1 **Redox-sensitive partitioning of vanadium and other heterovalent elements between apatite and**
2 **biotite in high silica magmas**

3 Peteris Rozenbaks and James M. Brenan

4 *Department of Earth and Environmental Sciences, Dalhousie University, Halifax, Canada*

5

6 **Abstract**

7 Apatite and biotite, ubiquitous minerals in a multitude of natural rocks, host a variety of

8 trace elements, including those whose valence state, and hence ionic radius and charge, can vary

9 over the oxygen fugacity (fO$_2$) of natural magmatic systems. In this study, we determine partition

10 coefficients (D values) between apatite (ap), biotite (bt), and glass (gl) in five suites of natural,

11 mostly silicic, metaluminous to peraluminous rocks of reduced to oxidized conditions (FMQ-2.8 to

12 +4.3; FMQ = fayalite-magnetite-quartz buffer). Elements considered include alkalis, alkaline earths,

13 rare earth elements, transition metals, metalloids, and high field strength elements, of which V, As,

14 Eu, Mo, Sn, and W are expected to be heterovalent over the fO$_2$ range considered.

15 Results reveal changes in partitioning of the heterovalent elements over the fO$_2$ range. With

16 increasing fO$_2$ from FMQ-2.8 to FMQ+2.8, values of D$^{bt/gl}$ for V decrease from ~580 to ~50 whereas

17 D$^{ap/gl}$ increases from ~0.6 to ~5. Arsenic becomes more compatible in apatite with D$^{ap/gl}$ increasing

18 from ~ 0.04 to ~1.6. Europium D$^{ap/gl}$ values increase from ~20 to ~90. Molybdenum D$^{bt/gl}$ decreases

19 from ~2 to ~0.1. Tin becomes more compatible with both minerals as fO$_2$ increases, with D$^{bt/gl}$

20 increasing from ~0.1 to ~1.0 and D$^{ap/gl}$ from ~0.05 to ~0.3. Although the uncertainty on D$^{ap/gl}$ for W

21 is too large to derive a meaningful fO$_2$ relation, values for D$^{bt/gl}$ decrease from ~0.13 to ~0.02 with

22 increasing fO$_2$. As vanadium shows counter variation in individual mineral/glass partitioning, the

23 apatite/biotite partitioning (D$^{ap/bt}$) sympathetically increases from ~0.003 to ~0.5 with increase in

24 fO$_2$.

25 In addition to shifts in the relative proportions of oxidized and reduced species with fO$_2$, the

26 observed partitioning relations for heterovalent elements could be caused by differences in other

27 parameters that affect the activity of single species, species proportions, temperature, etc. These

28 confounding aspects are assessed by comparison of the homovalent element partitioning data,

29 which are relatively constant for the samples investigated, and with a suggestion that larger D-

30   values involving one suite (Mascota, Mexico) are likely due to the stabilization of higher valence V

31   species in a more alkaline melt composition. Results therefore indicate that the observed variation

32   in heterovalent element partitioning is predominantly the result of $f\mathrm{O_2}$ control on element species

33   and corresponding ionic radius. With this interpretation, we present a preliminary vanadium

34   partitioning model that considers changes in the proportion of vanadium species with $f\mathrm{O_2}$ and

35   estimated values $D^{ap/bt}$ for vanadium species. Model results are used to estimate the $f\mathrm{O_2}$ of the

36   peraluminous South Mountain Batholith (Nova Scotia, Canada) and Palabora carbonatite (South

37   Africa) for which oxybarometry has not been straightforward. Estimated oxygen fugacities are

38   consistent with other redox indications, however, other factors, including melt and biotite

39   composition, need to be considered to enable general application of the model. The partitioning of

40   vanadium between apatite and ferromagnesian minerals has the potential of a novel oxybarometer,

41   applicable to a broad range of igneous rocks, including Fe-Ti poor plutonic systems.

42   Keywords: apatite, biotite, vanadium, partitioning, trace element

43

1. Introduction

45   Oxygen fugacity ($f\mathrm{O_2}$) is one of the fundamental thermodynamic variables in geological

46   systems as it drives redox reactions and controls phase stability (Frost, 1991). This in turn impacts

47   such aspects as the mineral paragenesis, rock solidus, magma and ore genesis, composition of fluids

48   and the mass transfer between solar system reservoirs (Gaillard et al., 2015; Moretti & Neuville, 2021;

49   Mungall, 2002; Taylor & Green, 1988). For heterovalent elements, oxygen fugacity is also linked to the

50   identity and relative proportions of chemical species through redox reactions (Carmichael & Ghiorso,

51   1990). As each element species has a specific charge and radius, a unique partitioning behavior

52   between coexisting phases could result. Thus, with proper calibration, heterovalent element

53   partitioning can be used as a proxy for igneous $f\mathrm{O_2}$ (Arató & Audétat, 2017c; Ballhaus et al., 1991;

54   Burnham et al., 2015; Mallmann & O'Neill, 2013; Smythe & Brenan, 2015).

55   Among the suite of trace elements in natural igneous systems, vanadium (V) is somewhat

56   unique as it can exist in four valence states - V^{2+}, V^{3+}, V^{4+}, V^{5+} (Sutton et al., 2005). At the most

57   common geological redox conditions of ±2 log units relative to the fayalite-magnetite-quartz (FMQ)

58   redox buffer (Cottrell et al., 2021), most of the vanadium is speciated as V^{3+} and V^{4+} (Canil, 1999).

59   These two species are expected to have similar partitioning behavior to Fe^{3+} and Ti^{4+} due to the

60   same valence and similar ionic radii (IR): 0.064 nm[1] (V^{3+}), similar to 0.0645 nm (Fe^{3+}) and 0.058 nm

61   (V^{4+}), similar to 0.0605 nm (Ti^{4+}). Thus, V^{3+} is most compatible with Fe^{3+}-bearing phases

62   (clinopyroxene, magnetite) and V^{4+} preferentially enters the titaniferous oxide minerals (Arató &

63   Audétat, 2017b; Mallmann & O'Neill, 2009). Similarly, V^{2+} mimics Fe^{2+} due to the same charge and near-

64   identical radii (0.079 and 0.078 nm, respectively) resulting in high compatibility in ferromagnesian

65   minerals, although this V species is sparse in terrestrial magmas (Sutton et al., 2005). Pentavalent

66   vanadium, similar to other highly charged ions (Nb^{5+}, Ta^{5+}), is expected to accumulate in the melt

67   phase as its size and charge make it generally incompatible with igneous rock forming mineral

68   structures (summarized in Ballouard et al., 2020). This rich variety of V species and partitioning

69   behaviors has enabled several experimentally calibrated vanadium oxybarometers for mineral-melt

70   systems that link V partitioning to magmatic redox state (Arató & Audétat, 2017c; Holycross & Cottrell,

71   2020, 2022; Mallmann & O'Neill, 2013; Sossi et al., 2018).

72   The application of mineral-melt oxybarometers, however, is often precluded by poorly

73   constrained or absent melt composition estimates (e.g., in hypabyssal and plutonic systems).

74   Therefore, oxybarometers involving intermineral partitioning are of use in systems for which the

75   melt phase cannot be characterized. In moderately oxidized, iron-bearing igneous rocks, oxygen

76   barometry involving coexisting cubic and rhombohedral oxides has been widely employed (Ghiorso &

77   Evans, 2008; Ghiorso & Sack, 1991). Unfortunately, this method can be infeasible for many systems

78   (e.g. chemically evolved granites, carbonatites) which are too iron-poor or have otherwise formed

79   outside the stability field of coexisting oxides. Therefore, the development of oxybarometers

80   involving heterovalent element partitioning between other rock-forming minerals is desirable. As a

81   recent example, Holycross and Cottrell (2022) demonstrated systematic changes in

82   rutile/clinopyroxene and rutile/garnet partitioning of vanadium over a large fO_2 range, and

83   therefore the potential for oxybarometry in appropriate bulk compositions (i.e., eclogites). The

84   changes in intermineral partitioning documented by Holycross and Cottrell (2022) are due to the

85   unique behavior of rutile, and its preferential acceptance of the V^{5+} species, which is otherwise

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[1] Unless otherwise specified, ionic radii (IR) are from Shannon (1976)

86   incompatible in ferromagnesian minerals. From the consideration of cation radius and charge of

87   vanadium species, as described below, we expect that apatite may behave in a similar way to rutile,

88   with a preference for pentavalent vanadium. Owing to its ubiquity in intermediate to felsic igneous

89   rocks, and its common coexistence with apatite (Clarke et al., 2021), we have focused in this case on

90   biotite to complete the intermineral partitioning pair.

91   Apatite, with the formula $^{IX}Ca_4{}^{VII}Ca_6(^{IV}PO_4)_6(F,OH,Cl)_2$, comprises a group of phosphate

92   minerals, with three available cation sites (IV-, VII- and IX-fold), and most igneous endmembers

93   distinguished by the occupant of the anion site (OH, Cl, F). In the VII- and IX-fold cation sites, Ca^{2+} is

94   commonly substituted by Sr^{2+}, Pb^{2+}, Na^+, REE^{3+}, and other similarly-sized cations (Pan and Fleet,

95   2002), which are significantly larger (> 0.1 nm) than any of the vanadium species. However, V^{5+} may

96   be compatible in the apatite structure as the oxyanion $(VO_4)^{-3}$ substituted for $(PO_4)^{-3}$, as evidenced

97   by the complete solid solution series between $Ca_{10}(PO_4)_6F_2$ and $Ca_{10}(VO_4)_6F_2$ confirmed by Kreidler &

98   Hummel (1970). Biotite, with the general formula $^{XII}K^{VI}(Mg_{0.6-1.8},Fe_{2.4-1.2})^{IV}(AlSi_3)O_{10}(OH,F,Cl)_2$, is a

99   trioctahedral mica, represented by solid solution between the ferruginous annite and magnesian

100   phlogopite endmembers. In its octahedral site, common replacements include Al^{3+} (eastonite-

101   siderophyllite substitution), Fe^{3+} and Ti^{4+} (Dymek, 1983), suggesting that V^{2+}, V^{3+}, and V^{4+} could

102   likewise be compatible. As demonstrated by Gao et al. (2023), although the pentavalent cations

103   Nb^{5+} and Ta^{5+} exhibit some level of compatibility in biotite ($D(Nb,Ta)^{bt/gl}$ of ~0.05 to 3), values of

104    $D(Ti^{4+})^{bt/gl}$ are at least 10x larger, therefore V^{5+} is expected to be the least compatible vanadium

105   species.

106   In terms of the anticipated change in apatite/biotite partitioning with fO_2, V^{5+} is expected to

107   have the highest D value for distribution between apatite and biotite, owing to its stability in the

108   apatite structure as the $(VO_4)^{3-}$ oxyanion. With decreasing charge and increasing ionic radius, other V

109   species are generally expected to become progressively less compatible in the apatite structure and

110   more compatible in biotite, thus resulting in decreasing D values. The bulk distribution of all V species,

111    $D(\Sigma V)^{ap/bt}$ is therefore dependent on the igneous speciation of V, which is controlled by the magmatic

112   fO_2 (Sutton et al., 2005). As oxidizing conditions will increase the relative abundance of high-valence

113   V species, enhanced partitioning of V into apatite over biotite is expected, thus linking $D(\Sigma V)^{ap/bt}$ to

114   the igneous fO_2 in a positive correlation. We test this hypothesis by measuring the partitioning of

115 vanadium and other trace elements, including those with several valence states, between apatite,

116 biotite, and glass in five natural igneous systems formed over a wide range of oxygen fugacity.

117 **3. Materials and methods**

118 **3.1 Sample suites**

119   Samples of five, previously well-described volcanic and plutonic rock suites were analyzed in

120 this study:

121   1) Revancha dyke and Cerro Esquinani stock from the Picotani intrusive suite, related to the

122   Macusani volcanics, southeastern Peru (Sandeman et al., 1997),

123   2) Tuk-Tuk dome, related to the Youngest Toba tuff member, Sumatra, Indonesia (Chesner

124   et al., 2020),

125   3) Fish Canyon tuff, Colorado, USA (Whitney & Stormer, 1985),

126   4) Mascota minette, Jalisco, Mexico (Carmichael et al., 1996), and

127   5) Umiakovik pluton of the Nain intrusive suite, Labrador, Canada (Emslie & Stirling, 1993).

128   The global distribution of the sample suites is shown in Figure 1, and relevant characteristics

129 are provided in Table 1. The suites were selected based on the criteria that they contain unaltered

130 biotite and apatite in a textural association suggesting phase equilibrium (i.e., planar contacts, lack

131 of reaction textures). Except for the samples from Umiakovik and Mascota, all others contain a

132 vitreous matrix, which enables determination of mineral-melt partitioning. Also considered is that

133 other intensive parameters, including crystallization temperature (T) and oxygen fugacity are

134 reasonably well known and span a sufficiently large range that meaningful relations between fO_2

135 and partitioning of redox-sensitive elements could be obtained. Independent estimates of fO_2 have

136 been published for all the suites except the Macusani subvolcanics, in which the fO_2 was determined

137 in this study using the Ce-in-zircon oxybarometer (Smythe & Brenan, 2016). Estimated oxygen

138 fugacities range from ~FMQ-2.8 (Macusani subvolcanics) to FMQ+4.3 (Mascota minette) and

139 temperatures of 700-800°C (Table 1). Compositionally, samples range in whole-rock silica content

140 from 48.7 to 73.2, and are metaluminous to strongly peraluminous with A/CNK (molar ratio

141 Al_2O_3/[$CaO+Na_2O+K_2O$]) values of 0.5-1.2 (note that the glass analyses, reported below somewhat

142 differ from these whole-rock values due to the presence of phenocrysts).

143   Samples were received from several collections. A Fish Canyon tuff hand sample from the

144   classic sampling locality in a road cut on Colorado (USA) Highway 160 (Gleadow et al., 2015) was

145   provided by Dr. Ray Donelick (Apatite.com Partners LLC). Three samples of Macusani subvolcanics

146   were sourced from several collections – MAC137 (Revancha dyke) and MAC160 (Cerro Esquinani

147   stock) hand samples were received from Dr. John Hanchar (Memorial University of Newfoundland)

148   and MAC2 thin sections (Revancha dyke) from Dr. Hamish Sandeman (Geological Survey of

149   Newfoundland and Labrador). A Mascota minette sample was selected from the collection of the

150   Smithsonian Institution (catalog number NMNH 117626-21). Two samples of Tuk-Tuk tuff (TT and

151   TT7), related to the Younger Toba tuff, were provided by Dr. Craig Chesner (Eastern Illinois

152   University). Material from the Umiakovik Pluton were received as mineral separates from the

153   Geochronology Laboratory Archive of the Geological Survey of Canada (sample EC-87-119, database

154   number Z1280).

155   As-received rock hand samples were split into cm-sized fragments, and both rock fragments

156   and mineral separates were mounted in 1" epoxy pucks, which were then prepared by grinding with

157   progressively finer SiC grit, followed by 1 micron, then 0.3 micron alumina powder. Polished thin

158   sections of the Mascota minette were prepared in the Petrography Laboratory at Saint Mary's

159   University (Halifax, Canada). Sample billets for polished thin sections were lapped flat and mounted

160   to frosted glass slides using epoxy. Sections were cut and lapped to ~100 microns thick, then

161   polished using monocrystalline diamond suspensions down to 3 microns. Final polishing was

162   performed using 0.06 micron amorphous colloidal silica suspension.

163   **3.2. Analytical methods**

164   Reflected light image sample maps at a magnification of 2x were acquired by digital image

165   acquisition of the entire mounts. Areas of particular interest were then investigated by imaging at

166   higher magnifications. High spatial resolution textural observations and some semi-quantitative

167   chemical data on apatite, biotite and glass were obtained using a TESCAN MIRA 3 LMU Variable

168   Pressure Schottky Field Emission Scanning Electron Microscope (SEM) at Saint Mary's University

169   (Halifax, Canada). A beam voltage of 20 kV, beam current of 0.2 nA and an approximate working

170   distance of 17 mm were used for all EDS spot analyses and imaging. The reflected light and

171   backscattered electron images were used to identify mineral textures and morphology to select

172 areas for further chemical analysis. Individual mineral grains were selected based on lack of zoning

173 or an outer uniform zone being at least 25 μm thick. Similarly, for matrix glass analysis, areas larger

174 than 25 μm and devoid of microcrysts were selected.

175   The major element composition of the mineral and glass phases was determined using the

176 JEOL JXA-8230 Electron Probe Micro-Analyzer (EPMA) at the University of Toronto. Analytes and the

177 phase-specific routine analytical conditions are summarized in Table 2. The spectral interference

178 from the Fe $L\alpha_{1,2}$ emission line (705 eV) on the F Kα line (676.8 eV) was determined by measuring

179 the F ka intensity in Fe-metal, which was then used to calculate an appropriate correction factor.

180 Analysis of Fe metal yielded F concentrations below detection limit ($\leq$0.02 wt%), confirming the

181 efficacy of this correction method. Analytical accuracy was checked by analysis of fused beads of

182 basalt reference materials BIR-1, BHVO-1 and a fragment of rhyolite glass CAM66. For BIR-1 and

183 BHVO-1 the relative difference between the reported and measured values did not exceed 5% for

184 oxides of >1 wt.% abundance. For CAM66, the relative difference was <1% for SiO_2, Al_2O_3, K_2O

185 (above 4 wt.%) and <15% for FeO, CaO, Na_2O (above 1 wt.%). Although not certified standards, we

186 also analyzed fragments of San Carlos biotite (Righter and Carmichael, 1996) and Durango apatite as

187 checks on accuracy and reproducibility between analytical sessions. For San Carlos biotite, the

188 relative difference between the reported (Righter & Carmichael, 1996) and measured values was

189 <3.6% for oxides above 0.2 wt.%. For Durango apatite, the relative difference between the reported

190 (Young et al., 1969) and measured values was <0.05% for CaO and P_2O_5, 5.2% for F, <3.5% for SiO_2

191 and Cl. Detailed precision and accuracy estimates are summarized in the Table ST1.

192   Trace element concentrations of apatite, biotite, and glass were determined using the laser

193 ablation ICP-MS facility located in the Health and Environments Research Centre (HERC) Laboratory

194 at Dalhousie University. The system employs a frequency quintupled Nd:YAG laser operating at 213

195 nm, coupled to a Thermo Scientific iCAP Q quadrupole mass spectrometer with He flushing the

196 ablation cell to enhance sensitivity (Eggins et al., 1998). Zircon from the Macusani suite of samples

197 was analyzed at the Micro-Analysis of Natural Trace-element and Isotope Systematics (MANTIS)

198 laboratory at University of New Brunswick. The system employs an ArF laser operating at 193 nm,

199 coupled to Agilent 7700x quadrupole mass-spectrometer using a mixture of He, Ar, and N as the

200 carrier gas as described by McFarlane & Luo (2012). The details of all the trace element analyses are

201 provided in Table 2. Each analytical session involved initial tuning using the NIST 610 glass reference

202 material, using ^{115}In to maximize sensitivity, ^{248}ThO/^{232}Th of <0.005 to minimize oxide production

203 and ^{238}U/^{232}Th of ~1 to monitor mass fractionation. Where possible, the analyses were carried out

204 in traverse track configuration to improve the signal stability. Factory supplied time resolved

205 software was utilized for the acquisition of individual analyses. A typical analysis involved 20

206 seconds of background acquisition with the ablation cell being flushed with the carrier gas, followed

207 by laser ablation for 60 seconds, then 40-60 seconds of cell washout. Analyses were collected in a

208 sequence in which two analyses were done on the NIST 610 standard reference material at the start

209 of the acquisition cycle, then after every 20 analyses on the unknowns including secondary

210 standards.

211 All LA-ICP-MS data reduction was done off-line using the Iolite version 4.0 software package

212 (Paton et al., 2011). Time-resolved signals were individually examined based on the major elements

213 in each phase and marker elements of potential contaminants – Na and K for glass and alkali

214 feldspars, Ca for apatite, hornblende, and plagioclase, Ti for ilmenite, Zr for zircon, REE for monazite.

215 Narrow spikes and otherwise anomalous spectra of the potential contaminant elements were used

216 as indicators of signal impurity from inclusions or adjacent phases. Spikes near the margins of

217 spectra were excluded by narrowing the signal selection, whereas the spectra containing multiple

218 spikes were discarded. Spectra with abnormal features were also discarded if the extracted

219 compositions deviated by >2 standard deviations from the mean content of the markers of the

220 potential contamination. Ablation yields were corrected by referencing to the EPMA-measured

221 concentration of internal standards (Table 2). As vanadium is an element of especial interest in this

222 study, care was made to consider and resolve any significant analytical interferences with isobaric

223 species that could affect analytical accuracy. Specific to halogen-bearing minerals like apatite and

224 biotite is the possible interference of the ^{35}Cl-^{16}O molecule on ^{51}V. The magnitude of this

225 interference was assessed by analyzing a synthetic endmember Cl-apatite (containing 6.81 wt% Cl;

226 provided by John Hanchar, Memorial University), which was assumed to be vanadium-free.   The

227 calculated vanadium concentration of this material, considered to be wholly from the ^{35}Cl-^{16}O

228 interference, is ~1.3 µg/g, resulting in a contribution of ~0.2 µg/g/wt% Cl. The highest Cl

229 concentrations in measured phases are 0.84 wt% in apatite (FCT), 0.24 wt% in biotite (TT7) and 0.12

230 wt% in glass (FCT), resulting in maximum interference contributions of 0.16, 0.05 and 0.02 µg/g in

231 apatite, biotite and glass, respectively. Reported vanadium concentrations reflect this minor

232 correction.

233 Comparison between the measured and reported values for secondary standards yields

234 average relative differences of ~7% for BIR-1 and BHVO-1 (Jochum et al., 2005) and ~14% for

235 Durango apatite (Marks et al., 2012). Measurements of our Durango apatite fragment were cross-

236 verified against the specimen at the MANTIS lab, with the median relative differences being ~4.6%.

237 Summaries of the major and trace element concentrations of the analyzed phases are provided in

238 the Supplementary Tables ST1-6.

239 **4. Results**

240 **4.1 Phase assemblage and textures**

241 *Fish Canyon tuff* is sampled at its relatively lithic-rich, lower part of the thick proximal

242 vitrophyre ignimbrite. The sample consists of plagioclase, sanidine, biotite, hornblende, quartz,

243 magnetite, titanite, and ilmenite phenocrysts in a matrix of microcrysts, phenocryst fragments, and

244 glass. The relative proportions within the phenocryst assemblage in the sample are close to the ones

245 reported by Whitney and Stormer (1985) - ~55% plagioclase, ~15% alkali feldspar, 10% biotite, 10%

246 hornblende, 5% quartz, 5% trace minerals. Matrix is predominantly composed of glass shards,

247 crystal and pumice fragments, devitrified glass with several pockets of massive, fresh glass. Biotite is

248 typically fresh, euhedral, often kinked, and compositionally uniform (Figure 2a), often contains

249 inclusions of apatite, Fe-Ti oxides, and zircon. Apatite is present as up to 300 µm long, euhedral,

250 equant to tabular phenocrysts and biotite-hosted inclusions. Texturally, apatite crystals are uniform,

251 featuring few inclusions of zircon and Fe-Ti oxides.

252 *Macusani subvolcanics* comprise samples from the Revancha dyke and the Cerro Esquinani

253 stock, which consist of plagioclase, sanidine, biotite phenocrysts with trace amounts of monazite,

254 apatite, ilmenite, and zircon set in a massive, uniform holohyaline matrix without any macroscopic

255 evidence of weathering or hydrothermal alteration. The Revancha dike exhibits a glass-rich (up to 74

256 vol%) margin (represented by MAC2) and a crystal-rich (up to 50 vol%) porphyritic interior,

257 separated by a flow-banded facies with an intermediate glass content (represented by MAC137;

258   Sandeman & Clark, 2003). MAC137 (Figure 2b) is rich in biotite phenocrysts and microphenocrysts,

259   typically reverse-zoned, particularly the older, larger phenocrysts, which commonly exhibit

260   resorption features. Iron numbers (molar Fe/[Fe+Mg]; Fe#) of the analyses bt02 (rim) and bt03

261   (interior, Figure 2b) are 0.48 and 0.51 respectively. The smaller biotite microphenocrysts, however,

262   are euhedral and lack zoning. Apatite is euhedral to subhedral, commonly equant, texturally uniform

263   without obvious zoning. Apatite crystals are present as microphenocrysts and biotite-hosted

264   inclusions. Apatite phenocrysts, up to hundreds of microns in size, host ubiquitous melt, zircon,

265   ilmenite, and monazite inclusions (Figure 2 c,d), few crystals feature inherited cores (Fig. 2e).

266   Mineral textures in the more crystal-poor MAC2 (Figure 2c) are generally the same as in MAC137.

267   Glass in both samples is unaltered, but rich in microlites with a few clear areas, typically surrounded

268   by perlitic cracks. In the Cerro Esquinani stock sample (MAC160), biotite is unzoned, with some

269   occurrences of partial resorption. Both apatite and zircon are present, but less abundant in Cerro

270   Esquinani than in the Revancha dyke. Zircon is rare, occurring as small (<30 μm), euhedral

271   microphenocrysts and as inclusions in other minerals (Supplementary Figure S1). Typical of igneous

272   zircons, the zircon grains exhibit concentric growth and sector zoning; inherited cores

273   (Supplementary Figure S1a) are comparatively uncommon.

274   *Tuk-Tuk tuff* samples are light gray-to-white, vesicular (6-7 vol%; Figure 3e), comprised of

275   glass (47-72 vol%), quartz (6-12 vol%), sanidine (1-12 vol%), plagioclase (9-34 vol%), biotite (1-4

276   vol%), and hornblende (≤ 2 vol%) with trace amounts of zircon, allanite, magnetite, ilmenite,

277   orthopyroxene, and apatite (Chesner et al., 2020). Biotite in both samples is euhedral and kinked

278   crystals are common. Biotite does not exhibit observable compositional zoning and resorption

279   features in biotite are rare. Biotite-hosted inclusions of zircon, monazite, magnetite, and feldspar

280   are common in both samples, and melt inclusions are rare. Biotite in TT7 contains ubiquitous

281   inclusions of columnar apatite crystals, which are more common than the free apatite phenocrysts.

282   Apatite crystals are typically <100 μm long, euhedral, compositionally uniform, and lack mineral or

283   melt inclusions. Sample TT, however, is completely devoid of apatite.

284   *The Mascota augite minette* sample consists of augite (~13 vol%), biotite (~10 vol%), and

285   apatite (~3 vol%) phenocrysts and microphenocrysts in a very fine-grained matrix of augite, biotite

286   and Fe-Ti oxides. Biotite is predominantly euhedral with the largest phenocrysts (>1000 μm)

287   exhibiting sieve textures, resorption features, and normal zoning. Smaller biotite crystals (<100 μm)

288   are uniform and euhedral. Compared to the other analysed biotite populations, Mascota biotite

289   contains much fewer inclusions of apatite and other minerals. Apatite is represented by euhedral,

290   columnar to tabular, up to 500 μm long crystals lacking any observable zoning and inclusions.

291   Apatite crystals in contact with biotite are usually not entirely surrounded by biotite.

292   *The Umiakovik biotite-hornblende granite* sample consists of alkali feldspar (43 vol.%), quartz

293   (25 vol.%), plagioclase (20 vol.%), biotite (7 vol.%), hornblende (5 vol.%) and trace amounts of

294   apatite, zircon, ilmenite, and fluorite (Emslie & Loveridge, 1992). Biotite is dark brown, often bent,

295   subhedral, up to 1-2 mm large crystals without noticeable zoning in reflected light or SEM. Biotite

296   occasionally contains up to 20 microns sized apatite and zircon inclusions. Apatite crystals are

297   typically up to 400 microns in size, are euhedral with a prismatic habit, and pale green to

298   transparent in color. Backscatter electron imaging reveals that approximately 30% of apatite

299   crystals exhibit a distinct darker, rounded core with >20 micron thick, bright rim. Inclusions in

300   apatite are rare, usually comprising micron-sized zircons.

301   **4.2. Major element compositions of the glasses**

302   The analysed suite of matrix glasses represents silica-rich (71-75 wt% SiO_2), moderately to

303   strongly peraluminous (A/CNK=1.0-1.4), K- (4.9-5.7 wt% K_2O) and Na-rich (2.4-3.0 wt% Na_2O),

304   rhyolitic melt compositions, poor in MgO, FeO, CaO, and TiO_2. The electron microprobe data totals

305   are typically 95-97 wt%, which suggests the presence of dissolved H_2O. Among other volatiles, F and

306   SO_3 were below detection limits (0.2 and 0.1 wt% respectively), whereas Cl contents vary between

307   0.03 wt% (Macusani subvolcanics) and 0.12 wt% (FCT) with intermediate values of 0.08-0.09 wt% in

308   the Tuk-Tuk samples. Within the rather uniformly rhyolitic sample suite, Macusani subvolcanics

309   stand out as the most peraluminous and least alkaline (Figure 3), thus overlapping with the

310   genetically related effusive Picotani and Quenamari samples reported by Pichavant et al. (2024).

311   Glass from the Fish Canyon tuff represents the most potassic and silicic compositions, and the Tuk-

312   Tuk tuffs are the most sodic and calcic in the sample group (Figure 3).

4.3. Major element composition of mineral phases

Biotite compositional diversity is reflected by their values of Fe# (iron number; $(Fe^{2+}/Fe^{2+}/Mg)$; molar basis), which describes the solid solution between phlogopite and annite (Figure 4). Iron number varies more between, than within most groups, thus resulting in discrete Fe# ranges for MM (0.15-0.21), FCT (0.38-0.42) , TT and TT7 (0.57 – 0.61), MAC160 (0.45-0.52), and UP (0.83-0.90). The Revancha biotite Fe# range is broader (0.24-0.53), which corresponds to a relatively higher variability in all other major element abundances, some of which (positive - Al, Mn, Cl, negative - Na) exhibit a covariation with Fe#, whereas others (Ti, F) do not. For Revancha biotites, which are the most Mg-rich (Fe#>0.42), the Ti content is highly variable (0.2 – 0.7 a.p.f.u.), whereas the more Fe-rich biotites show less variation in Ti (0.34 - 0.42).

Across the analyzed rock suites, other major element abundances in biotite overlap, leaving only few signature outliers. The strongly peraluminous composition of the Macusani subvolcanics is reflected in biotite with a slightly increased abundance of total Al and tetrahedral Al, the latter corresponding to a decreased silica content due to the common Al-Si substitution in the tetrahedral site. Based on the MnO content, the biotite suites can be divided into low-Mn biotite (MAC and MM) and high-Mn (FCT, TT, UP) biotite (Figure 4c). The Umiakovik biotite, which is annite-rich and generally variable in its major element content, is particularly low in Na, just exceeding the detection limit of 0.02 wt% (Fig. 4d).

The major element content of apatite is generally uniform across the suites – Ca contents typically exceed 9.5 a.p.f.u., which almost entirely fills the 7-fold and 9-fold coordination sites. Tetrahedral sites are primarily filled with P (5.6-5.8 a.p.f.u.) with a minor Si component (0.1-0.2 a.p.f.u.). The anion site is dominated by F (1-2 a.p.f.u.), leaving <1 a.p.f.u. of OH⁻, and trace amounts of Cl in a negative correlation with Fe in apatite (Figure 5). Mascota apatite has an exceptionally high Si content (~0.2 a.p.f.u.) compared to apatite from other suites (~0.1 a.p.f.u.).

4.4. Trace element compositions

The trace element content of the analyzed glasses are normalized to the average upper crust (Rudnick & Gao, 2003) in Figure 6, where elements are grouped according to their chemical classification as alkalis (Li, Rb, Cs), alkaline earth (Sr, Ba), transition metal (Sc, V, Mn, Co, Ni, Cu, Zn,

Mo), metalloid (Ga, Ge, Cd, In, Sn, Pb, Bi), rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), and high field strength elements (Zr, Nb, Hf, Ta, W). Within each group the elements are ordered according to mass number. Relative to crustal abundances, the analyzed glasses are enriched in most alkalis, high field-strength elements and post-transition metals, but depleted in alkaline earth elements (except Ba) and transition metals. In their rare-earth element compositions, the matrix glasses are relatively depleted in intermediate REE (FCT and TT) or heavy REE (MAC) with a distinct negative Eu anomaly in MAC and TT. Macusani glasses are generally the most enriched in incompatible elements (with anomalously high Li, Cs, As, In, Sn concentrations in all Macusani glasses, Bi, Pb, Rb, Sb, U, W in Revancha glasses, and Zn in Cerro Esquinani glasses). The abundance of heterovalent elements in matrix glasses often strongly vary across the sample suite. Vanadium is relatively depleted in all glasses with the normalized abundance varying between ~0.04 in Fish Canyon tuff to ~0.008 in Revancha glasses. Molybdenum is generally enriched (up to ~5x the upper crustal abundance in Fish Canyon tuff), however, in Cerro Esquinani glass it is slightly depleted. Arsenic, indium, and tin are all most enriched (4-20x) in the Revancha dyke, and are slightly depleted (0.9-0.5x) in Fish Canyon tuff. Tungsten and uranium are also the most enriched in Revancha glasses (~7 x) and least enriched (1-2x) in Tuk-Tuk glasses.

The trace element abundances of biotite were found to correlate with their major element composition. Within the low-Al biotite group (all but MAC biotites), most of the trace elements correlate with the Fe#: Cs, Ge, Pb, Rb, Sc, Sn, Ta, V are in a positive correlation whereas Ba, Co, Cu, Eu, Hf, Ni, Sr, and Zr correlate negatively with Fe# (Supplementary Figure S5). The aluminous biotites of the evolved Macusani suite are enriched in trivalent (In, REE, Sc, As), pentavalent (P, Nb, Ta), other incompatible elements (Rb, Pb, Ge, Bi) and vanadium relative to the less aluminous biotites.

Apatite strontium content correlates with the bulk rock silica content in a trend (in order of increasing Sr) of UP-MAC137-MAC2-TT7-MAC160-FCT-MM. Within this series, Ba, V, Zn, Zr increase and REE+Y decrease with increasing Sr. MAC and MM apatite populations record the broadest Sr ranges (554-179 µg/g and 7875-5365 µg/g, respectively) and reveal compositional trends: in MM, Ba, REE, Mn, Ta, Th, Ti, V are in a positive correlation with Sr, whereas in MAC, Ba, LREE, Th, V, Zr are in positive correlation and HREE, Mn are negatively correlated with Sr. Apatite from the Umiakovik pluton show the largest variability in compatible trace elements (REE, Y, U, Th) without any

13

370 correlation to Sr. Instead, the silica content is in a positive correlation with trivalent (Ga, As, REE+Y),

371 tetravalent (Ge, Zr, Hf, Th), and other highly charged ions (Ta, W, U) and Rb, without correlation to

372 Mn, Fe, and Sr. The magnitude of the Eu anomaly (Eu/Eu*$_{CN}$, where Eu*=(Sm x Gd)$^{0.5}$ and all element

373 concentrations are normalized to McDonough & Sun (1995) chondritic abundances) in UP apatites

374 strongly correlates with the Si content. The variation of trace elements in Macusani apatites is

375 similar to that of other apatites.

4.5. Apatite and biotite chemistry as tracers of evolution of Macusani subvolcanics

377 The measured biotite and apatite compositions in the Ravencha dyke samples (MAC2,

378 MAC137) from the Macusani subvolcanics show a high degree of variability in their major (Fig. 4a-d)

379 and trace element abundances (Supplementary Figure S4-5), which often do not follow the

380 expectations for a continuous liquid line of descent (e.g. Fe# and Al^{IV} in biotite, total REE content in

381 apatite, F/Cl in either mineral). This compositional heterogeneity has been attributed to a thermal

382 pulse and volatile (H$_2$O, Cl, F) influx due to mafic magma underplating (Sandeman & Clark, 2004). To

383 extract empirical partition coefficients that represent equilibrium mineral and glass compositions

384 therefore requires identification of co-crystallizing phase assemblages.   Based on biotite Fe#, F/Cl,

385 Na, and Rb/K (Fig. 4d-g), two distinct biotite generations can be distinguished in these samples: 1)

386 more primitive, magnesian (Fe# <0.41), F-rich (F/Cl >30), and Rb-poor (Rb/K <0.008) and 2) more

387 evolved, ferrous (Fe# >0.46), Cl-rich (F/Cl <15), and Rb-rich (Rb/K >0.010). Here we consider the

388 more evolved second generation biotite as in equilibrium with the surrounding glass, which is

389 supported by biotite-glass Fe-Mg exchange and interelement partitioning systematics consistent

390 with previous experimental studies (see below). In contrast to the Revencha dyke, sample MAC160

391 from the Cerro Esquinani stock yielded biotite with a more narrow compositional range, which is

392 overall similar to the more evolved Revancha dyke group, but the latter with lower Rb/K values.

393 Biotite in MAC160 is compositionally uniform and considered to have formed in a single

394 crystallization event.

395 In Macusani samples, two apatite generations can be distinguished based on Sr and

396 chondrite-normalized La/Sm, (La/Sm)$_{CN}$: one with low Sr (170-400 µg/g) and low La/Sm (0.6-1.2) and

397 the other with high Sr (450-560 µg/g) and high La/Sm (1.3-2.2) (Supplementary Figure 9). Both

398 compositional parameters can be associated with a control by plagioclase. As LREE are more

14

399 compatible in plagioclase than HREE (Bindeman & Davis, 2000; Pichavant et al., 2024), co-precipitation

400 with plagioclase diminishes the $(La/Sm)_{CN}$ ratio. As well, a decrease in Sr content in apatite is known

401 to reflect fractionation of a Ca-rich phase, such as plagioclase (e.g., Belousova et al. (2001)). For the

402 Revancha dyke, the impact of a thermal event has been to destabilized plagioclase, as evidenced by

403 dissolution features (Sandeman & Clark, 2004), which in turn would liberate Sr to the melt. Due to the

404 absence of other abundant and stable Ca-bearing phases in the Macusani subvolcanics, Sr is

405 expected to accumulate in the melt and result in progressively increasing Sr content in apatite. Thus,

406 the earlier apatite compositions, which crystallized together with plagioclase prior to the thermal

407 event, are expected to have relatively lower Sr and La/Sm values, whereas the post-thermal apatite

408 is expected to record an increase in both these parameters. Therefore, apatite with $(La/Sm)_{CN}>1.2$

409 and Sr>400 µg/g are accepted as the latest generation of apatite in Macusani subvolcanics and in

410 equilibrium with the host glass.

411 **4.6. Trace element mineral/melt partition coeffcients**

412   Empirical partition coefficients (D(element)$^{A/B}$), defined as C^A/C^B, have been calculated from

413 mean trace element concentrations (µg/g weight basis) in the phase A (C^A) divided by trace element

414 concentrations in the phase B (C^B). The associated uncertainty on partition coefficients is calculated

415 from:

416 $\sigma = D^{A/B} \times \sqrt{\left(\frac{SD}{X}\right)^2_A + \left(\frac{SD}{X}\right)^2_B}$, in which σ is the uncertainty of $D^{A/B}$ and SD is the standard deviation

417 of the measurements of the element X in each phase. A summary of the mineral/melt partition

418 coefficients for all elements that were above the limit of detection is provided in Tables 3 and 4 and

419 plotted in Figure 7.

420 *Apatite.* Values of $D^{ap/gl}$ are summarized in Figure 7a, which includes comparison to the results of

421 experimental studies on basaltic-andesitic systems at 1.0 GPa and 1250 °C (Prowatke & Klemme,

422 2006), basanitic-granitic systems at 950-1120 °C, 0.75-2.0 GPa (Watson & Green, 1981), basaltic

423 system at 1050 – 1100 °C, 1.0 GPa (Ji & Dygert, 2024) and a study of a natural phonolite system at

424 950±25 °C and 0.2 GPa (Li et al., 2023). Also considered were the experiments of Stokes et al. (2019),

425 carried out in compositions ranging from trachyte to basalt at 1250-1400°C and 1.0 GPa. Among the

426 measured trace elements, the REE are the most compatible in apatite, with the lowest $D^{ap/gl}$ values

427   for alkalis (Rb, Cs). The compatibility of the REE is a downward concave function of atomic number

428   with the highest D values recorded for Gd and the lowest being La and Lu. Overall, the empirical rare

429   earth element D values are up to 10x higher than the range reported in experimental studies, the

430   origin of which is discussed in the section below on mineral-melt equilibrium. Other compatible

431   trace elements include Ge and Mn with D values in all suites of ~20 and 10, respectively. $D(Ge)^{ap/gl}$

432   has not been previously reported but likely follows Si substituting for $(PO_4)^{3-}$ as the oxyanion

433     $(GeO_4)^{4-}$ (Pan & Fleet, 2002). Values of $D(Mn)^{ap/gl}$ are consistent with experimental determinations

434   involving highly polymerized (NBO/T = 0.03 – 0.10) and peraluminous melts (ASI = 1.0–1.3) reported

435   by Stokes et al. (2019). Empirical partition coefficients for Sr, Th, U correspond to the upper limits of

436   the range recorded in the experimental studies of Ji & Dygert (2024).Values of $D(V)^{ap/gl}$ from the

437   natural samples range between 0.5 and 4, generally increasing with the fO_2 estimated for each suite,

438   with a further discussion of this provided below; we are unaware of any previous experimental

439   measurements of $D(V)^{ap/gl}$ for comparison. Transition metals are increasingly incompatible with

440   increasing atomic number, ranging from $D(Cu)^{ap/gl}$ ~1 to $D(Zn)^{ap/gl}$ ~0.1, with the latter values for

441     $D(Zn)^{ap/gl}$ consistent with the range reported by Ji & Dygert (2024). Apatite-melt partition

442   coefficients for Pb coincide with the lower limit of the experimentally determined range reported by

443   Prowatke & Klemme (2006) and Li et al. (2023). Like V, $D^{ap/gl}$ for Sn and Bi have not been reported from

444   experiments, with Bi showing weak incompatibility ($D^{ap/gl}$ of ~0.3 to 1), similarly for Sn, although the

445   D range is larger (0.05 to 1) and reflects some fO_2 dependence (see below). Elements from the LIL

446   and HFSE groups are the least compatible in apatite, with D values generally below 0.1, overlapping

447   with the range of determinations from Prowatke and Klemme (2006), although the corresponding

448   uncertainties are large due to the low abundance of these elements in the natural samples.

449   *Biotite.* Values of $D^{bt/gl}$ are assembled in Figure 7b and compared to the experimental

450   determinations of Icenhower and London (1995), Stepanov and Hermann (2013), Pichavant et al.,

451   (2016), Gion et al. (2018), Were and Keppler (2021), Wei et al. (2024) and empirical determinations

452   from glassy volcanic rock suites (El Hoyazo dacite, SE Spain; Acosta-Vigil et al., 2010) including

453   previous measurements for the FCT (Bachmann et al., 2005) and the effusive Macusani suites

454   (Pichavant et al., 2024) related to the Macusani subvolcanics analyzed in this study. Previous biotite-

455   melt partitioning experiments were done on rhyolitic compositions over the temperature range of

456 600-1000 °C, pressures from 0.1 to 2.5 GPa and most fO_2 near FMQ+1, but Wei et al. (2024)

457 investigated FMQ-1 to FMQ+8.

458   Of the elements considered, the transition metals are generally the most compatible in

459 biotite, with the largest $D^{bt/gl}$ for V, Co, and Ni (>50), and other transition metals (Sc, Mn, Zn, Cu)

460 being moderately compatible ($D^{bt/gl}$ 1-10). Alkalis, alkali earth metals, and metalloids are moderately

461 compatible ($D^{bt/gl}$ 1-10; Ba, Rb, Ga, In) to moderately incompatible (Li, Cs, Sr, Ge, Pb, Bi with $D^{bt/gl}$

462 0.1-1). High field strength elements (Zr, Hf, W, Mo) are strongly incompatible ($D^{bt/gl}$ = 0.5-0.01).

463 $D(Nb)^{bt/gl}$ (2-10) exceeds the $D(Ta)^{bt/gl}$ (0.6-3) in all cases. Rare earth elements are the most

464 incompatible group with $D(REE+Y)^{bt/gl}$ <0.2, except Eu with $D^{bt/gl}$ of 0.1 to 1.0.   The empirically

465 determined $D^{bt/gl}$ values determined in this study, overlap with the experimentally determined

466 range of partitioning coefficients. The values $D^{bt/gl}$ for Co, Ni, Zn, Mn, Nb, Ta, Ba, Rb, Cs, Mo, Eu, Gd,

467 Zr overlap with the experimental determinations by Were & Keppler (2021). Indium $D^{bt/gl}$ was found to

468 be sensitive to the biotite composition by Gion et al. (2018). Our empirical determinations

469 correspond with the experimental values by Gion et al. (2018) despite the natural biotites having a

470 higher annite component than any of the synthetic biotites reported by Gion et al (2018). For Y, Sc,

471 Ge, and Hf, we are not aware of any experimentally established $D^{bt/gl}$, however, our findings agree

472 with the other empirical determinations. Partition coefficient values for Sr (0.05-0.22) are within the

473 range found by Icenhower & London (1995), below the $D(Sr)^{bt/gl}$ value (0.57) reported by Were &

474 Keppler (2021) in a single, more calcic melt (1.87 wt% CaO, compared to <1.1 wt% in our samples and

475 Icenhower & London experiments) at 800 °C. Our determined range of $D(Li)^{bt/gl}$ (0.1-0.7) overlaps

476 with results from experiments in peraluminous systems (0.4-1.0) by Pichavant et al. (2016), and are

477 close to the range of $D(Li)^{bt/gl}$ (0.8-1.7) determined in three peraluminous experiments by Icenhower

478 & London (1995). Both sets of experiments indicate that $D(Li)^{bt/gl}$ is negatively correlated with melt

479 ASI and positively correlated with biotite Al^{IV} content, thus implying a melt and/or mineral

480 compositional effect on lithium partitioning. Results are also consistent with values measured by

481 Pichavant et al. (2016) whose melt composition (72.6-75.7 wt% SiO_2) and biotite Al^{IV} content (2.33-

482 2.56 a.p.f.u.) are close to our natural samples (72.3-74.8 wt% SiO_2 in glass, 2.28-2.61 Al^{IV} a.p.f.u. in

483 biotite).

484   Partitioning systematics for vanadium, tungsten, europium, and tin indicate a redox-

485   sensitivity. Vanadium $D^{bt/gl}$ decreases from 586 to 56 with increasing fO_2 with the range

486   corresponding to the results from El Hoyazo dacite (335-15) by Acosta-Vigil et al. (2012).

487   Experimental determinations of $D(V)^{bt/gl}$ by Were & Keppler (2021) point to a more moderate

488   compatibility (23-47) in biotite, however, their measurements were carried out in Ti-poor biotites

489   (<1.6 wt% TiO_2) in comparison to our compositions (3.9-4.5 wt% TiO_2). As discussed in Section 5.2,

490   TiO_2 content is expected to enhance vanadium partitioning. Values of $D^{bt/gl}$ for W decrease from

491   0.16 to 0.02 with increasing oxidation. This is below the determinations reported by Pichavant et al.

492   (2024) for the Macusani volcanics (0.38±0.06) and from the experiments of Were & Keppler (2021)

493   (1.2±0.8), but agrees with the findings of Dailey et al. (2018) involving the Spor Mountain topaz

494   rhyolite (0.06±0.06). As tungsten is predominantly hexavalent even at the most reducing terrestrial

495   fO_2 conditions(O'Neill et al., 2008), this element is expected to be incompatible with most rock-

496   forming minerals (Arevalo & McDonough, 2008; Fonseca et al., 2014), which is inconsistent with the

497   relatively large partition coefficients reported by Were & Keppler (2021). The value of $D^{bt/gl}$ for Sn

498   varies between ~0.1 and 3, with an increase in values with fO_2 of the sample suite. This result is

499   consistent with the experimental measurements of $D(Sn)^{bt/melt}$ reported by Wei et al. (2024) in

500   which values increase from ~0.02 at FMQ-1 to ~3 at FMQ+8.

501   The empirical biotite-melt partition coefficients presented here are also generally consistent

502   with values reported for mineral/glass pairs from similar samples. Bachmann et al. (2005) measured

503   a number of the same trace elements in biotite and glass (as well as other phenocryst phases) from

504   samples of the FCT and showed similar values to our empirical determinations (Supplementary

505   Figure S8). Our results from the MAC subvolcanic samples are in general agreement with the results

506   for the Macusani tuffs reported by Pichavant et al. (2024) (Supplementary Figure S7), except values

507   for $D(Li)^{bt/gl}$ of 0.14-0.57 determined in this study are much lower than the value of ~3.7 reported for

508   the Macusani tuffs. Values of D(Li) for the Macusani subvolcanics are consistent with results from

509   other suites in this study along with experimental determinations of Pichavant et al. (2016) and

510   Acosta-Vigil et al. (2012) involving melts of dacitic composition. Pichavant et al. (2024) suggest that a

511   secondary Li enrichment or redistribution in tuffs could have altered the Li content in phenocrysts

512   and matrix. Furthermore, we note that the composition of biotite from the samples for which $D^{bt/gl}$

were measured by Pichavant et al (2024) differ somewhat from those measured here, in that the Macusani tuffs are generally more compositionally evolved, with higher Fe# (~0.65 – 0.80), Al_2O_3 (19.0-21.4 wt.%), and Rb content (912-2242 µg/g) compared to our samples (Fe#<0.54, Al_2O_3<19.7 wt.%, Rb<1150 µg/g). How these differences influence Li partitioning are not completely clear, although of the intensive parameters that affect $D(Li)^{bt/gl}$, Icenhower and London (1995) document an overall decrease in $D(Li)^{bt/gl}$ with increasing temperature. We therefore speculate that the overall more evolved nature of the Macusani tuff biotites could suggest a lower crystallization temperature, and therefore a higher value of $D(Li)^{bt/gl}$.

4.7. Oxybarometry of Macusani subvolcanics

Apart from qualitative assessments by Pichavant et al. (1988a) and Sandeman & Clark (2003), the fO_2 of Macusani igneous rocks, including the Macusani subvolcanics, has not been determined quantitatively. This is necessary, however, to assess fO_2 controls on heterovalent element partitioning. Here, we use the major and REE compositions of Macusani zircon and glass compositions along with the Ce-in-zircon oxybarometer of Smythe & Brenan (2016) to determine the oxygen fugacity of the Revancha dyke (measured in sample MAC137) and the Cerro Esquinani stock (MAC 160) samples. As described above, zircon occurs in both sample suites as small (<50 µm), euhedral crystals, exhibiting well-developed, concentric growth zoning, with rare textural evidence for inheritance. In total, 24 zircon and 75 glass analyses were obtained from these samples. Analysis of the zircons was particularly challenging because of their small size, and therefore susceptibility to contamination by the laser sampling inclusions of other minerals, or surrounding glass. To minimize the non-zircon contribution, the time-resolved spectrum for each zircon analysis was carefully reviewed, and the REE and zircon-incompatible element (Na, Al) patterns were used to filter those subject to contamination within the ablated volume. Following this, 11 measurements from the Revancha dyke and 4 measurements from the Cerro Esquinani stock were accepted as representative of uncontaminated zircon trace element compositions.

The oxybarometer of Smythe & Brenan (2016) uses the concentrations of Ce in zircon and melt, as well as estimates of $D(Ce^{3+})^{zrn/melt}$ and $D(Ce^{4+})^{zrn/melt}$ obtained from linear interpolation of trivalent REE and tetravalent element (Th, U, Hf, Zr) partition coefficients expressed as a function of ionic radii (Shannon, 1976) to calculate the proportions of the Ce^{3+} and Ce^{4+} species in the melt.

542   Results are then compared to a calibration that expresses species proportions as a function of fO_2,

543   melt composition (including H_2O content) and temperature. Zircon crystallization temperatures

544   were calculated using Ti concentrations following the expression of Ferry & Watson (2007) and Ti

545   activity following Borisov & Aranovich (2020). The melt H_2O content estimate (4.2 wt% for MAC137,

546   4.8 wt% for MAC160) is based on the EPMA totals, which agrees with the H_2O estimate in Macusani

547   tuffs (4.5-6.5 wt%) reported by Pichavant & Montel (1988). The measured trace element

548   concentration of zircon, and resulting oxygen fugacities are provided in the Supplementary Table S1.

549   The oxybarometry results suggest similar, reduced fO_2 values for both Macusani subvolcanic units:

550   FMQ-2.8±1.1 for the Revancha dyke and FMQ-1.9±1.0 for the Cerro Esquinani stock. This is

551   consistent with the absence of magnetite and the very low hematite content (<1% Fe_2O_3) in ilmenite

552   from the Revancha dyke and Macusani tuffs (Pichavant et al., 1988b; Sandeman & Clark, 2003).

553   **5. Discussion**

554   **5.1. Evidence for crystal-melt equilibrium**

555   *Textural evidence*

556   Biotite crystals have been observed in all of the analyzed samples, occuring as ubiquitous,

557   lamellar phenocrysts and microphenocrysts. Phenocrysts are chemically uniform and euhedral in

558   FCT and TT samples, whereas the larger biotites from both MAC and MM samples frequently exhibit

559   resorption features and compositional zoning observable in both optical and BSE imaging. Free

560   microphenocrysts, however, are commonly euhedral and unzoned, with the exception of the

561   Revancha dyke, where reversly zoned biotite is present (Fig. 2c).

562   Apatite in the sample suite is present in trace amounts as microphenocrysts and biotite-

563   hosted inclusions. Apatite microphenocrysts are commonly euhedral, and tabular to equant. In most

564   samples apatite is chemically uniform, with rare cases of concentric growth zoning or inherited,

565   partially resorbed cores, as observable in BSE imaging (Fig. 2e). Apatites from the UP, however,

566   commonly display bright, up to 20-30 μm thick rims in BSE images, suggesting at least two stages of

567   apatite growth. In most samples, apatite phenocrysts are free from inclusions, with the exception of

568   Revancha dyke samples, where apatite phenocrysts (ocasionally exceeding 1000 μm size) contain a

569   multitude of mineral (monazite, zircon) and melt inclusions.

570   As natural intra-crystal and intercrystal compositional variation is present in at least some of

571   the samples, further verification of mineral-melt equilibria must be provided, as described in the

572   sections that follow.

573   *Mineral /melt equilibria*

574   Comparison to experimentally established major element exchange coefficients (K_d) and

575   trace element D values for mineral/melt partitioning enable evaluation of the chemical equilibrium

576   between biotite, apatite, and glass from the natural samples. Biotite-glass major element

577   equilibrium was assessed using Fe-Mg exchange partitioning, expressed as K_d(Fe-Mg) = (Fe/Mg)$_{biotite}$

578   x (Mg/Fe)$_{melt}$ (Fe and Mg as molar proportions). Figure 8a provides a comparison of K_d(Fe-Mg) values

579   determined in the natural samples to the results of the experimental studies involving water-

580   saturated granitic melts (Were & Keppler, 2021; Icenhower & London, 1997). Results of the

581   experimental studies suggest an overlapping range of K_d(Fe-Mg) from 0.060 to ~0.177 that would be

582   characteristic of biotite and granitic melts in equilibrium. The range of K_d(Fe-Mg) from the natural

583   samples is 0.06 to 0.277, which is similar to the experimentally determined values, consistent with

584   Fe-Mg exchange equilibrium.

585   Experimentally established values of D(Sr)$^{ap/gl}$ (Prowatke & Klemme, 2006; Watson & Green,

586   1981) were used to assess apatite-melt equilibrium. Strontium was selected for verification of

587   equilibrium due to its measureable abundance in the analyzed glasses and high compatibility in

588   apatite. Most of the D(Sr)$^{ap/gl}$ values obtained in this study are similar to or greater than the highest

589   values reported from experiments (~5; Prowatke and Klemme, 2006). Significantly, Prowatke and

590   Klemme (2006) found a strong negative correlation between the melt CaO content and D(Sr)$^{ap/gl}$,

591   with the highest partition coefficients recorded for the most CaO poor melts (i.e.,~5 wt% CaO;

592   Figure 8b). A less pronounced trend is also seen in the results from Watson and Green (1981).

593   These data are shown in Figure 8b, along with values determined in this study. Our results plot at

594   the low CaO (i.e., <1 wt%) extension of the experimentally-determined correlation. Therefore,

595   although D(Sr)$^{ap/gl}$ measured for the natural samples do not overlap with the experimental

596   measurements, values seem to be predicted from the trends established by the experimental data.

597   Another test for mineral-melt equilibrium is to compare partition coefficients for isovalent

598   series of elements to expectations of the so-called lattice strain model, as formulated by Blundy and

599   Wood (1994). In this model, the total change in free energy for the substitution of a trace element,

600   I, for the "primary" cation, J, on a normal lattice site, can be represented by the reaction:

601
$$\Delta G_I^0 = \Delta G_J^0 + \Delta G_{strain}^{melt} - \Delta G_{strain}^{crystal} \ (1)$$

602   where ΔG_J^0 and ΔG_I^0 describe the free energy of melting for the I and J end-members, ΔG_{strain}^{melt} and

603   $\Delta G_{strain}^{crystal}$ refer to the strain energies induced by replacing one mole of J by one mole of I in an

604   infinite J-endmember melt and crystal. As the strain energy of substitution into the melt is

605   insignificant, the equilibrium constant, K_I, for the I-J substitution can be expressed as:

606
$$K_I = exp\left(\frac{-\Delta G_J^0 + \Delta G_{strain}^{crystal}}{RT}\right) = K_0 exp\left(\frac{\Delta G_{strain}^{crystal}}{RT}\right) (2).$$

607   Assuming that the activity coefficient of the J-endmember is constant and near unity and the activity

608   of both end-members in melt are identical (which is likely due to the the identical charge) the

609   equilibrium constants in Eq. 2 can be related to the partition coefficients (D):

610
$$D_I = D_0 exp\left(\frac{-\Delta G_{strain}^{crystal}}{RT}\right) (3),$$

611   where D_I and D_0 are the mineral/melt coefficient of I and J, respectively, the latter being unhindered

612   by strain related to entering the crystal lattice.

613   By applying the Brice (1975) expression of the mechanical strain energy around a

614   homovalent cation defect as a function of Young's Modulus (E) of a host crystal, the size of the

615   lattice site (r_0), the substituent cation (r_i), and Avogadro's number (N_A), Blundy and Wood

616   formulated the trace element partition coefficient at specific pressure (P), temperature (T), and

617   composition (X) as a function of the "strain-compensated partition coefficient" [$D_0(P,T,X)$] as:

618
$$D_I(P,T,X) = D_0(P,T,X) \cdot exp\left[\frac{-4\pi E N_A\left[\frac{r_0}{2}(r_i-r_0)^2+\frac{1}{3}(r_i-r_0)^3\right]}{RT}\right] (4)$$

619   in which R is the gas constant and T is degrees K. Assuming crystal-melt equilibrium, at constant P,T

620   and X, D_i values for a series of isovalent trace elements is a function of r_i with the maxima at strain-

22

621 free substitution (r_i=r_0) and decrasing D_i as the mismatch between r_i and r_0 (and therefore the

622 mechanical strain in the crystal lattice) increases. Thus, plots of D_l versus r_l, termed Onuma diagrams

623 (Onuma et al., 1968), result in concave functions with maxima at D_0 and r_0, and the width of the

624 parabola decreasing with increasing E. The value of r_0 is primarily controlled by the mineral

625 composition, whereas E is controlled by the ionic charge (Wood & Blundy, 2013). The correlation

626 between D_l and the r_0-r_l mismatch has been confirmed experimentally and empirically in a great

627 number of mineral/silicate melt partitioning studies (e.g., Beattie, 1994; Lee et al., 2007; Shimizu et al.,

628 2017; van Westrenen & Draper, 2007; Zajacz & Halter, 2007) including several focused on biotite

629 (LaTourrette et al., 1995; Schmidt et al., 1999; Were & Keppler, 2021) and apatite (Klemme & Dalpé, 2003; Li

630 et al., 2023; Prowatke & Klemme, 2006). Thus, results for mineral-melt equilibrium are tested by

631 adherence to the expectations from the successful Blundy-Wood lattice strain model.

632 In applying the Blundy-Wood model, temperatures of crystal-melt equilibrium were

633 estimated from the Ti-in-biotite calibration of Henry et al. (2005) due to the peraluminous and

634 titania-rich sample compositions, which are saturated with ilmenite or other Fe-Ti oxide phase.

635 Values of D_0, r_0, and E were determined using least squares regression for each isovalent series of

636 trace element D_l values (Supplementary Table ST7). Values of r_i for a specific trace element will

637 depend on both ionic charge and coordination (Shannon, 1976), and were therefore selected with

638 guidance from previous partitioning and mineral structural studies (Padilla & Gualda, 2016; Pan & Fleet,

639 2002; Pichavant et al., 2024; Were & Keppler, 2021) and size-charge considerations. Partitioning arrays

640 are shown in Figures 9 and 10 for apatite and biotite, respectively.

641 The apatite structure contains three types of cation sites: VII- and IX-fold coordination

642 (generally occupied by Ca with r_0 being 0.106 in VII-fold and 0.118 in IX-fold coordination) along with

643 tetrahedrally coordinated site typically containing phosphorous with IR=0.017 nm (Pan & Fleet, 2002).

644 Here it is assumed that all of the ions with IR exceeding 0.07 nm in VIII-fold coordination solely enter

645 the VII- and IX-fold sites, with radii corresponding to an intermediate VIII-fold coordination.

646 Divalent and trivalent cations are the most compatible with the VII- and IX-fold coordinated

647 sites. Both of the isovalent arrays adhere to concave D_i-r_l functions with similar r_0 values (0.111-

648 0.113 nm for divalent and 0.106-0.108 for trivalent ions) with the trivalent array recording higher E

649   (270-349 MPa) and D_0 (103 – 177) than the divalent series (E=250-303 MPa, D_0=64-129). The

650   proximity of D_0 of the trivalent series to the Ca^{VII} site indicates a REE preference for entering in the

651   smaller Ca^{VII} site, supported by earlier studies (Pan & Fleet, 2002). The larger r_0 values of the divalent

652   array place it between the two Ca sites thus suggesting an even divalent ion distribution between

653   Ca^{VII} and Ca^{IX}. Several of the less compatible divalent elements (Zn, Mg, Pb, Ba), however, show

654   deviations from fitted D_i-r_i functions. Each of these elements show a preference for one of the Ca

655   sites: Pb, Ba, Zn preferentially enter the Ca^{VII} site, but Mg the Ca^{IX} site (Elliott, 1994; Pan & Fleet, 2002).

656   The partitioning of Mg, however, is enhanced by high melt polymerization with the effect amplified

657   at low temperature (Zhan et al., 2022). Experimentally determined D_{Mg} in low-P-T silicaceous

658   peraluminous systems exceed unity (Trend 2 - Zhan et al., 2022), which coincides with the elevated

659   D_{Mg} values (up to 6.0) in the Macusani samples.

660   Similar to the trivalent series, the tetravalent series (Hf-Zr-Th) with r_0=0.106-0.109 indicate

661   affinity for the Ca^{VII} site as previously described by Luo et al. (2009). Related to the tetravalent

662   series, the ratio of D_U/D_{Th} is below 1 in the reduced Macusani rocks, equals 1 in Tuk-Tuk tuff, and

663   exceeds 1 in the oxidized Fish Canyon tuff. While thorium exists exclusively in the tetravalent state,

664   uranium in silicate melts can be present in valence states (Schreiber, 1983) of U^{4+} (IR=0.100 nm in

665   VIII-fold coordination), U^{5+} (IR=0.084 nm in VII-fold coordination), U^{6+} (IR=0.081 nm in VII-fold

666   coordination). With its charge and size being the closest to Ca^{2+} in VII-fold coordination, U^{4+} is the

667   most compatible in the apatite structure (Clarke & Altschuler, 1958). Thus, D_U/D_{Th} is likely to vary as a

668   function of $U^{4+}/\Sigma U$ in melt, which at least in part is controlled by the fO$_2$, which stabilizes the more

669   compatible U^{4+} under reduced conditions (Fonseca et al., 2014).

670   Monovalent ions are generally incompatible (D_i<0.1) in the apatite structure. The arrays of

671   Na-K-Rb reach the maxima at near r_{Na} (r_0=0.115-0.120), which suggests a preference for entering the

672   larger, IX-fold coordination site. D_{Li}, however, exceeds the values expected from the monovalent r_i-

673   D_i fit. The relatively lower IR of lithium (0.092 nm in VIII-coordination with no data about any higher

674   coordination) could lead to a preference for a lower coordination.

675   Although the relative apatite-melt partitioning of the trivalent REE + Y is consistent with the

676   lattice strain model, as mentioned previously, absolute values of partition coefficients for this

677   element group are up to 10 times higher than those reported in previous experimental studies

678   (Watson & Green, 1981; Prowatke & Klemme, 2006). Mineral or melt composition effects may serve as

679   possible explanations, as past work has shown that the $D(REE)^{ap/gl}$ increases both with the Si content

680   in apatite and the degree of melt polymerization, the latter simply expressed as melt SiO_2 content.

681   The Si contents of the apatites measured in this study are comparable to those produced in past

682   experiments, so that is an unlikely cause. However, the natural glasses are significantly more

683   evolved (SiO_2 = 72-75 wt.%) than the range from previous experimental studies (SiO_2 = 36-70 wt%).

684   Prowatke & Klemme (2006) combined their data with the results from Watson and Green (1981) to

685   show that $D(Sm)^{ap/gl}$, a representative REE, increases approximately exponentially with melt SiO_2

686   content. This relationship is shown in Figure 11, along with results from this study, Little Glass

687   Mountain (LGM) rhyolite (USA) reported by Brophy et al. (2011), and from Erebus (Antarctica),

688   reported byLi et al. (2023) Values of $D(Sm)^{ap/gl}$ determined in this study are similar to those

689   measured for the LGM sample, which is consistent with overlapping glass SiO_2 concentrations. All

690   datasets seem to project smoothly from the experimental results, suggesting that the unusually

691   large values of $D(Sm)^{ap/gl}$ (and by extension other REE + Y) measured in this study are the result of

692   melt composition control.

693   As for biotite, its structure comprises three kinds of cation sites – XII-fold coordinated

694   (usually hosting LILE, e.g. K), VI-fold coordinated, most commonly hosting di- and trivalent elements

695   (e.g., Mg, transition metals, REE), and a IV-fold coordinated site, typically occupied by Si or Al

696   (Bailey, 1984). The Onuma diagram for biotite-melt partitioning (Figure 10) reveals five groups of

697   concave isovalent element arrays: monovalent elements in XII-fold coordination (comprising Na, K,

698   Rb, Cs), divalent elements in VI-fold coordination (Mg, Co, Fe, Mn), trivalent elements in VI-fold

699   coordination Ga, Sc, In, Lu, Yb, Y), trivalent elements in IV-fold coordination (Al, Ga, In) , and

700   tetravalent elements in IV-fold coordination (Si, Ge, Hf, Zr). For the XII-fold coordinated site, the

701   monovalent element array peaks at r_0 = 0.164-0.170 nm with D_0 = 1.6-2.1, consistent with K as the

702   most suitable occupier. Divalent Ba^{XII} has an IR=0.161 nm, which results in high $D(Ba)^{bt/gl}$ values (2.4-

703   8.4), however, developing a meaningful Brice fit for divalent elements is precluded by the large

704   uncertainties of $D(Ca)^{bt/gl}$ and the electron configuration of Pb, which leads to formation of partial

705   covalent bonds, which do not obey the Wood-Blundy r_i-D_i model (Engel et al., 1975; Were & Keppler,

706   2021). The biotite octahedral site is known to accommodate cations of several valence states

707   (Nickel, 1954). In this study, two isovalent arrays are fitted: divalent elements form the higher D tier

708   with r_0= 0.065 – 0.070 nm and D_0 = 165-447, compared to the trivalent cation array with overlapping

709   r_0 = 0.067-0.072 and lower D_0 values = 2.7-13.0. The r_0 value of the divalent array appears to

710   decrease with increasing Al content and the opposite is true for the trivalent array. In the divalent

711   series, Mg^{2+} (IR=0.072 nm in VI-fold coordination) is the closest to r_0 thus it is the most compatible

712   element. In the trivalent series, the octahedral site r_0 values are similar to the ionic radii of Ga and

713   Sc (0.062 and 0.0745 nm, respectively) and positively correlate with the biotite alumina content thus

714   implying that the size of the octahedral cation sites for divalent and trivalent elements is altered by

715   the abundance of Al. Ionic radii of several highly-charged ions are close to the r_0 of the octahedral

716   site: Ti^{4+} (IR=0.0605 nm), V^{3+} (0.064 nm), V^{4+} (0.058 nm), Nb^{5+} and Ta^{5+} (both 0.064 nm), Sn^{4+} (0.069

717   nm), which explains their compatibility in the analized biotite suites. Given that the D_i-r_i curves for

718   the highly charged elements would be much narrower than that of divalent elements (Blundy &

719   Wood, 1994), even a minor change in the r_0 of the site due change to the crystal chemistry can

720   strongly alter the D_i values of the HFSE, therefore biotite Al^{VI} could be important when considering

721   and comparing the D values of other, octahedrally coordinated elements.

722   In general, the empirical partitioning measurements are consistent with experimental

723   measurements, either as overlapping values, or on the extension of trends with other melt

724   composition parameters (e.g., wt% CaO, wt% SiO_2). Onuma diagrams defined for biotite- and

725   apatite-melt partitioning of similarly-sized isovalent cations display parabolic relations with values of

726   r_o and D_o consistent with the major substituent cations for a particular site. Results therefore

727   suggest that the mineral/melt partitioning of the trace elements measured for the natural samples

728   broadly adhere to the systematics established by the experimental database, and by extension,

729   reflect crystal-melt equilibrium.

730   **5.2. Redox control on heterovalent element partitioning**

731   Amongst the group of elements for which empirical partition coefficients have been

732   determined, several are expected to have multiple valence states over the range in fO_2 of terrestrial

733   magmas. These include V (2+, 3+, 4+, 5+), As (3+, 5+), Eu (2+, 3+), Mo (4+, 6+), Sn (2+, 4+) and W (4+,

734   6+) (Canil, 1999; Mallman and O'Neill, 2009; Maciag & Brenan, 2020;Drake, 1975; Linnen et al., 1995;

735   1996; Holzheid et al., 1975; Fonseca et al., 2014). As shown in Figure 12, all of these elements show

736   a systematic variation in values of $D^{mineral/glass}$ with the estimated fO_2 of each magmatic suite, which

737   here we ascribe to a predominant control of fO_2 on the ionic radius and charge of progressively

738   changing proportions of cation species.

739   The partitioning of vanadium between biotite and melt is highest (up to 585) in the most

740   reduced end of the sample suite (Macusani subvolcanics), while the lowest $D(V)^{bt/gl}$ is found in the

741   most oxidized rocks (Fish Canyon tuff). The opposite trend is observed for $D(V)^{ap/gl}$. The difference is

742   further amplified if apatite/biotite partitioning is considered – $D(V)^{ap/bt}$ changes from 0.001 in the

743   reduced MAC137 to 0.547 in the oxidized Mascota minette. As described in the introduction, the VI-

744   fold coordination ionic radii of the species V^{2+}, V^{3+}, V^{4+}, V^{5+} are 0.079, 0.064. 0.058 and 0.054 nm,

745   respectively, hence the V^{2+} and V^{4+} species are suitable substituting for divalent Mg or Fe and Ti^{4+},

746   leading to their compatibility in biotite at lower fO_2, but relative exclusion of V^{5+} at higher fO_2. Only

747   V^{5+} exhibits a potential for being compatible in the apatite structure, as the oxyanion $(VO_4)^{-3}$ can

748   substitute for $(PO_4)^{-3}$ (Pan & Fleet, 2002). Apatite VII- and IX-fold coordinated sites (usually occupied

749   by Ca^{2+}), however are too large to accommodate any of the other vanadium species. As the higher

750   charged V species are stabilized in oxidized melts, the higher abundance of more compatible V^{5+} is

751   expected to enhance the overall vanadium compatibility in apatite, which is consistent with the

752   observed increase in $D(V)^{ap/gl}$ with fO_2.

753   In contrast to vanadium, values of $D(Sn)^{mineral/melt}$ increase with fO_2 for *both* biotite and

754   apatite, and this sympathetic relation results in essentially constant values of $D(Sn)^{ap/bt}$ (0.40±0.24)

755   over the fO_2 range of the sample suites. The change in the biotite- and apatite-melt partition

756   coefficients likely reflects the difference in compatibility of the Sn^{2+} and Sn^{4+} species, and their

757   changes in proportion with fO_2. At ~FMQ and below, Sn^{2+} is the predominant species in

758   peraluminous melt compositions (Linnen et al., 1996; Farges et al., 2006), with an estimated ionic

759   radius of 0.111 nm in VI-fold coordination (Uchida et al., 2002). Divalent Sn is therefore a poor fit for

760   isovalent substitution with Mg^{2+} (IR = 0.072 nm) or Fe^{2+} (IR = 0.078 nm) in biotite, whereas Sn^{4+}

761   (IR=0.069 nm) is close in size to Ti^{4+} (IR = 0.061 nm). The increase in $D(Sn)^{bt/gl}$ with increasing fO_2 is

27

762 therefore consistent with an increased abundance of Sn^{4+} and its preferential substitution for Ti^{4+} in

763 the biotite structure. This interpretation is consistent with the experimental results of Wei et al.

764 (2024) who found strong positive correlations between D(Sn) and D(Ti) for biotite and other

765 ferromagnesium minerals obtained under highly oxidized conditions, at which the Sn^{4+} species

766 would dominate. As for apatite, although the Sn^{2+} species would be a suitable fit for either of the

767 two large cation sites in apatite (IR = 0.106 and 0.118 nm in VII- and IX-fold coordination), this is

768 inconsistent with low values of $D(Sn)^{ap/gl}$ for the lowest fO_2 samples. However, when ionized to the

769 2^+ state, tin donates two 5p electrons and obtains a stable filled $5s^2$ electron configuration, resulting

770 in an inert pair effect. This likely plays an inhibiting role for the incorporation of Sn^{2+} into apatite

771 (and likely biotite as well), which would otherwise be a suitable fit from size considerations alone. In

772 contrast to the 2^+ species, Sn^{4+} lacks the filled shell configuration, and therefore would have a higher

773 affinity for the apatite structure. In tetrahedral coordination, the IR of Sn (0.055 nm) is relatively

774 close to the IR of Ge (0.039 nm), which is one of the most compatible trace elements in the apatite

775 structure ($D(Ge)^{ap/gl}$ of ~8-20). Therefore, despite Sn^{4+} being a poorer fit than Sn^{2+}, the more

776 favorable bonding environment for the former seems to overcome this size mismatch, accounting

777 for the increase in $D(Sn)^{ap/gl}$ with fO_2.

778 Arsenic is found to become more compatible in apatite with increasing fO_2 (from 0.04 to

779 1.6). This element was not detected in biotite from most samples, however, thus precluding

780 $D(As)^{bt/gl}$ estimates. In silicate melts, arsenic is present as As^{3+} and As^{5+} in proportions primarily

781 controlled by the fO_2 with the As^{3+} being the dominant species in natural silicate melts (Maciag &

782 Brenan, 2020). Pentavalent arsenic, however, likely is compatible with apatite as it enters solid

783 solutions with apatites forming the arsenate endmembers (Pan & Fleet, 2002), where As^{5+} (IR = 0.0335

784 nm in tetrahedral coordination) substitutes for P^{5+} (IR = 0.017 nm). Due to the size and charge

785 mismatch As^{3+} (IR = 0.058 in octahedral coordination) is much less likely to enter any of the cation

786 sites in apatite structure. Thus, the increasing compatibility of As in apatite could be caused by a

787 shift to higher melt As^{5+}/As^{3+} values, a prediction borne out by the apatite/melt partitioning

788 experiments reported in Maciag (2023) involving felsic melt compositions.

789   Tungsten is incompatible in both minerals, with $D(W)^{bt/gl}$ decreasing with fO_2, but no

790   systematic change in $D(W)^{ap/gl}$ across the same fO_2 interval. The decrease in $D(W)^{bt/gl}$ could result

791   from a change in speciation from W^{4+} to W^{6+}, as W^{4+} has an IR=0.066 nm, allowing a good fit into the

792   biotite octahedral site, with an appropriate charge compensation mechanism (e.g., $^{VI}Fe^{3+} + {}^{IV}Si^{4+} =$

793    $^{VI}W^{4+} + {}^{IV}Al^{3+}$). On the contrary, partitioning of W^{6+} into either biotite or apatite is inhibited by the

794   large excess of charge, and the general exclusion of W^{6+} from silicate minerals is well documented

795   (e.g., Fonseca et al., 2014). Although the change in $D(W)^{bt/gl}$ seems consistent with a change in

796   speciation, available W solubility data indicates that the fO_2 at which the transition from W^{4+} to W^{6+}

797   takes place is ~FMQ-7 (O'Neill et al., 2008), which is far more reduced than the conditions recorded

798   by the sample suite. In contrast, Fonseca et al. (2014) provide evidence from mineral-melt

799   partitioning experiments for the presence of W^{4+} and W^{6+} in the range of FMQ to FMQ-4, as

800   revealed by large changes in the $D(W)^{mineral/melt}$ for olivine and pyroxene. Fonseca et al. (2014)

801   account for this discrepancy with the solubility data by proposing that melt composition may play a

802   role in W speciation, either by the stabilization of the $CaWO_4$ complex (O'Neill et al., 2008) or by

803   affecting the fO_2 of the W^{4+} to W^{6+} transition. In terms of the latter, by analogy to the geochemically

804   similar molybdenum, it has been shown that melt compositions in the $MgO-Al_2O_3-SiO_2$ system

805   exhibit the Mo^{4+} to Mo^{6+} transition at almost 2 log units higher fO_2 than melts in the $CaO-Al_2O_3-SiO_2$

806   system (O'Neill and Eggins, 2002). Fonseca et al. (2014) emphasize that even small changes in the

807   fO_2 of the W^{4+} to W^{6+} transition could impact partitioning given the large differences in the

808   compatibility of the two species. Our results for Mo partitioning between biotite and glass, indeed,

809   follow a similar pattern to tungsten with decreasing compatibility ($D(W)^{bt/gl} = 2 - 0.1$) reflecting a

810   transition from the compatible Mo^{4+} (IR = 0.065 nm in octahedral coordination) to the highly

811   charged, incompatible Mo^{6+} (IR = 0.059 nm), which takes place at more oxidized conditions (~FMQ-

812   4; Holzheid et al., 1994), closer to the fO_2 range of the sample group. Therefore, a higher proportion

813   of the compatible Mo^{4+} could lead to a higher $D(Mo)^{bt/gl}$ values in comparison $D(W)^{bt/gl}$. As

814   molybdenum was not detected in most of the sampled apatite compositions, $D(Mo)^{ap/gl}$ could not be

815   determined.

816   Values of $D(Eu)^{bt/gl}$ do not show a systematic change with fO_2, however, $D(Eu)^{ap/gl}$ increases

817   with more oxidizing conditions (Figure 12a). Europium in silicate melts is present in two valence

818   states – Eu^{2+} and Eu^{3+} (Drake, 1975) . Experimental studies have shown that both valence states are

819   present over the fO_2 range represented by the sample suite, and that the $Eu^{3+}/\Sigma Eu$ increases with

820   fO_2 (as well as T, and decreasing melt polymerization; Burnham et al., 2015). Due to the larger size

821   (0.120 nm in VII-fold coordination), Eu^{2+} is expected to be less compatible than Eu^{3+} (0.101 pm in VII-

822   fold coordination) with either cation site in apatite. The observed increase in $D(Eu)^{ap/gl}$ with

823   increasing fO_2 is therefore consistent with the preferential uptake of the more compatible Eu^{3+}

824   relative to Eu^{2+}.

825   **5.3. Estimate of the redox control on vanadium intermineral partitioning systematics**

826   As mineral/melt partitioning of vanadium for apatite and biotite follow diverging trends with

827   fO_2, results suggest that the intermineral partitioning of vanadium is a potential oxybarometer. As

828   discussed above, the observed change in $D(V)^{ap/bt}$ is generally consistent with differences in species

829   compatibility into the apatite and biotite structures as predicted from ionic radius and charge.

830   However, a concern is whether the increase in $D(V)^{ap/bt}$ with fO_2 is simply due to the fO_2 control on

831   vanadium speciation, or reflects other factors that could influence species proportions without a

832   change in fO_2, notably melt composition. This latter effect arises because the redox equilibria

833   between the species of multivalent elements are controlled by the balance between the three kinds

834   of oxygen bonding in the silicate melts: singly bonded O-, doubly bonded O^0, and O^{2-}, free oxygen

835   (Fincham & Richardson, 1954; Moretti, 2005). O^0 forms a covalent bond with Si^{4+} or other highly

836   charged network formers in tetrahedral coordination (thus earning the name of bridging oxygens or

837   T), but O- form ionic bonds with network modifiers and are therefore denoted as 'non-bridging

838   oxygens' (NBO). The balance between the three kinds of oxygens in silicate melts is described in the

839   following equation:

840      $2\ O\text{-} \leftrightarrow O^0 + O^{2-}$ (5)
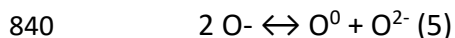
841   The ratio of NBO/T describes the melt structure and viscosity with its values ranging

842   between 0 (fully polymerized melt) and 4 (fully depolymerized melt), yet in natural silicate melts, it

843   generally varies between 0 and 1 (Mysen, 1983). NBO/T is inversely correlated to the melt basicity

844   (Λ), which is controlled by the activity of the metal network modifiers. Thus, the melt polymerization

845   and its acid-base character, which determines the stability of heterovalent element ligands, are

846   linked. Generally, the oxidation-reduction equilibria are expected to shift toward the more oxidized

847   species with increasing melt basicity (higher NBO/T), which coincides with lower polymerization

848   (Cicconi et al., 2020). However, as the heterovalent element equilibria are subject to both redox and

849   acid-base chemistry, the potential amphoteric nature of one of the species (e.g., Fe^{3+}) can be

850   affected by additional significant variables. For example, in peraluminous systems, increasing alkali

851   content leads to stabilization of Fe^{2+}, while the opposite is true in metaluminous and peralkaline

852   systems. This illustrates the neccesity for experimental investigations of compositional controls of

853   each equilibrium, which have proven to be essential in a number of studies on heterovalent element

854   species and partitioning including iron (Cicconi et al., 2015; Dingwell & Virgo, 1987; Lange & Carmichael,

855   1987; Ottonello et al., 2001), sulphur (Nash et al., 2019; O'Neill & Mavrogenes, 2002), tin (Linnen et al.,

856   1996), cerium (Smythe & Brenan, 2015), and vanadium (Arató & Audétat, 2017a; Leuthold et al., 2023;

857   Mallmann & O'Neill, 2013; Sossi et al., 2018). The melt structural control of vanadium species in silicate

858   systems is experimentally studied by McKeown et al. (2011) and Wang et al. (2016). McKeown et al.

859   measured the V speciation in borosilicate glasses synthesized at 1050 °C and 0.1 MPa with varying

860   alkali contents. They found a positive correlation between the melt Na_2O content and the average V

861   oxidation state in the glass, measured by XANES. They remark that this is consistent with with the

862   results for Cr in less polymerized melts reported by Berry et al. (2006), in which a higher proportion

863   of network modifying cations stabilizes the Cr^{3+} over Cr^{2+}. Similarly, in their study of the CaO-MgO-

864   Al_2O_3-SiO_2-VO_x system, Wang et al (2016) found that a higher basicity, defined as

865     $(CaO+MgO)/(SiO_2+Al_2O_3)$, stabilizes the higher oxidation state of vanadium. As redox reactions are

866   endothermic, higher temperatures are expected to stabilize the reduced species – this is confirmed

867   by the Wang et al., (2016) experiments for several compositions. Therefore, we interpret the

868   unusually large values of $D(V)^{ap/bt}$ for the Mascota sample as likely the result of melt composition

869   (see below), even though the equilibration temperatures (1080-1100°C) are higher than for the

870   other sample suites (634-825°C).

871   To verify that the observed vanadium partitioning patterns originate predominantly from the

872   redox control on heterovalent element species instead of melt structural controls, we likewise plot a

873   set of homovalent elements against the sample fO_2 state. In Figure 13a, a set of trivalent,

874   tetravalent, and pentavalent element $D^{ap/bt}$ values from all samples except the Mascota minette are

875   plotted in the fO_2 space. Results from the Mascota minette are excluded due to the effect of

876   significantly higher alkali content, which sets them apart from the rest of the analyzed samples with

877   overlapping T ranges (Table 1) and comparable peraluminous compositions (Figure 3). Within the

878   peraluminous, low-T group, the $D^{ap/bt}$ values of homovalent elements show no correlation with the

879   sample fO_2, thus precluding any role of melt structure overprinting the redox effect on heterovalent

880   element partitioning. Following the experimental studies of McKeown et al. (2011) and Wang et al.

881   (2016), the relatively high value of $D(V)^{ap/bt}$ measured in the Mascota minette sample is likely due to

882   the enchanced stabilization of V^{5+} due to the alkaline melt composition, which outweighs the shift

883   towards the less oxidized species due to the increased temperature, as described previously. This

884   illustrates the intricate interplay between the intensive parameters controlling the speciation of

885   vanadium and its partitioning between the igneous species.

886   **6.0 Geological implications**

887   **6.1. Preliminary formulation of an apatite-biotite oxybarometer**

888   Towards quantifying the redox control on vanadium partitioning between apatite and biotite,

889   and its use in oxygen barometry, we present a preliminary partitioning model that takes into

890   account the change in proportion of the vanadium species with fO_2, with estimates of the

891   partitioning of the endmember vanadium species.

892   The relevant model parameters are identified by first considering the relation describing the

893   individual apatite-melt and biotite-melt partition coefficients ($D(V)^{bt,ap/melt}$), expressed as:

894    $D(V)^{ap,bt/melt} = \{C(V^{3+})^{bt,ap} + C(V^{4+})^{bt,ap} + C(V^{5+})^{bt,ap}\}/ \{C(V^{3+})^{melt} + C(V^{4+})^{melt} + C(V^{5+})^{melt}\}$ (6)

895   In which $C(V^{x+})^{bt,ap}$ and $C(V^{x+})^{melt}$ are the concentrations of the vanadium species in apatite or biotite,

896   and melt, respectively. The contribution from V^{2+} is assumed to be insignificant under the relatively

897   oxidized conditions of the sample suites considered (Sutton et al., 2005). For each vanadium

898   species, the individual mineral/melt partition coefficients can be expressed as:

899    $D(V^{x+})^{ap,bt/melt} = C(V^{x+})^{ap,bt}/C(V^{x+})^{melt}$ (7)

900   Which can be substituted into equation 6 to remove the apatite or biotite compositional terms to

901   yield:

902    $D(V)^{ap,bt/melt} = \{ D(V^{3+})^{ap,bt/melt} C(V^{3+})^{melt} + D(V^{4+})^{ap,bt/melt} C(V^{4+})^{melt} + D(V^{5+})^{ap,bt/melt} C(V^{5+})^{melt}\}/$

903    $\{C(V)^{total,melt}\}$ (8)

904   In which $C(V)^{total,melt}$ is the sum of the contributions of each vanadium species to the total

905   concentration in the melt. Considering just apatite/biotite partitioning ($D(V)^{ap/bt}$) yields the relation:

906    $D(V)^{ap/bt} = \{D(V^{3+})^{ap/melt} C(V^{3+})^{melt} + D(V^{4+})^{ap/melt} C(V^{4+})^{melt} + D(V^{5+})^{ap/melt} C(V^{5+})^{melt}\}/ \{\{D(V^{3+})^{bt/melt}$

907    $C(V^{3+})^{melt} + D(V^{4+})^{bt/melt} C(V^{4+})^{melt} + D(V^{5+})^{bt/melt} C(V^{5+})^{melt}\}\}$ (9)

908   In terms of the speciation of vanadium, the relative proportions are governed by the homogenous

909   redox equlibria:

910                    $V^{3+}O_{1.5(melt)} + ¼ O_2 = V^{4+}O_{2(melt)}$ (10)

911                    $V^{3+}O_{1.5(melt)} + ½ O_2 = V^{5+}O_{2(melt)}$ (11)
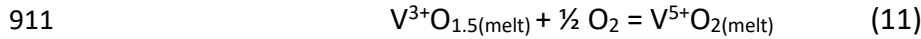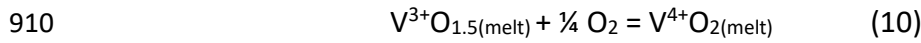
912   Assuming ideal solution behavior of the vanadium species (the activity of V^{x+} is therefore equal to

913   the mole fraction, X_{Vx+}), the corresponding equilibrium constants, $K(10)_{eq}$ and $K(11)_{eq}$ are:

914                    $K(6)_{eq} = X_{V4+O2(melt)} / \{X_{V3+O1.5(melt)} * fO_2^{1/4}\}$ (12)

915                    $K(7)_{eq} = X_{V5+O2(melt)} / \{X_{V3+O1.5(melt)} * fO_2^{1/2}\}$ (13)

916   The abundance of vanadium species at a given fO_2 is determined using values of $K(6)_{eq}$ and $K(7)_{eq}$

917   estimated by Sossi et al. (2018) for a granitic composition measured from experiments done at 0.5

918   GPa and 800°C using magnetite-melt partitioning systematics. Estimates of $D^{ap/bt}$ for the

919   endmember vanadium species were chosen from similar, homovalent "surrogate" trace elements,

920   i.e., Ga (IR = 0.062 nm) for V^{3+} and Ti (IR = 0.060 nm) for V^{4+}. For $D(V^{5+})^{ap/bt}$, however, no suitable

921   "surrogate'' homovalent elements are available as both Nb and Ta have almost 2x larger ionic radii

922   in comparison to V^{5+}, therefore the value of $D(V^{5+})^{ap/bt}$ was determined by least squares

923   minimization to match the modeled $D(\Sigma V)^{ap/bt}$ values to the measured ones. Estimates for the

924   endmember $D(V^{x+})$ are provided in Table 6. The value for $D(V^{5+})^{ap/bt}$ of 0.165 regressed from the data

925   is consistent with the lattice strain-based $D^{ap/bt}$ systematics for other pentavalent elements – P^{5+} (IR

926   = 0.017 nm) and identically-sized Ta^{5+} and Nb^{5+} (IR=0.064 nm). Assuming $D(P)^{ap/bt}$ as the upper D

927   limit (element strongly concentrated in apatite) and $D(Ta)^{ap/bt}$ as the lower limit (element strongly

928   concentrated in biotite), the modeled $D(V^{5+})^{ap/bt}$ value falls within the expected D interval, describing

929   a lesser compatibility in apatite and a moderate compatibility with biotite.

930   The apatite/biotite vanadium partitioning systematics were subsequently calculated using

931   equations 9, 12 and 13 and a comparison of the calculated and measured partitioning is provided in

932   Figure 14a. As can be seen, with the exception of the Mascota minette sample, the model provides

933   a very good description of the data for the suites with similar, peraluminous compositions, capturing

934   values within analytical uncertainty. Results of this modelling indicate that the high compatibility of

935   V^{3+} and V^{4+} in biotite and their low compatibility in apatite leads to V^{5+} as being the most important

936   species, as its abundance and $D^{ap/bt}$ almost entirely determines the total $D(V)^{ap/bt}$. The model,

937   although preliminary, therefore provides a first insight into the controls of vanadium intermineral

938   partitioning, and it seems clear that factors that affect the V^{5+} speciation and partitioning will

939   influence the accuracy of this method in oxybarometry. As mentioned in section 5.3, a number of

940   studies have already shown that aspects of melt composition, particularly the presence of network-

941   modifying cations, such as alkalis and alkaline earth elements, will affect the species proportions,

942   and hence vanadium partitioning, at a given fO_2.

943   **6.2 Example of application to natural apatite and biotite-bearing samples**

944   Currently, the most precise oxybarometry methods are based on the equilibrium between

945   coexisting Fe-Ti oxides (Andersen & Lindsley, 1988; Carmichael, 1967; Ghiorso & Evans, 2008; Spencer &

946   Lindsley, 1981) with other methods formulated from the mineral/melt partitioning of heterovalent

947   elements (Arató & Audétat, 2017c; Burnham et al., 2015; Smythe & Brenan, 2016). Despite the

948   widespread application of these approaches, oxybarometry of plutonic igneous systems, or those

949   lacking one or both Fe-Ti-oxides, remains a challenge. Although a comprehensive application of

950   apatite-biotite oxygen barometry awaits additional experimental calibration, and the more

951   widespread availability of vanadium concentration data for apatite, we present here two examples

952   of how the method could be applied to rock suites for which direct fO_2 determinations are

953   unavailable.

954   The chosen suites represent samples provided from our own research collection for which

955   coexisting apatite and biotite were measured using the indentical analytical protocols as described

956 in section 3.2. The suites comprise samples from the peraluminous South Mountain Batholith

957 (SMB), Nova Scotia, Canada (Brenan et al., 2023) and the Palabora carbonatite, South Africa (Dixon,

958 1979). Petrographic relations indicate that samples from both suites were saturated in only a single

959 Fe-Ti oxide phase during crystallization (ilmenite in SMB and magnetite in Palabora). Importantly for

960 comparative purposes, each has other petrological indications of the prevailing redox conditions.

961 Both samples from the SMB and Palabora carbonatite contain petrographic evidene for co-

962 saturation in apatite and biotite as reflected by ubiquitous biotite-hosted apatite inclusions (Figure

963 15). Biotite crystallization temperatures for the SMB are estimated to be in the range of 603-722°C

964 (Brenan et al., 2023), so temperatures and melt compositions are similar to the natural calibration

965 dataset. Temperatures for Palabora reported by Solovova et al. (1998) indicate apatite crystallized

966 at 720-750 °C, overlapping the results of olivine-magnetite thermometry (510-760 °C) reported by

967 Braunger et al. (2020). Although crystallization temperatures are similar to the natural calibration

968 suite, the host carbonatite melt composition is silica-poor and significantly richer in network

969 modifying cations.

970 The vanadium content of apatite and biotite from 20 samples encompassing 9 constituent

971 plutons of the SMB and one sample from the Palabora transgressive carbonatite facies are reported

972 in Supplementary Table ST4 and ST5. Values of $D(V)^{ap/bt}$ were calculated from coexisting pairs fom

973 each sample, and the mean and standard deviation of values are compared to the preliminary

974 partitioning model in Figure 14b. For the SMB, the range in $D(V)^{ap/bt}$ is 0.0008 to 0.0190 and

975 suggests biotite-apatite equilibration under generally reducing conditions, with the mean $D(V)^{ap/bt}$ of

976 0.0052 corresponding to ~FMQ-1.5. As far as other fO_2 estimates for the SMB, previous

977 experimental studies (summarized in Bucholz et al., 2018) have shown that, at a given temperature,

978 biotite Fe/(Fe+Mg) increases with decreasing fO_2, consistent with a shift to the left of the

979 heterogenous redox equilibrium:

980 $\quad$ $KFe^{2+}_3AlSi_2O_{10}(OH)_2 + 0.75\ O_2 = KAlSi_3O_8 + 1.5\ Fe_2O_3{}^{melt} + H_2O$ $\quad$ (15)
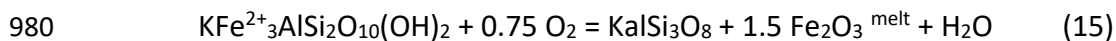
981 Applying this equilibrium to the multicomponent natural system, Brenan et al. (2023) used the

982 MELTS thermodynamic model to track biotite compositional evolution in SMB samples as a function

983 of fO_2, with results indicating biotite crystallization within a narrow fO_2 interval of FMQ to FMQ-1.

984   Also consistent with this indication of generally reduced conditions are previous fO_2 estimates for

985   the SMB based on Ce-in-zircon oxygen barometry yielding FMQ to FMQ-5 (Bickerton et al., 2022).

986   The mean $D(V)^{ap/bt}$ from the carbonatite sample of 0.186 (± 0.046) indicates a higher

987   abundance of highly charged vanadium in the melt compared to the SMB, suggestive of more

988   oxidizing conditions. However, the measured $D(V)^{ap/bt}$ exceeds the model curve. Assuming that the

989   measured $D(V)^{ap/bt}$ represents equilibrium, then the unusually high value for $D(V)^{ap/bt}$ may be

990   influenced by other factors besides fO_2. As discussed in section 5.3, several previous studies have

991   shown that melt composition may affect the vanadium speciation, with a higher proportion of

992   oxidized species stabilized in less polymerized melts containing greater abundances of network

993   modifying cations (McKeown et al., 2011; Wang et al., 2016 and references therein). The same

994   interpretation is applied to explain the elevated $D(V)^{ap/bt}$ for the Mascota minette sample.

995   Carbonate melts represent an extreme endmember in terms of structure and composition, with

996   very low SiO_2, high alkali and alkaline earth element concentrations, and a largely ionic liquid

997   structure (Jones et al., 2013). The extent to which the speciation determinations from silicate melt

998   based studies can be used to interpret partitioning involving carbonate melt is uncertain. However,

999   Jones et al. (1995) report the results of silicate melt-carbonate melt partitioning experiments which

1000   may offer some insights. Their experiments done at 1250°C and 1 GPa reveal a simple linear

1001   decrease $lnD^{silicate/carbonate}$ with increasing Z/r, in which Z is the ionic charge and r the ionic radius (in

1002   angstroms). Results revealed two groupings, however, divided according to Z/r < or > 7, with higher

1003 $D^{silicate/carbonate}$ for Z/r > 7, therefore indicating that the V^{5+} species (Z/r = 9.2) would be more strongly

1004   partitioned into the carbonate relative to the V^{3+} or V^{4+} species (Z/r of 4.7 and 6.9, respectively).

1005   Thus, there is some evidence, albeit indirect, that the more highly changed V^{5+} species may be

1006   preferentially stabilized in carbonate melt, relative to the more reduced species, thus accounting for

1007   the anomalously high values of $D^{ap/bt}$ measured for the Palabora sample. In addtion to melt

1008   structure, biotite composition could also play a role, in that the Palabora biotite is Al- and Ti-poor

1009   compared to the reference group (Supplementary Table 2), which could hinder the uptake of V^{3+}

1010   and V^{4+} and amplify the melt composition-induced shift towards a higher $D(V)^{ap/bt}$ value. Despite

1011   the likely complications imposed by other factors, the relatively oxidized conditions for the Palabora

1012   sample implied by the high value of $D(V)^{ap/bt}$ are broadly consistent with some independent

1013 measures of sample redox state. For example, the only primary Fe oxide mineral in the sample is

1014 magnetite, which together with coexisting tetraferriphlogopite, implies a moderately high fO_2

1015 (Giebel et al., 2019). Also, using the composition of ilmenite exsolved from host magnetite, Milani et

1016 al. (2017) tracked a T-fO_2 path of re-equilibration with maximum temperatures at 560-590 °C, and

1017 fO_2 of ~FMQ+1. This agrees with measurements reported by Braunger et al. (2020), using a similar

1018 method which suggesting an fO_2 of ~FMQ+0.9 (±0.4) at T=570-650 °C.

5. Conclusions

1019

1020   Results reported in this study show that the partitioning of vanadium and other heterovalent

1021 elements (As, Eu, Mo, Sn, W) between apatite, biotite and high silica glass show changes with

1022 sample redox state. With increasing fO_2 from FMQ-2.8 to FMQ+2.8, vanadium becomes more

1023 compatible in apatite, (D(V)$^{ap/gl}$ from ~0.6 to ~5), and less compatible in biotite, (D(V)$^{bt/gl}$ from ~580

1024 to ~50). Over the same fO_2 interval, tin compatibility increases in both minerals (D(Sn)$^{ap/gl}$ from 0.05-

1025 0.3, D(Sn)$^{bt/gl}$ from 0.1-1), europium compatibility increases in apatite (D(Eu)$^{ap/gl}$ from ~20-~90), and

1026 tungsten compatibility decreases in biotite (D(W)$^{bt/gl}$ from ~0.13 to ~0.02). Given the diverging fO_2

1027 trends for D(V)$^{bt/gl}$ and D(V)$^{ap/gl}$, the vanadium partitioning between apatite and biotite is amplified

1028 from values of ~0.003 at FMQ-2.8 to ~0.5 at FMQ+4.3. Comparison of partitioning for an internally

1029 consistent dataset of homovalent elements also collected in this study suggests that the changes in

1030 partitioning behaviour of the heterovalent elements are primarily controlled by the fO_2. Based on

1031 these results, a preliminary model of D(V)$^{ap/bt}$ applicable to high-silica, peraluminous systems is

1032 developed. The model reveals that the species abundance and D$^{ap/bt}$ of V^{5+} almost entirely

1033 determines the total D(V)$^{ap/bt}$. Vanadium intermineral partitioning in the peraluminous South

1034 Mountain Batholith (SMB) implies reducing conditions (~FMQ-1.5) consistent with fO_2

1035 determinations from independent phase-equilibria-based models and zircon-melt partitioning. The

1036 elevated D(V)$^{ap/bt}$ values measured for the Palabora carbonatite indicate a high proportion of V^{5+}

1037 during crystallization, which in part could reflect more oxidizing conditions, but also be influenced

1038 by melt and/or mineral composition controls. Further experimental studies of vanadium

1039 partitioning between apatite and biotite are necessary to quantify these effects.

1040   Previous experimental studies of mineral-melt partitioning relations involving

1041 ferromagnesian phases (pyroxene, olivine, Fe-Ti oxides; Arató & Audétat, 2017a; Mallmann & O'Neill,

1042 2009, 2013)) for vanadium have established that D(V) decreases with increasing fO_2, owing to the

1043 increasingly poor mismatch between the higher valence vanadium species and the dominant

1044 substituent cations in these phases. Because of this sympathetic partitioning relationship,

1045 intermineral partitioning of vanadium involving these phases shows little change with fO_2. Minerals

1046 that exhibit exceptions to this behavior are rutile (Holycross & Cottrell, 2020, 2022) and apatite (this

1047 study), in which the V^{5+} species is the most compatible.   Although the distribution of rutile is

1048 somewhat more restricted to specific igneous bulk compositions, apatite is a ubiquitous phase in

1049 compositions ranging from lunar basalts to high silica rhyolites (McCubbin & Jones, 2015; Webster &

1050 Piccoli, 2015). Hence, the change in apatite/biotite partitioning of vanadium documented in this

1051 study is almost certainly to be seen for the cases of apatite in equilibrium with pyroxenes, olivine

1052 and Fe-Ti oxides, providing the basis for a number of potentially new oxybarometers applicable to a

1053 range of rock-types.

1063

partitioning coefficients (For comparison, studies in natural systems: FCT - Bachmann et al. (2005), AV – Acosta-Vigil et al. (2012), Petal 2024 – Pichavant et al. (2024). Experimental studies: Getal 2018 – Gion et al. (2018), W&K, 2021 – Were & Keppler (2021), Petal 2016 - - Pichavant et al. (2016)).

Figure 8. Mineral/melt chemical equilibria in the glass-phyric suites analyzed in this study. **A)** Biotite-glass Mg-Fe equilibrium. Gray lines represent the K_D for Mg-Fe exchange between biotite and melt established by Were and Keppler (2021), mean value marked as a solid line, dashed lines mark the maximal and minimal $K_D(Fe-Mg)$ values. Black dashed lines mark the range of $K_D(Fe-Mg)$ values determined by Icenhower & London (1997). Equilibrium in Were & Keppler experiments was approached by a prolonged duration of the experiments (30-45 days) and was confirmed using textural evidence and chemical uniformity of the phenocrysts and matrix glass. B) Apatite/glass partition coefficient of strontium ($D(Sr)^{ap/gl}$) as a function of glass CaO. Experimental data from Prowatke & Klemme (2006) and Watson & Green (1981). Prowatke and Klemme suggested trend of D(Sr) in the mafic compositions in a correlation with the melt CaO. Data in this study lay near the minimum CaO with high D(Sr) values suggesting a continuation from the felsic Watson & Green compositions.

Figure 9. Major and trace element $D^{ap/gl}$ values as a function of ionic radius in VIII-fold coordination. Curves are produced as least square regressions to Eq. 4 for Na, K, Rb in monovalent array, Zn, Mg, Fe, Ca, Sr, Ba in divalent array, REE and Y in trivalent array, Hf, Zr, Th in tetravalent array. Pentavalent elements (P, Nb, Ta) lack sufficient datapoints to model the r_i-D_i relationships. When selecting the D values for the isovalent array fits, several elements were excluded from the regression (Li for monovalent, Ga for trivalent, Si, Ti, Ge for tetravalent array) as their IR are sufficiently small to enter the tetrahedral site, thus reducing the IR. Similarly, the heterovalent elements (V, W, U) are not included in the fitting. Symbols from Fig. 4. Error bars depict uncertainty of D, propagated from standard errors of element concetrations in apatite and glass.

Figure 10. Major and trace element $D^{bt/gl}$ values as a function of ionic radii. Curves are produced as least square regressions to Eq. 4. for Na, K, Cs in XII-fold coordinated monovalent array, Mg, Co, Fe, Mn in VI-fold coordinated divalent array, Si, Ge, Hf, Zr in IV-fold coordinated tetravalent array. In the Al^{VI}-rich Macusani biotite, it is assumed that the trivalent trace elements (Ga, In, Sc, Lu, Yb, Y) exclusivelly enter the octahedral sites, whereas in the less-aluminous biotites of FCT and TT the two smallest trivalent trace elements (Ga, In) enter the tetrahedral site and the other, larger trivalent ions enter the octahedral site. Symbols from Fig. 4. Error bars depict uncertainty of D, propagated from standard deviations of element concetrations in biotite and glass.

Figure 11. Comparison of empirical and experimental ap/gl partition coefficients for samarium as a function of the SiO_2 content of the coexisting melt demonstrating the large increase in partition coefficients with increasing SiO_2. Experimental data from Prowatke and Klemme (2006; P&K) and Watson and Green (1981; W&G); Empirical data from Brophy et al (2011; B et al), Li et al. (2023) and this study.

1138 **Figure 12.** Redox sensitive heterovalent element partitioning between biotitite and melt (a), apatite
1139 and melt (b), apatite and biotite (c). Error bars depict the reported range of fO_2 and D uncertainty
1140 propagated from standard errors of the element concentrations.

1141 **Figure 13.** Homovalent element apatite/biotite partitioning coefficients as a function of oxygen
1142 fugacity (a) and inverse temperature (b). Sample group for $D^{ap/bt}$-1/T correlation includes all
1143 samples, the Dap/bt-fO2 correlation is based on all samples except Mascota minettte.

1144 **Figure 14.** a) Model of the $D(\Sigma V)^{apatite/biotite}$ as a function of oxygen fugacity. Inputs: surrogate $D(V^{3+})$
1145 = D(Ga), $D(V^{4+})$ = D(Ti), $D(V^{5+})$ = approximation from D(Nb) and D(Ta) given in the legend,
1146 abundances of V species from Sossi et al. (2018). High-T model is based on the surrogate
1147 homovalent element D values in Mascota minette, low-T model is based on the rest of the sample
1148 group. b) Variation of $D(\Sigma V)^{apatite/biotite}$ in South Mountain Batholith (purple) and Palabora
1149 carbonatite (green). Vanadium partitioning between apatite and biotite suggests fO_2 below FMQ in
1150 South Mountain Batholith whereas the D values in the Palabora carbonatite correspond with
1151 stronger oxidation.

1152 **Figure 15.** Backscattered electron images showing the textural relations for biotite and apatite
1153 indicating co-crystallization of both phases. A) Palabora carbonatite (xxx facies) and B) peraluminous
1154 South Mountain Batholith (sample BM0001, Cloud Lake Pluton)

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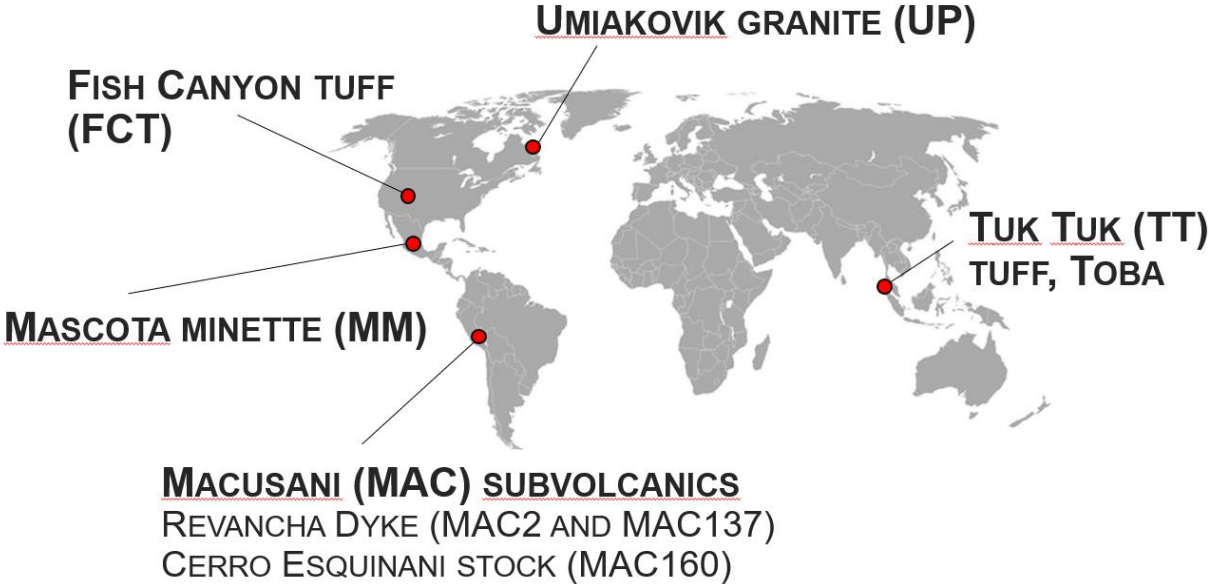1378   Situ Accessory Mineral Dating in Thin Sections. *Geoscience Canada*, *39*(3), 158.

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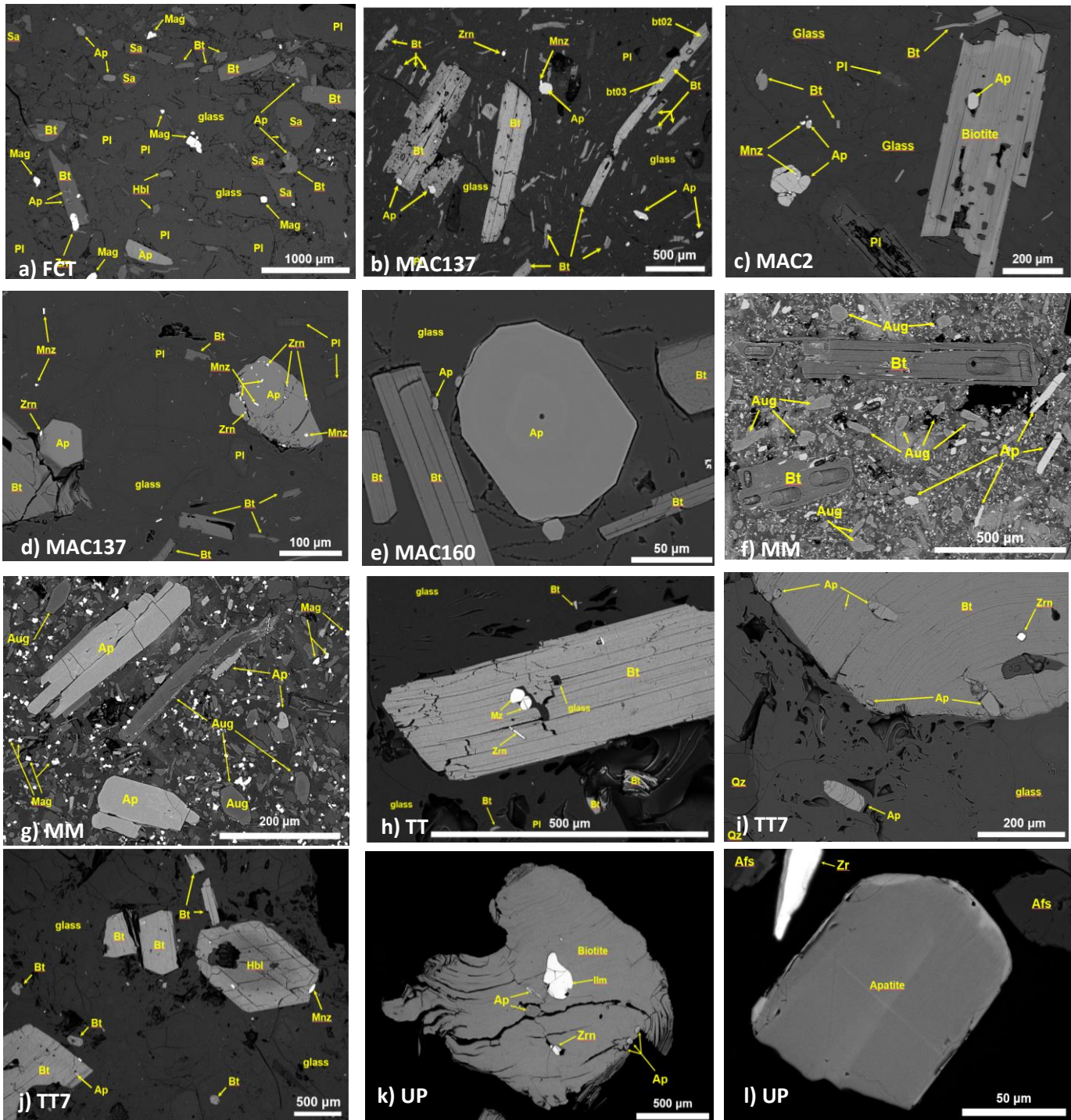
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1495   **Figures**

UMIAKOVIK GRANITE (UP)

FISH CANYON TUFF (FCT)

TUK TUK (TT) TUFF, TOBA

MASCOTA MINETTE (MM)

MACUSANI (MAC) SUBVOLCANICS
REVANCHA DYKE (MAC2 AND MAC137)
CERRO ESQUINANI STOCK (MAC160)

1496

1497   **Figure 1.**

1498

Figure 2.

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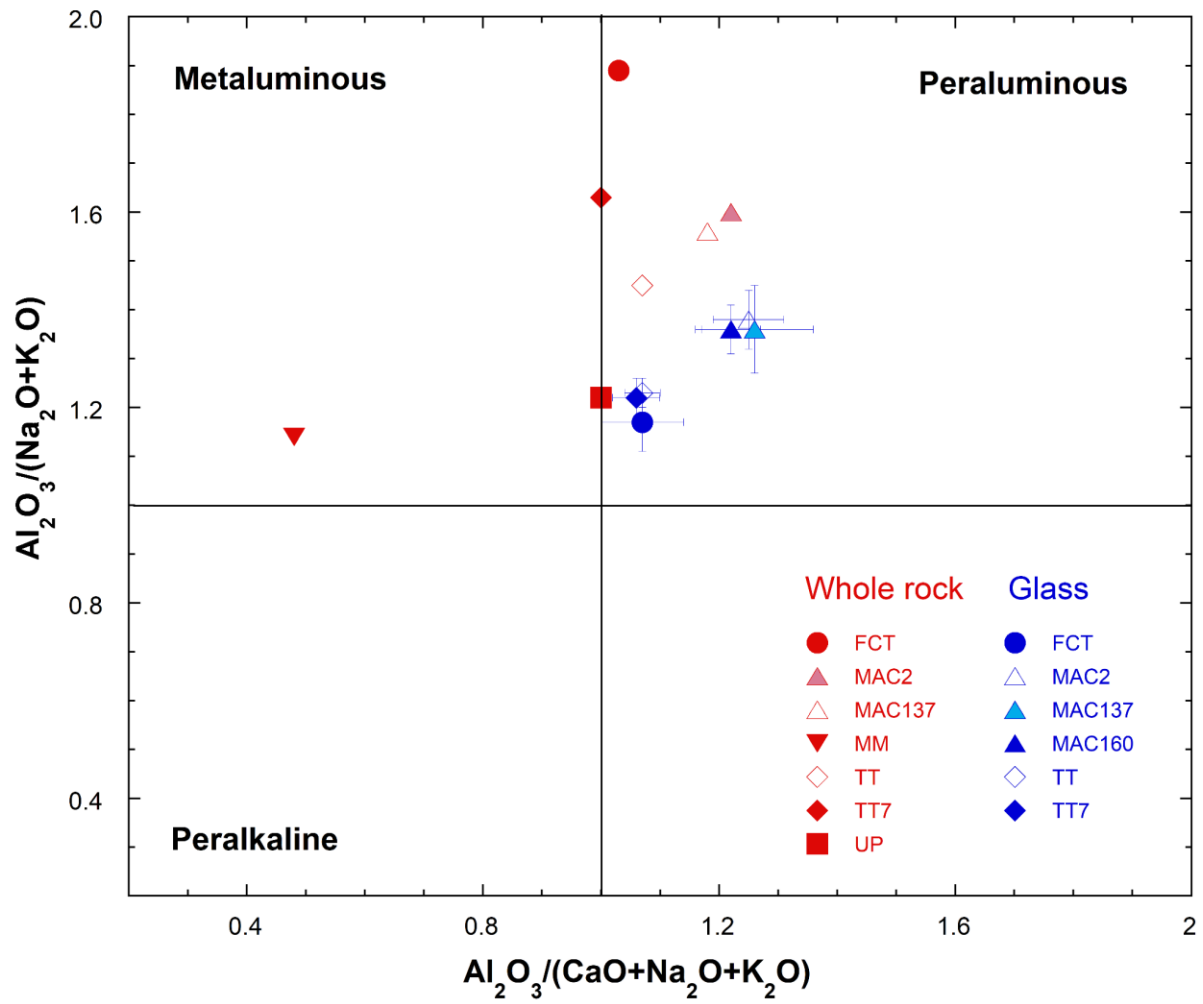
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1502   **Figure 3 .**

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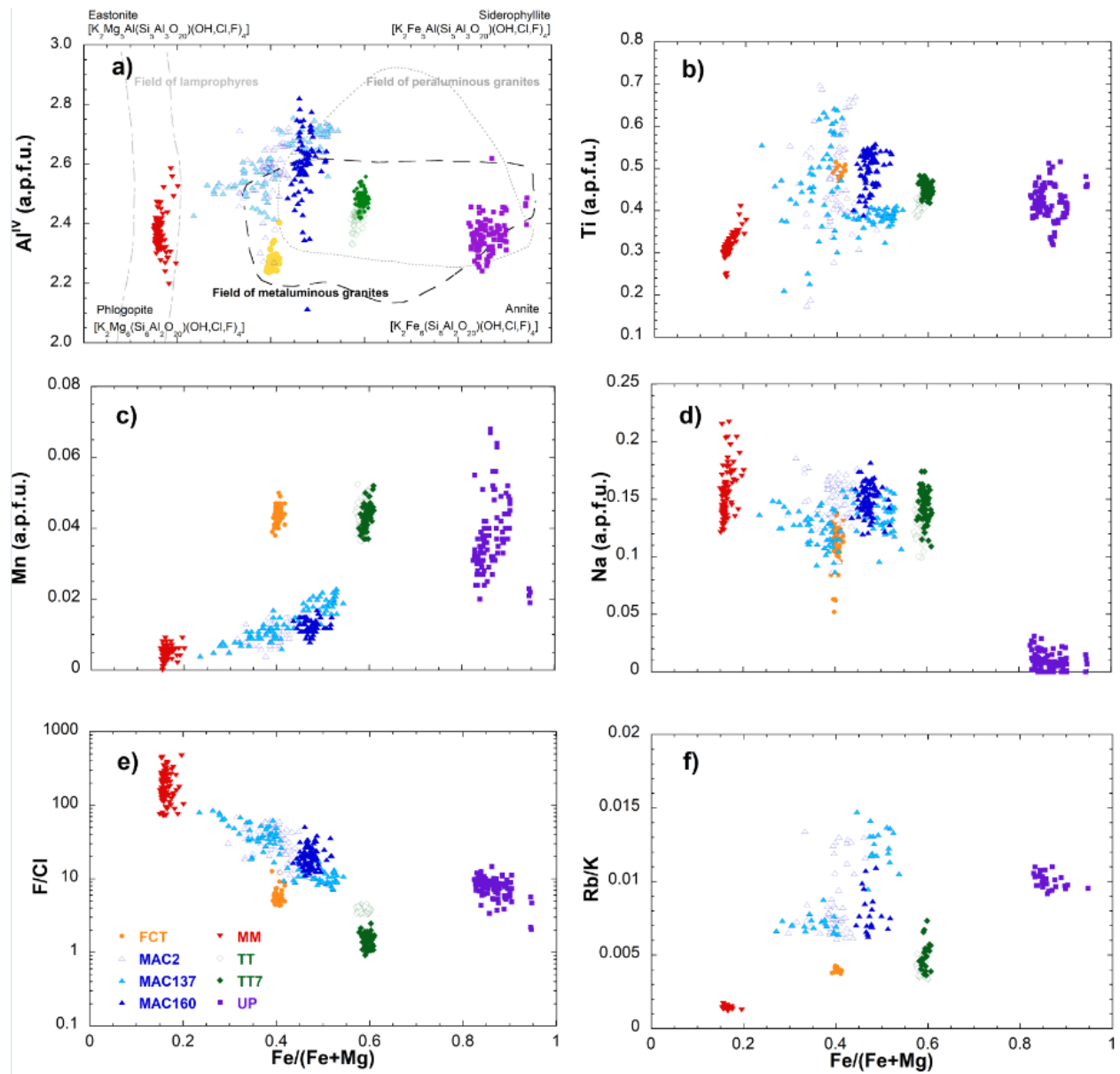
1504

1505   **Figure 4.**

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a)

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b)

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1510 **Figure 5.**

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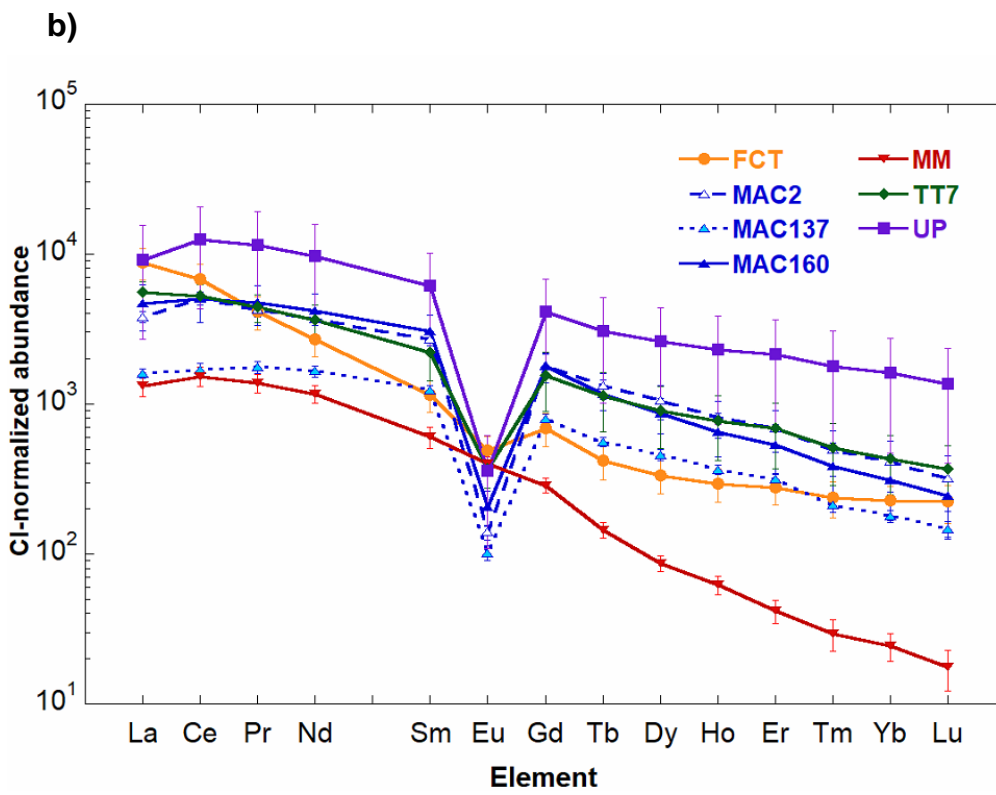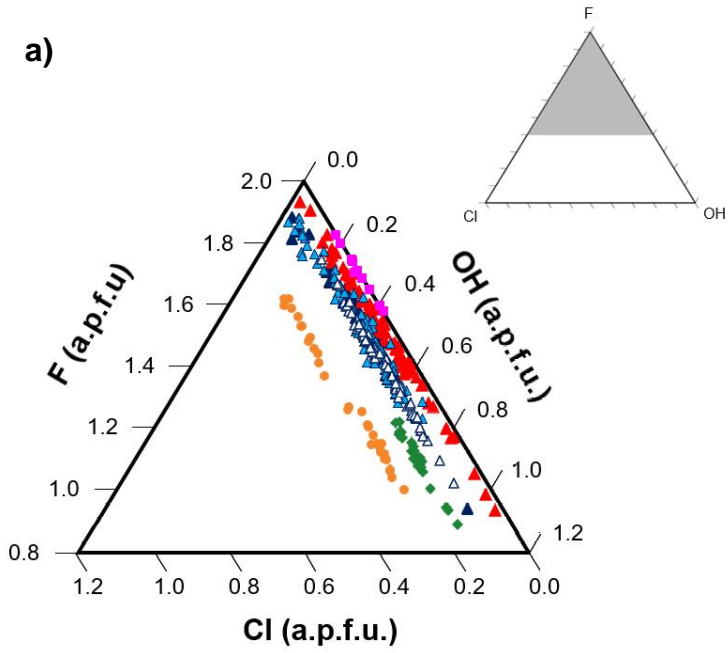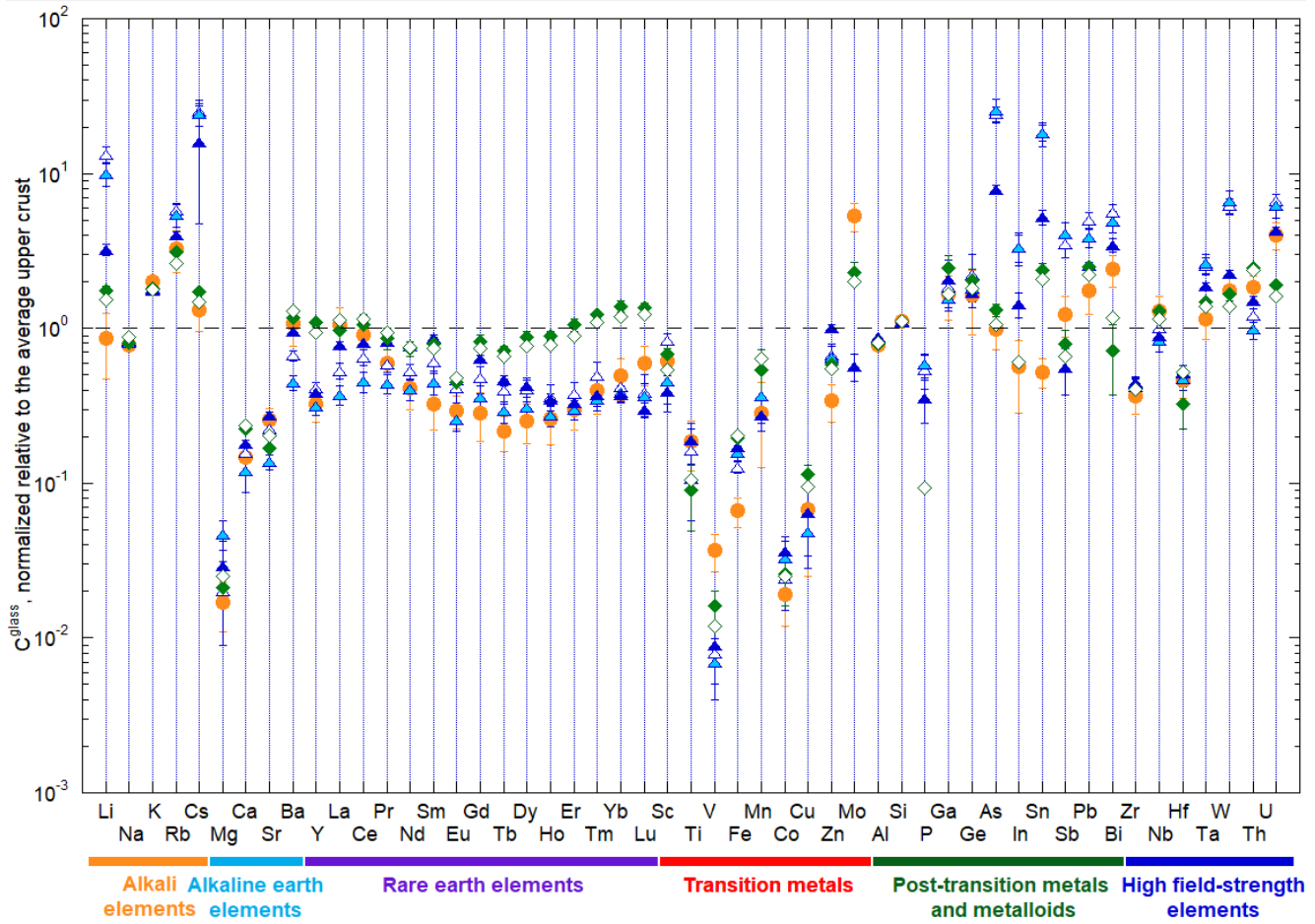
1511
1512 **Figure 6.**

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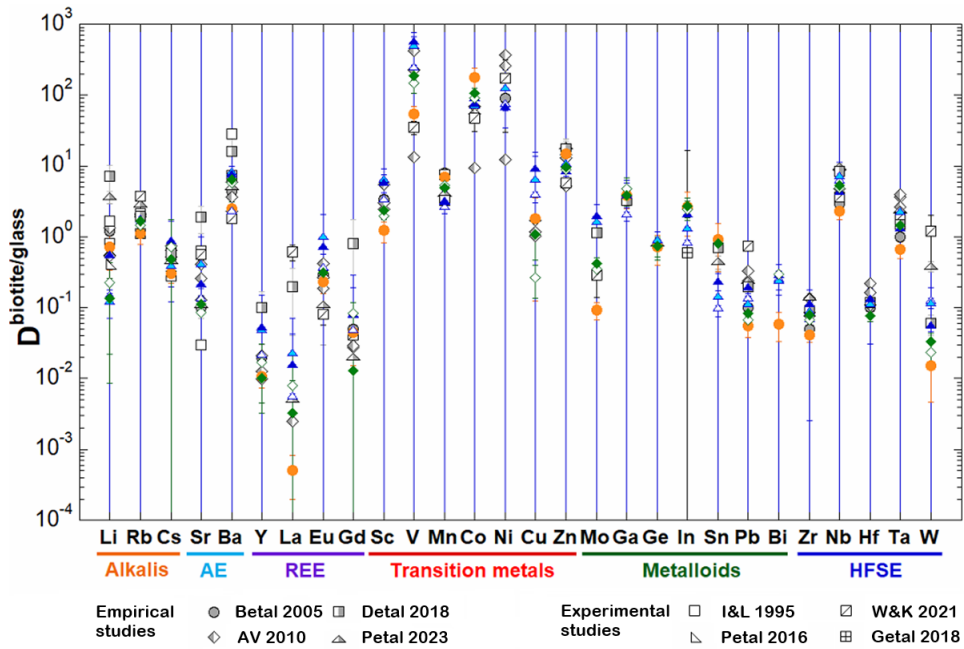
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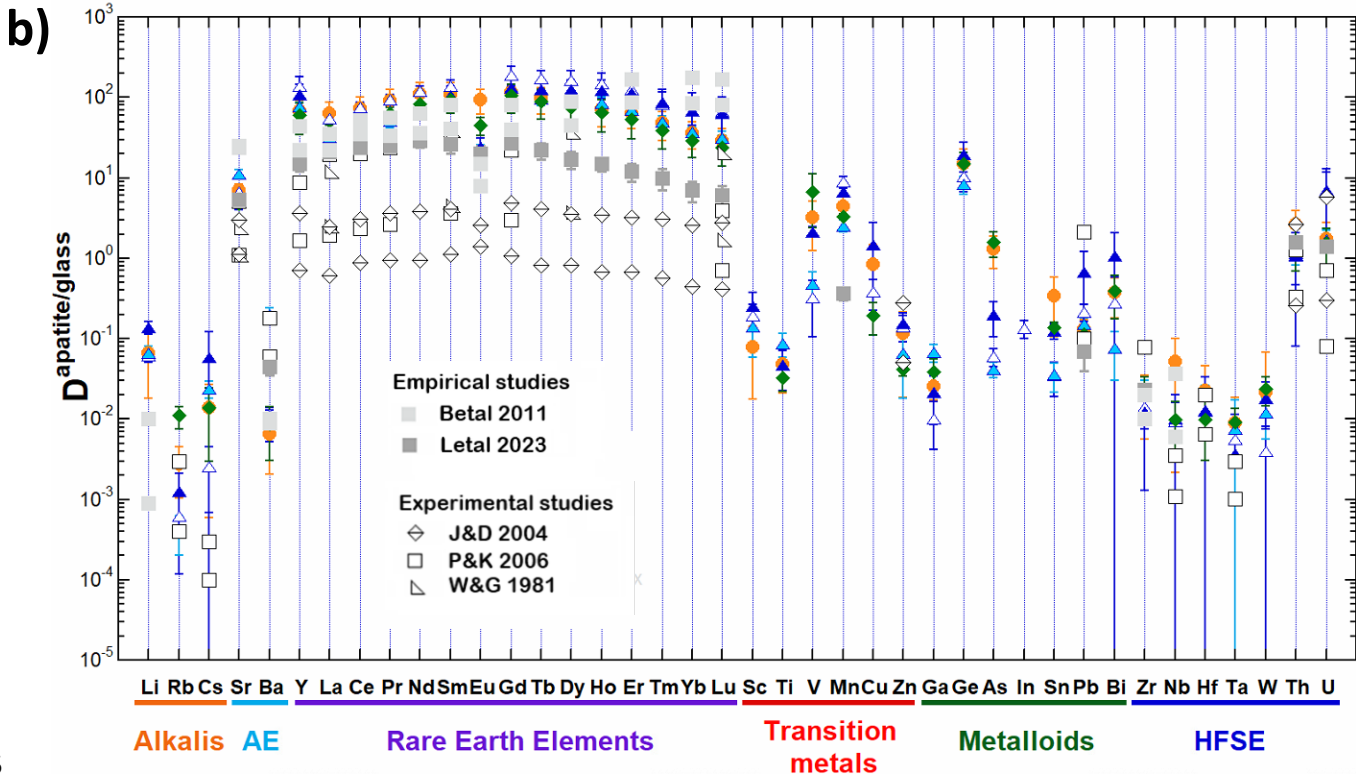
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1516   **Figure 7.**
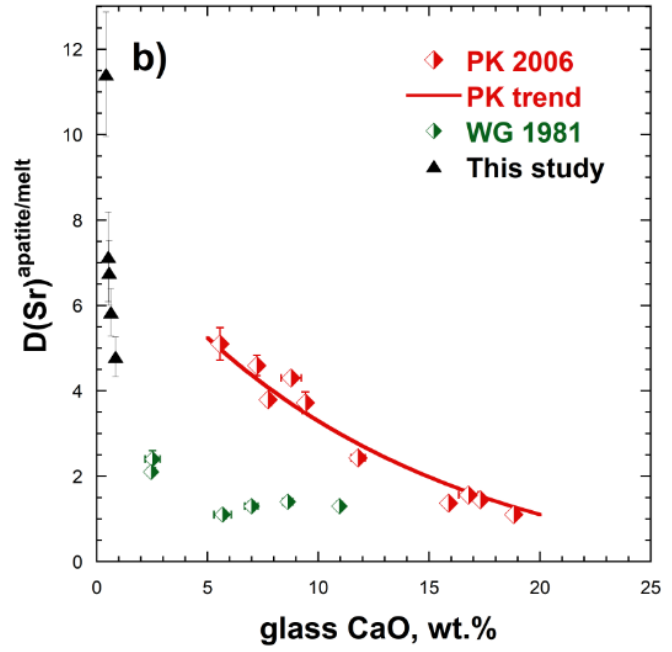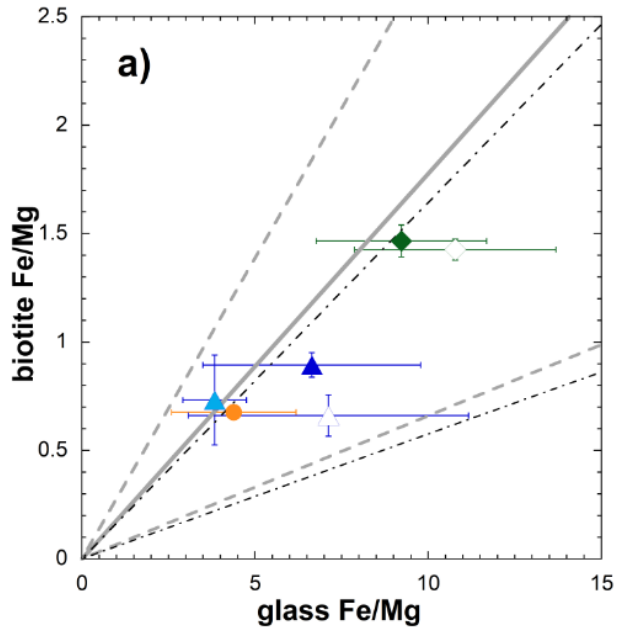
1517

1518   **Figure 8.**

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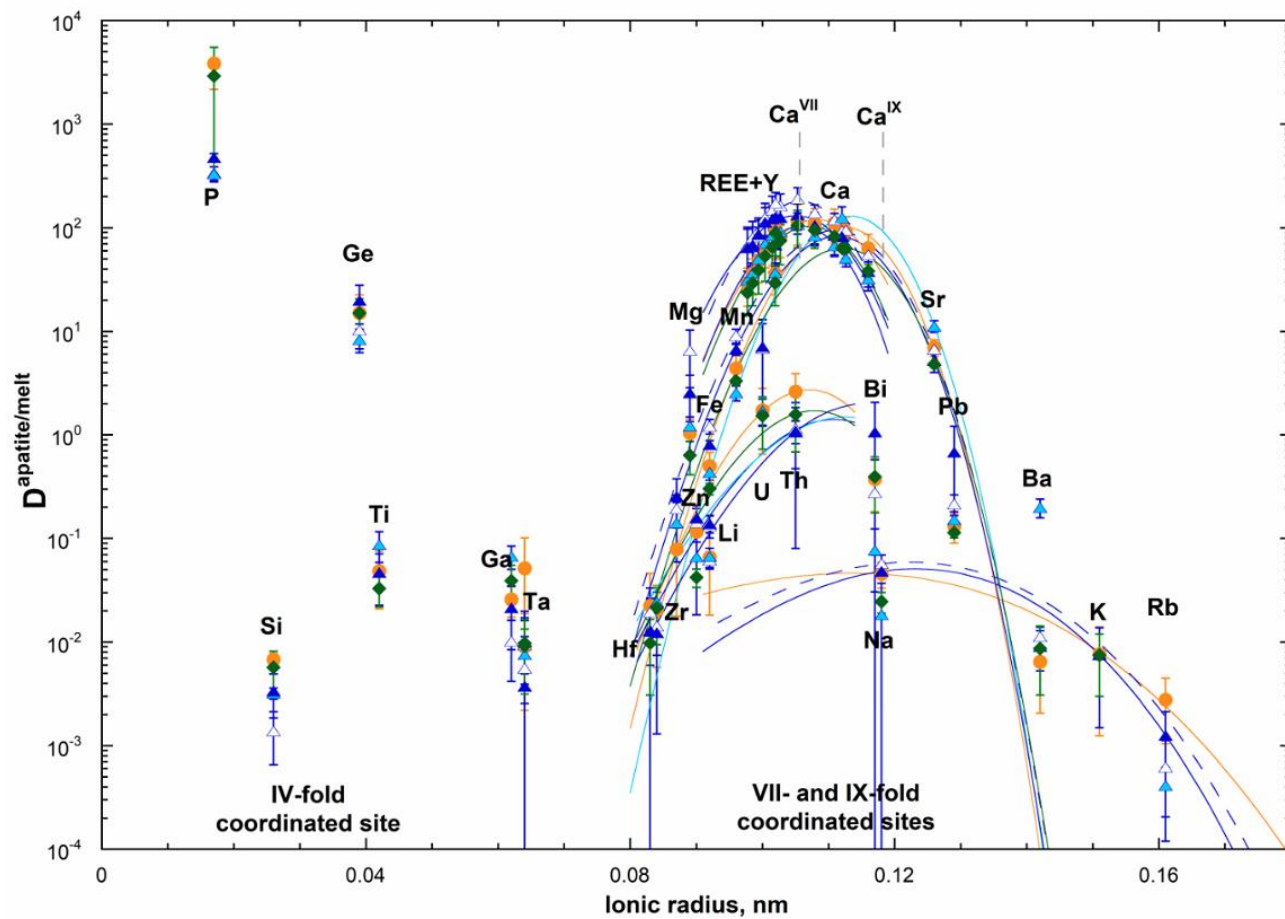
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1521 **Figure 9.**

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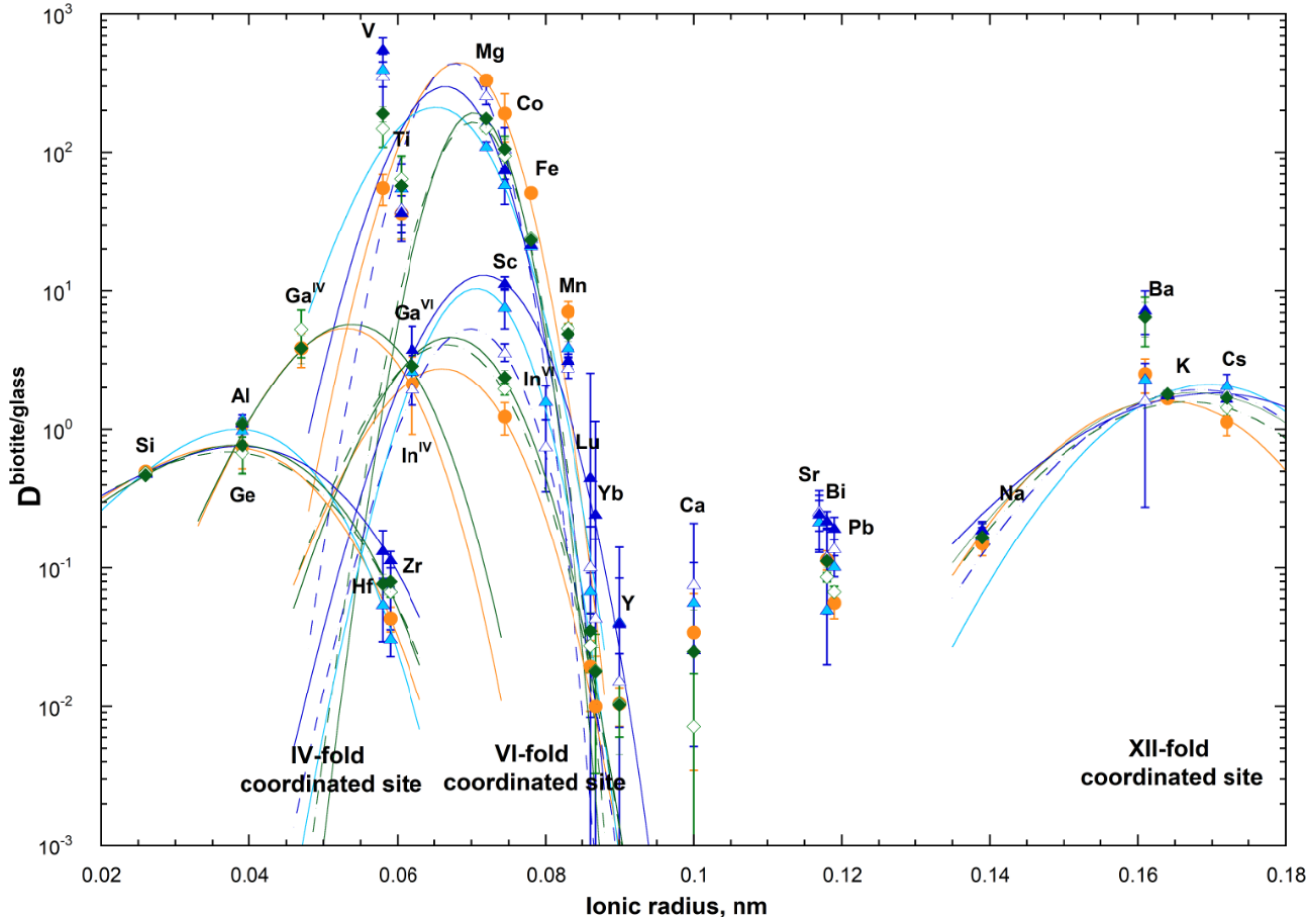
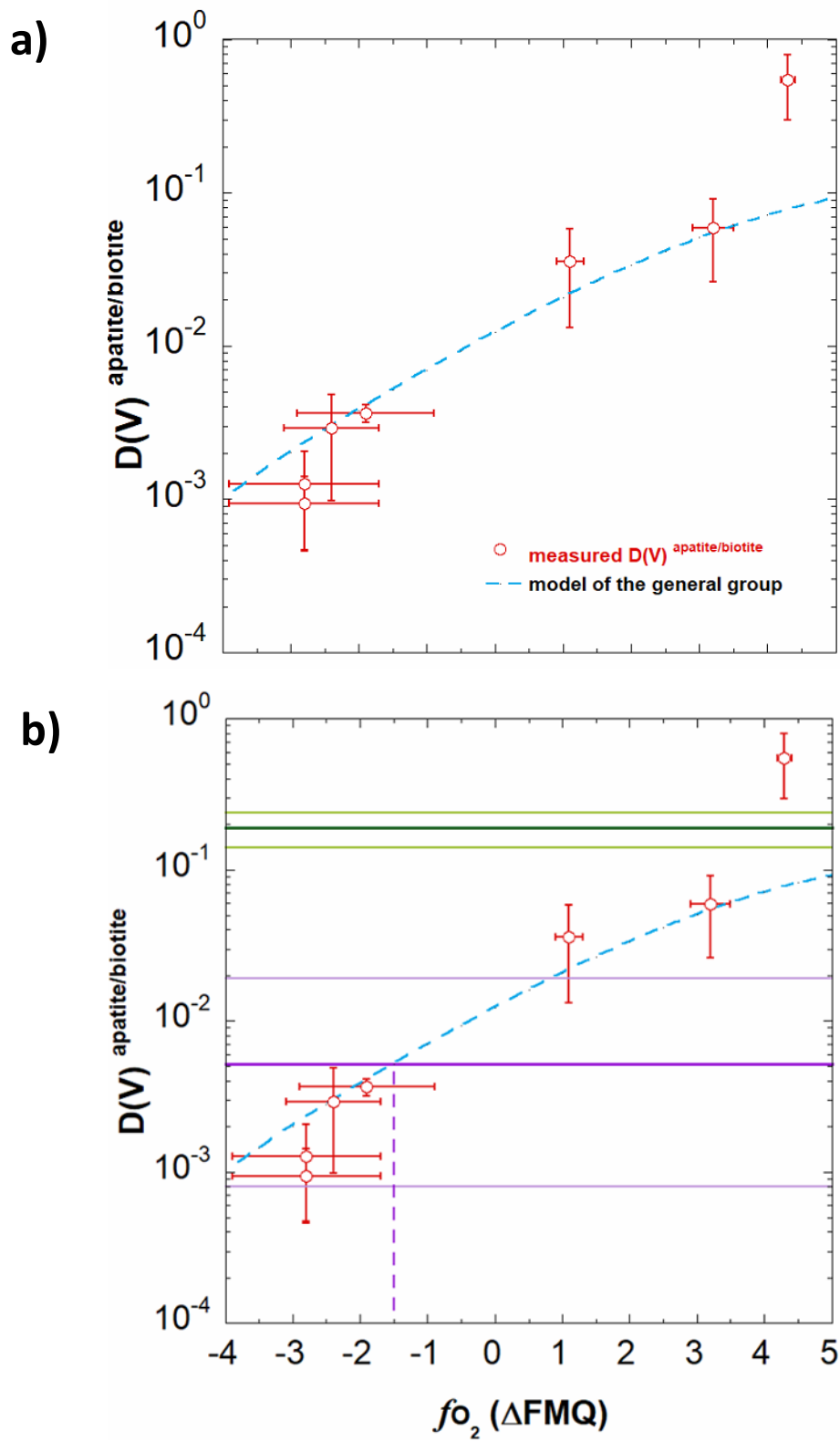

1524

1525 **Figure 10.**

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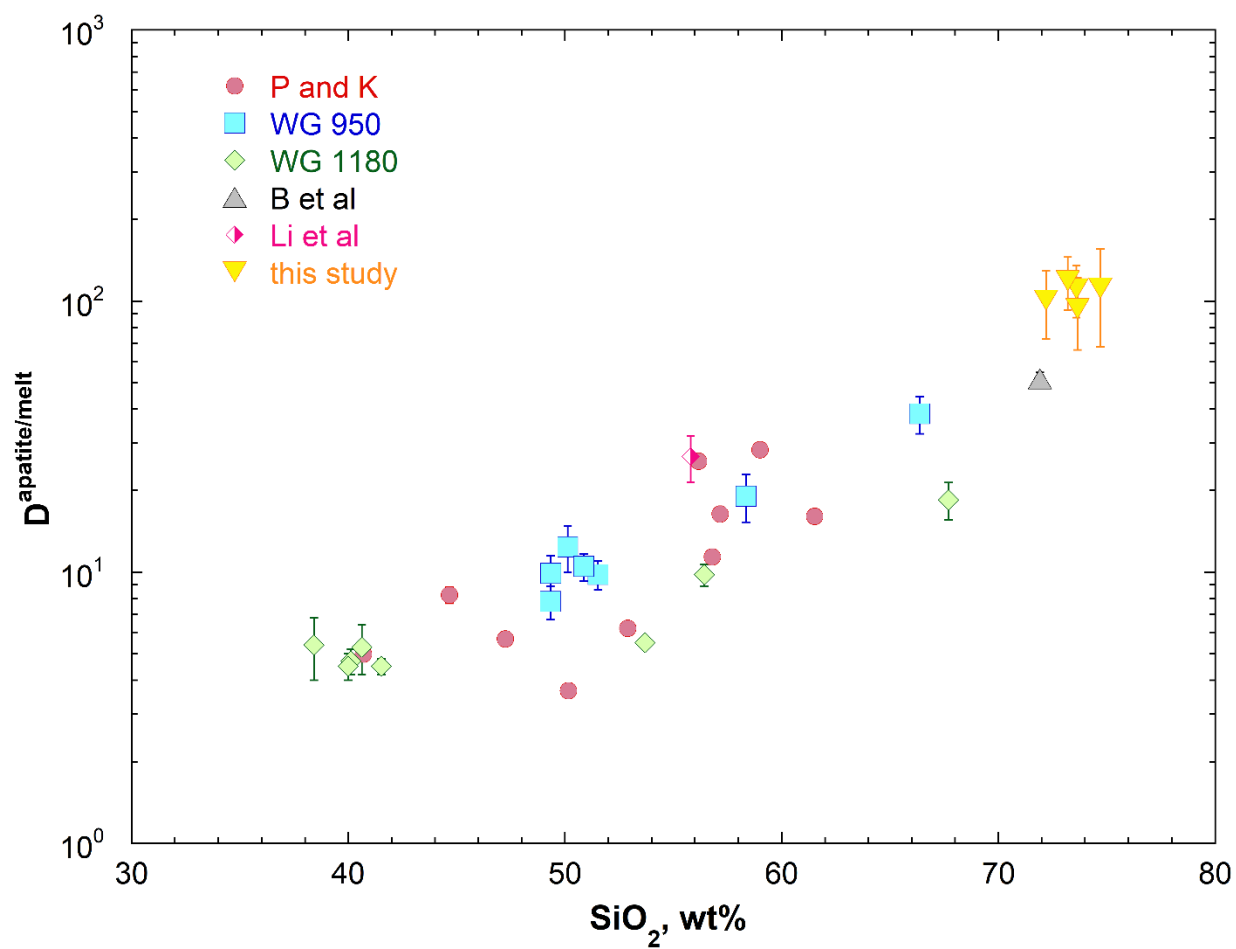
Figure 11.

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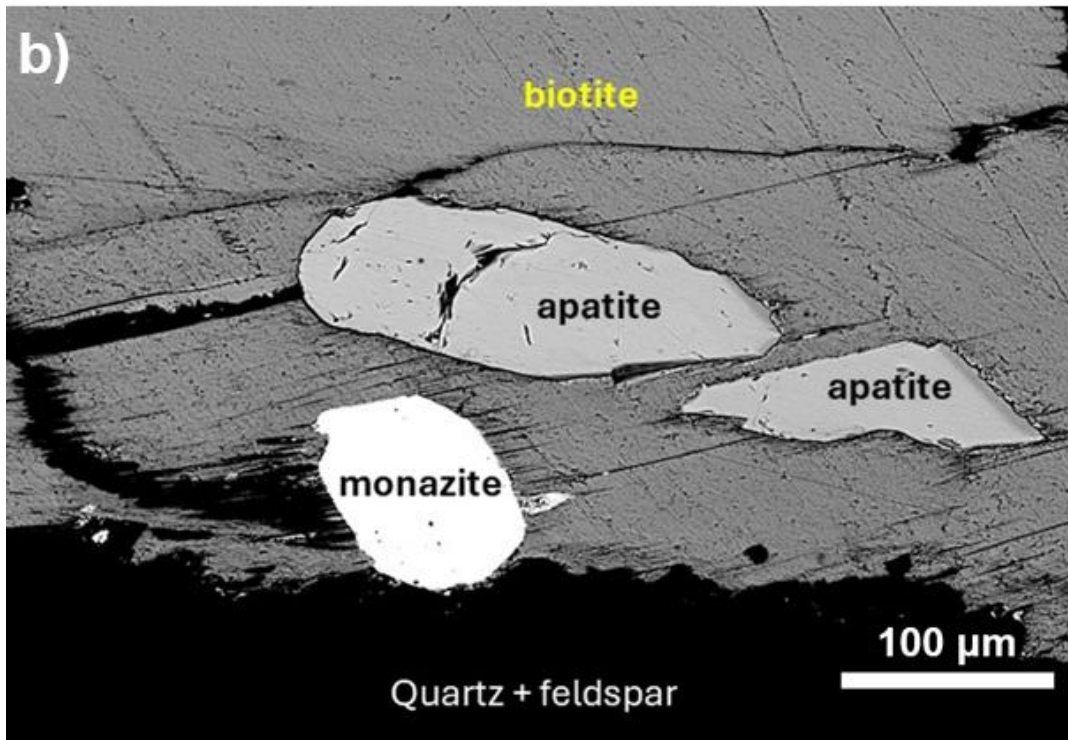1532   **Figure 12.**

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a) Trivalent elements — Y, Sc, Ga

b) Tetravalent elements — Zr, Hf, Ge, Ti

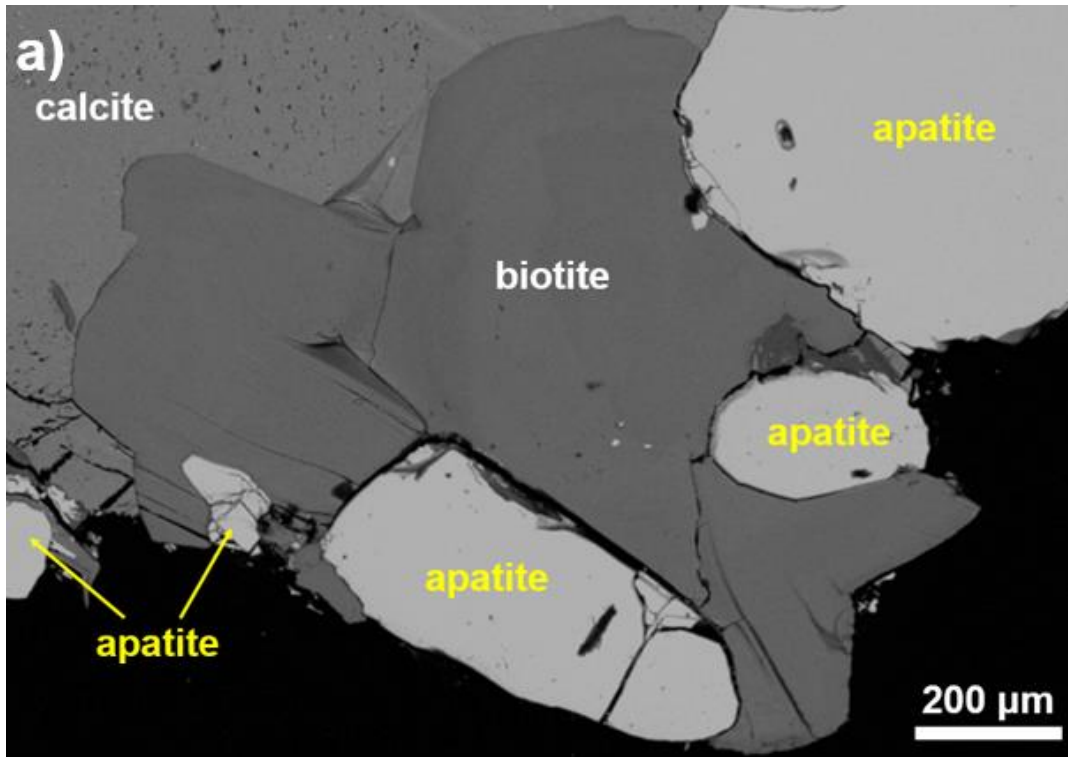**c)** Pentavalent elements — Nb, Ta

fO_2 (ΔFMQ)

1533   **Figure 13**.

a)

b)
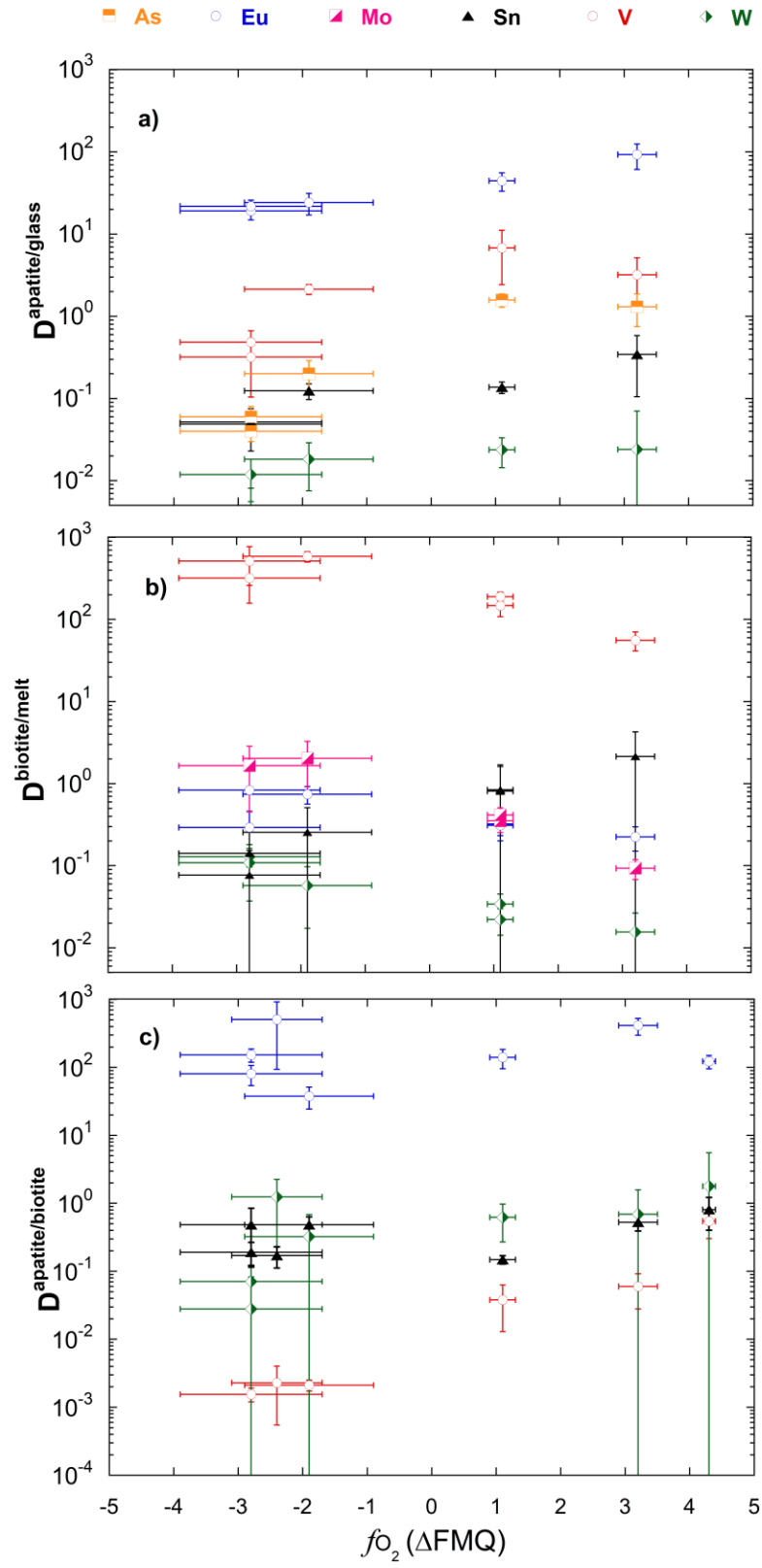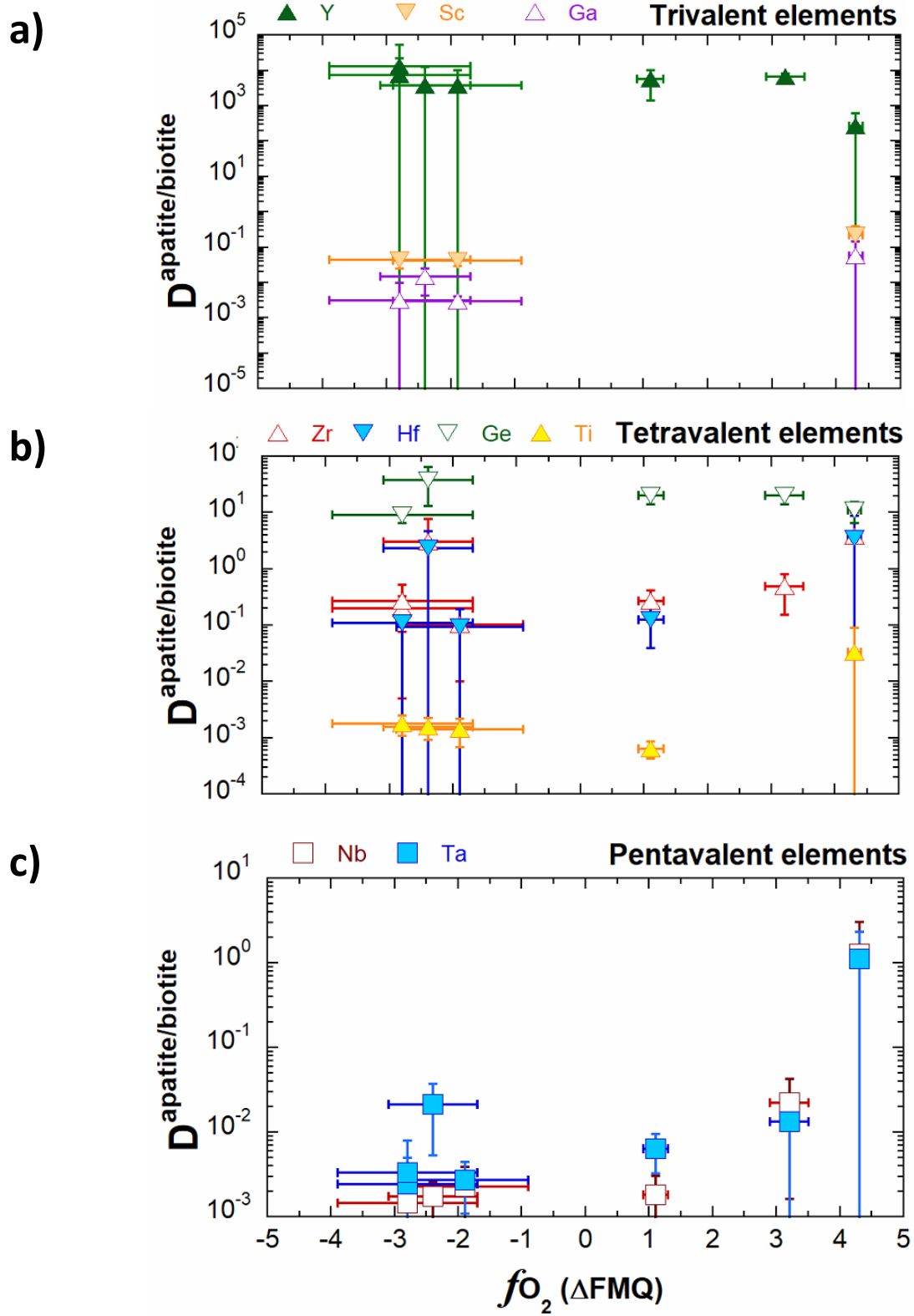
1534   **Figure 14.**

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1538 **Figure 15.**

1539 **Tables**

1540 **Table 1.** Summary of the analysed samples. Oxybarometry methods: cerium-in-zircon (Smythe &
1541 Brenan, 2016) for MAC (this study), UP (Smythe & Brenan, 2016); whole-rock iron oxidation state
1542 (Ghiorso & Sack, 1995) for MM (Carmichael et al., 1996), Fe-Ti oxide oxybarometry (Ghiorso & Sack,
1543 1991) for FCT (Whitney & Stormer, 1985) and TT (Chesner, 1998).

Sample	Petrology (phase assemblage)	SiO$_2$ (wt%)	A/CNK	fO$_2$ (ΔFMQ)	T (°C)
Fish Canyon tuff, FCT	Dacitic ignimbrite (Pl + Gl + Afs + Qz + Hbl + Bt + Ttn + Mag + Ilm + Ap + Zrn)	62.4-65.2	1.03	+2.8 ±0.3	700–760 (Johnson & Rutherford, 1989)
Revancha dyke, MAC2, MAC137	Cordierite-biotite rhyodacite (Gl + Pl + Bt + Crd + Qz + Afs + Ap + Ilm + Mnz + Zrn)	67.7-67.8	1.18-1.22	-2.8 ±1.1	634-693 (Sandeman & Clark, 2003)
Cerro Esquinani stock, MAC160	Biotite rhyodacite (Gl + Pl + Bi + Qz + Sil + Ap + Ilm + Mnz + Zrn)	66.8-71.7	1.13-1.28	-1.9 ±1.0	-
Mascota minette, MM	Augite minette (Aug + Bt + Ap + Mag)	48.7	0.47	+4.2 ±0.1	1080-1100 (Carmichael et al., 1996)
Tuk Tuk tuff, TT	Rhyolite (Gl + Pl + Qz + Bt + Afs + Hbl + Zr + Aln + Mag + Ilm + Mnz ± Ap)	69.8-72.7	1.00-1.07	+1.2 ±0.2	701-780 (Chesner, 2012)
Umiakovik granite, UP	Biotite-hornblende granite (Afs + Qz + Pl + Bt + Hbl + Ilm + Ap + Zrn + Fl)	73.2	1.00	-2.4 ±0.7	725-825 (Emslie & Stirling, 1993)

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1546 **Table 2.** Microanalytical conditions of EPMA and LA-ICP-MS used in this study.

Phase	**Zircon** (n=25)	**Apatite** (n=319)	**Biotite** (n=374)	**Glass** (n=289)
EPMA conditions	15 kV accelerating voltage, 10 nA beam current, 10 μm spot size			15 kV accelerating voltage, 10 nA beam current, 10 μm spot
Primary standards	Standards for zircon analysis were zircon (Zr), (Hf), (Y), (P)	synthetic fluorapatite (Ca, P, F); tugtupite (Cl); garnet (Fe, Si, Al); pyrolusite (Mn); albite (Na); biotite (K, Mg); K kaersutite (Ti)	Biotite (Fe, Al, Si, K, Mg), pyrolusite (Mn), kaersutite (Ca, Ti), albite (Na), tugtupite (Cl) and apatite (F)	BHVO-1 (Ca, Na, Mg, Al, Fe, Si); sanidine (K); rutile (Ti); chromite (Cr); pyrolusite (Mn); synthetic fluorapatite (P, F); tugtupite (Cl); barite (Ba); celestite (Sr); pyrrhotite (S)
Count time	20 s for all analytes, except F (90 s) and Cl (40 s) in apatite, biotite, and glass			
Secondary standards	Synthetic zircon	Durango apatite	San Carlos biotite, DJ biotite	BIR-1 and CAM66
LA-ICP-MS conditions	10 Hz repetition rate, ~5 J/cm^2, 15-100 μm spot size depending on the crystal size and availability of crystal-free domains in glass. 15-25 μm spot size for zircon.			
Analytes	^{23}Na, ^{27}Al, ^{29}Si, ^{31}P, ^{43}Ca, ^{44}Ca, ^{49}Ti, ^{55}Mn, ^{56}Fe, ^{89}Y, ^{90}Zr ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{178}Hf, ^{232}Th, ^{238}U	^{7}Li, ^{27}Al, ^{29}Si, ^{31}P, ^{43}Ca, ^{45}Sc, ^{47}Ti (glass, biotite), ^{49}Ti (apatite), ^{51}V, ^{52}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{61}Ni, ^{63}Cu, ^{65}Cu, ^{66}Zn, ^{69}Zn, ^{73}Ge, ^{75}As, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{95}Mo, ^{111}Cd, ^{113}In, ^{115}In, ^{118}Sn, ^{121}Sb, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{178}Hf, ^{181}Ta, ^{182}W, ^{206}Pb, ^{208}Pb, ^{209}Bi, ^{232}Th, ^{238}U		
Dwell time	10 ms (most analytes), 30 ms (^{139}La, ^{141}Pr)	10 ms (most analytes), 30 ms (^{51}V), 5 ms (^{27}Al, ^{29}Si, ^{31}P, ^{57}Fe)		
Primary standard	NIST 610 glass			
Secondary standard, internal standard isotope	Zircon 91500, ^{90}Zr	Durango apatite, apatite nano-powder pellet (myStandards GmbH), ^{43}Ca	DJ biotite, ^{27}Al	BIR-1, BHVO-1, ^{43}Ca

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Table 3. Trace element partitioning between apatite and glass.

Element	FCT	SD	MAC2	SD	MAC137	SD	MAC160	SD	TT7	SD
Li	**0.07**	0.05	**0.06**	0.01	**0.07**	0.01	**0.14**	0.03	-	-
Rb	**0.0028**	0.0017	**0.0006**	0.0005	**0.0004**	0.0002	**0.0013**	0.0009	**0.0110**	0.0034
Cs	**0.014**	0.013	**0.003**	0.002	**0.024**	0.006	**0.058**	0.063	**0.014**	0.011
Sr	**7.0**	1.3	**6.7**	0.6	**11.2**	1.4	**5.2**	1.2	**4.8**	0.3
Ba	**0.006**	0.004	**0.011**	0.003	**0.199**	0.041	**0.009**	0.004	**0.009**	0.006
Y	**69**	22	**137**	43	**77**	11	**109**	39	**60**	25
La	**63**	23	**55**	8	**32**	5	**38**	13	**38**	6
Ce	**73**	28	**76**	12	**35**	6	**53**	16	**45**	8
Pr	**92**	35	**94**	15	**51**	9	**69**	23	**63**	12
Nd	**111**	40	**119**	18	**67**	13	**84**	31	**83**	19
Sm	**110**	43	**140**	26	**84**	17	**105**	35	**95**	31
Eu	**93**	32	**19**	4	**22**	4	**24**	7	**45**	11
Gd	**118**	49	**191**	52	**107**	21	**133**	38	**106**	42
Tb	**98**	35	**172**	46	**96**	17	**127**	35	**89**	36
Dy	**82**	30	**163**	49	**92**	16	**126**	39	**75**	31
Ho	**72**	29	**149**	52	**85**	15	**122**	42	**65**	28
Er	**63**	22	**126**	45	**71**	12	**113**	44	**53**	23
Tm	**48**	19	**83**	34	**50**	9	**86**	38	**39**	16
Yb	**36**	14	**80**	35	**37**	6	**68**	33	**29**	12
Lu	**29**	12	**66**	35	**31**	7	**64**	33	**24**	10
Sc	**0.08**	0.06	**0.20**	0.07	**0.14**	0.08	**0.26**	0.12	-	-
Ti	**0.05**	0.03	-	-	**0.09**	0.03	**0.05**	0.02	**0.03**	0.01
V	**3.2**	2.0	**0.3**	0.2	**0.5**	0.2	**2.1**	0.3	**6.8**	4.4
Mn	**4.4**	1.4	**9.1**	1.4	**2.5**	0.4	**6.7**	0.8	**3.3**	0.2
Cu	**0.83**	0.64	**0.39**	0.16	-	-	**1.47**	1.29	**0.19**	0.09
Zn	**0.12**	0.10	**0.14**	0.05	**0.07**	0.05	**0.16**	0.05	**0.04**	0.01
Ga	**0.026**	0.008	**0.010**	0.006	**0.067**	0.017	**0.022**	0.013	**0.039**	0.016
Ge	**15**	7	**10**	4	**8**	2	**20**	8	**15**	6
As	**1.31**	0.56	**0.06**	0.02	**0.04**	0.01	**0.20**	0.09	**1.58**	0.29
In	-	-	**0.13**	0.03	-	-	-	-	-	-
Sn	**0.34**	0.24	**0.04**	0.02	**0.04**	0.01	**0.12**	0.03	**0.14**	0.02
Pb	**0.13**	0.04	**0.22**	0.05	**0.15**	0.03	**0.68**	0.54	**0.11**	0.01
Bi	**0.38**	0.19	**0.28**	0.30	**0.08**	0.05	**1.07**	1.00	**0.39**	0.22
Zr	**0.020**	0.015	**0.014**	0.007	**0.024**	0.006	**0.012**	0.011	**0.021**	0.012
Nb	**0.052**	0.049	**0.009**	0.011	-	-	**0.010**	0.006	**0.010**	0.007
Hf	**0.022**	0.024	**0.020**	0.014	**0.013**	0.013	**0.013**	0.013	**0.010**	0.007
Ta	**0.0090**	0.0097	**0.0056**	0.0057	**0.0076**	0.0095	**0.0037**	0.0012	**0.0092**	0.0042
W	**0.021**	0.046	**0.004**	0.004	**0.012**	0.006	**0.018**	0.011	**0.024**	0.009
Th	**2.6**	1.3	**1.2**	0.7	**1.1**	0.3	**1.1**	1.0	**1.6**	0.9
U	**1.7**	1.1	**6.9**	4.9	**1.7**	0.5	**7.1**	5.9	**1.5**	0.8

1554 **Table 4.** Trace element partitioning between biotite and glass.

1555

Element	FCT	1σ	MAC2	1σ	MAC137	1σ	MAC160	1σ	TT	1σ	TT7	1σ
Li	**0.72**	0.38	**0.15**	0.05	**0.12**	0.05	**0.57**	0.18	**0.23**	0.21	**0.14**	0.13
Rb	**1.1**	0.3	**1.6**	0.2	**1.8**	0.6	**1.6**	0.2	**1.5**	0.2	**1.7**	0.3
Cs	**0.31**	0.09	**0.40**	0.12	**0.40**	0.20	**0.89**	0.77	**0.72**	1.06	**0.48**	0.21
Sr	-	-	**0.14**	0.07	**0.42**	0.57	**0.22**	0.03	**0.09**	0.01	**0.11**	0.01
Ba	**2.5**	0.9	**2.4**	1.8	**8.4**	10.0	**7.9**	2.1	**5.8**	2.6	**6.5**	1.8
Y	**0.011**	0.003	**0.022**	0.009	**0.050**	0.100	**0.054**	0.044	**0.017**	0.014	**0.010**	0.006
La	**0.001**	0.000	**0.006**	0.004	**0.023**	0.048	**0.016**	0.026	**0.008**	0.014	**0.003**	0.006
Eu	**0.235**	0.076	**0.379**	0.173	**1.020**	1.073	**0.743**	0.179	**0.310**	0.116	**0.310**	0.077
Gd	**0.045**	0.030	**0.050**	0.031	**0.081**	0.205	**0.082**	0.113	**0.082**	0.036	**0.013**	0.017
Sc	**1.2**	0.4	**3.5**	0.7	**6.7**	2.5	**5.9**	1.7	**1.9**	0.2	**2.4**	0.3
V	**54**	14	**253**	109	**515**	255	**586**	85	**146**	39	**190**	25
Mn	**7.1**	2.1	**2.7**	0.6	**3.3**	1.1	**3.2**	0.3	**5.3**	0.4	**4.9**	0.6
Co	**177**	66	**93**	35	**73**	28	**77**	19	**92**	34	**106**	19
Ni	-	-	**77**	31	**130**	96	**68**	7	-	-	-	-
Cu	**1.8**	1.7	**4.1**	4.4	**6.7**	6.9	**9.3**	6.2	**0.3**	0.1	**1.1**	0.6
Zn	**14.7**	4.0	**8.8**	1.9	**11.1**	3.9	**8.8**	1.1	**9.0**	0.8	**9.6**	1.4
Mo	**0.09**	0.03	-	-	**1.66**	1.21	**2.03**	-	**0.35**	0.10	**0.42**	0.09
Ga	**3.8**	1.3	**2.1**	0.5	**4.0**	2.3	**4.2**	1.6	**4.8**	2.1	**3.9**	0.9
Ge	**0.7**	0.3	-	-	**0.9**	0.3	-	-	**0.7**	0.2	**0.7**	0.3
Cd	-	-	-	-	-	-	-	-	-	-	-	-
In	**2.7**	1.6	**0.9**	0.4	**1.3**	0.6	**2.1**	0.7	**2.5**	0.8	**2.7**	0.9
Sn	**0.93**	0.61	**0.10**	0.05	**0.15**	0.07	**0.24**	0.07	**0.80**	0.10	**0.81**	0.20
Pb	**0.06**	0.02	**0.14**	0.04	**0.11**	0.03	**0.20**	0.04	**0.07**	0.01	**0.08**	0.01
Bi	**0.06**	0.03	**0.26**	0.08	**0.24**	0.09	**0.29**	0.11	**0.30**	-	-	-
Zr	**0.04**	0.01	**0.07**	0.03	**0.09**	0.09	**0.12**	0.02	**0.07**	0.01	**0.08**	0.01
Nb	**2.3**	0.6	**6.4**	1.8	**7.4**	3.8	**4.4**	1.6	**5.0**	0.7	**5.4**	0.7
Hf	-	-	-	-	**0.12**	0.08	**0.13**	0.05	-	-	**0.08**	0.01
Ta	**0.7**	0.2	**2.3**	0.9	**2.3**	1.3	**1.4**	0.7	**1.5**	0.3	**1.4**	0.3
W	**0.02**	0.01	**0.13**	0.03	**0.12**	0.07	**0.06**	0.04	**0.02**	0.01	**0.03**	0.01

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1558 **Table 5.** Trace element partitioning between apatite and biotite.

	FCT		MAC2		MAC137		MAC160		MM		PAL		TT7	
	Mean	SD	**Mean**	SD	**Mean**	SD	**Mean**	SD	**Mean**	SD	**Mean**	SD	**Mean**	SD
Li	0.091	0.057	0.410	0.135	0.541	0.226	0.242	0.084	0.405	0.370	0.021	0.009	-	-
Rb	0.00249	0.00135	0.00038	0.00031	0.00023	0.00012	0.00077	0.00054	0.13001	0.14160	0.00003	0.00001	-	-
Cs	0.04472	0.04127	0.00650	0.00487	0.06030	0.03014	0.06569	0.06254	0.32989	0.23581	0.00002	0.00002	0.02844	0.02525
Sr	-	-	48	25	27	36	24	6	35	11	384	423	43	4
Ba	0.0026	0.0017	0.0047	0.0036	0.0238	0.0287	0.0012	0.0006	0.0462	0.0681	0.0003	0.0001	0.0013	0.0009
Co	0.009	0.009	0.019	0.004	0.010	0.005	0.008	0.003	0.037	0.036	0.034	0.011	0.009	0.007
Ni	0.037	0.020	0.007	0.007	0.015	0.010	0.011	0.008	0.004	0.004	0.032	0.018	-	-
Zn	0.008	0.006	0.016	0.005	0.006	0.005	0.018	0.006	0.279	0.252	0.002	0.002	0.004	0.001
Pb	2.4	0.3	1.6	0.5	1.3	0.3	3.5	2.8	-	-	15.8	7.4	1.4	0.1
Y	6455	1978	6221	3010	1542	3089	2030	1817	273	302	675	1423	5863	4002
La	125374	74029	9432	6550	1370	2813	2318	3813	247	501	1159	3180	11555	21539
Gd	2613	1634	3840	2401	1322	3328	1621	2269	515	726	425	513	8272	11560
Sc	0.06	0.05	0.06	0.02	0.02	0.01	0.04	0.02	0.26	0.18	0.02	0.01	-	-
Ga	0.007	0.001	0.0048	0.003	0.017	0.010	0.0051	0.003	0.073	0.085	0.00170	0.001	0.010	0.005
In	-	-	0.16	0.05	-	-	-	-	-	-	0.45	0.41	-	-
Bi	6.3	3.8	1.1	1.2	0.3	0.2	3.6	3.6	7.4	13.2	77.1	41.0	-	-
Ge	20.6	6.2	-	-	9.1	2.6	-	-	11.2	4.5	18.8	7.0	20.4	6.3
Zr	0.49	0.34	0.20	0.13	0.27	0.26	0.11	0.10	3.83	6.31	0.33	1.43	0.27	0.15
Hf	-	-	-	-	0.11	0.14	0.09	0.10	3.44	5.37	0.12	0.29	0.13	0.09
Th	2337	2370	180	219	99	252	94	184	50	102	469	942	3487	4715
Si	-	-	-	-	0.005	0.001	0.008	0.002	0.093	0.131	0.003	0.001	0.021	0.015
Ti	-	-	-	-	0.0018	0.0007	0.0014	0.0007	0.0338	0.0577	-	-	0.0007	0.0002
Nb	0.022	0.021	0.001	0.002	-	-	0.002	0.002	1.288	1.772	0.009	0.006	0.002	0.001
Ta	0.013	0.014	0.002	0.003	0.003	0.005	0.003	0.002	1.118	1.249	0.002	0.003	0.006	0.003
P	-	-	-	-	2513	1986	2344	2586	2804	2521	975	2419	-	-
Eu	396	126	51	22	21	22	33	12	123	43	101	49	144	48
V	0.0589	0.0326	0.0013	0.0008	0.0009	0.0005	0.0037	0.0005	0.5468	0.2493	0.1858	0.0530	0.0358	0.0227
Mn	0.62	0.08	3.32	0.62	0.78	0.26	2.08	0.26	1.08	0.36	0.44	0.11	0.68	0.07
Cu	0.46	0.38	0.09	0.10	-	-	0.16	0.12	0.36	0.31	0.21	0.32	0.18	0.12
Sn	0.37	0.10	0.34	0.22	0.24	0.14	0.52	0.17	0.80	0.41	0.46	0.17	0.17	0.04
W	1.41	3.17	0.03	0.03	0.10	0.08	0.32	0.29	4.13	6.84	47.54	59.22	0.72	0.35

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1560   **Table 6.** $D(V)^{ap/bt}$ values used for the vanadium species in the partitioning model.

V species	D surrogate	D value
V^{3+}	Minimal $D(Ga^{3+})$	0.0048
V^{4+}	Mean $D(Ti^{4+})$	0.0004
V^{5+}	Least squares fitting	0.1651

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Supplementary figures
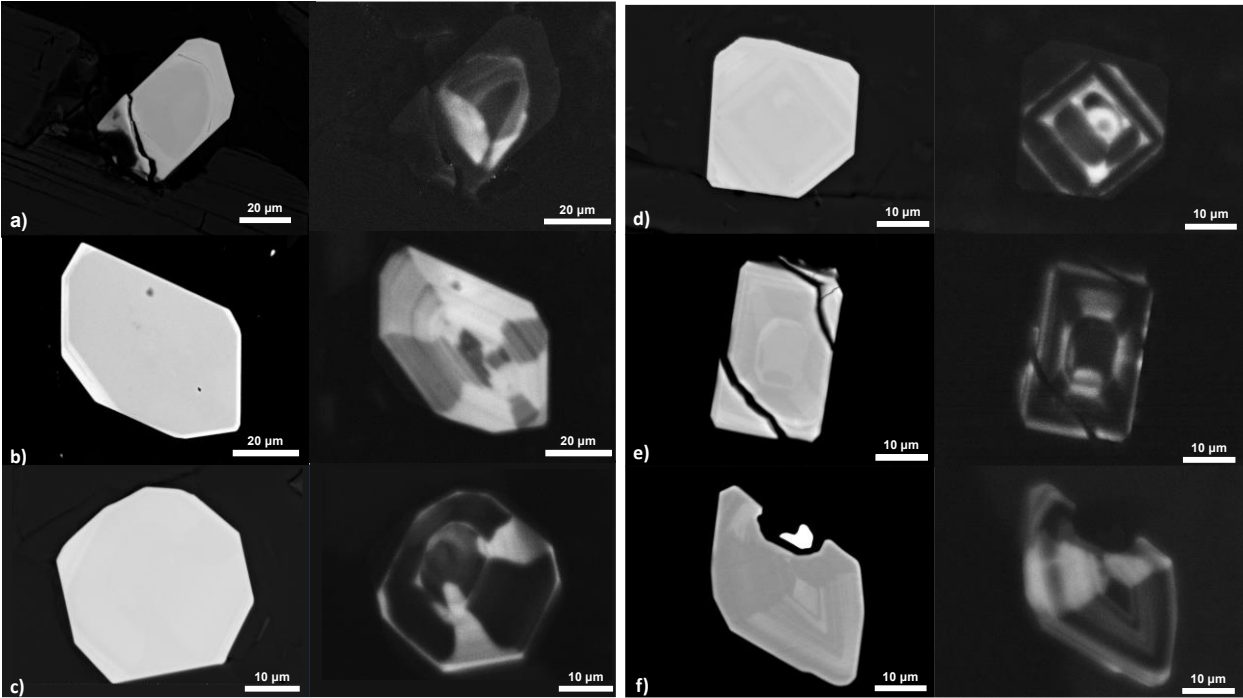
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Supplementary Figure S1. Examples of Macusani zircon textures in BSE (left) and cathodoluminescence (CL) images: a) MAC137.1_zr03, b) MAC137.1_zr04, c) MAC137.3_zr03, d) MAC137.3_zr04, e) MAC160.1_zr01, f) MAC160.1_zr03. The zircons are typically small (<50 μm), euhedral, and exhibit well-developed, concentric growth zoning, typical to igneous zircon (Corfu et al., 2003). Few crystals, e.g. S1a, contain an inherited core.
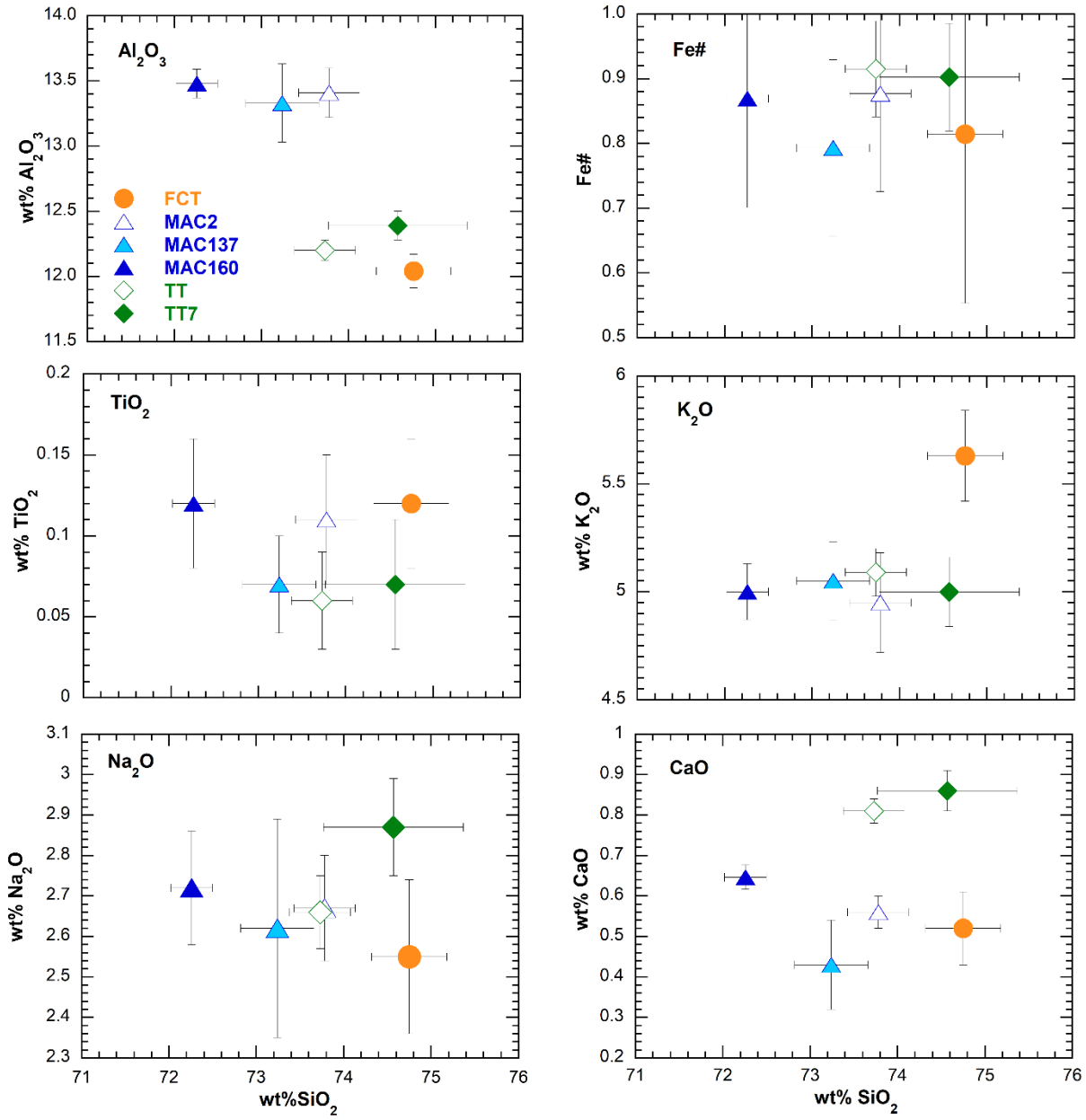
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Supplementary Figure S2. Major element composition of the glass suite.

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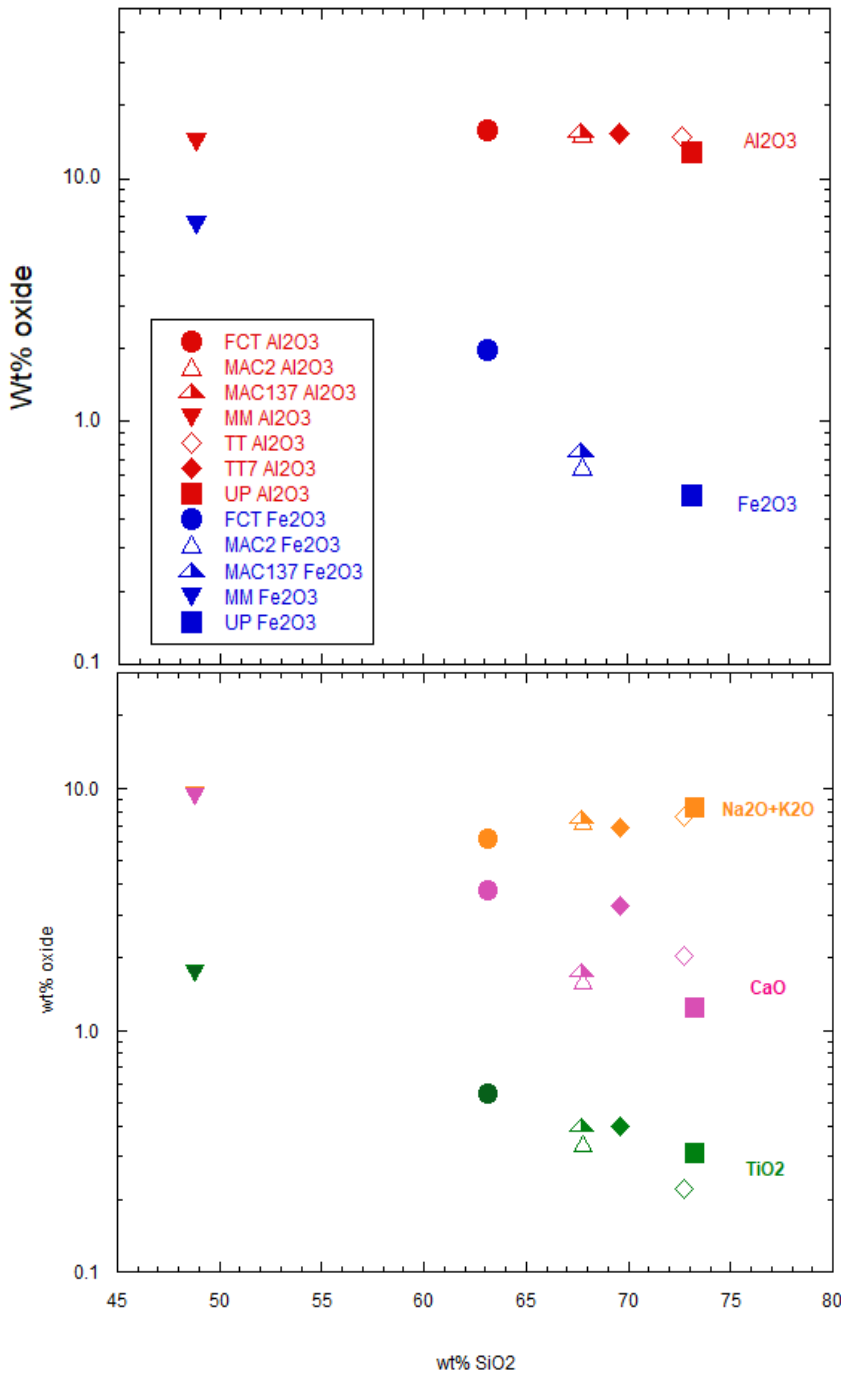
1596 **Supplementary Figure S3.** Whole rock reported major element composition: FCT from Whitney &
1597 Stormer (1985), MAC2 and M137 from Sandeman & Clark (2003), MM from Carmichael et al. (1996),
1598 TT7 from Chesner et al. (2020), UP from Emslie & Stirling (1993). Composition of the sample TT is
1599 assumed to be the same as TT5 of Chesner et al. (2020), due to the proximity of the locations of the
1600 two sampling sites.

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1602   *Apatite*

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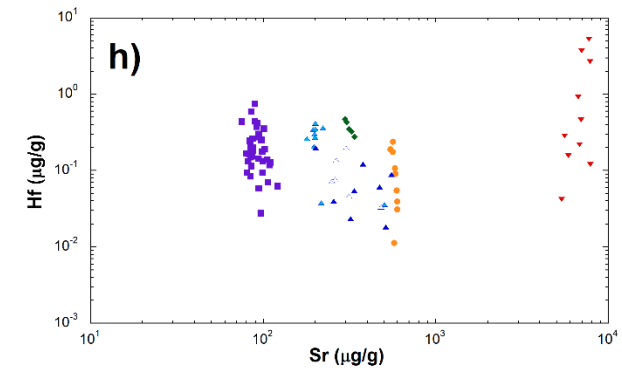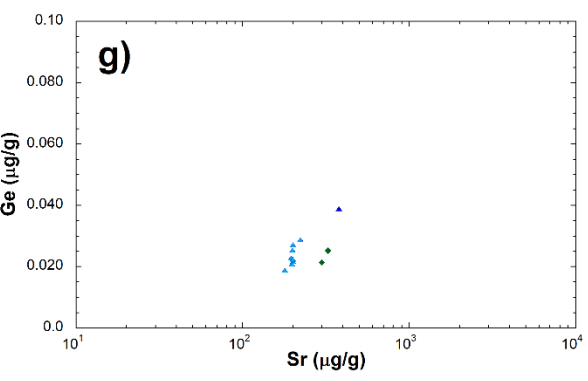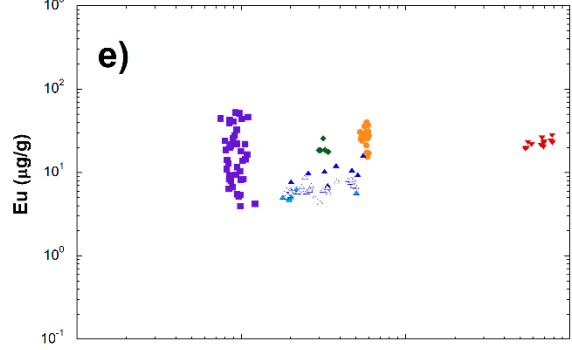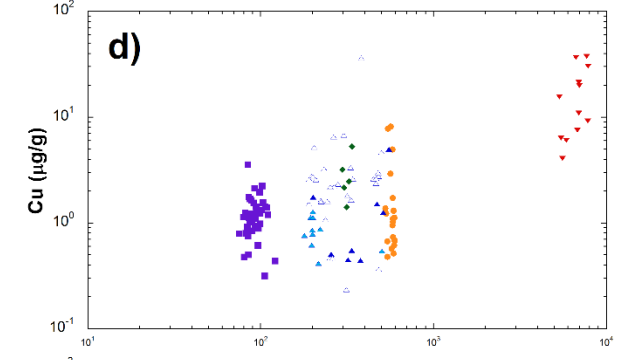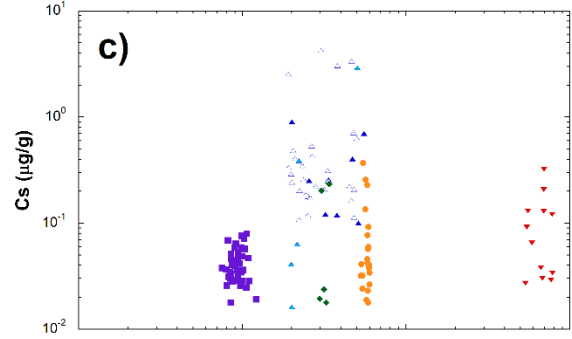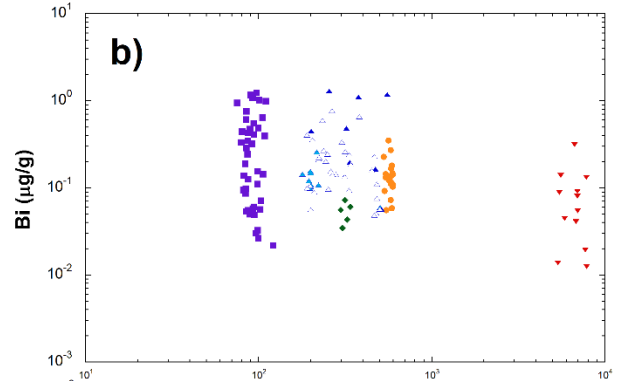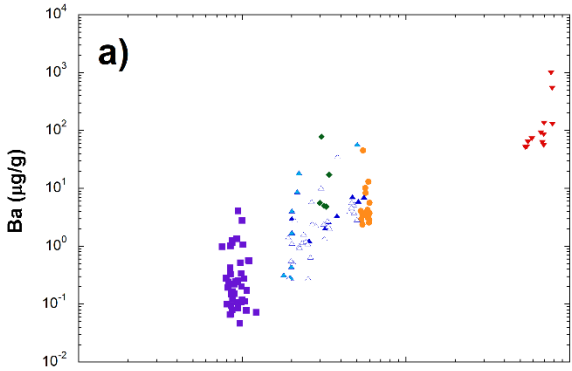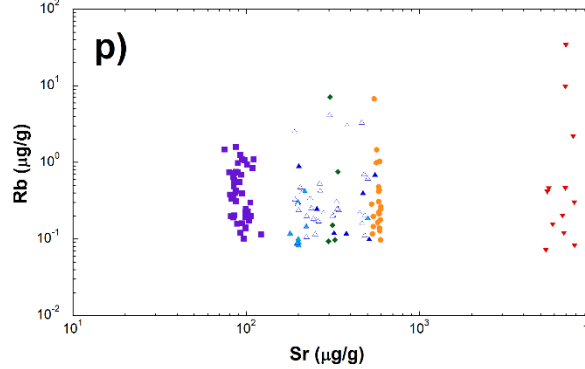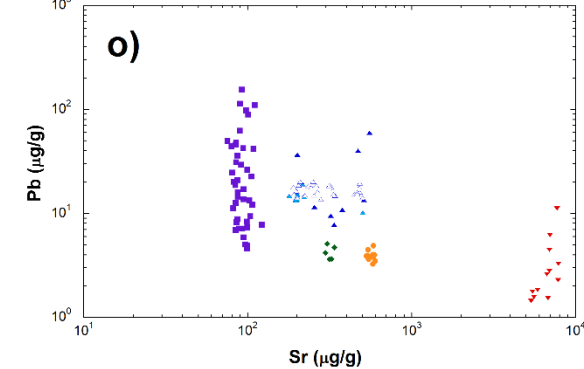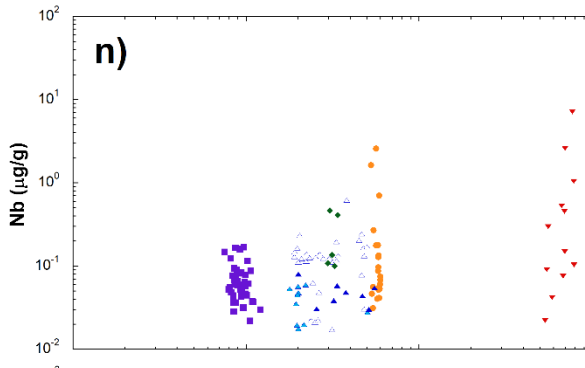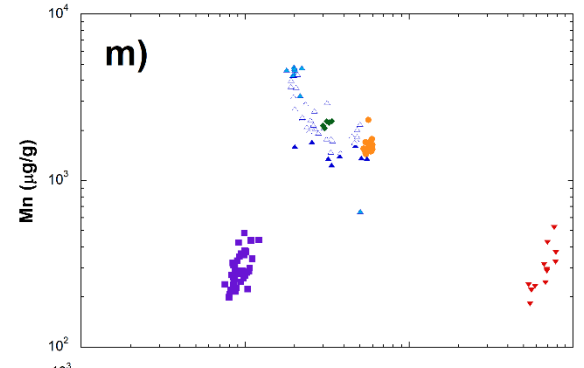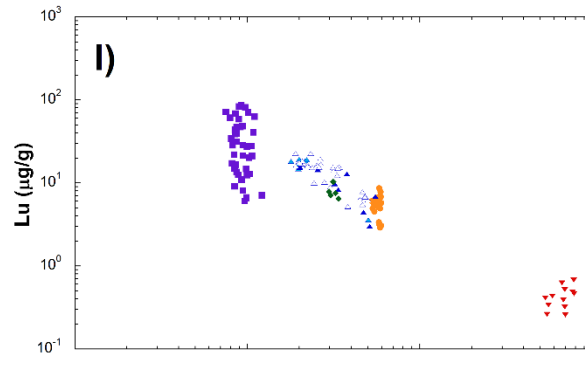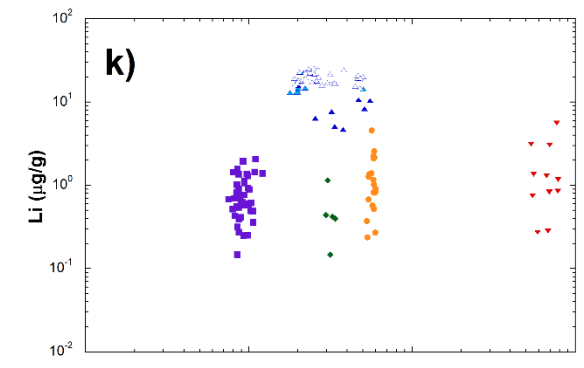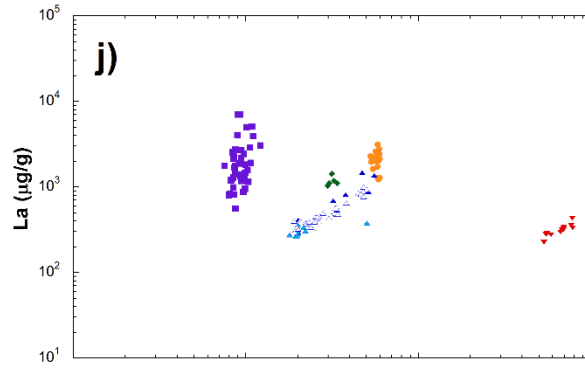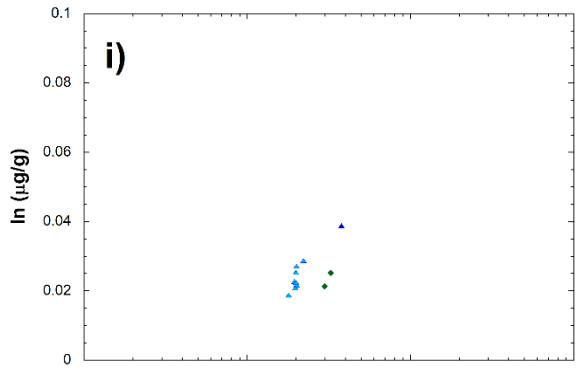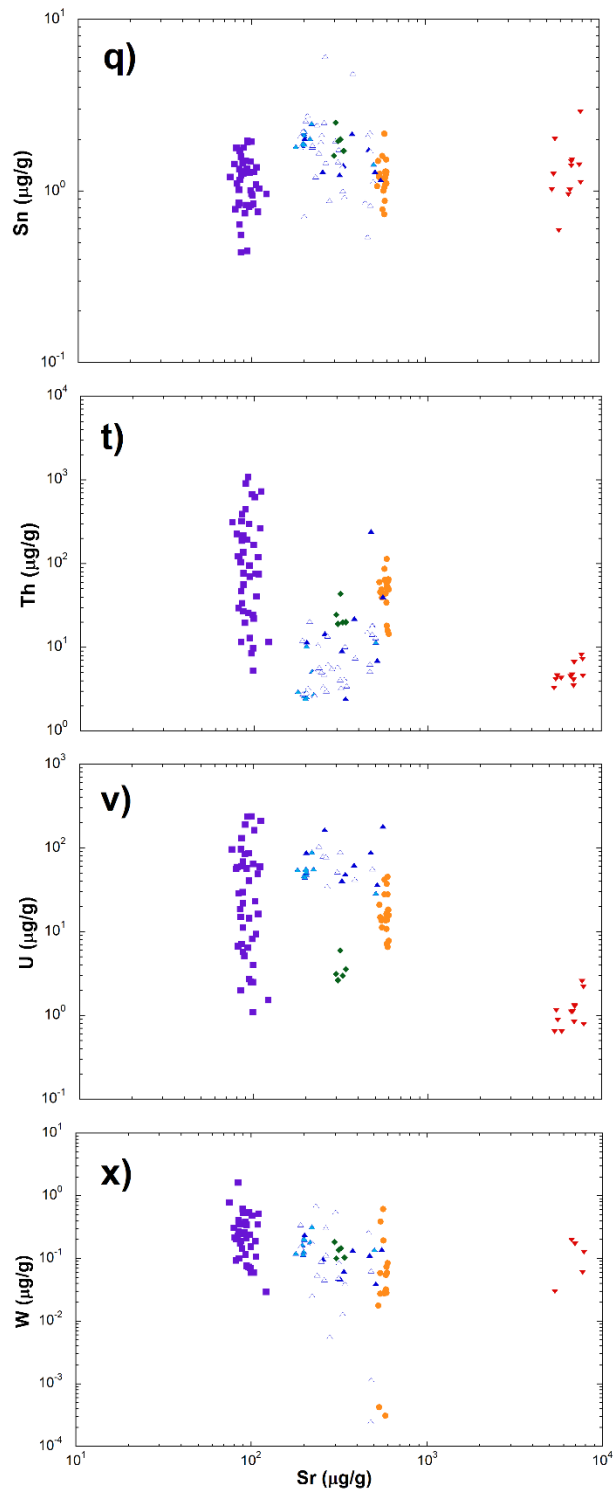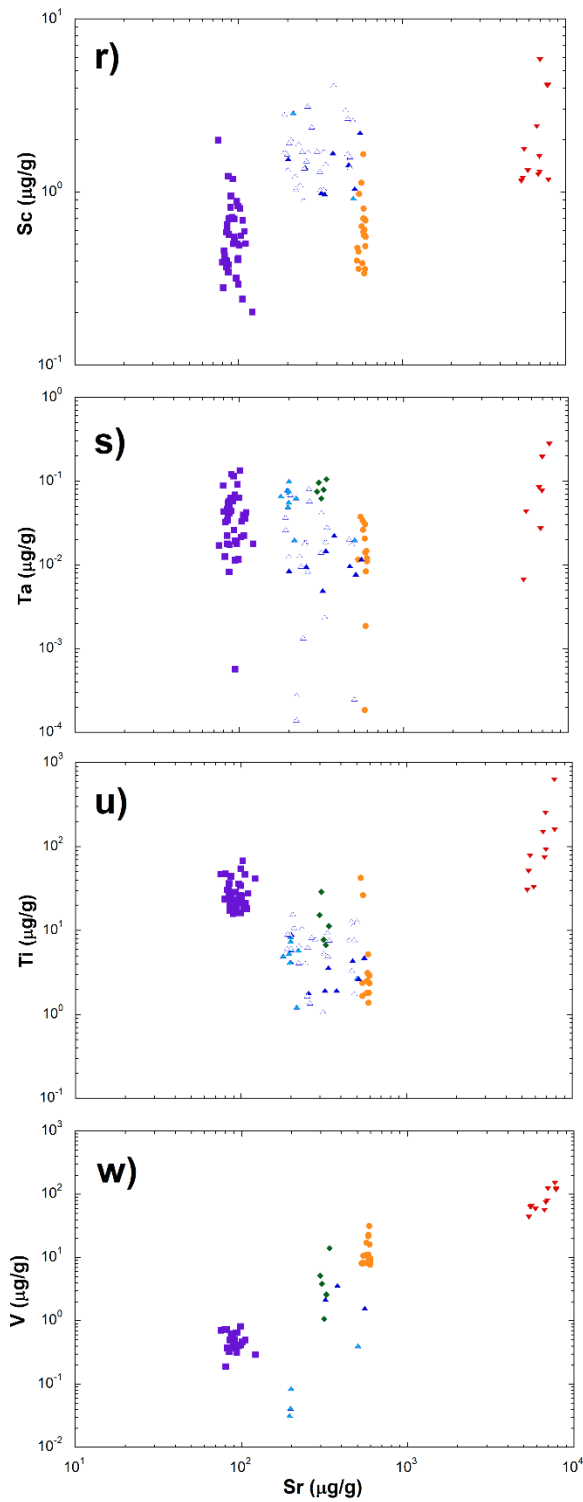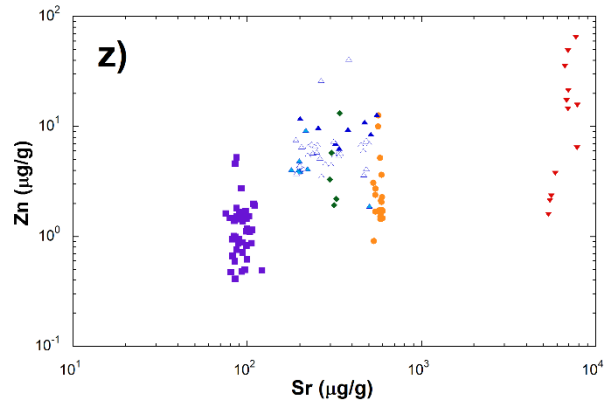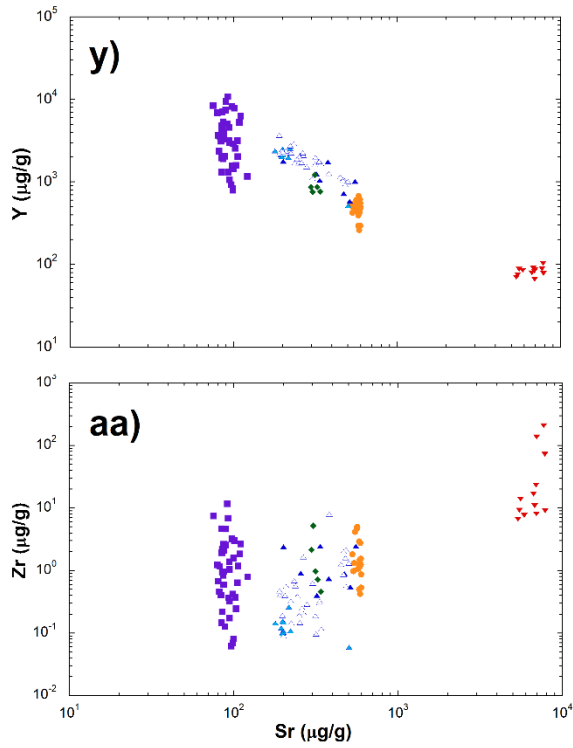
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1609   **Supplementary Figure S4.** Apatite trace element composition. Symbols from Fig. 8.

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1615   *Biotite*

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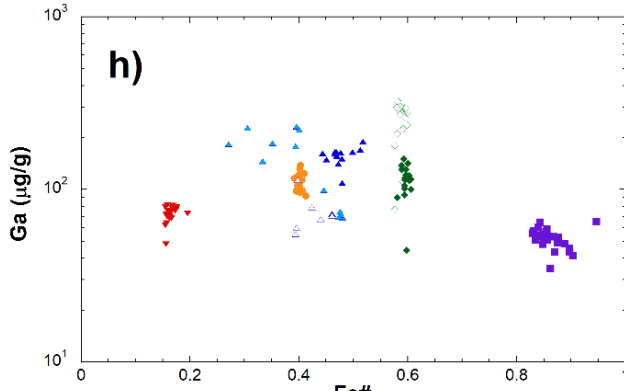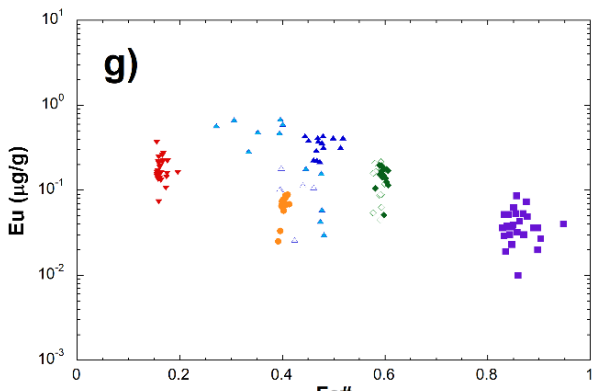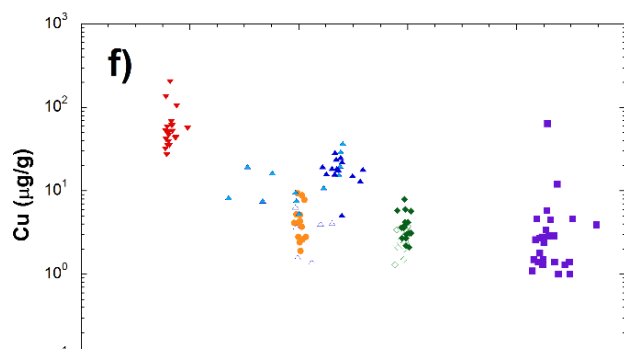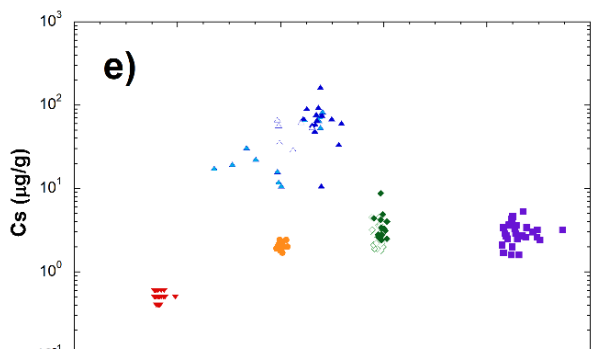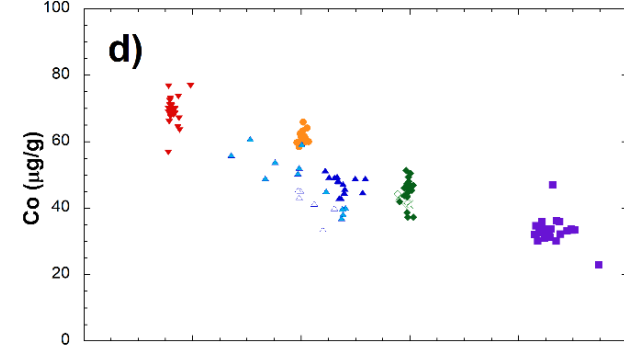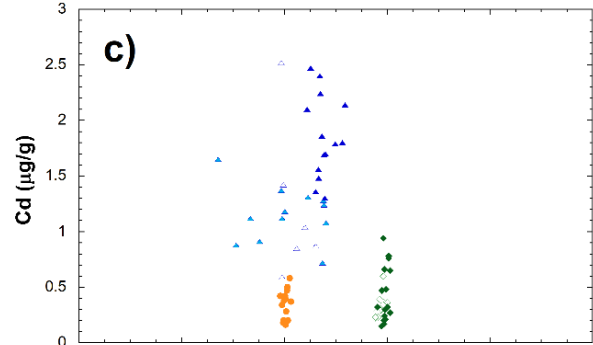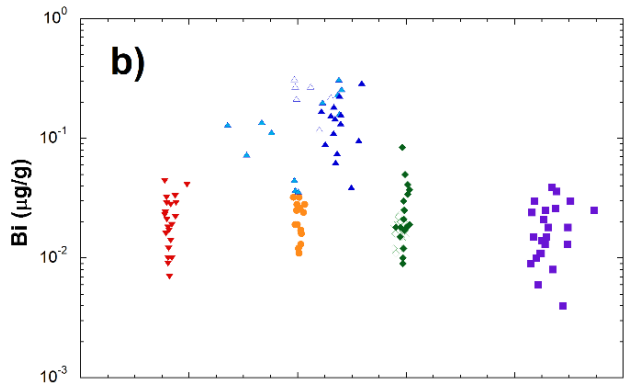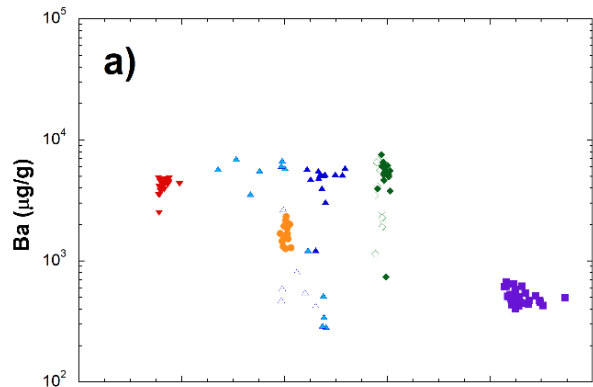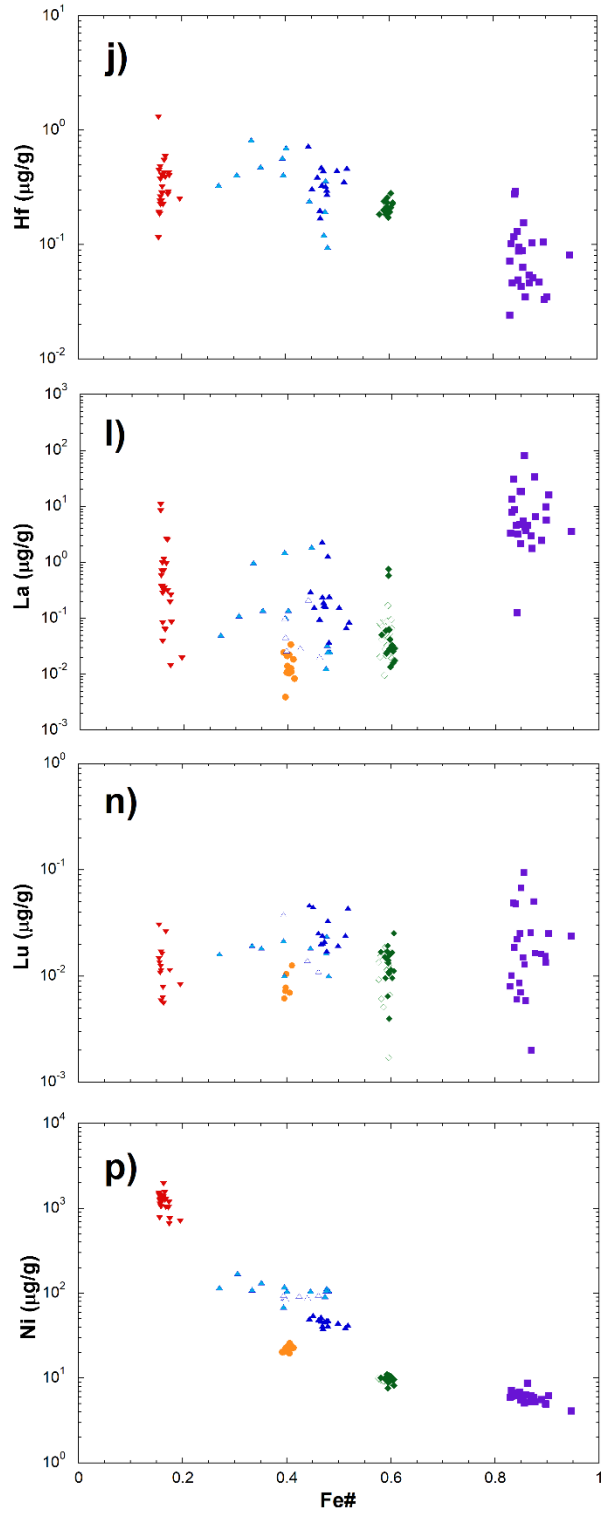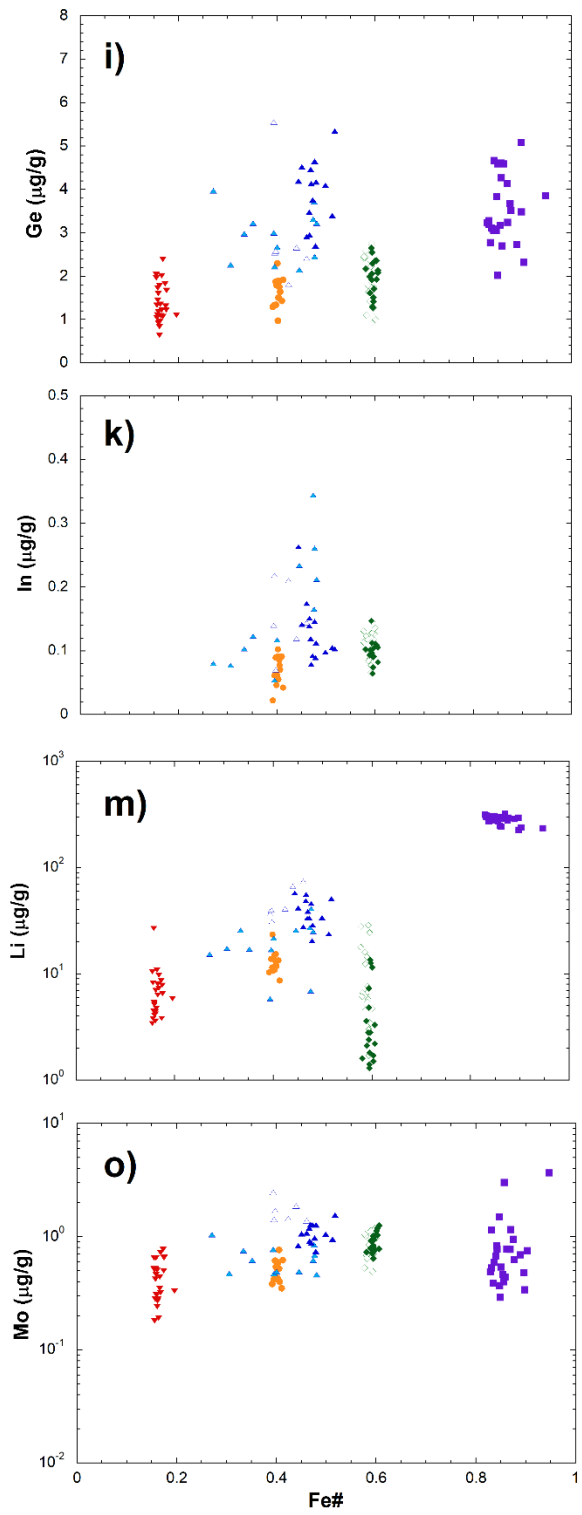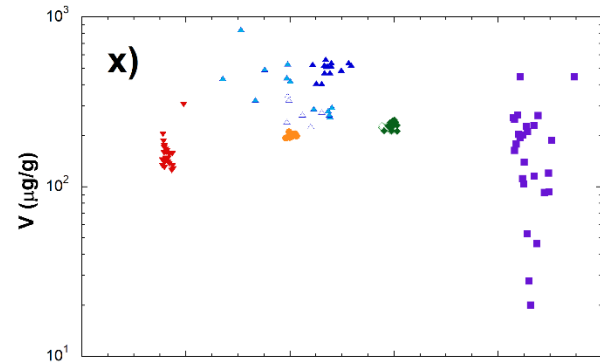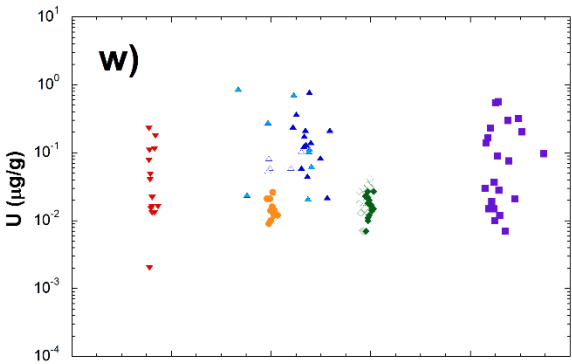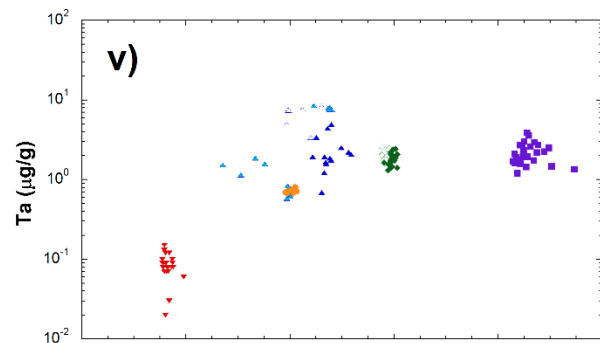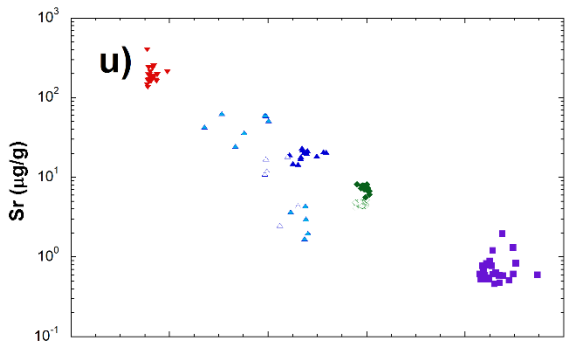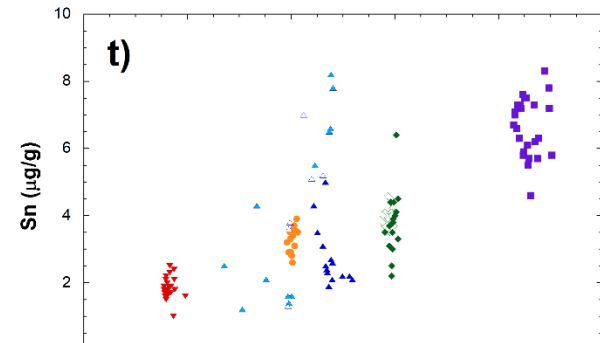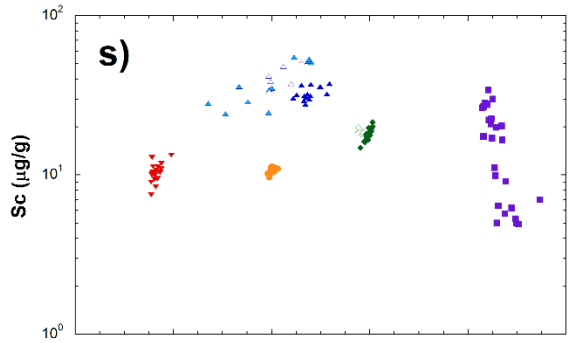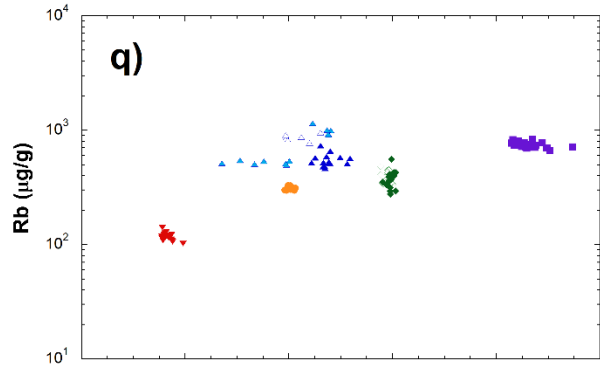
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Supplementary Figure S5. Biotite trace element composition. Symbols from Fig. 8.

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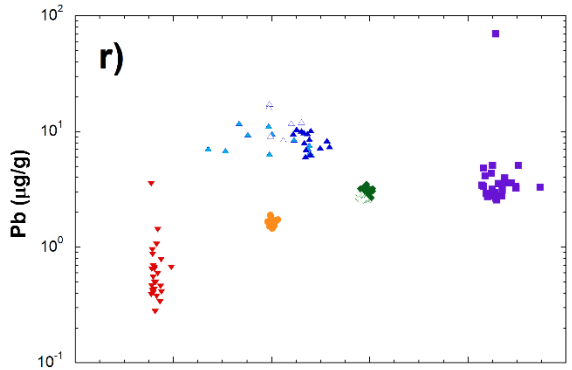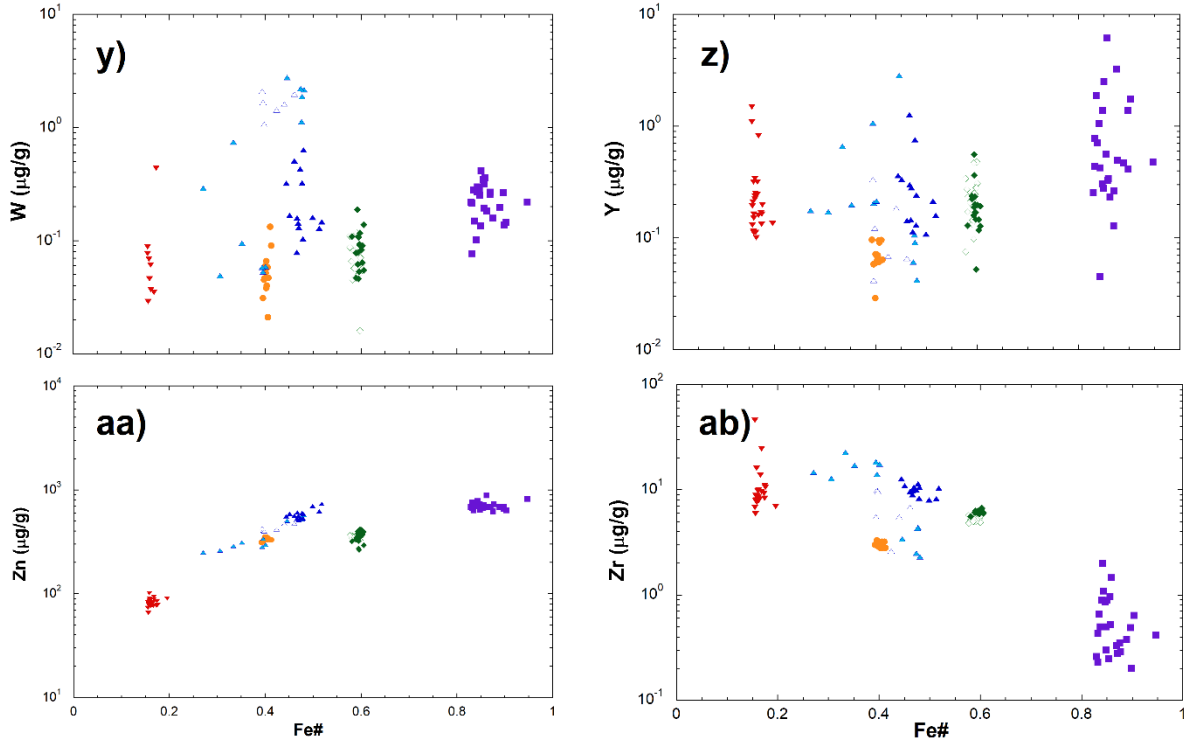
1624   *Glass*

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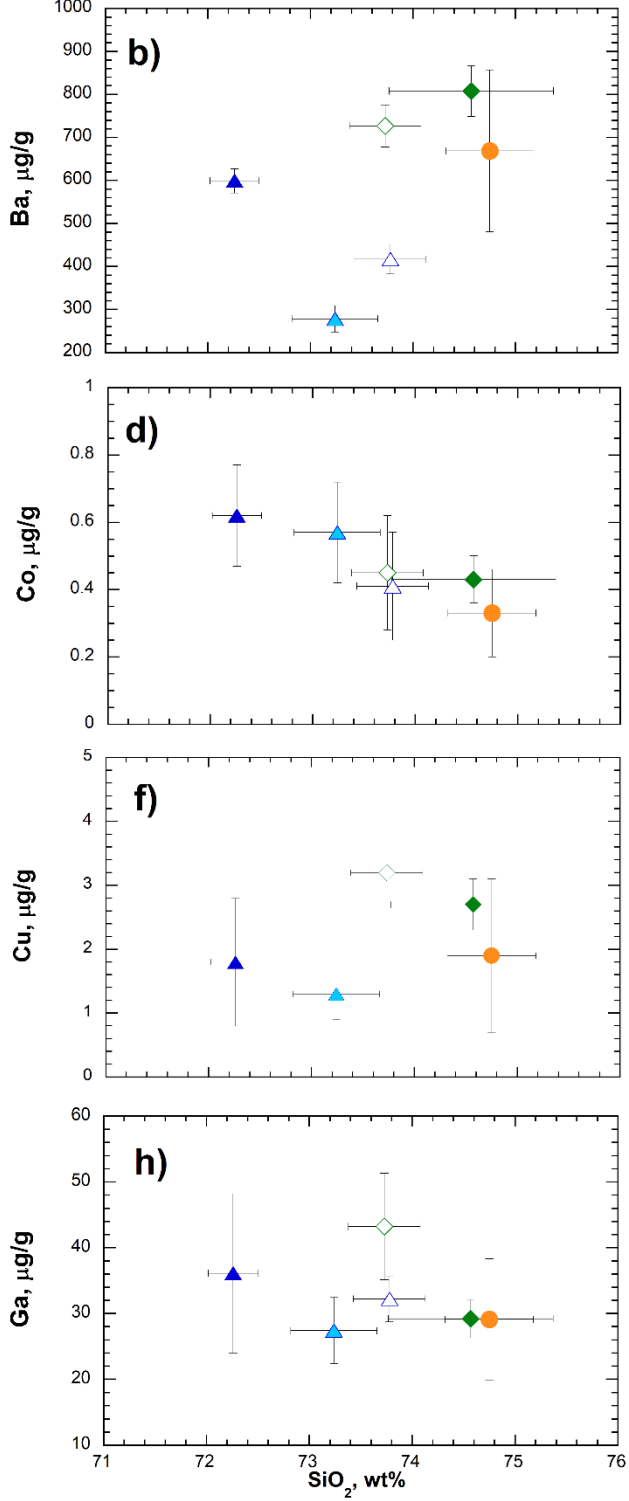
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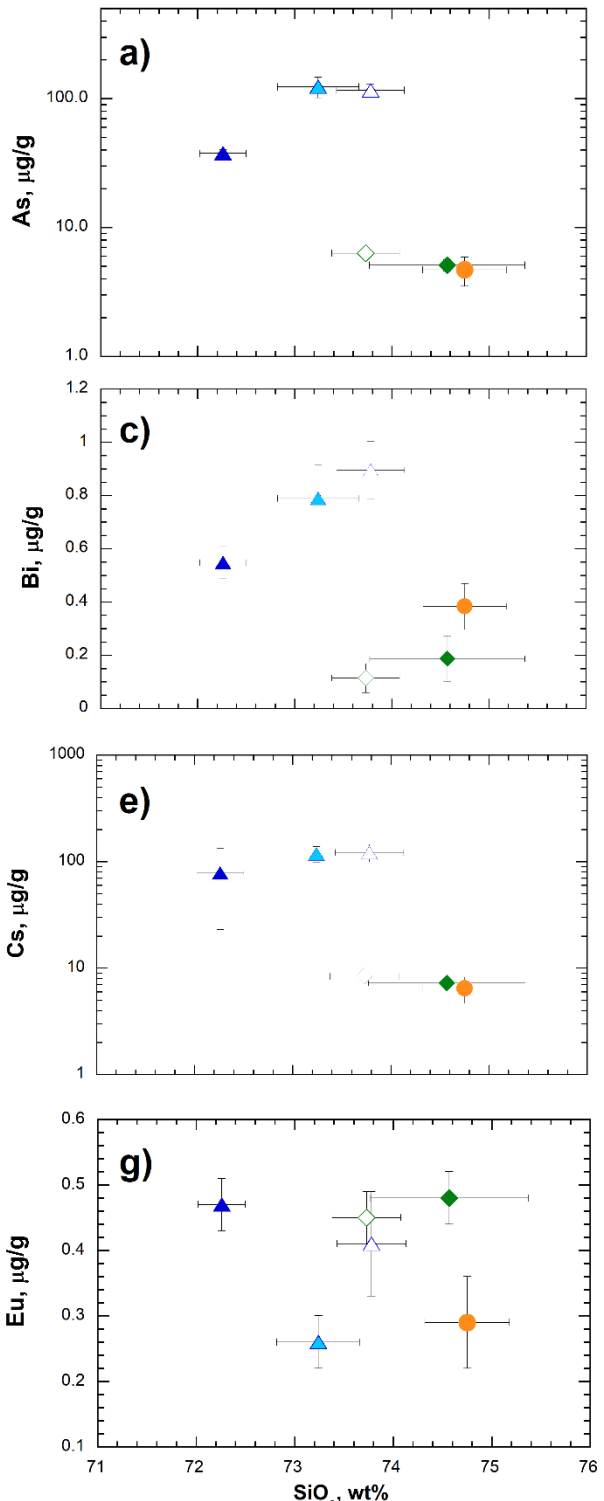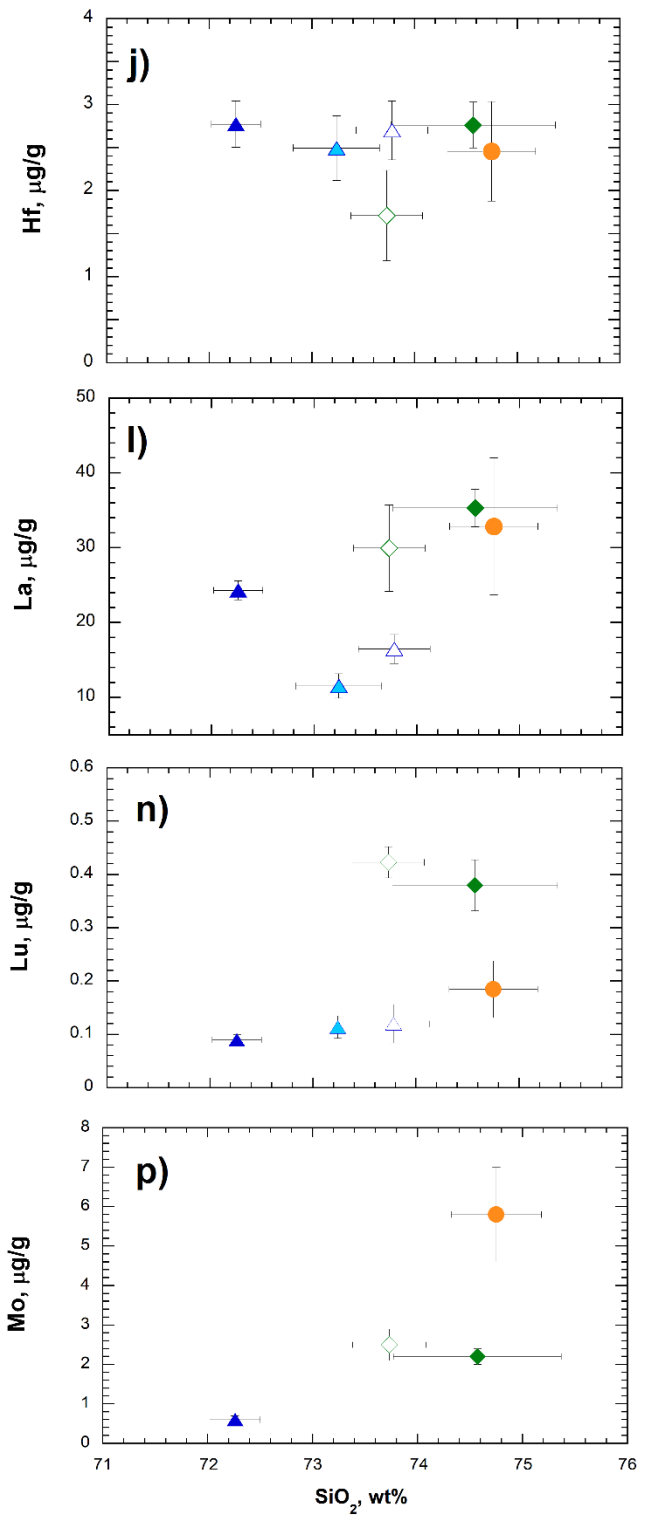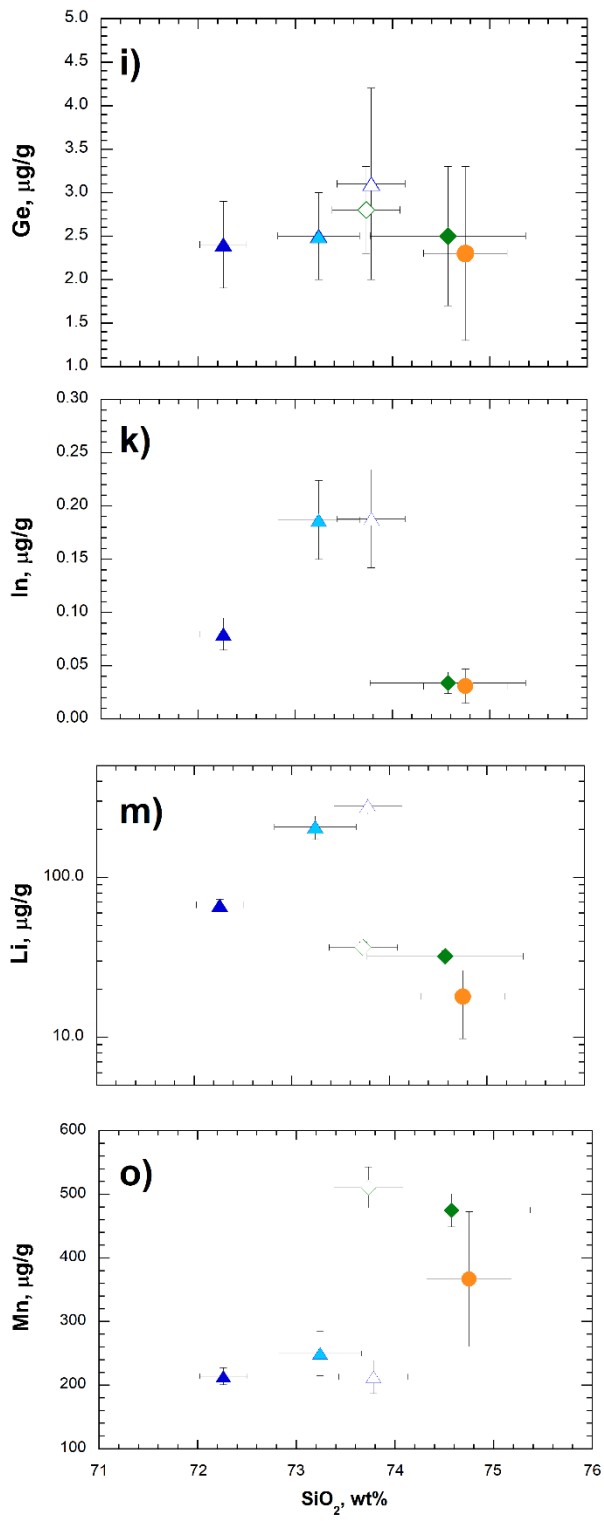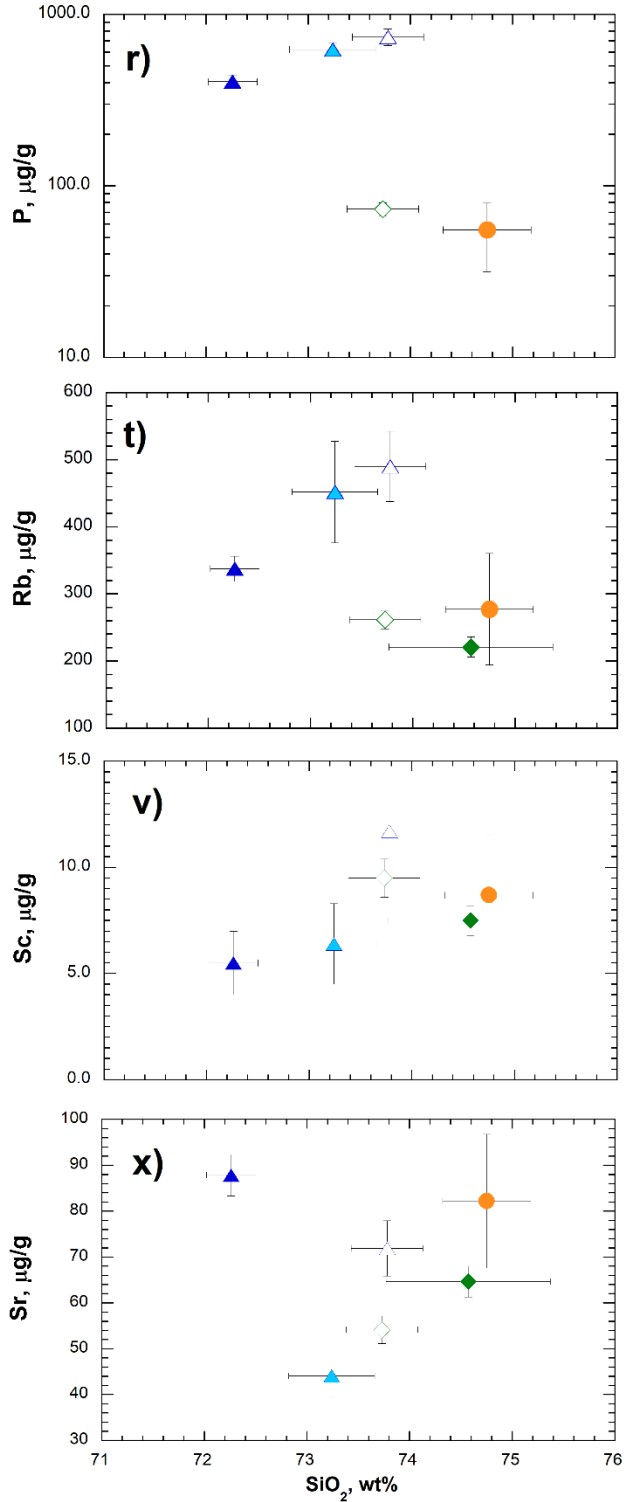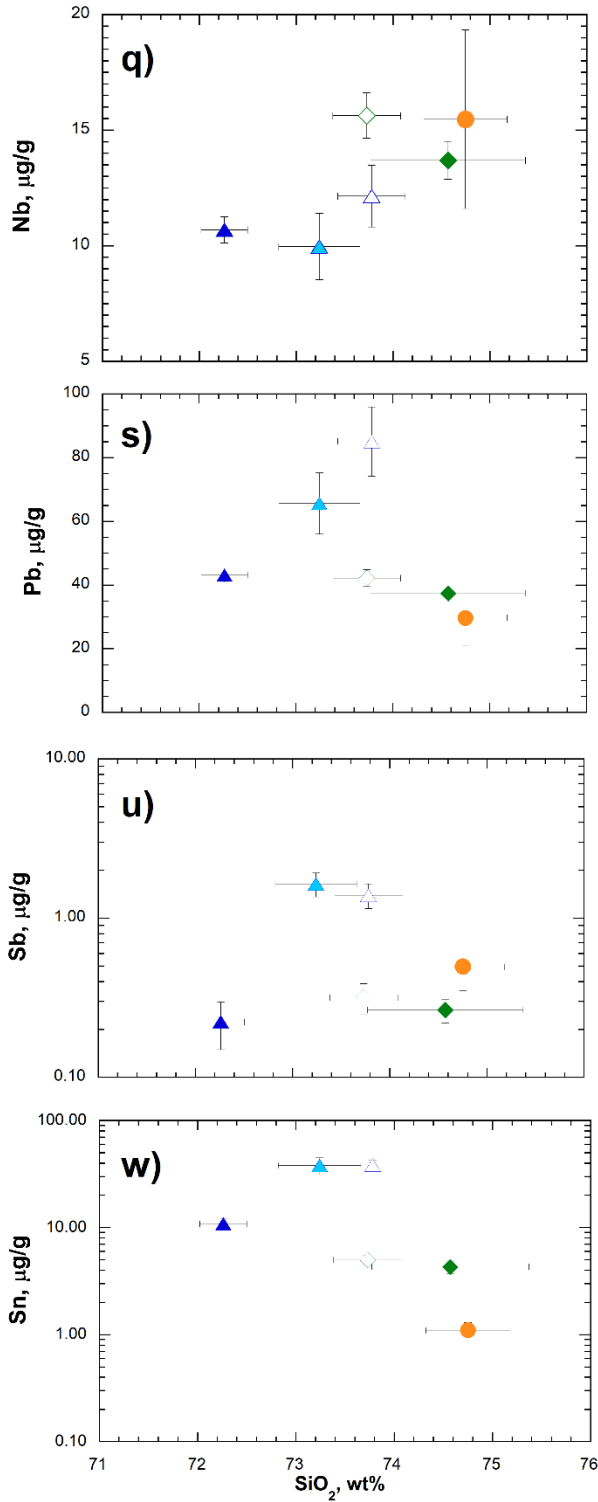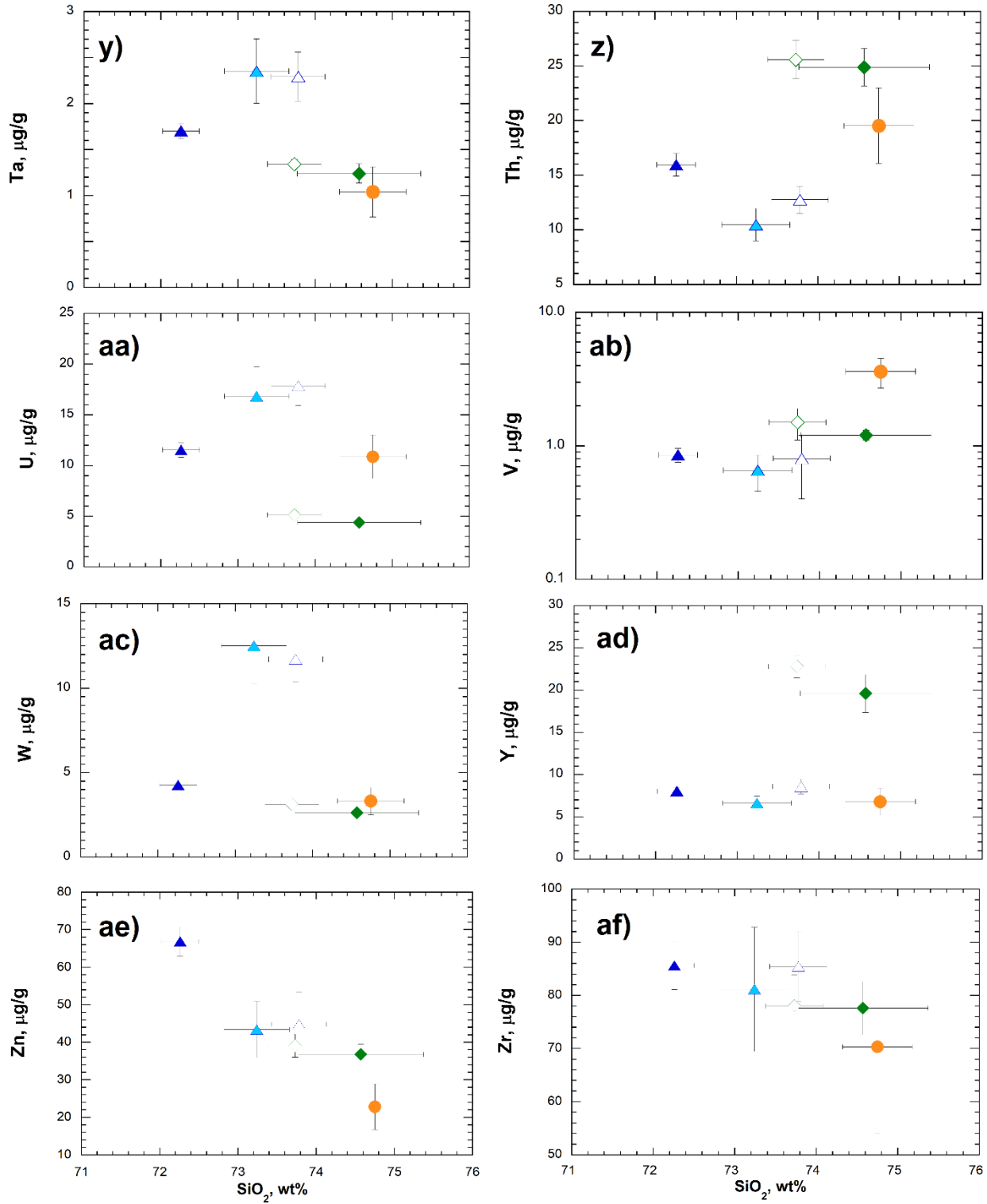
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Supplementary Figure S6. Glass trace element composition. Symbols from Fig. 8.

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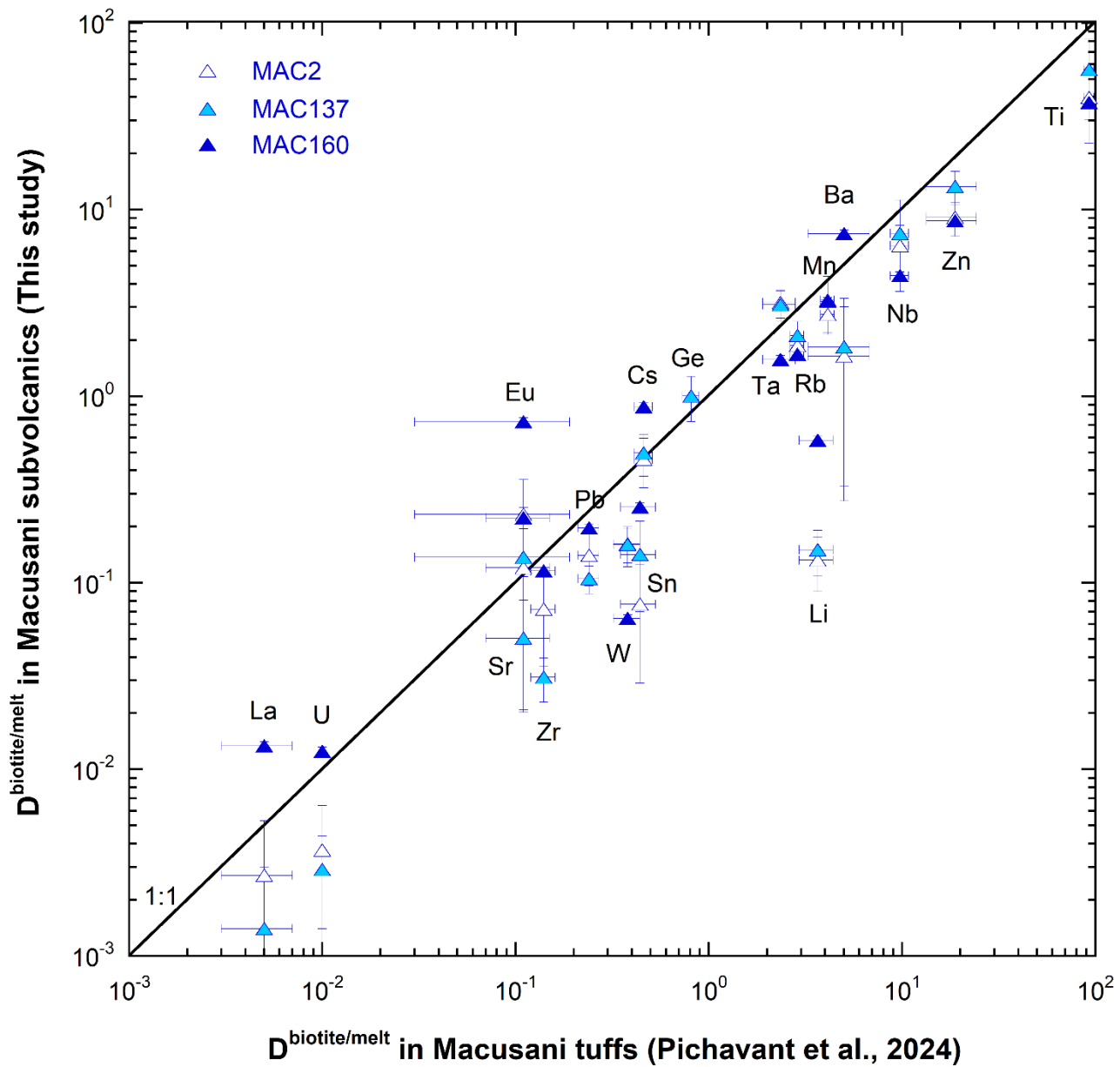
Supplementary Figure S7. Comparison of trace element D values obtained from Macusani tuffs (Pichavant et al., 2024) and subvolcanics (MAC2, MAC137, MAC160) from this study.

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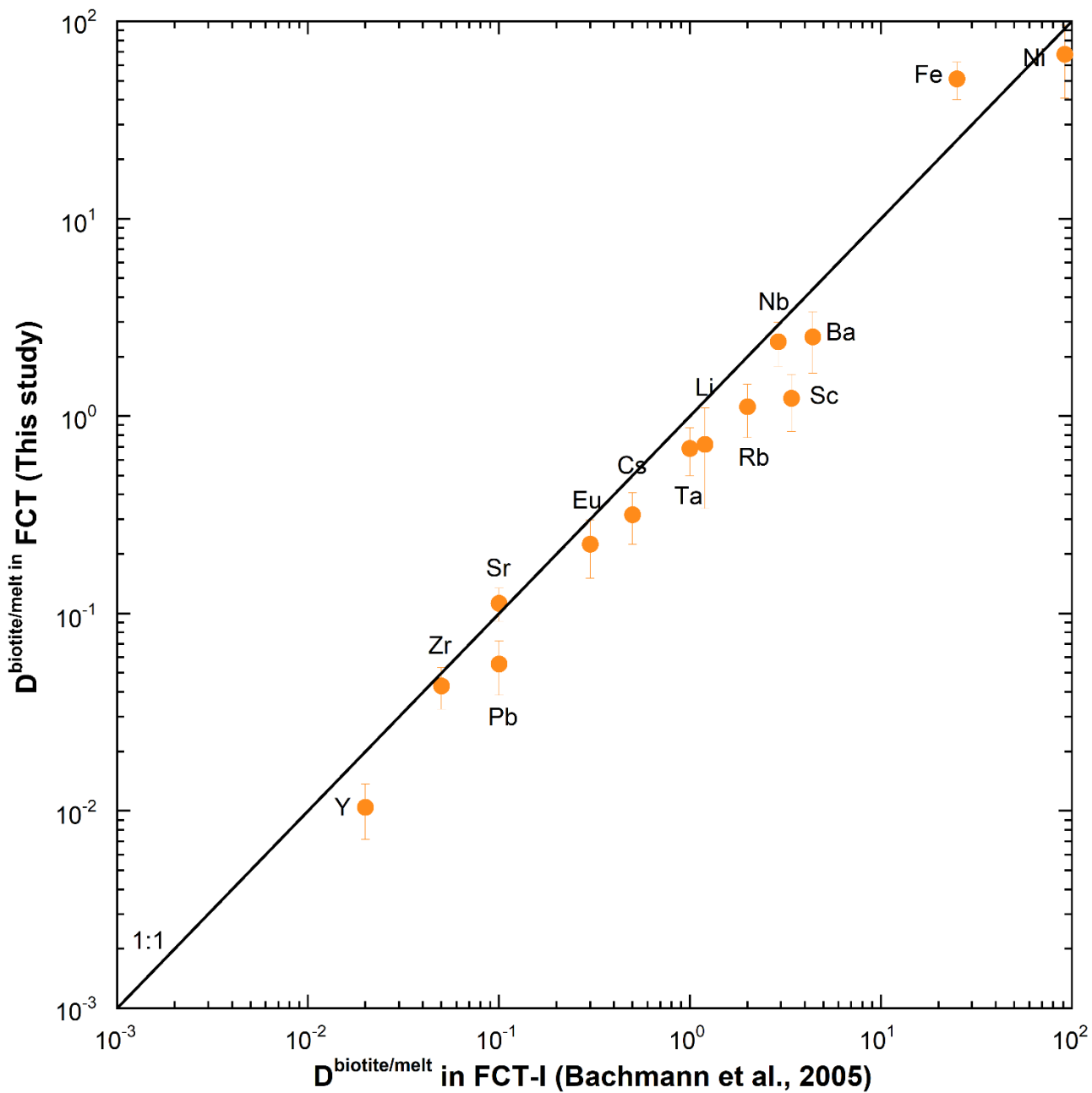
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Supplementary Figure S8. Comparison of trace element D values in the Fish Canyon tuff by
Bachmann et al. (2005) and this study.

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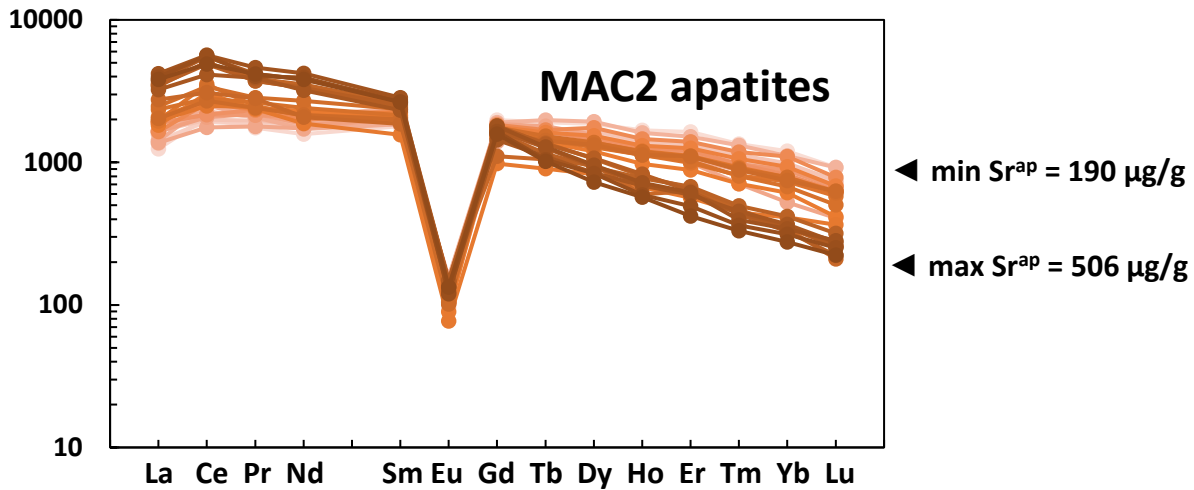
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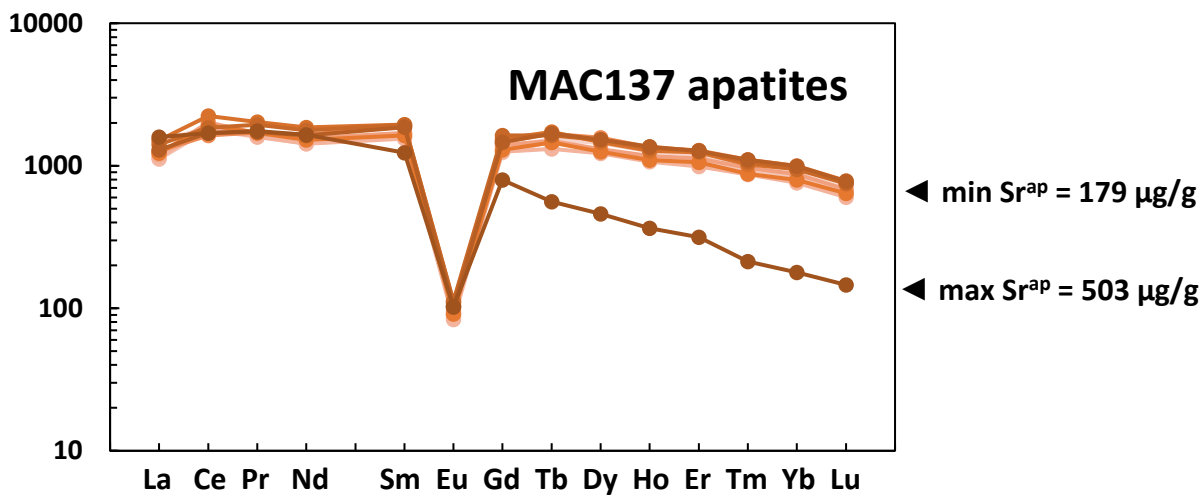
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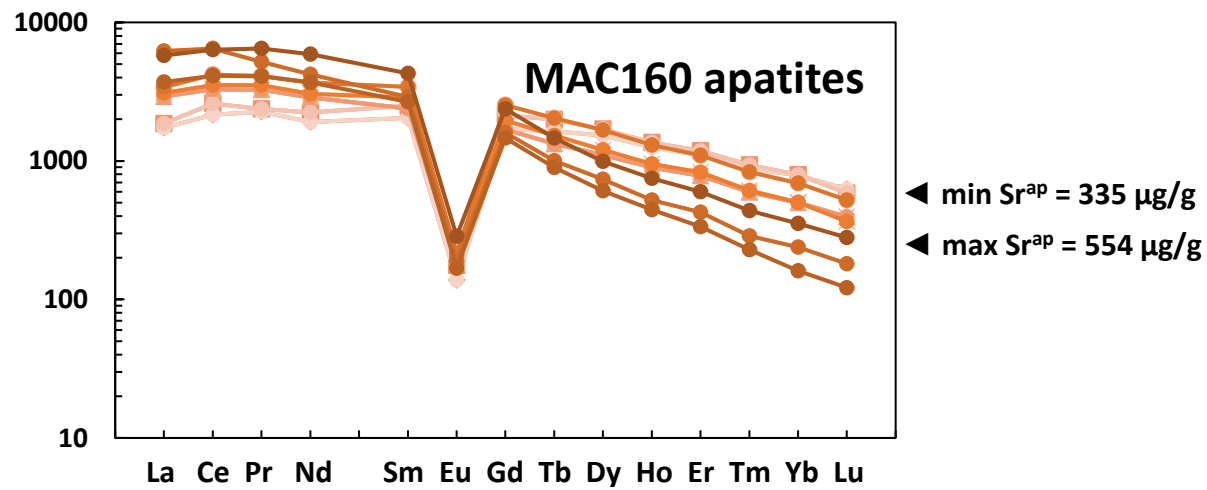
Supplementary Figure S9. Chondrite-normalized REE abundance in Macusani apatites. Tone of the graph corresponds with the apatite Sr (Sr^{ap}) content, darker colour denoting higher Sr abundance. In all samples, the La/Lu and La/Sm ratios are observed in the Sr-richer apatites.

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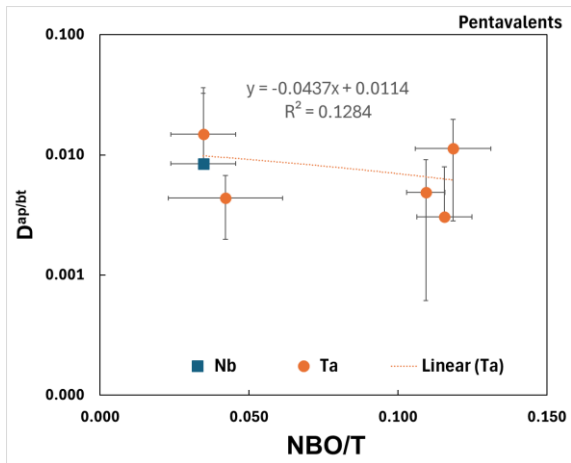
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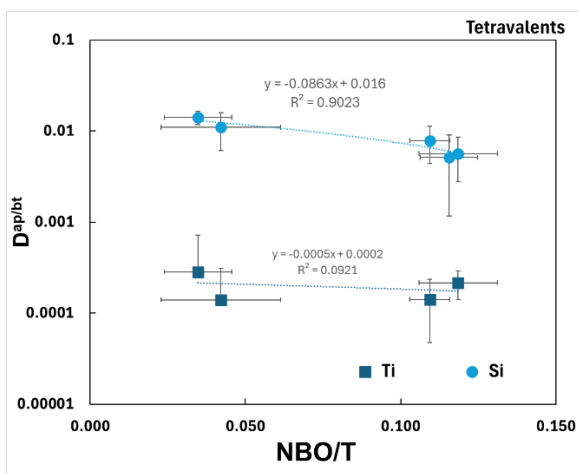
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Supplementary Figure S10. Homovalent element $D^{ap/bt}$ as a function of melt polymerization
(NBO/T).

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1656   **Supplementary Table S1.**

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1659 **Supplementary Table S2.** Results of the least square fits.

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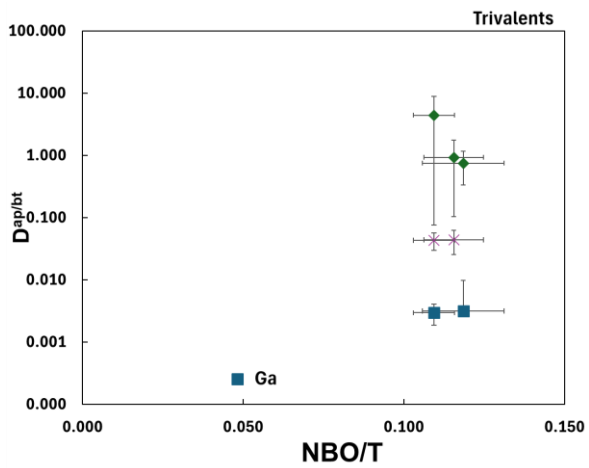| Mineral	Valence	Coord.	Sample	D_0	1 σ	r_0, nm	1 σ	E, MPa	1 σ	R^2	χ^2
Apatite	+1	VIII-	MAC2	**0.050**	-	**0.115**	-	**22**	-	0.988	0.0000
			MAC160	**0.044**	-	**0.120**	-	**30**	-	1.000	0.0000
			TT7	**0.024**	-	**0.120**	-	**30**	-	0.999	0.0000
	+2	VIII-	FCT	**102.7**	0.859	**0.112**	0.000	**289**	11	1.000	3.5
			MAC2	**95.6**	2.832	**0.111**	0.001	**250**	22	0.996	32.6
			MAC137	**128.8**	3.291	**0.113**	0.001	**303**	26	0.999	8.8
			MAC160	**82.7**	1.174	**0.111**	0.000	**251**	12	0.999	6.2
			TT7	**63.5**	0.562	**0.112**	0.000	**253**	9	1.000	1.6
	+3	VIII-	FCT	**121.7**	5.660	**0.108**	0.000	**270**	34	0.912	881.6
			MAC2	**158.9**	7.266	**0.106**	0.000	**311**	39	0.904	1517.0
			MAC137	**107.0**	5.839	**0.106**	0.000	**349**	49	0.886	945.9
			MAC160	**176.5**	6.901	**0.106**	0.000	**282**	31	0.920	1416.5
			TT7	**103.0**	5.261	**0.107**	0.000	**318**	40	0.910	706.9
	+4	VIII-	FCT	**2.726**	-	**0.107**	-	**225**	-	1.000	0.0001
			MAC2	**1.001**	-	**0.106**	-	**213**	-	1.000	0.0000
			MAC137	**1.199**	-	**0.109**	-	**162**	-	0.999	0.0010
			MAC160	**6.551**	-	**0.108**	-	**276**	-	1.000	0.0001
			TT7	**1.624**	-	**0.108**	-	**185**	-	1.000	0.0007
Biotite	+1	XII-	FCT	**1.607**	0.220	**0.164**	0.003	**55**	21	0.967	0.0506
			MAC2	**1.931**	0.042	**0.168**	0.001	**48**	4	0.999	0.0029
			MAC137	**2.117**	0.092	**0.170**	0.001	**55**	9	0.996	0.0116
			MAC160	**1.827**	0.154	**0.170**	0.002	**31**	8	0.977	0.0396
			TT7	**1.581**	-	**0.167**	-	**44**	-	1.000	0.0000
			TT7	**1.838**	0.049	**0.168**	0.001	**41**	4	0.998	0.0040
	+2	VI-	FCT	**447.3**	61.900	**0.068**	0.001	**738**	162	1.000	21.5
			MAC2	**441.0**	342.170	**0.068**	0.005	**1017**	879	0.998	78.8
			MAC137	**211.0**	166.090	**0.065**	0.007	**479**	370	0.998	15.7
			MAC160	**298.1**	236.350	**0.066**	0.006	**694**	557	0.998	32.7
			TT7	**165.3**	19.948	**0.070**	0.001	**1008**	349	0.998	21.8
			TT	**192.7**	18.529	**0.070**	0.001	**1151**	329	0.999	19.5
	+3	IV-	FCT	**5.384**	-	**0.053**	-	**463**	-	1.000	0.0000
			TT7	**5.753**	-	**0.054**	-	**421**	-	1.000	0.0000
	+3	VI-	FCT	**2.752**	32.080	**0.066**	0.090	**378**	2369	1.000	0.0001
			MAC2	**5.337**	0.136	**0.070**	0.000	**599**	21	0.999	0.0067
			MAC137	**10.425**	0.081	**0.071**	0.000	**675**	7	1.000	0.0020
			MAC160	**12.962**	0.099	**0.072**	0.000	**489**	8	1.000	0.0034
			TT	**4.122**	23.120	**0.067**	0.043	**397**	1238	1.000	0.0001
			TT7	**4.635**	23.256	**0.067**	0.039	**421**	1239	1.000	0.0001
	+4	IV-	FCT	**0.757**	-	**0.037**	-	**256**	-	1.000	0.0000
			MAC137	**1.003**	0.006	**0.038**	0.000	**336**	7	1.000	0.0000
			MAC160	**0.755**	-	**0.039**	-	**196**	-	0.998	0.0001
			TT	**0.688**	-	**0.037**	-	**209**	-	1.000	0.0000
			TT7	**0.771**	0.016	**0.038**	0.000	**244**	13	0.999	0.0003

1661

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1662 **Supplementary Material 1 - Sample descriptions**

1663   **Macusani subvolcanic suite, Puno, SE Peru**

1664   *General geology*

1665   The strongly peraluminous (ACNK>1.1) Macusani subvolcanics, stratigraphically assigned to

1666 the Crucero intrusive supersuite, are exposed in the Picotani, Quenamari, and Cayconi mesetas

1667 (plateaus) of the Central Andean Inner Arc of southeastern Peru. Crucero supersuite is comprised of

1668 two temporally and geochemically distinct assemblages – Picotani and Quenamari groups. Picotani

1669 intrusive suite (24.5-23.2 Ma) consists of monzogranitic hypabyssal rock bodies, temporally

1670 associated with a bimodal volcanic sequence of the Picotani group (Sandeman et al., 1997). Two

1671 bodies containing vitreous matrix – Revancha dyke and Cerro Esquinani stock – are analyzed in this

1672 study.

1673   Revancha dike is a ≤5 m wide and >400 m long cordierite-, biotite-bearing monzogranite

1674 body, located in the south of the Quenamari plateau, in the vicinity of the significantly larger (>20

1675 km^2) Ninahuisa stock. The bulk composition of the Revancha dike is rhyodacitic (67-68 wt.% SiO_2, 4-5

1676 wt.% K_2O, 3 wt.% Na_2O) and peraluminous (A/CNK = 1.1-1.2). It intrudes a country rock of similar

1677 mineral and chemical composition (Sandeman et al., 1997). The dike is interpreted as a pristine,

1678 hypabyssal analogue of the S-type monzogranites found in the Lachlan Fold belt of SE Australia

1679 (Sandeman & Clark, 2003). Dike emplacement temperatures are in the range of 634-693°C estimated

1680 from two-feldspar thermometry (Fuhrman & Lindsley, 1988). The oxidation state of the Revancha

1681 magma is considered to be low due to the occurrence of near-stoichiometric $FeTiO_3$ compositions of

1682 unaltered ilmenite (Sandeman & Clark, 2003). This is supported by Ce-in-zircon oxybarometry (Smythe

1683 & Brenan, 2016) measured for the samples from this study which yielded a ΔFMQ of -2.9 (± 1).

1684   The age of the Revancha dike has been determined using biotite $^{40}Ar/^{39}Ar$ spectra, yielding

1685 integrated ages of 24.07±0.09 Ma (Sandeman et al., 1997) and 24.18±0.72 Ma (Clark et al., 1990).

1686   The samples of the Revancha dyke (MAC2 and MAC137) were obtained from the collection

1687 of Dr. Hamish Sandeman (Newfoundland Geological Survey) and have been previously analyzed by

1688 .Sandeman et al. (1997) and Sandeman & Clark (2003).

1689   Cerro Esquinani stock is exposed in ca. 1.2 km^2 area near the southern edge of the Picotani

1690   Meseta. It consists of vitreous biotite monzogranite, which intruded biotite-bearing rhyodacitic tuff

1691   of the Cerro Huancahuancane formation. Compared to the Revancha dyke, the stock is similarly

1692   peraluminous (A/CNK=1.1-1.3), more potassic (5-8 wt.%) and less sodic (1.6-2.9 wt.%) (Sandeman et

1693   al., 1997). Biotite of the stock yield a total fusion date of 24.84±0.06 Ma, which overlaps with the

1694   recorded dates of the Cerro Huancahuancane rhyodacite flow, which suggests a genetic link

1695   between the two formations (Sandeman et al., 1997). Temperature, pressure, and fO_2 for this

1696   intrusive body have not been previously established.

1697   The sample of Cerro Esquinani stock (MAC160) was received from Dr. John Hanchar

1698   ((Memorial University of Newfoundland). It has been previously analyzed by Sandeman et al. (1997).

1699   *Sample descriptions*

1700   *Revancha dyke (MAC2 and MAC137)*

1701   Revancha monzogranite contains phenocrysts of plagioclase, sanidine, biotite, and cordierite

1702   with accessory sillimanite, apatite, zircon, monazite, and ilmenite set in a holohyaline matrix. The

1703   dike exhibits a glass rich (up to 74 vol%) margin and a crystal-rich (up to 50 vol%) porphyritic

1704   interior, separated by a flow-banded facies with an intermediate glass content (63-68 vol%). The

1705   dike does not contain any macroscopic evidence of weathering or hydrothermal alteration

1706   (Sandeman & Clark, 2003). Sample MAC137 (Figure X) is a biotite microphenocryst-rich sample of the

1707   glassy, flow-banded Revancha dike facies. Older, larger biotite phenocrysts exhibit both resorption

1708   features and sieved textures. Darker rims of the larger phenocrysts represent reverse zoning with

1709   progressive enrichment in Mg towards the crystal edges. Iron numbers (Fe#) of the analyses bt02

1710   (rim) and bt03 (interior, Figure 4a) are 0.48 and 0.51 respectively. In contrast, microphenocrysts are

1711   euhedral with no observable zoning. MAC2 (Figure X) is a sample of the crystal-poor facies of the

1712   Revancha dike glassy chill margin. Similarly to MAC137, the larger biotite phenocrysts exhibit

1713   reverse and oscillatory zoning and sieve texture. Biotite microphenocrysts are euhedral with no

1714   observable zoning.

1715   *Cerro Esquinani stock (MAC160)*

1716   Cerro Esquinani monzogranite contains predominantly plagioclase and biotite together with

1717   rare sanidine and quartz phenocrysts and trace amounts of sillimanite, zircon, apatite, monazite,

1718   ilmenite in a vitreous matrix (Sandeman et al., 1997). In the MAC160 handsample, compared to the

1719   Revancha dyke samples, flow banding and bent biotite flakes are rare. Large and medium-sized

1720   biotite crystals (>200 µm) exhibit resorption features, which are more present than in Revancha

1721   dyke, apart from the resorption features, the crystals are euhedral. MAC160 contains very few fine

1722   biotite flakes (<100 µm) are significantly less abundant. Biotite zoning is present only in the largest

1723   crystals, which are normally zoned. Apatite in MAC160 is less abundant and smaller in size than in

1724   Revancha samples. Most of apatite crystals are euhedral, few crystals are rounded presumably by

1725   dissolution. The matrix glass is scattered with <5 µm Fe-Ti oxide microlites, which are not present in

1726   Revancha samples.

1727

1728   **Tuk-Tuk lava dome, Toba, Sumatra, Indonesia**

1729   *General geology*

1730   The Toba samples (TT and TT7) are sourced from the Tuk-Tuk lava domes, located along the

1731   NE shore of Samosir Island, at the centre of the Toba caldera (Sumatra; Chesner et al., 2020). The

1732   samples were obtained from the personal collection of Dr. Craig Chesner (Eastern Illinois University).

1733   The lava domes represent the youngest volcanic activity associated with the Toba caldera, having

1734   extruded following the climactic eruption that produced the underlying youngest Toba tuff (YTT).

1735   Chesner et al. (2020) report weighted mean $^{39}Ar/^{40}Ar$ ages from Tuk-Tuk dome sanidine phenocrysts

1736   of 74.1 to 75.8 Ka, in agreement with the range of 74.5 to 75.2 Ka for sanidine from the YTT. The

1737   Tuk-Tuk dome samples are considered to be virtually identical to the YTT in terms of phenocryst

1738   mineralogy, textures and geochemistry (Chesner et al., 2020). For the associated upper YTT

1739   members, Chesner (1998) reported crystallization temperatures of 713-761°C and oxygen fugacity

1740   values of FMQ +1.0 to +1.4 based on Fe-Ti oxide oxybarometry.

1741   *Sample description*

1742   The Tuk-Tuk lave dome samples are light gray-to-white, vesicular (6-7 vol%), comprised of

1743   glass (47-72 vol%), quartz (6-12 vol%), sanidine (1-12 vol%), plagioclase (9-34 vol%), biotite (1-4

1744   vol%), and hornblende (≤ 2 vol%) with trace amounts of zircon, allanite, magnetite, ilmenite,

1745   orthopyroxene, and apatite (Chesner et al., 2020). Biotite in both samples is euhedral and kinked

1746   crystals are common. Unlike hornblende crystals, biotite does not exhibit observable compositional

1747   zoning and resorption features in biotite are rare. Biotite-hosted inclusions of zircon, monazite,

1748   magnetite, and feldspar are common in both samples, melt inclusions are rare. Biotite in TT7

1749   contains ubiquitous inclusions of acicular apatite. Sample TT, however, is completely devoid of

1750   apatite.

1751

1752   **Fish Canyon tuff, Colorado, US**

1753   *General geology*

1754   The Fish Canyon Tuff (FCT) is one of the 17 major (>100 km^3) ash-flow sheets of the San Juan

1755   volcanic field located in the southern part of Colorado (USA; Lipman et al., 1970). Despite its

1756   enormous volume (~ 5000 km^3), the FCT is remarkably uniform in composition (e.g., ~68.0±0.5 wt%

1757 SiO_2). The entire tuff sheet forms a single cooling unit with a common, <10 m thick basal vitrophyre

1758   layer. The sample analysed in this study was provided by Dr. Ray Donelick collected at the classic site

1759   (Gleadow et al., 2015) of the Fun Valley Ranch on Highway 160, Colorado (USA). Recent age

1760   determinations on FCT phenocrysts yield values of 28.37 (± 0.05) Ma by the $^{238}U/^{206}Pb$ method on

1761   zircon and 28.04 (± 0.18) by the $^{40}Ar/^{39}Ar$ method on sanidine, with coexisting biotite, hornblende

1762   and plagioclase yielding 0.2 to 0.3 Ma older ages (Bachmann et al., 2007). Johnson & Rutherford

1763   (1989) used the composition of coexisting Fe-Ti oxides to determine a magma crystallization

1764   temperature of 760 (± 30) °C and oxygen fugacity of FMQ+3.0. These workers also determined the

1765   pressure in the Fish Canyon magma chamber to be 240 (± 50) MPa (equivalent to depth of 7.9 km)

1766   using Al-in-hornblende geobarometry. Melt inclusions trapped in quartz and hornblende

1767   phenocrysts from the FCT record compositions identical to matrix glass (Johnson & Rutherford, 1989),

1768   suggesting little compositional evolution of the FCT magma between phenocryst growth and

1769   eruption.

1770   *Sample description*

1771   Samples contain phenocrysts of plagioclase, sanidine, biotite, hornblende, quartz, magnetite,

1772   titanite, and ilmenite in a matrix of microcrysts, phenocryst fragments, and glass. The relative

1773   proportions within the phenocryst assemblage are close to constant (~55% plagioclase, ~15% alkali

1774   feldspar, 5% quartz, 10% biotite, 10% hornblende, 5% trace minerals) and their modal abundance in

1775   the tuff depends on the crystallinity of the rock (35-50%; Whitney and Stormer, 1985). Matrix glass

1776   commonly features fiamme textures, but in numerous pockets the glass is massive and fresh. Biotite

1777   is typically fresh, euhedral, often kinked, and compositionally uniform (Figure 4e), often contains

1778   inclusions of apatite, feldspars and hornblende.

1779

1780   **Mascota minette, Jalisco, W Mexico**

1781   *General geology*

1782   Mascota volcanic field is located in the Jalisco Block of western Mexico, where the Rivera Plate (a

1783   separated fragment of the Farallon plate) subducts beneath the North American Plate along the

1784   Middle America trench. The field spans an area of ~2000 km^2 and contains ~87 small cones and

1785   lava flows of minette, absarokite, basic hornblende lamprophyre, basaltic andesite, and andesite (R.

1786   A. Lange & Carmichael, 1990). Mascota minettes represent the youngest volcanism in the region, their

1787 ^{40}K-^{40}Ar ages on biotite are between 0.489±0.08 and 0.061+0.192 Ma (Carmichael et al., 1996).

1788   Phenocryst assemblage of augite minettes (sampled in this study) record a crystallization

1789   temperature of 1080-1100°C, determined by experiments of phologopite and augite saturation in a

1790   related augite minette. Equilibration pressure of augite and olivine minettes of Mascota volcanic

1791   field is estimated to be between 5 and 15±4kbar, based on TiO_2 and BaO partitioning between

1792   phlogopite and matrix (Righter & Carmichael, 1996). Oxidation state of augite minettes (FMQ+4.3;

1793   Carmichael et al., 1996) was resolved using Fe_2O_3/FeO ratio in matrix (Kress & Carmichael, 1991).

1794   *Sample description*

1795   Sample has been provided by Smithsonian Institution (number NMNH 117626-21) and has

1796   been previously analysed by (Carmichael et al., 1996) as M.18.

1797   The sample consists of phlogopite (~5 vol%), augite (~13 vol%) phenocrysts and

1798   microphenocrysts in a very fine-grained groundmass (~79 vol%) of phlogopite and sanidine. Apatite,

1799   zircon, magnetite, and ilmenite are present in trace amounts both in the phenocryst assemblage

1800   and groundmass. Phlogopite phenocrysts occur as reddish brown tabular, <1 mm large flakes.

1801   Inclusions in biotite are rare, usually ilmenite and zircon. Apatites are euhedral, colourless, up to 60

1802   microns large prismatic to acicular crystals.

1803

1804   **Umiakovik pluton, Labrador, Canada**

1805   *General geology*

1806   Umiakovik pluton is represented by sample EC 87-119, previously analyzed by (Emslie & Stirling,

1807   1993).

1808   Umiakovik pluton, located in northern Labrador (Canada) belongs to the Nain Plutonic suite, an

1809   example of anorthosite-charnokite-mangerite-granite (ACMG) suites of Mesoproterozoic. The Nain

1810   plutonic suite intrudes the Torngat orogen region between the Nain and Rae cratons of the

1811   Canadian Shield. Within the suite, two spatially and temporarily distinct intrusive sequences (1363-

1812   1319 Ma in NW and 1319-1289 Ma in SE) are recognized. Emplacement of the Umiakovik pluton is

1813   the final intrusive episode of the first sequence.

1814   Umiakovik composite pluton consists of biotite and biotite-hornblende granite, fayalite-pyroxene

1815   quartz monzonite and granite facies, and rare monzodiorite occurrences adjacent to the contact

1816   with anorthosite. The boundaries between the fayalite-, pyroxene-, and hornblende-bearing facies

1817   are gradational, however the hornblende-biotite and biotite granites (sampled in this study) intrude

1818   the fa- and py-bearing facies as dykes and sheets. EC 87-119 sample, which represents the latter bt-

1819   hbl-granite, produced zircon $^{207}Pb/^{206}Pb$ age of 1316+2/-3Ma in agreement with K-Ar ages for biotite

1820   (1302±19 Ma) and hornblende (1322±18 Ma). Corresponding to the field relationships, these ages

1821   are marginally younger than the 1319±2 Ma zircon $^{207}Pb/^{206}Pb$ age of the of the fayalite quartz

1822   monzodiorite (Emslie & Loveridge, 1992). Emplacement pressure estimate, based on Al-in-hornblende

1823   geobarometer (Johnson & Rutherford, 1989), is 3.7±0.5 kbar. This corresponds within error to the

1824   garnet-cordierite and hypersthene-olivine-quartz equilibria (Hensen & Green, 1972; 1973) in the

1825   mineral assemblage in the metamorphic aureole of Nain plutonic suite, which suggests 3.5±1 kbar

1826   (Berg, 1977; 1979).

1827   Late-stage crystallization temperature 750-800° C is based on equilibration of pyroxene- and olivine-

1828   bearing facies and presence of inverted pigeonite in the monzodiorite facies (Emslie & Stirling, 1993).

1829   Given that the sampled facies does not contain olivine and pyroxene, a more accurate and

1830   representative temperature estimate (e.g., Henry et al., 2005) is necessary. The oxidation state of

1831   Umiakovik pluton has been initially estimated by the intersection of isopleths defined by the

1832   hematite content in ilmenite and the Fe^{3+}/Fe^{2+} ratio of biotite, ranging between FMQ-1 and FMQ-4

1833   (Emslie & Stirling, 1993). Subsequent Ce-in-zircon oxybarometry narrowed the fO$_2$ range to FMQ-

1834   2.4±0.7 (Smythe & Brenan, 2016).

1835   *Sample description*

1836   Sample EC 87-119 is a representative sample of biotite-hornblende granite. It consists of alkali

1837   feldspar (43 vol.%), quartz (25 vol.%), plagioclase (20 vol.%), biotite (7 vol.%), hornblende (5 vol.%)

1838   and trace amounts of apatite, zircon, ilmenite, and fluorite (Emslie & Loveridge, 1992). Biotite is dark

1839   brown, often bent, subhedral, up to 1-2 mm large crystals without noticeable zoning in reflected

1840   light or SEM. Biotite occasionally contains up to 20 microns large apatite and zircon inclusions.

1841   Apatite crystals are typically up to 400 microns large prismatic, euhedral, pale green, transparent

1842   crystals. In SEM, approximately 30% of apatite crystals exhibit a distinct darker, rounded core with

1843   >20 micron thick, bright rim. Inclusions in apatite are rare, usually few microns large zircons.