/melt partition
10 coefficients of Fe³⁺ and Fe²⁺ (DFe³⁺ and DFe²⁺). However, no systematic DFe³⁺ and
11 DFe²⁺ are reported due to the difficulties in analyzing Fe³⁺ of silicate minerals. Here,
12 we conducted hydrous experiments at 900–1100 °C and 1–2 GPa and determined
13 systematically DFe³⁺ and DFe²⁺ using a novel method. With the obtained partition
14 coefficients, we investigated the redox evolution by performing fractional
15 crystallization modelling. The almost invariable redox state during arc magma
16 differentiation implies an oxidizing mantle predated the Great Oxidation Event if it was
17 triggered by the increasing oxidizing capacity of volcanic gases.

18
19
20 The Earth's mantle regulates the secular evolution of the atmosphere by dominating the
21 redox state (described by oxygen fugacity, fO_2) of mantle-derived magmas and
22 emanated volatiles therein¹⁻⁴. Arc magmas, deriving from sub-arc mantle, contain
23 abundant volatiles^{5,6} and may undergo extensive differentiation from basaltic, through
24 andesitic and dacitic, to rhyolitic compositions on the way to eruption⁷⁻⁹. Differentiation
25 may significantly affect the fO_2 of the erupted magmas and the oxidizing capacity of
26 the expelled volatiles, and thus augment or abate the capacity of the mantle in regulating
27 the atmospheric compositions. But how and if fO_2 evolves during arc magma
28 differentiation remains hotly debated. Some studies suggest that arc magmas beneath
29 thick crust will be continuously oxidized due to garnet fractionation, which increases

30 the $\text{Fe}^{3+}/\text{Fe}_T$ ratio of the residual melt because garnet prefers Fe^{2+} over Fe^{3+} ^{10,11}. Other
31 studies suggest, based on mineral oxybarometer or direct analysis of melt $\text{Fe}^{3+}/\text{Fe}_T$
32 ratios, that the $f\text{O}_2$ of arc magmas remains nearly constant during magmatic
33 differentiation, regardless of the crustal thickness¹²⁻¹⁶. The debate arises mainly from
34 the lack of mineral/melt partition coefficients of Fe^{3+} and Fe^{2+} during arc magma
35 differentiation.

36 Iron is the most abundant multivalent elements on Earth and the magmatic $f\text{O}_2$,
37 reflected by the $\text{Fe}^{3+}/\text{Fe}_T$ ($\text{Fe}_T = \text{Fe}^{3+} + \text{Fe}^{2+}$) ratio of the magma, is thus largely
38 controlled by the behavior of ferric (Fe^{3+}) and ferrous (Fe^{2+}) iron^{17,18}. In a closed
39 magmatic system, crystallization of Fe-bearing minerals will fractionate the $\text{Fe}^{3+}/\text{Fe}^{2+}$
40 (i.e. $\text{Fe}^{3+}/\text{Fe}_T$) ratio of the magma and change the $f\text{O}_2$ of the system¹⁹. Specifically,
41 fractional crystallization of a mineral that preferentially partitions Fe^{2+} over Fe^{3+} (i.e.
42 $D\text{Fe}^{3+}/D\text{Fe}^{2+} < 1$, $D\text{Fe}^{3+}$ and $D\text{Fe}^{2+}$ are the mineral/melt Fe^{3+} and Fe^{2+} partition
43 coefficients) will impart a higher $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio on the residual melt, resulting in an
44 elevated $f\text{O}_2$ of the system, and vice versa. Therefore, constraints on $D\text{Fe}^{3+}$, $D\text{Fe}^{2+}$ and
45 $D\text{Fe}^{3+}/D\text{Fe}^{2+}$ for the major crystallizing minerals and their equilibrium melts are
46 essential in deciphering the redox evolution during arc magma differentiation.

47 The major Fe-bearing minerals during arc magma differentiation include olivine
48 (ol), clinopyroxene (cpx), amphibole (amp), garnet (grt) and Fe-oxides. The $D\text{Fe}^{2+}$ for
49 these minerals can be determined by performing high pressure experiments at reducing
50 conditions where Fe is almost present exclusively as Fe^{2+} ^{20,21}. Most published reducing
51 experiments are buffered by graphite, where $\text{Fe}^{2+}/\text{Fe}_T$ ratios exceed 0.95–0.98²²⁻²⁵.
52 Therefore, the bulk iron partition coefficient ($D\text{Fe}_T$) obtained from the very reducing
53 experiments can approximately represent $D\text{Fe}^{2+}$. For the case of $D\text{Fe}^{3+}$, it approximates
54 0 for ol because ol contains negligible Fe^{3+} due to the steric limitations in the crystal
55 structure²⁶. For Fe-oxides, [magnetite (mag) and spinel (spl)], the $D\text{Fe}^{3+}$ can be readily
56 determined because the mineral Fe^{3+} content can be accurately calculated from the
57 mineral composition determined, e.g. by electron microprobe^{21,27}. However, $D\text{Fe}^{3+}$ for
58 silicate minerals (cpx, amp and grt) are only sporadically reported^{21,28-30} and the results
59 are inapplicable to arc magma differentiation because the experiments were performed

60 at dry or high temperature (>1100 °C) conditions. The lack of systematic $D\text{Fe}^{3+}$ for
 61 silicate minerals at conditions pertinent to arc magma differentiation mainly results
 62 from the following difficulties. Firstly, the proportion of Fe^{3+} rarely exceeds 0.8 in high
 63 pressure experiments^{18,31}; secondly, Fe^{3+} analysis of hydrous silicate melts remains a
 64 difficult task³²; thirdly, unlike for Fe-oxides, the Fe^{3+} content of silicate minerals cannot
 65 be accurately calculated from their composition²⁶; at last, an accurate analytical method
 66 for determining Fe^{3+} in silicate minerals by X-ray absorption near edge structure
 67 (XANES) remains to be established, especially for anisotropic minerals such as
 68 pyroxenes³³.

69 Here, we performed high temperature and pressure (HTP) experiments and
 70 determined $D\text{Fe}^{3+}$ for silicate minerals (cpx, amp, grt) with high precision following a
 71 novel method. The method circumvents the above difficulties by determining $D\text{Fe}^{3+}$
 72 according to the relation: $D\text{Fe}^{3+} = \frac{D\text{Fe}_T - D\text{Fe}^{2+}}{(\text{Fe}^{3+}/\text{Fe}_T)^{\text{melt}}} + D\text{Fe}^{2+}$. The HTP experiments were
 73 performed in a piston-cylinder apparatus at 900–1100 °C and 1–2 GPa (Supplementary
 74 Table 1), covering the typical T–P ranges of arc magma differentiation (cf. ^{9,34}). The
 75 obtained partition coefficients can thus be directly applied to constrain the redox
 76 evolution during arc magma differentiation.

77

78 **Determination of $D\text{Fe}^{3+}$ from a novel method**

79 $D\text{Fe}^{3+}$ can be determined according to the following equation (details for the derivation
 80 of the equation are reported in the SI text):

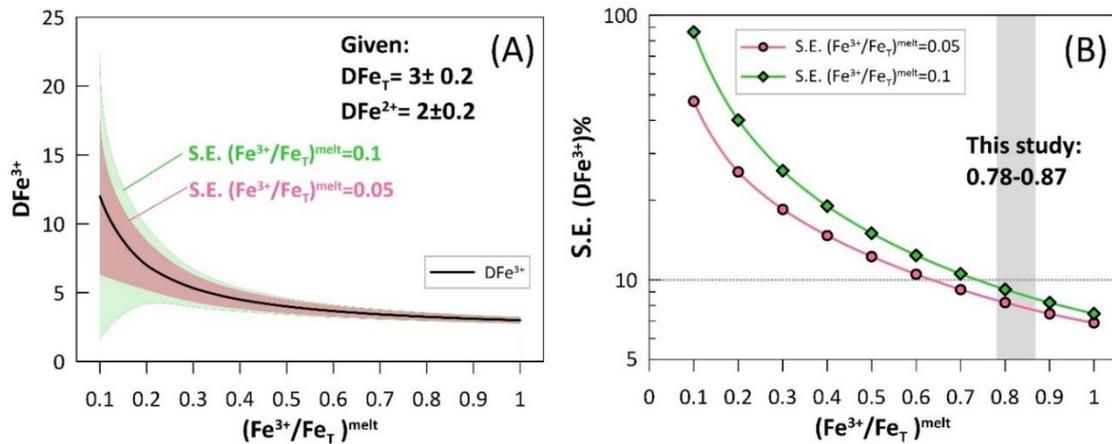
$$81 \quad D\text{Fe}^{3+} = \frac{D\text{Fe}_T - D\text{Fe}^{2+}}{(\text{Fe}^{3+}/\text{Fe}_T)^{\text{melt}}} + D\text{Fe}^{2+} \quad (1)$$

82 Equation (1) indicates that $D\text{Fe}^{3+}$ can be obtained when $D\text{Fe}_T$, $D\text{Fe}^{2+}$ and melt $\text{Fe}^{3+}/\text{Fe}_T$
 83 $[(\text{Fe}^{3+}/\text{Fe}_T)^{\text{melt}}]$ are accurately constrained. For an experiment with known $f\text{O}_2$, $D\text{Fe}_T$ is
 84 readily determined by analyzing the FeO_T content of the minerals and coexisting melt,
 85 while $(\text{Fe}^{3+}/\text{Fe}_T)^{\text{melt}}$ can be calculated from the experimental $f\text{O}_2$, temperature, pressure,
 86 and melt compositions using well-calibrated equations^{17,18}. Therefore, we can
 87 determine $D\text{Fe}^{3+}$ when $D\text{Fe}^{2+}$ is precisely constrained and measured.

88 According to equation (1), the propagated uncertainty of $D\text{Fe}^{3+}$ can be expressed
 89 by the following equation:

$$\delta DFe^{3+} = \sqrt{\left(\frac{1}{(Fe^{3+}/Fe_T)^{melt}}\right)^2 (\delta DFe_T)^2 + \left(1 - \frac{1}{(Fe^{3+}/Fe_T)^{melt}}\right)^2 (\delta DFe^{2+})^2 + \frac{(DFe_T - DFe^{2+})^2}{(Fe^{3+}/Fe_T)^{melt^4}} (\delta(Fe^{3+}/Fe_T)^{melt})^2} \quad (2)$$

90
 91 Where δ represents the standard error of each variable (e.g., δDFe_T denotes the S.E. of
 92 DFe_T). As shown in equation (2), the S.E. of DFe^{3+} acquired by this method mainly
 93 depends on the accuracy of the $(Fe^{3+}/Fe_T)^{melt}$ value because DFe_T and DFe^{2+} can be
 94 accurately determined. With equations (1) and (2), we tested the effect of $(Fe^{3+}/Fe_T)^{melt}$
 95 on the accuracy of DFe^{3+} assuming that $DFe_T = 3 \pm 0.2$ and $DFe^{2+} = 2 \pm 0.2$ and the S.E. of
 96 $(Fe^{3+}/Fe_T)^{melt}$ varies from 0.05 to 0.1. The calculated DFe^{3+} and the propagated
 97 uncertainty are shown in Fig. 1. It is evident that the lower S.E. in $(Fe^{3+}/Fe_T)^{melt}$ always
 98 results in lower S.E. of DFe^{3+} (Fig. 1A). More importantly, at a given S.E. of
 99 $(Fe^{3+}/Fe_T)^{melt}$, the S.E. of DFe^{3+} decreases dramatically with increasing $(Fe^{3+}/Fe_T)^{melt}$
 100 and the relative uncertainty is $< 10\%$ at $(Fe^{3+}/Fe_T)^{melt} > \sim 0.7$ (Fig. 1B). The dramatic
 101 decrease in the S.E. of DFe^{3+} with increasing $(Fe^{3+}/Fe_T)^{melt}$ indicates that DFe^{3+} can be
 102 accurately determined at highly oxidizing conditions (e.g., S.E. $< 10\%$ at Ru–RuO₂
 103 buffered conditions as in this study).



104
 105 **Fig. 1. Schematic diagram showing the effect of $(Fe^{3+}/Fe_T)^{melt}$ on the propagated standard**
 106 **error (S.E.) of DFe^{3+} for $DFe_T = 3 \pm 0.2$ and $DFe^{2+} = 2 \pm 0.2$.** (A) The effect of $(Fe^{3+}/Fe_T)^{melt}$ on
 107 the absolute S.E. of DFe^{3+} . The black curve represents the calculated DFe^{3+} . The trumpet-
 108 shaped coloured areas denote the absolute S.E. of DFe^{3+} assuming an S.E. of 0.05 (circle-filled)
 109 and 0.10 (diamond-filled) for $(Fe^{3+}/Fe_T)^{melt}$. (B) The effect of $(Fe^{3+}/Fe_T)^{melt}$ on the relative S.E.
 110 of DFe^{3+} . The grey shaded area highlights the $(Fe^{3+}/Fe_T)^{melt}$ range of our experiments,
 111 suggesting that the S.E. of DFe^{3+} calculated from equation (1) is $< 10\%$ relative. Note that
 112 change the DFe_T and DFe^{2+} could change the absolute values of the calculated DFe^{3+} and S.E.,
 113 but will not affect the general trend of the DFe^{3+} and S.E..

115 **Regression of DFe^{2+} from reducing experiments**

116 For ferromagnesian minerals, DFe^{2+} can be expressed by DMg (magnesium partition
117 coefficient) following the relation: $DFe^{2+} = a*DMg + b$, where a and b are
118 constants^{35,36}. We here confirmed that amphibole conforms to this relation because the
119 ratio of DFe^{2+} and DMg ($Kd_{Fe^{2+}-Mg}^{amp/melt}$) never changes with temperature, pressure or
120 mineral compositions (see Fig. S1 and Supplementary Text). At reducing conditions,
121 where iron is almost exclusively present as Fe^{2+} , DFe_T is approximated by DFe^{2+} , thus
122 enabling us to determine the relation between DFe^{2+} and DMg.

123 To determine the relation between DFe^{2+} and DMg for amp, we collected
124 amphibole–melt pairs from HTP experiments and picked out the experiments
125 performed under reducing conditions for the regression^{9,28,34,37,38}. The criteria for the
126 filtration of the experiments were: 1) we preferred experiments performed in graphite
127 capsules because iron was mainly present as Fe^{2+} (with melt $Fe^{2+}/Fe_T > 0.95$)²²⁻²⁵; 2)
128 for experiments performed in noble metals capsules, we calculated the $(Fe^{3+}/Fe_T)^{melt}$
129 from the reported fO_2 using the algorithms of Zhang et al.¹⁸ or from the coexisting ol-
130 melt pair using the ol- oxybarometry of Blundy et al.²⁰ and then chose the experiments
131 with the calculated $(Fe^{3+}/Fe_T)^{melt} < 0.1$. Finally, 36 experiments met the criteria
132 (Supplementary Table 2), which were regressed to obtain the following equation:

$$133 \quad \text{Amp: } DFe^{2+} = 0.2919* DMg + 0.0460 \quad (n=36, aad=0.14, R^2=0.81) \quad (3)$$

134 Where aad is the average absolute deviation. Details for the regression are reported in
135 Fig. S2. For cpx and grt, the relations between DFe^{2+} and DMg are from a related
136 manuscript:

$$137 \quad \text{Cpx: } DFe^{2+} = 0.3822*DMg - 0.0287*DMg^2 \quad (n=126, aad=0.06, R^2=0.85) \quad (4)$$

$$138 \quad \text{Grt: } DFe^{2+} = 0.5843* DMg - 0.1210 \quad (n=44, aad=0.09, R^2=0.99) \quad (5)$$

139 P-values for DMg in the regressions are far less than 0.05. The high R^2 and low S.D.
140 demonstrate the reliability and accuracy of the parameterized equations.

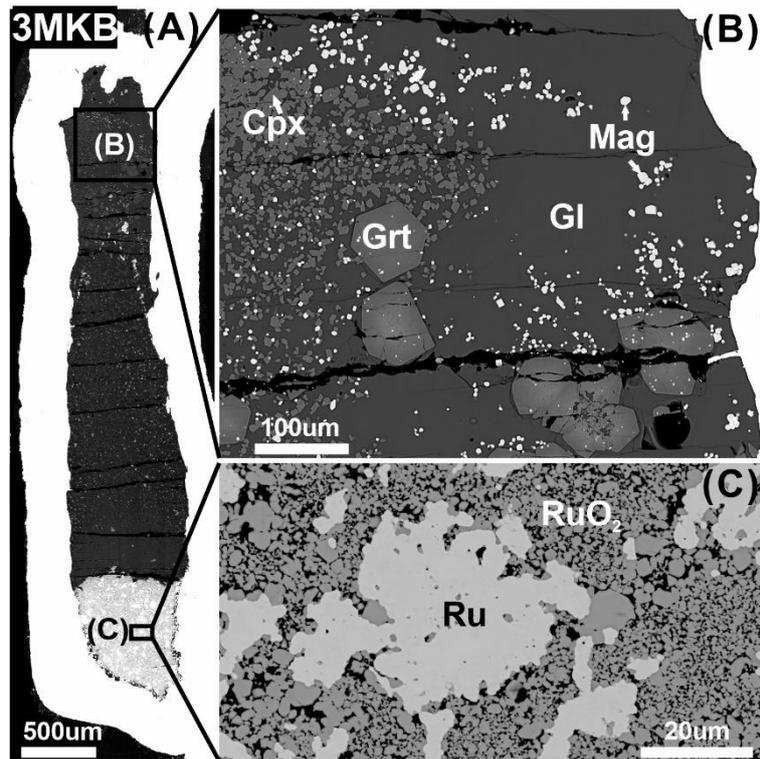
141

142 **Results**

143 Twelve experiments were successfully synthesized at 900–1100 °C, 1–2 GPa and
144 Ru–RuO₂ buffered conditions (see later Materials and Methods part and Supplementary
145 Table 1). Both Ru and RuO₂ present at the end of each experiment (Fig. 2), indicating
146 the validity of the fO_2 buffer. The experimental run products include melt,
147 clinopyroxene, amphibole, garnet and Fe-oxides. The melts usually quenched to clear
148 glasses with some of them containing tiny (usually < 3 μm) vesicles caused by H₂O
149 exsolution during quenching. The minerals were generally euhedral with crystal sizes
150 varying from <10–15 μm (clinopyroxene, amphibole and Fe-oxides) to up to 50 μm
151 (garnet) (Fig. 2).

152 **Melt compositions and (Fe³⁺/Fe_T)^{melt}**

153 The quenched melts are compositionally homogeneous (Supplementary Table 3). On
154 an anhydrous basis, melts from the 1.0 GPa experiments are basaltic-andesitic to
155 andesitic (55.16–62.97% SiO₂) and those from the 2.0 GPa experiments are andesitic
156 to dacitic (61.85–67.38% SiO₂). At each pressure, melt SiO₂ and K₂O increase, but
157 MgO and FeO_T decrease with temperature decreasing from 1100 °C to 900 °C. Because
158 metallic Ru and RuO₂ coexist after the experiments, the experimental fO_2 can be
159 accurately calculated using the algorithm of O'Neill and Nell³⁹. The calculated
160 log₁₀(fO_2) ranges from –5.23 to –2.71 and the relative fO_2 varies from FMQ+5.4 to
161 FMQ+6.4 (FMQ, the fayalite–magnetite–quartz buffer⁴⁰).



162

163 **Fig. 2. Representative BSE images showing the run products of Exp. 3MKB.** (A) An
 164 overview of the longitudinal section of the sample capsule. (B) An enlarged image showing the
 165 euhedral minerals and coexisting quenched glass. (C) The coexistence of Ru and RuO₂
 166 indicating the validity of the fO_2 buffer. Abbreviations: Grt, garnet; Cpx, clinopyroxene; Mag,
 167 magnetite; Gl, quenched glass.

168

169 The $(Fe^{3+}/Fe_T)^{melt}$ can be calculated from the experimental fO_2 , temperature,
 170 pressure and melt composition using the well-calibrated algorithms^{17,18,41}. The
 171 compositional effect in O'Neill et al.⁴¹, which is inherited from Jayasuriya et al.⁴², may
 172 be inaccurate by overestimating the effects of P₂O₅^{43,44}. Therefore, we calculated
 173 $(Fe^{3+}/Fe_T)^{melt}$ using the algorithms of Kress and Carmichael¹⁷ (equation A-6) and
 174 Zhang et al.¹⁸ (equation 10-b), respectively. The $(Fe^{3+}/Fe_T)^{melt}$ calculated by these two
 175 methods agree with each other within an error of ± 0.05 (Fig. S3), indicating their
 176 reliability. In keeping with related manuscript, here we adopt the $(Fe^{3+}/Fe_T)^{melt}$
 177 calculated using the algorithm of Zhang et al.¹⁸. The calculated $(Fe^{3+}/Fe_T)^{melt}$ values
 178 range from 0.73 to 0.85, showing a slight increase with decreasing temperature and
 179 pressure. Considering that the difference in the calculated $(Fe^{3+}/Fe_T)^{melt}$ from the Kress

180 and Carmichael¹⁷ and the Zhang et al.¹⁸ algorithms is <0.05, we employed an absolute
181 uncertainty of 0.05 for the calculated $(\text{Fe}^{3+}/\text{Fe}_T)^{\text{melt}}$ in the following calculations. The
182 calculated CFe^{3+} and CFe^{2+} in melt ranges from 1.18–4.28 wt% and 0.19–1.09 wt%,
183 respectively. Considering Fe^{3+} as a network-forming cation, the calculated melt NBO/T
184 (degree of depolymerization) values range from 0.02 to 0.38.

185

186 **Mineral compositions**

187 The mineral compositions of cpx, amp and Fe-oxides from single experiments are
188 homogeneous, indicating the attainment of equilibrium. Although garnet zonation
189 occurs in some experiments, the garnet rims should approach equilibrium with the
190 coexisting melts as confirmed by their homogeneous compositions. Therefore, the
191 compositions of garnet rim and the adjacent melt were used in subsequent calculations
192 of the partition coefficients (Supplementary Table 3).

193 Cpx occurs in both 1 and 2 GPa experiments. Crystals have $\text{En}_{36.3-49.3}\text{Fs}_{6.5-17.4}$
194 $\text{Wo}_{44.2-48.5}$ (En, enstatite; Fs, ferrosilite; Wo, wollastonite), containing 3.32–11.73 wt
195 % Al_2O_3 and < 3.3 wt % Na_2O . The cpx from Exp. 11MKB (1 GPa, 1000 °C) splits into
196 two distinct compositional groups: one (h-Al) is high in Al_2O_3 and FeO_T ($\text{Al}_2\text{O}_3=6.14$
197 wt%; $\text{FeO}_T=6.56$ wt%) and the other (l-Al) is low in Al_2O_3 and FeO_T ($\text{Al}_2\text{O}_3=3.32$ wt%;
198 $\text{FeO}_T=4.12$ wt%). The distinct compositions in cpx are commonly recognized in both
199 experimental and natural samples^{9,45-47}. As demonstrated by Welsch et al.⁴⁸, such
200 compositional differences represent different crystal orientations rather than
201 disequilibrium. Amp also occurs in both 1 and 2 GPa experiments, classifying as
202 pargasite or magnesio-hastingsite^{49,50}. FeO_T and Al_2O_3 contents in amps range from
203 6.54 wt% to 8.56 wt% and 14.03 to 17.07 wt%, respectively. Grt occurs only in the 2
204 GPa runs and they are dominantly composed of $\text{Pyr}_{63.0-68.3}\text{Grs}_{13.8-17.4}\text{Alm}_{4.9-7.8}\text{And}_{2.1-4.2}$
205 $\text{Spe}_{6.7-10.1}$ (Pyr, pyrope; Grs, grossular; Alm, almandine; And, andradite; Spe,
206 spessartite). Their FeO content increases systematically from 4.76 wt% at 900 °C to
207 6.52 wt% at 1100 °C. Fe-oxides occur in all of the experiments and classifying as
208 magnetite and spinel. The magnetite and spinel crystals are composed of
209 $\text{Spl}_{0.4-0.8}\text{Her}_{4.7-12.4}\text{Mfr}_{4.3-7.6}\text{Mag}_{65.6-75.5}\text{Chr}_{2.6-6.3}\text{Usp}_{7.2-8.8}$ and $\text{Spl}_{10.7-32.1}\text{Her}_{4.2-10.4}$

210 Mfr_{27.7–48.8}Mag_{8.9–19.8}Chr_{2.1–2.9}Usp_{0.0–0.1}, respectively (Spl, spinel; Her, hercynite; Mfr,
211 magnesioferrite; Mag, magnetite; Chr, chromite; Usp, ulvöspinel)⁵¹. Mag contains
212 4.9–6.2 wt% TiO₂, 1.1–1.9 wt% MgO and 2.1–5.76 wt% Al₂O₃, and Spl contains
213 ~0.2–0.4 wt% TiO₂, 12.3–13.8 wt % MgO and 7.7–25.6 wt% Al₂O₃.

214

215 **D_{FeT}, D_{Fe²⁺}, D_{Fe³⁺}, and D_{Fe³⁺/D_{Fe²⁺}}** for minerals

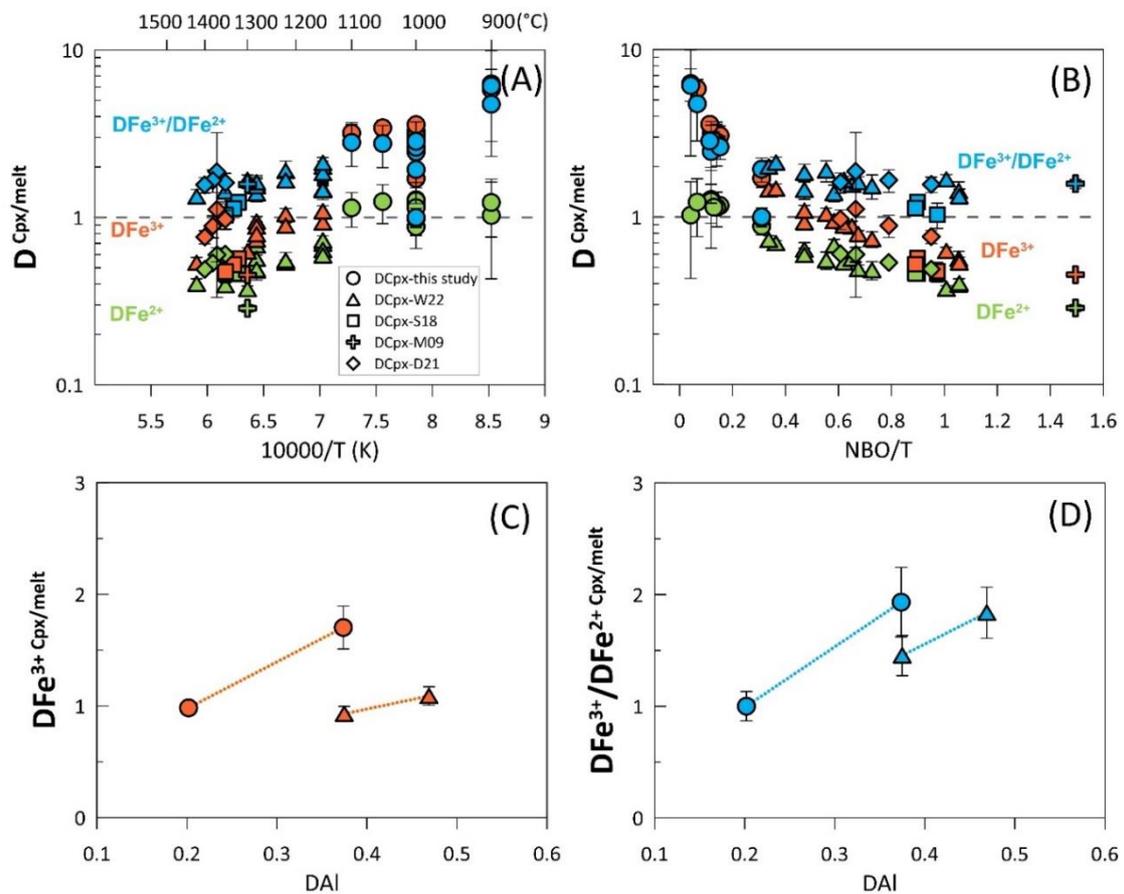
216 D_{FeT} for both silicate minerals and Fe-oxides were determined by dividing the FeO_T
217 content of the minerals by that of the coexisting melts. For silicate minerals (cpx, amp
218 and grt), the D_{Fe²⁺} values were calculated from the relations between D_{Fe²⁺} and DMg
219 [Eqs. (3)–(5)] and D_{Fe³⁺} values were then calculated from D_{FeT}, D_{Fe²⁺} and
220 (Fe³⁺/Fe_T)^{melt} using equation (1). For Fe-oxides (mag and spl), we directly calculated
221 FeO and Fe₂O₃ contents of the minerals based on the charge balance of chemical
222 formula, and then D_{Fe²⁺} and D_{Fe³⁺} were respectively determined by dividing the FeO
223 and Fe₂O₃ contents of the minerals by those of the melts. We also verified the accuracy
224 of the D_{Fe³⁺} by calculating it using the (Fe³⁺/Fe_T)^{melt} obtained respectively from Kress
225 and Carmichael¹⁷ (equation A–6) and Zhang et al.¹⁸. The excellent agreement (fig. S4)
226 demonstrated the accuracy of the determined D_{Fe³⁺}. Additionally, the D_{Fe³⁺/D_{Fe²⁺}} for
227 each mineral was calculated from the conjugated D_{Fe³⁺} and D_{Fe²⁺}. With the above
228 methods, we also calculated the D_{Fe²⁺}, D_{Fe³⁺} and D_{Fe³⁺/D_{Fe²⁺}} from the oxidizing
229 experiments of King et al.²⁸, Sorbadere et al.⁵² and Davis and Cottrell²¹, and reported
230 D_{Fe²⁺}, D_{Fe³⁺} and D_{Fe³⁺/D_{Fe²⁺}} from Mallmann and O’Neill²⁹ for comparison
231 (Supplementary Table 4).

232 Cpx from this study shows ranges of 0.23–3.19 for D_{FeT}, 0.88–1.27 for D_{Fe²⁺},
233 0.98–6.28 for D_{Fe³⁺}, and 1.00–6.11 for D_{Fe³⁺/D_{Fe²⁺}}, respectively (Supplementary
234 Table 4a). Generally, D_{FeT}, D_{Fe²⁺}, D_{Fe³⁺} and D_{Fe³⁺/D_{Fe²⁺}} all decrease with
235 temperature (T) and melt NBO/T as exhibited by both our experiments and literature
236 data (Fig. 3A–B). In addition, D_{Fe³⁺} and D_{Fe³⁺/D_{Fe²⁺}} increase with the DAI (partition
237 coefficient of Al₂O₃) (Fig. 3C–D). Considering the effects of T, NBO/T and DAI, our
238 results are consistent with literature data regardless of the pressure. Importantly, the
239 D_{Fe³⁺/D_{Fe²⁺}} for cpx is always ≥1, indicating that the crystallization of cpx will lower

240 $\text{Fe}^{3+}/\text{Fe}_T$ ratio and $f\text{O}_2$ of the residual melt. Because the NBO/T and temperature are
 241 positively correlated, we regressed $\text{D}\text{Fe}^{3+}/\text{D}\text{Fe}^{2+}$ using temperature and DAI for the
 242 convenience of subsequent redox modelling and obtained the following equation:

243 $\text{Cpx: D}\text{Fe}^{3+}/\text{D}\text{Fe}^{2+} = -8.8638 + 4.9634 \cdot \text{DAI} + 11898/T$, $n=23$, $R^2=0.76$ (6)

244 In the regression, we only used data from this study and related manuscript because D-
 245 values from these two studies were determined using the same method. P-values for
 246 each parameter are far less than 0.05. The small P-values and relatively high R^2 indicate
 247 the reliability and accuracy of the regression.



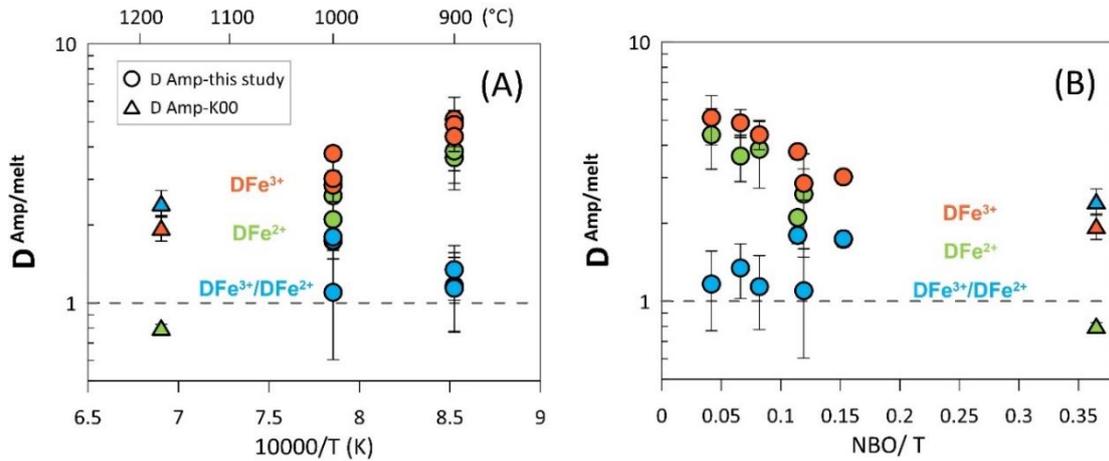
248 **Fig. 3. DFe^{3+} , DFe^{2+} and $\text{D}\text{Fe}^{3+}/\text{D}\text{Fe}^{2+}$ for cpx and melt.** (A) DFe^{3+} , DFe^{2+} and $\text{D}\text{Fe}^{3+}/\text{D}\text{Fe}^{2+}$
 249 as a function of $10000/T$. (B) DFe^{3+} , DFe^{2+} and $\text{D}\text{Fe}^{3+}/\text{D}\text{Fe}^{2+}$ as a function of melt NBO/T. (C)
 250 DFe^{3+} vs. DAI. (D) $\text{D}\text{Fe}^{3+}/\text{D}\text{Fe}^{2+}$ vs. DAI. Data cited are from W22: related manuscript, S18:
 251 Sorbadere et al.⁵², M09: Mallmann & O'Neill²⁹ and D21: Davis et al.²¹.
 252

253 Amp shows ranges of 2.80–5.01 for DFe_T , 1.73–4.39 for DFe^{2+} , 2.85–5.11 for
 254 DFe^{3+} and 1.10–1.80 for $\text{D}\text{Fe}^{3+}/\text{D}\text{Fe}^{2+}$ at our experimental conditions (Supplementary
 255 Table 4b). Similar to cpx, the DFe_T , DFe^{2+} and DFe^{3+} decrease with T and melt NBO/T
 256 (Fig. 4A–B). But the effects of T and NBO/T on $\text{D}\text{Fe}^{3+}/\text{D}\text{Fe}^{2+}$ of Amp are indiscernible.

257 We note that the $D_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ values calculated from the most oxidizing experiment of
 258 King et al.²⁸ is generally consistent with our results. Here we propose an average
 259 $D_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ of 1.38 from our experiments.

260
$$\text{Amp: } D_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 1.38 (\pm 0.31) \quad (7)$$

261 Because the $D_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ is always >1 , similar to cpx, amp crystallization will lower
 262 $\text{Fe}^{3+}/\text{Fe}_T$ and f_{O_2} of the residual melt.

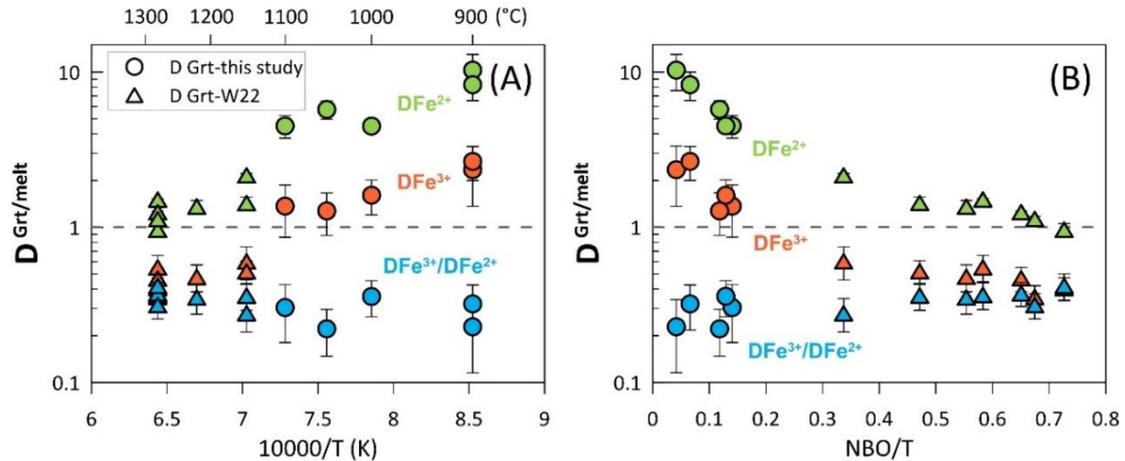


263
 264 **Fig. 4. $D_{\text{Fe}^{3+}}$, $D_{\text{Fe}^{2+}}$ and $D_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ between amp and melt. (A) $D_{\text{Fe}^{3+}}$, $D_{\text{Fe}^{2+}}$ and**
 265 **$D_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ as a function of $10000/T$. (B) $D_{\text{Fe}^{3+}}$, $D_{\text{Fe}^{2+}}$ and $D_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ as a function of melt**
 266 **NBO/T. K20 indicates D-values obtained from the most oxidizing experiments in King et al.²⁸.**

267 The D_{Fe_T} , $D_{\text{Fe}^{2+}}$, $D_{\text{Fe}^{3+}}$ and $D_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ for grt respectively ranges from 2.06 to
 268 3.47, 4.49 to 10.29, 1.27 to 2.66 and 0.22 to 0.36 (Supplementary Table 4c). As
 269 highlighted by our and related manuscript's experiments, D_{Fe_T} , $D_{\text{Fe}^{2+}}$ and $D_{\text{Fe}^{3+}}$
 270 decrease with T and melt NBO/T (Fig. 5A–B). But $D_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ is almost invariable
 271 (Fig. 5A–B) with an average of 0.33 ± 0.06 ($n=12$).

272
$$\text{Grt: } D_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.33 (\pm 0.06), n=12 \quad (8)$$

273 Contrary to cpx and amp, grt crystallization will increase $\text{Fe}^{3+}/\text{Fe}_T$ and f_{O_2} of the
 274 residual melt because its $D_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ is always <1 .



275
 276 **Fig. 5. DFe³⁺, DFe²⁺ and DFe³⁺/DFe²⁺ for grt and melt.** (A) DFe³⁺, DFe²⁺ and DFe³⁺/DFe²⁺ as
 277 a function of 10000/T. (B) DFe³⁺, DFe²⁺ and DFe³⁺/DFe²⁺ as a function of NBO/T. References
 278 data cited are from W22: related manuscript.

279 In our experiments, mag shows values of 18.93–54.96 for DFe_T, 47.20–167.42 for
 280 DFe²⁺, 14.94–42.46 for DFe³⁺ and 0.24–0.38 for DFe³⁺/DFe²⁺ (Supplementary Table
 281 4d). For spl, the DFe_T, DFe²⁺, DFe³⁺ and DFe³⁺/DFe²⁺ respectively range from 10.64 to
 282 15.97, 8.29 to 19.55, 12.49 to 16.96 and 0.87 to 1.52 (Supplementary Table 4e).
 283 Consistent with literature data, DFe_T, DFe²⁺, DFe³⁺ for both mag and spl decrease with
 284 T and melt NBO/T (Fig. 6). We also observed that the DFe³⁺/DFe²⁺ for mag increases
 285 slightly with T and NBO/T, but the DFe³⁺/DFe²⁺ for spl increases strongly with T and
 286 NBO/T (Fig. 6). Intriguingly, because the DFe³⁺/DFe²⁺ is < 1 for mag and generally >
 287 1 for spl, mag crystallization will elevate Fe³⁺/Fe_T ratio and *f*O₂ of the residual melt, but
 288 spl crystallization has the opposite effect. The common view proposes that magnetite
 289 crystallization will decrease Fe³⁺/Fe_T and *f*O₂ of the residual melt by assuming that
 290 magnetite contains abundant Fe³⁺ (Fe³⁺: Fe²⁺=2:1)^{11,53}. On the contrary, our results
 291 reveal the opposite effect for mag crystallization because neither natural nor
 292 experimental mag is pure end member of Fe₃O₄⁵⁴. Using the results from this study and
 293 related manuscript, the DFe³⁺/DFe²⁺ for mag and spl can be regressed as the following
 294 equations:

295 Mag: $D_{Fe^{3+}/Fe^{2+}} = 0.9118 - 769.1/T$, $n=12$, $R^2=0.83$ (9)

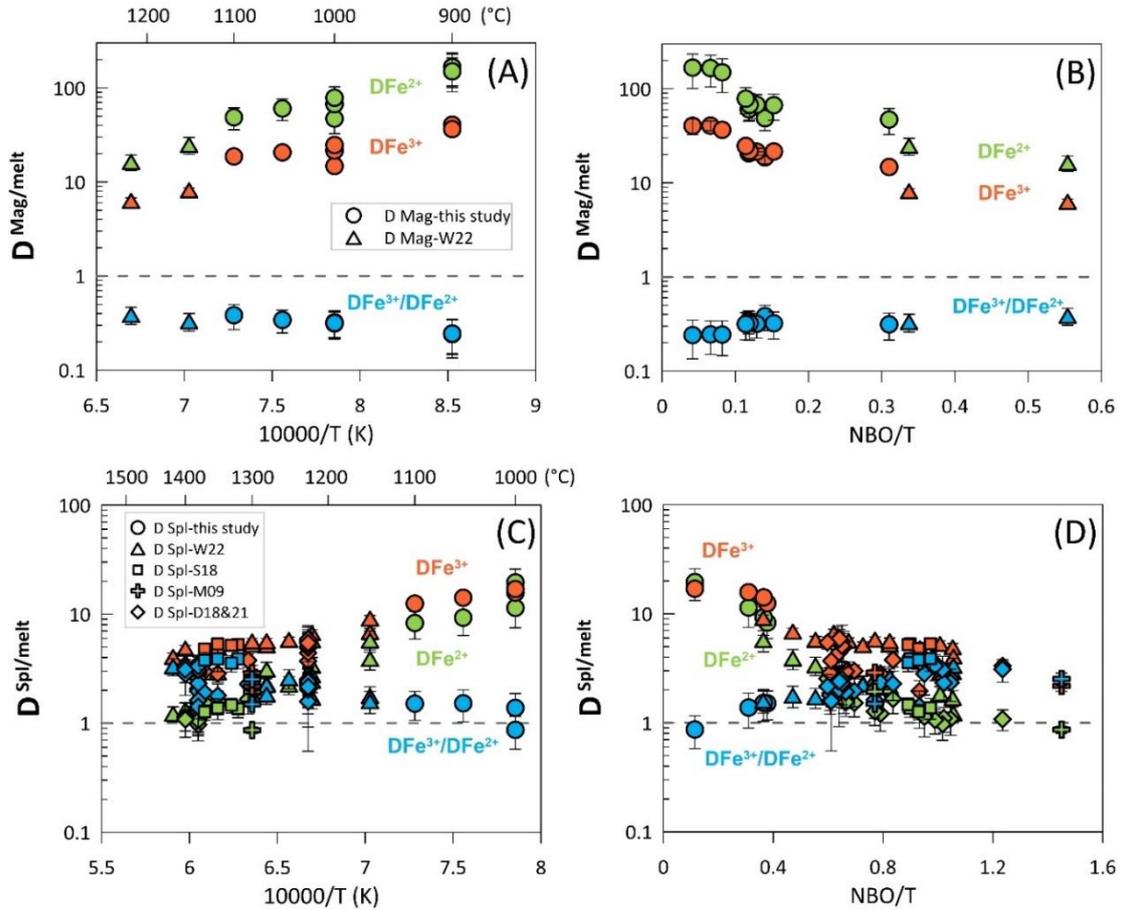
296 Spl: $D_{Fe^{3+}/Fe^{2+}} = 9.7005 - 11142.3/T$, $n=17$, $R^2=0.79$ (10)

297 For the convenience of the redox modelling, we also regressed $D_{Fe^{2+}}$ using T and
 298 obtained the following equations:

299 $Mag: \ln D_{Fe^{2+}} = -5.0371 + 11832.8/T, n=12, R^2=0.93$ (11)

300 $Spl: \ln D_{Fe^{2+}} = -7.4720 + 12918.7/T, n=17, R^2=0.95$ (12)

301 The high R^2 and low p-values (<0.05) demonstrate the reliability and accuracy of these
 302 regressions.



303 **Fig. 6. $D_{Fe^{3+}}$, $D_{Fe^{2+}}$ and $D_{Fe^{3+}/D_{Fe^{2+}}}$ for Fe-oxides (mag and spl) and melt. (A) $D_{Fe^{3+}}$,**
 304 **$D_{Fe^{2+}}$ and $D_{Fe^{3+}/D_{Fe^{2+}}}$ as a function of $10000/T$ for mag. (B) $D_{Fe^{3+}}$, $D_{Fe^{2+}}$ and $D_{Fe^{3+}/D_{Fe^{2+}}}$**
 305 **as a function of melt NBO/T for mag. (C) $D_{Fe^{3+}}$, $D_{Fe^{2+}}$ and $D_{Fe^{3+}/D_{Fe^{2+}}}$ as a function of**
 306 **$10000/T$ for spl. (D) $D_{Fe^{3+}}$, $D_{Fe^{2+}}$ and $D_{Fe^{3+}/D_{Fe^{2+}}}$ as a function of melt NBO/T for spl.**
 307 **References data are cited from W22: related manuscript, S18: Sorbadere et al.⁵², M09:**
 308 **Mallmann & O'Neill²⁹ and D21: Davis et al.²¹.**

310 To summarize, D_{Fe_T} , $D_{Fe^{2+}}$ and $D_{Fe^{3+}}$ for silicate minerals and Fe-oxides all
 311 decrease with T and melt NBO/T . $D_{Fe^{3+}/D_{Fe^{2+}}}$ for cpx decreases with T and NBO/T ,
 312 but that for mag and spl increases with T and NBO/T . No obvious pressure effect on

313 D_{Fe_T} , $D_{Fe^{2+}}$ and $D_{Fe^{3+}}$ and $D_{Fe^{3+}/Fe^{2+}}$ was observed. More importantly, the
314 crystallization of cpx, amp and spl will lower Fe^{3+}/Fe_T and fO_2 of the residual melt
315 because their $D_{Fe^{3+}/Fe^{2+}}$ values are generally > 1 . However, the crystallization of grt
316 and mag has an opposite effect because their $D_{Fe^{3+}/Fe^{2+}}$ values are < 1 . How the fO_2
317 evolves during arc magma differentiation should therefore depends on the crystallizing
318 mineral assemblages and the bulk mineral/melt partition coefficient of $D_{Fe^{3+}}$ and
319 $D_{Fe^{2+}}$.

320 **Discussion**

321 **Redox evolution during arc magma differentiation**

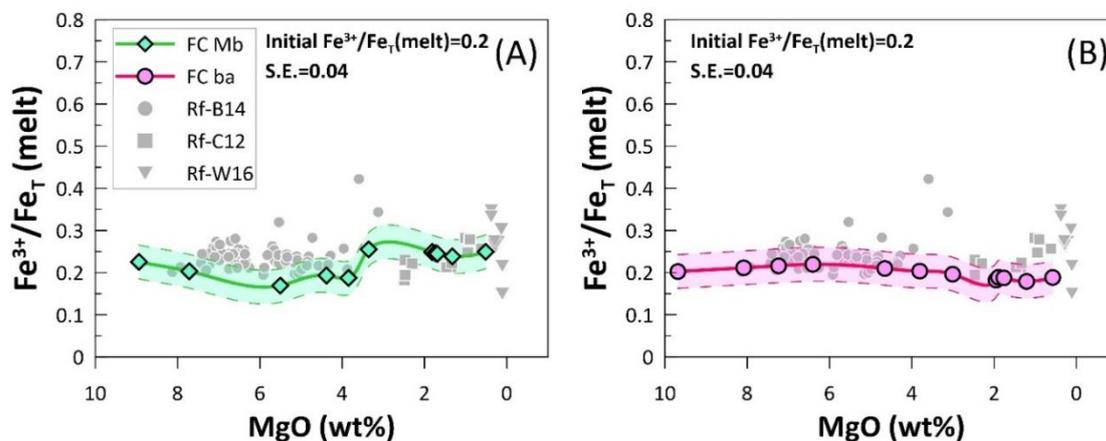
322 The redox evolution during arc magma differentiation is dictated by Fe^{3+}/Fe_T of the
323 derivative melt. How Fe^{3+}/Fe_T of the melt changes depends on $D_{Fe^{3+}/Fe^{2+}}$ of the
324 minerals and the crystallizing mineral assemblage. Here, we model the redox evolution
325 during arc magma differentiation by combining the determined $D_{Fe^{3+}/Fe^{2+}}$ from this
326 study and the reported crystallizing mineral assemblages from Ulmer et al.⁹. Ulmer et
327 al.⁹ experimentally determined the liquid line of descent (LLD) of typical primitive arc
328 magmas at 1 GPa using a high-Mg basalt and a high-Mg basaltic andesite, respectively.
329 Their experiments successfully reproduce the LLD of arc magmas and should mimic
330 the differentiation processes of arc magmas, which enable us to explore redox evolution
331 of typical arc magmas.

332 During arc magma differentiation, the Fe^{3+}/Fe^{2+} (i.e., Fe^{3+}/Fe_T) ratio of the melt
333 reflects the redox state of the magma, while the MgO content of the residual melt
334 records the degree of crystallinity. Therefore, we can investigate redox evolution during
335 magma differentiation by exploring how the melt Fe^{3+}/Fe_T ratio evolves with decreasing
336 melt MgO (Supplementary Table 5). At each differentiation step, MgO content and
337 Fe^{3+}/Fe_T ratio of the melt can be calculated from the bulk D_{totMg} , $D_{totFe^{2+}}$ and $D_{totFe^{3+}}$
338 between crystallizing minerals and residual melt. The bulk D-values of Mg, Fe^{2+} and
339 Fe^{3+} at each step are respectively weighted average of mineral DMg , $D_{Fe^{2+}}$ and $D_{Fe^{3+}}$
340 and the mineral fraction. At a given step (in every 30 or 50 °C), the fraction of each
341 mineral is as reported in Ulmer et al.⁹ and the DMg for each mineral can be calculated
342 from the MgO content of the experimental minerals and melt. $D_{Fe^{2+}}$ for each mineral

343 at the step can then be derived from the calculated DMg according to Eqs. (3)–(5) or
344 from the experimental temperature following Eqs. (11)–(12). After that, the
345 $D\text{Fe}^{3+}/D\text{Fe}^{2+}$ ratio for each mineral can be estimated from Eqs. (6)–(10) and thus $D\text{Fe}^{3+}$
346 can be determined from the derived $D\text{Fe}^{2+}$ and estimated $D\text{Fe}^{3+}/D\text{Fe}^{2+}$. For
347 orthopyroxene, the $D\text{Fe}^{2+}$ was calculated from DMg using the regression in the related
348 manuscript and the $D\text{Fe}^{3+}/D\text{Fe}^{2+}$ were determined following the relation between
349 $D\text{Fe}^{3+}/D\text{Fe}^{2+}$, temperature, and DAI (Supplementary Table 4f). For plagioclase, the
350 $D\text{Fe}^{3+}$ and $D\text{Fe}^{2+}$ values were calculated based on the empirical equations from
351 Lundgaard and Tegner⁵⁵.

352 Following the above rationale, we modelled the redox evolution during arc magma
353 differentiation given an initial $\text{Fe}^{3+}/\text{Fe}_T$ of 0.20 (± 0.04), which is the average of the least
354 degassed primitive arc basalts^{15,56,57}. The fractional crystallization modelling for the
355 high-Mg basalt and the high-Mg basaltic andesite is shown in Fig. 7. The details of the
356 modelling are reported in Supplementary Table 5. As shown in Fig. 7, $\text{Fe}^{3+}/\text{Fe}_T$ of the
357 derivative melts shows limited variation during the differentiation of arc magmas.
358 Specifically, during the differentiation of the high-Mg basalt, $\text{Fe}^{3+}/\text{Fe}_T$ of the derivative
359 melts ranges from 0.17–0.26, showing a slight decrease and an increase at MgO interval
360 of 7.7–5.5 wt% and 3.9–3.4 wt%, respectively (Fig. 7A). The decrease in $\text{Fe}^{3+}/\text{Fe}_T$ was
361 induced by extensive crystallization of cpx and spl and the increase in $\text{Fe}^{3+}/\text{Fe}_T$ was
362 caused by mag crystallization. For the basaltic andesite, $\text{Fe}^{3+}/\text{Fe}_T$ of the derivative melts
363 range from 0.18–0.22 and is almost invariable during differentiation (Fig. 7B). The
364 modelling results reproduce the observed $(\text{Fe}^{3+}/\text{Fe}_T)^{\text{melt}}$ from natural samples and
365 indicate that the $f\text{O}_2$ of arc magmas remains invariable during differentiation^{13-16,56,58}.
366 Beneath thick crust, grt may fractionate and thus elevate $\text{Fe}^{3+}/\text{Fe}_T$ of the residual melt¹⁰.
367 However, recent studies demonstrated that arc magmas evolve mainly in the stability
368 field of amp rather than grt, even for thick crust in Andes^{59,60}. Therefore, our modelling
369 results should represent a universal phenomenon considering that arc magmas evolve
370 in a limited pressure range (amphibole stability field). We emphasize that although
371 crystallization of a single mineral may elevate or lower $\text{Fe}^{3+}/\text{Fe}_T$ and $f\text{O}_2$ of the residual

372 melt, the $\text{Fe}^{3+}/\text{Fe}_T$ and $f\text{O}_2$ remain largely invariable because the fractionation capacities
373 of the minerals on $\text{Fe}^{3+}/\text{Fe}_T$ are counterbalanced.



374

375 **Fig. 7. Redox evolution of a high-Mg basalt (mb) and a high-Mg basaltic andesite (ba)**
376 **revealed by $\text{Fe}^{3+}/\text{Fe}_T$ of the derivative melts. (A) Redox evolution of a hydrous high-Mg**
377 **basalt. (B) Redox evolution of a high-Mg basaltic andesite. The fractionation models are based**
378 **on the LLD reported by Ulmer et al.⁹. Because our experiments and literature data cover a**
379 **temperature range of 900–1420 °C, the redox modelling is restricted to ≥ 900 °C to avoid large**
380 **uncertainties. $\text{Fe}^{3+}/\text{Fe}_T$ ratios of the arc magmas are compiled from Brounce et al.⁵⁶, Crabtree**
381 **and Lange¹² and Waters et al.¹⁶.**

382

383 Because the redox state of arc magmas barely changes during magmatic
384 differentiation, the subaerial magmas and volcanic gases should inherit the redox state
385 from mantle sources. Therefore, a well-reasoned inference could be: oxidizing volcanic
386 gas must derive from an oxidized mantle. If the Great Oxidation Event (GOE) was
387 triggered by increasing oxidizing capacity of volcanic gases^{2,3}, our results propose that
388 the mantle must have become oxidized around the GOE as has also been proposed by
389 other recent studies^{4,61,62}.

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397 **Methods**

398 **High pressure experiments**

399 All the experiments were conducted at 1–2 GPa and 900–1100 °C on a piston cylinder
400 apparatus at X. The starting material was a synthetic, medium-K basalt glass (MKBN2)
401 containing 49.04 wt% SiO₂, 0.68 wt% TiO₂, 15.83 wt% Al₂O₃, 11.77 wt% FeO_T, 0.1
402 wt% MnO, 7.06 wt% MgO, 8.72 wt% CaO, 3.65 wt% Na₂O, 1.14 wt% K₂O, 0.20 wt%
403 Cr₂O₃ and 0.10 wt% NiO. Another 0.7 wt% MnO and ~700ppm La was doped to this
404 composition for other purpose. For each sample, we first loaded 5–10 wt% of H₂O
405 followed by the Ru–RuO₂ mixture (the *f*O₂ buffer, Ru:RuO₂=1:1 wt%) at the bottom of
406 the platinum (Pt) capsule (2.0 OD; 1.7 mm ID; 6 mm length). Then, ~6 mg starting
407 material were filled into the Pt capsule, which was then welded shut. The mass ratio of
408 the Ru–RuO₂ mixture and the starting material was adjusted to ~0.67. The use of the
409 Ru–RuO₂ buffer maintains oxidizing conditions and prevents Fe loss during the
410 experiments^{18,31,41,63}. Besides, the Ru–RuO₂ buffer will not change the phase relations
411 because Ru is relatively insoluble in silicate melts [<100 ppm,⁴¹]. Finally, the welded
412 sample were checked for leaks by drying in an oven at 110 °C for more than 2 hours
413 and then weighing. The Pt sample containers were then wrapped into a half-inch
414 assembly and loaded into the piston cylinder. The experimental temperature was
415 controlled by a thermos-controller and monitored by a Pt–Pt₉₀Rh₁₀ (S-type)
416 thermocouple with an error of $\pm 2^\circ\text{C}$. Considering the temperature gradient, the
417 temperature uncertainty of our experiments is within $\pm 15^\circ\text{C}$. A friction correction of
418 13% was applied for the 1/2 inch assembly and the pressure uncertainty is < 0.1 GPa.
419 The experimental durations range from 75 to 126 hours, depending on the temperature
420 (Supplementary Table 1). After the experiments, the samples were sectioned, mounted
421 in epoxy resin, and polished for later backscattered electron imaging and electron
422 microprobe analysis (EPMA).

423 **EPMA analysis**

424 The run products were observed under a Carl Zeiss SUPRA55 SAPHIR field
425 emission scanning electron microscope and analyzed using a JEOL JXA-8230 EPMA
426 at X. The EPMA analytical conditions were set to an accelerating voltage of 15 kV, a
427 beam current of 20 nA and a nominal 0 μm beam diameter for minerals. For quenched
428 melts, the beam diameter was varied from 10–20 μm , depending on the size of the glass
429 pools. Peak counting time was 10 s for all the elements; background counting time was
430 5 s. The primary standards were: olivine for Si; rutile for Ti; pyrope for Al; fayalite for
431 Fe; bustamite for Mn; hornblende for Mg and Ca; orthoclase for K; and Albite for Na.
432 Data reduction was performed by using a ZAF correction. A dry glass⁶⁴ was used as a
433 secondary standard to monitor the analytical accuracy and precision. The recorded
434 relative precision is better than $\pm 2\%$ for SiO_2 , Al_2O_3 , and CaO , $\pm 5\%$ for TiO_2 , FeO ,
435 MnO , MgO , K_2O and $\pm 10\%$ for Na_2O . The analytical results are reported in
436 Supplementary Table 3.

437

438 **Data availability**

439 All data needed to evaluate the conclusions in the paper are present in the paper and/or
440 the Supplementary information. Additional data related to this paper may be requested
441 from the authors.

442

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637 **Author contributions**

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639 **Competing interests**

640 The authors declare that they have no competing interests.

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642 **Additional information**

643 Supplementary information is available for this paper.

644

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