1  Platinum-group element geochemistry of the volcanic rocks associated with the Jaguar and

2  Bentley Cu-Zn volcanogenic massive sulfide (VMS) deposits, Western Australia: Implications

3  for the role of chalcophile element fertility on VMS mineralization.

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5  Jung-Woo Park[1,2][*] and Ian Campbell[2]

6  [1] School of Earth and Environmental Sciences, Seoul National University, Seoul 08826, South

7  Korea

8  [2] Research School of Earth Sciences, Australian National University, Canberra, ACT 2601,
9  Australia

10  * Corresponding author: jung-woo.park@snu.ac.kr

11

**Abstract**

We report whole-rock major, trace, and platinum-group element (PGE) geochemistry of volcanic rocks from the Teutonic Bore complex that hosts the Jaguar and Bentley Cu-Zn volcanogenic massive sulfide (VMS) deposits. This study aims to understand their sulfide saturation history and chalcophile element evolution during differentiation of the Jaguar and Bentley magmas, and investigate the role of chalcophile element fertility on the formation of VMS deposits.

The fractionated primitive mantle-normalized trace element patterns, with negative Nb and Ti anomalies of basalts, andesites, dacites and rhyolites from Jaguar and Bentley are similar to each other. The trace elements and PGE show continuous variations when plotted against fractionation indices such as Yb, which can be explained by a two-stage fractional crystallization model: Stage 1 Rayleigh fractionation of plagioclase + clinopyroxene + Cr-spinel, and Stage 2 the fractional of plagioclase + clinopyroxene + magnetite + 0.1 wt.% sulfide liquid. Dolerites, which postdate the mineralization, differ from the other rock types and require a different magma source.

Andesite and basalt are the most PGE-enriched lithologies in Jaguar and Bentley. The PGE behave incompatibly in the early stage of magma differentiation at < 4 ppm Yb, whereas they abruptly decrease at > 4 ppm Yb, indicating sulfide saturation at this point. When Pd/MgO and Pd/Pt are used as chalcophile element fertility indicators, the andesite before sulfide saturation (< 4 ppm Yb) is as fertile as the magmas associated with porphyry Cu-only deposits. In contrast, the andesite after sulfide saturation and other lithologies are characterized by markedly depleted fertility similar to those of barren suites. This suggests that sulfide-undersaturated andesite, and probably basalt, may have been a significant source for Cu in the Jaguar and Bentley Cu-Zn VMS deposits. However, the Au fertility of the Jaguar and Bentley andesite

36    must have been low and not enough to form Au-rich VMS deposits because their Pd/MgO and

37    Pd/Pt values are 5-10 times lower than those of andesite and dacite from the modern Au-rich

38    seafloor massive sulfide deposits. This can be explained if ore formation occurred shortly after

39    sulfide saturation. If the amount of sulfide melt to precipitate was small, Au, with its high

40    partition coefficient into immiscible sulfide melts, would have been largely stripped from the

41    silicate melt whereas Cu, with its lower partition coefficient, would be little affected. Our study

42    shows that chalcophile element fertility may play an important role in the formation of VMS

43    deposits, especially in controlling the Au contents of the ore, if the magmatic-hydrothermal

44    component is the dominant source for metals in VMS systems.

**Introduction**

There are two principal hypotheses for the source of the metals in volcanogenic massive sulfide (VMS) deposits, the wall rock leaching, and magmatic-hydrothermal hypotheses. In the former, the metals are leached from the wall rocks above a sub-volcanic magma chamber, which drives convection in the overlying volcanic rocks. The latter requires them to be deposited from a magmatic fluid, derived from an underlying magma chamber (Campbell et al., 1981; Franklin et al., 2005; Yang and Scott, 1996; Huston et al., 2011; de Ronde et al. 2011; Patten et al., 2020). Both sources may contribute to the formation of VMS deposits, although their relative contributions may vary.

Studies of seafloor massive sulfide (SMS) deposits, the modern equivalent of VMS systems, provide critical information as to the source of metals and S in VMS systems. The presence of advanced argillic alteration and native sulfur with negative $\delta^{34}S$ values in some arc-related SMS deposits require the input of a magmatic component into the ore-forming hydrothermal fluid (Huston et al., 2011). The arc-associated SMS deposits discharge vent fluids with significantly higher magmatic volatile and metal contents such as $SO_2$, $H_2S$, $CO_2$ and Fe than those at mid-ocean ridge (MOR) settings (de Ronde et al., 2001, 2011, 2014; Massoth et al., 2003; Lupton et al., 2006, 2008; Resing et al., 2007, 2009; Butterfield et al., 2011). It has been suggested that these volatiles are responsible for transporting economic metals such as Au and Cu from the sub-volcanic magma chambers to the SMS systems (de Ronde et al., 2005, 2011, 2014; Berkenbosch et al., 2012; Gruen et al., 2014). These observations, together with the higher concentrations of Au, As, Sb, and Hg in sulfides from some arc-related SMS deposits compared with those associated with MOR, suggest higher magmatic input into the former. A recent mass balance study (Patten et al., 2020) on Izu-Bonin arc oceanic crust, and associated VMS mineralization, showed that leaching alone could not explain the enrichment of Se, S,

69  and Au in the mineralized samples and significant metal fluxes from magmatic-hydrothermal

70  fluids are necessary.

71      The Teutonic Bore complex of Western Australia hosts three Archean Cu-Zn VMS deposits:

72  the Teutonic Bore, Jaguar and Bentley, over a distance of about 8 km (Fig. 1; Belford, 2010).

73  The steeply dipping banded massive sulfide layers are hosted by a sequence of pillow basalt

74  with intercalated dacite breccias and sedimentary rocks (Hallberg and Thomson, 1985; Belford,

75  2010; Belford et al., 2015). Multi-sulfur isotope studies for the Teutonic Bore, Jaguar and

76  Bentley deposits (Chen et al., 2015) have shown that the $\Delta^{33}S$ of the ores is slightly negative

77  from –0.46 to –0.05 ‰, in contrast to pyrites from wall rocks, which include sedimentary rocks

78  that range from +0.19 to +6.20 ‰. Chen et al. (2015), based on the S isotope results, argued

79  that the ore S is a mixture of magmatic and seawater S, dominated by the former with a

80  negligible contribution from the country rocks. Given that S is the major anion in the VMS ore

81  and the major component of the ligands, together with Cl, which transport Cu and Au in the

82  ore-forming fluids (Huston, 1997), it is likely that Cu and Au in the ores from the Teutonic

83  Bore, Jaguar and Bentley deposits were mainly derived from an underlying magma body.

84      If the above argument is correct, the Cu and Au ore potential of the volcanic package is likely

85  to be mostly dependent on the nature of the fractionation process in the underlying magma

86  chamber, and especially on the timing of sulfide saturation relative to volatile saturation in the

87  evolving melt (Park et al., 2013; 2015; 2019). Early sulfide saturation leads to depletion of the

88  chalcophile elements, which include Cu and Au, so that they are unavailable to enter the

89  magmatic-hydrothermal fluid when the magma becomes volatile saturated (Cocker et al., 2015;

90  Park et al., 2019). Alternatively, if sulfide saturation occurs late, after or shortly before volatile

91  saturation, the chalcophile elements are concentrated by fractional crystallization and are

92  available to enter the fluid phase when the magma eventually become fluid-saturated (Park et

93    al., 2019). Note that the effect of sulfide segregation will be limited for Zn and Pb due to their

94    affinity for sulfide phases being weaker than Cu and Au.

95    Platinum-group element (PGE) have been used to test the hypothesis that the time of sulfide

96    saturation, relative to volatile saturation, controls the fertility of porphyry Cu and porphyry Cu-

97    Au deposits (Cocker et al., 2015; Park et al., 2019; Hao et al. 2017; 2019; Lowczak et al., 2018).

98    The PGEs are preferred for two reasons, first because their partition coefficients into an

99    immiscible sulfide melt are at least two orders of magnitude higher than Cu, and an order of

100   magnitude higher than Au (Mungall and Brenan, 2014); and second because the PGEs are less

101   mobile than Cu and Au in seafloor hydrothermal settings (Crocket et al., 2000; Park et al.,

102   2016).

103   In this study, we report the results of major and trace element analyses, including PGEs, in

104   volcanic rocks from the Jaguar and Bentley Cu-Zn VMS deposits using a NiS fire assay-isotope

105   dilution method, which has a detection limit of 15 ppt (part per trillion) for Pt and Pd, and ca.

106   1 ppt for the other PGE. The aim was to determine the point at which the evolving magma

107   systems, which produced the Jaguar and Bentley VMS deposits, reached sulfide saturation, and

108   to ascertain its influence on the evolution of the chalcophile elements. We also discuss the role

109   of chalcophile element fertility on Cu and Au mineralization in VMS ore deposits by

110   comparing PGE data of volcanic rocks that host the Jaguar and Bentley Cu-Zn VMS deposits

111   with those of the Pual Ridge and Niuatahi Au-rich SMS deposits.

112

113   **Geological setting**

114   The Teutonic Bore, Jaguar and Bentley VMS deposits are located in the Teutonic Bore

115   volcanic complex in the northern Gindalbie Domain of the Kurnalpi terrane, Eastern Goldfields

116    Superterrane (EGST), Western Australia (Belford et al., 2015). The Archean EGST is

117    composed of deformed and metamorphosed volcanic and sedimentary rocks, which were later

118    intruded by granite batholiths (Barley et al., 2008). The volcanic and sedimentary rocks were

119    deposited between ~2930 and ~2650 Ma and underwent low to medium grade greenschist

120    facies metamorphism (Swager et al., 1992; Cassidy et al., 2002). Late granitoids, with ages

121    from 2680 to 2660 Ma, intruded into the greenstone belts (Cassidy et al., 2002), which were

122    subjected to major N-S to NNE-SSW trending faulting (Swager, 1997).

123    The Gindalbie Domain hosts four major volcanic complexes: Melita, Teutonic Bore, Spring

124    Well, and Jeedamya. They range in age from $2694 \pm 4$ Ma to $2676 \pm 5$ Ma (Nelson, 1995;

125    Nelson, 1997a; Nelson, 1997b; Brown et al., 2002; Kositcin et al., 2008). The Melita and

126    Teutonic Bore complexes are characterized by high field strength element (HFSE) enriched

127    bimodal volcanism, whereas the Spring Well and Jeedamya complexes consist of calc-alkaline

128    intermediate and silicic volcanic rocks (Barley et al., 2008). The role of subduction in the

129    petrogenesis of the volcanic rocks is contentious. Belford et al. (2015) invoked a back-arc

130    setting for the Gindalbie Domain adjacent to the Teutonic Bore; however, Barnes and Van

131    Kranendonk (2014) suggested that plume-related magmatism accompanied by magma mixing

132    and crustal assimilation can explain the geochemistry of felsic and intermediate volcanic rocks

133    in the Eastern Goldfields superterrane. Regardless of whether or not subduction is required,

134    young $Nd_{DM}$ ages and juvenile Pb isotope signatures, compared to those of the surrounding

135    volcanic units, indicates that the VMS mineralization occurred along rift margins such as a

136    continental-rift or back-arc basin rift system (Huston et al., 2014; Hollis et al., 2015).

137    The Teutonic Bore complex hosts the Teutonic Bore, Jaguar, and Bentley VMS deposits (Fig.

138    1). Hallberg and Thompson (1985) investigated the geologic setting of the Teutonic Bore

139    deposit, and a summary of their study follows. The oldest exposed rocks are amygdaloidal

140 andesites that are overlain first by pillowed basalts, and then by rhyolitic volcanic and

141 volcanoclastic rocks. The felsic rocks are, in turn, overlain by a second sequence of pillowed

142 basalts that host most of the mineralization. The basalts are interspersed with polymict

143 conglomerate and greywacke layers or lenses. The massive sulfide ore body occurs 0 and 150

144 m stratigraphically above the boundary between the rhyolite and basalt. Dolerite sills and dykes

145 intrude all of the volcanic units. Nelson (1997b) reported a SHRIMP zircon U-Pb age of 2692

146 $\pm$ 4 Ma for a hanging-wall porphyritic dacite from the Teutonic Bore. Hayman et al. (2014)

147 reported thermal ionization mass spectrometry (TIMS) zircon U-Pb ages of 2692.6 $\pm$ 1.5Ma

148 and 2694.2 $\pm$ 0.6 Ma for a hanging-wall rhyolite dyke (Jaguar) and the footwall rhyolite

149 (Bentley), respectively.

150 Belford (2010) and Belford et al. (2015) studied the stratigraphy, geochemistry, and

151 petrology of the host successions of the Jaguar VMS deposit. The following is a summary of

152 Belford et al. (2015). The oldest unit of the Jaguar deposit is massive coherent andesite with

153 thickness > 50 m. Its lower contact is not exposed. The andesite unit is intruded by a rhyolite

154 dome, which is overlain by andesite that erupted on the seafloor. Basalt conformably overlies

155 the andesite with no interflow sediment separating the units. Sedimentary facies are rare in the

156 footwall of the Jaguar deposit, suggesting a high rate of volcanic accumulation and that

157 volcanic hiatus are short or absent. The basalt is overlain by a laminated chert and pumice rich

158 facies, which in turn is overlain by coherent and polymict dacites forming a series of small

159 domes that were extruded onto the seafloor. The Jaguar massive sulfide body is hosted by the

160 coherent dacites and their associated volcanoclastic rocks, which together are classified as the

161 mineralized package by Belford et al. (2015). Later dolerite dykes crosscut all of the facies

162 described above.

163

164 **Samples**

165     The coherent volcanic rocks analyzed for this study were collected from four drill holes:

166 13JUDD002, 12JADD002, 09BTDD029, and 09BTDD025 (Electronic Supplementary

167 Material (ESM) Table 1; Fig. 2). These holes cover most of the coherent volcanic lithofacies

168 that hosts the Jaguar and Bentley deposits. The samples are fresh to the extent that they still

169 preserve primary igneous textures despite prevalent regional greenschist facies metamorphism

170 and local hydrothermal alteration. The igneous rock classification of the Jaguar and Teutonic

171 Bore areas has been performed using HFSE, which are immobile during greenschist

172 metamorphism (Hallberg and Thompson, 1984; Belford et al., 2015). In this study, we used

173 Ti/Zr to classify the major igneous rock types. The Ti/Zr criteria are: rhyolite < 4 < dacites <

174 12 < andesite < 50 < basalt (Hallberg, 1984). Note that Ti/Zr = 50, instead of 60 as suggested

175 in Hallberg (1984), has been used to discriminate between andesite and basalt. Y/Zr was also

176 used as an index to classify the rocks as tholeiite (2 < Y/Zr <4.5), transitional (4.5 < Y/Zr < 7),

177 or calc-alkaline (7 < Y/Zr < 25) (MacLean and Barrett, 1993).

178     Drill hole 13JUDD002 is an underground hole that was drilled from the same level as the

179 mineralized package toward the stratigraphic footwall. It cuts andesite, basalt, and dolerite,

180 which are considered to be part of the footwall, but distal to the mineralized and footwall

181 rhyolites. The dolerite shows sharp upper and lower contacts with andesite and basalt, with

182 well-developed chilled margins. This suggests late intrusion of dolerite into the andesite and

183 basalt sequences in the mineralized package. The basalts are interspersed with layers of wacke,

184 chert, and siltstone from 40 to 70 m. Between 400 m and 430 m, where they are close to the

185 footwall rhyolite, they are partly brecciated and intercalated with feldspathic and quartz phyric

186 rhyolite. Weak pyrite and chalcopyrite veining occurs in the brecciated basalt-rhyolite zone.

187 The footwall rhyolite is silicified and has experienced sericitization and chloritization. A total

188   of twenty-two samples were collected from this core, consisting of two andesites from the

189   mineralized package and two andesites, six basalts, and five rhyolite samples from footwall

190   and seven dolerite samples.

191   Drill hole 12JADD002 is one of the three northernmost holes designed to investigate the

192   lithology of the northeastern Jaguar area. It cuts through the hanging-wall basalt, andesite and

193   rhyolite, and the footwall basalt and rhyolite as well as dolerite. The rocks between 212 m and

194   480 m are weakly deformed and sheared. At 310 m, the host rock is partially replaced by 30%

195   pyrite, which is interpreted to be the distal end of the main Jaguar ore body. A total of twenty

196   samples were collected from this hole. They include four basalts, two rhyolites and one andesite

197   from the hanging-wall sequence, together with three basalts and four rhyolite samples from the

198   footwall sequence, and four dolerite samples.

199   Drill hole 09BTDD029 was drilled through the hanging-wall, the mineralized package

200   lithofacies, and footwall rhyolite of the Bentley deposit. The hanging-wall volcanic facies from

201   this hole consists mainly of andesite. A total of thirteen samples consisting of nine hanging-

202   wall andesite-, two foot-wall rhyolites, and five dolerites were collected from this hole.

203   Drill hole 09BTDD025 crosses from the hanging-wall lithofacies through the main massive

204   Cu-Zn sulfide ore body into the footwall rhyolite. The hanging-wall volcanic facies consist of

205   basalt, andesite, and rhyolite. A total of twenty-three samples were collected, consisting of five

206   andesites, three basalts, and three rhyolites from the hanging-wall sequence along with five

207   footwall rhyolite and four massive and stringer ore samples.

208   Six additional footwall volcanic and intrusive rocks from the Bentley deposit were collected

209   from drill holes 12TRDD016, 13TRDD009, 09TRDD032, and 13TRDD001, which include

210   three andesites, one dacite, and two dolerite samples. One footwall rhyolite was also collected

211     from drill hole 13TRDD014 from the Teutonic Bore deposit.

212     Coherent volcanic rocks, with small amounts of phenocrysts (<~10 modal %), were used in

213     this study. The rhyolite is composed of a fine-grained matrix with quartz phenocrysts (< 1-2

214     mm). The matrix minerals are dominantly quartz, sericite, and chlorite and show varying

215     degree of silicification. The andesite is amygdaloidal and aphyric to feldspar-phyric. The round

216     and elongated amygdales (~1-3 mm) are filled with quartz or carbonate minerals. Overall the

217     size of plagioclase laths varies from 1 to 3 mm. In some cases, the plagioclase phenocrysts and

218     microcrystalline matrix are replaced with sericite, carbonate, and chlorites. Basalt is

219     dominantly aphyric. Microtextures vary from sub-ophitic texture with plagioclase laths and

220     pyroxene to intersertal with plagioclase and microrites.

221

222     **Analytical techniques**

223     Major element analysis

224     The major element compositions of twenty-three samples were measured by X-ray

225     fluorescence (XRF) analysis at Genalysis Laboratories in Perth, Western Australia, using the

226     whole-rock lithium borate fusion XRF package FB1/XRF20. The results are reported in Table

227     1. A further thirty-two samples, including seventeen of the samples that had been analyzed by

228     XRF, were selected for whole rock analysis by electron microprobe. The samples were crushed

229     in a steel jaw crusher and milled in a tungsten carbide mill at the Australian National University

230     (ANU). About 0.5 g of each sample powder was fused in a graphite crucible in an open furnace

231     at 1400 ℃ for 1 hour and quenched in tap water. The quenched glass was mounted on an

232     epoxy disk, and the major element compositions were measured by Cameca SX100 microprobe

233     at ANU with an accelerating voltage of 15 KeV, beam current of 10 nA and beam diameter of

234  10 μm. The results are reported in ESM Table 2. The probe data differ from the XRF data by

235  more than 10% for some samples, particularly in FeO, MnO, $Na_2O$, and $P_2O_5$. The discrepancy

236  is attributed to incomplete fusion in the absence of the Li-borate flux, a conclusion supported

237  by patches of microcrystals in glass chips of some felsic samples. Systematically low

238  microprobe FeO data can be attributed to the formation of Fe metal phases during fusion, which

239  results in depletion of FeO in a silicate melt. However, $SiO_2$ contents measured by the two

240  methods vary by less than 10 % (ESM Fig. 1). The $SiO_2$ contents were used to calculate trace

241  element concentrations of the samples during LA-ICP-MS data reduction.

242

243  Trace element analysis by LA-ICP-MS

244   A total of twenty-nine samples were analyzed for trace elements by LA-ICP-MS at ANU.

245  The sample powder (~0.6 g) was mixed with Li-borate flux with a sample/flux ratio of 1/3. The

246  mixture was dried at 400 ℃ for 10 min, fused at 1050 ℃ for 8 min and then poured onto a

247  graphite mold to make a glass disk. The laser system consists of a Lambda Physik Complex

248  110 excimer laser ($\lambda = 193$ nm) and ANU-designed HelEx cell combined with an Agilent 7700x

249  ICP-MS. The analyses were performed at the laser pulse rate of 5 Hz, beam size of 81 μm, and

250  energy density of ~ 3 $J/cm^2$. NIST 610 glass was used as the external standard for calculating

251  the trace element concentrations with reference to the Si content of the glass as determined

252  either by XRF or electron microprobe. Averages of three to five analyses of each sample are

253  reported in Table 2. Seven analyses of the USGS reference material BCR-2g were carried out

254  along with unknown samples in order to check the reproducibility and precision of the analyses.

255  The measured BCR-2g values agree well with those reported by Jochum et al. (2008) within

256  the quoted uncertainties. The percentage relative difference (%RD) is less than 6% for all

257  elements except for Cr (15 %), Ni (11 %), Cu (16 %) and Zn (25 %). The reproducibility,

258  calculated as relative standard deviation (1σ) based on counting statistics, was mostly less than

259  4 % (Table 2).

260

261  Platinum-group element and Re analysis by a Ni-sulfide fire assay and isotope dilution method

262      Twenty-three samples were analyzed for PGE and Re following the method described by

263  Park et al. (2012). Briefly, 5 g sample powder was mixed with Ni, S, and sodium borax powder

264  (sample: Ni : S : sodium borate = 10 : 1 : 2: 10) on a weighing paper, and the mixture was

265  poured into a porcelain Coors$^{TM}$ crucible. The PGE spikes ($^{99}$Ru, $^{105}$Pd, $^{185}$Re, $^{191}$Ir, and $^{195}$Pt)

266  were added to the mixture. The crucible containing the mixture and spike was then placed into

267  the second crucible containing 0.1 g of flour and covered by a porcelain lid. The sample mixture

268  was dried at 100 ℃ for 60 min, fused at 1100 ℃ for 30 min, and quenched in the air by

269  removing the crucible from the furnace. During fusion, $N_2$ gas was introduced at a flow rate of

270  ~0.03 m$^3$/min. After quenching, Ni-sulfide beads containing the PGE were collected and

271  dissolved in 150 ml of 6 N HCl, and the solution was filtered through a Millipore filter paper.

272  The filter was digested in 4 ml of aqua regia. After the complete digestion of the filter paper,

273  the solution was dried to ~100 μl and diluted with 2 % nitric acid. The final solution was

274  analyzed by an Agilent 7700x ICP-MS at ANU. The sensitivities were ~2−3 × 10$^5$ cps per

275  ppb for mass 89, 140, and 205. Argide and oxide production rates were measured using pure

276  solutions of Ni, Cu, Zn, Co, Hf, Mo, and Zr to correct molecular isobaric interferences on the

277  PGE. The argide production rate ranges from 0.002% to 0.004% and oxide rate from 0.2% to

278  0.6%. The molecular interferences on all PGE were < 0.1% except Ru for which the Ni argide

279  interference was < 30 % for all samples but JB44605 where the interference was 68 %. This is

280  largely due to the Ru content of JB44605 being close to the limit of detection. Concentrations

281  of Pd, Pt, Ir, Ru, and Re were determined by isotope dilution method using the $^{105}$Pd/$^{108}$Pd,

282 $^{195}Pt/^{194}Pt$, $^{191}Ir/^{193}Ir$, $^{99}Ru/^{101}Ru$, and $^{185}Re/^{187}Re$, respectively. Rhodium concentrations were

283 calculated using the method described in Park et al. (2012).

284 Average procedural blanks determined from four analyses using 10 g of sodium borax, 1 g

285 of Ni and 0.5 g of S were 0.9 ± 0.1 ppt for Ir, 1.9 ± 0.4 for Ru, 0.9 ± 0.1 ppt for Rh, 7.5 ± 1.8

286 ppt for Pt, 14 ± 3.3 ppt for Pd and 21 ± 4.0 ppt for Re. The blank corrected PGE data are

287 reported in Table 3. The method detection limits (MDL), taken to be two standard deviations

288 of the procedural blanks, were 0.2 ppt Ir, 1 ppt Ru, 0.3 ppt Rh, 4 ppt Pt, 8 ppt Pd, and 8 ppt Re.

289 The uncertainties (1σ) arising from ICP-MS counting statistics, the PGE calibration standard,

290 and blank subtraction are given. Multiple analyses of the CANMET TDB-1 reference material

291 were performed to test the accuracy and precision of the measurements (Table 3). The results

292 agree well with the values previously reported by Meisel and Moser (2004), and Peucker-

293 Ehrenbrink et al. (2003).

294

295 **Results**

296 Major and trace element

297 Although the samples were selected on a least-altered basis, the major element geochemistry

298 of Jaguar and Bentley volcanic rocks has, to some extent, been affected by hydrothermal

299 alteration and greenschist facies metamorphism. Selected major elements are plotted against

300 $SiO_2$ in ESM Fig. 2. $Al_2O_3$, CaO show negative correlations with $SiO_2$, suggesting they may

301 represent magmatic trends. However, MgO, FeO, $K_2O$, and $Na_2O$ data are scattered, which can

302 be attributed to moderate hydrothermal alteration.

303 High field strength elements (Ti, Zr, Y, Nb, REE, Hf, Ta, and Th) and some transition metals

304 (V, Cr, Ni, and Co) are considered to be chemically immobile at moderate degrees of

305    hydrothermal alteration and greenschist facies metamorphism (Pearce and Cann, 1973;

306    Winchester and Floyd, 1977; Whitford et al., 1989; MacLean and Barrett, 1993). The samples

307    analyzed in this study are compared with the geochemical data of 243 core samples from the

308    Jaguar and 240 core samples from the Bentley in terms of the immobile elements in ESM Fig.

309    3. The samples from this study represent most of the rock types that occur in the two deposits,

310    except for the calc-alkaline andesite and the dacite (ESM Fig. 3). The calc-alkaline andesites

311    of the Jaguar deposit are found mostly in hanging-wall units, whereas footwall andesites have

312    transitional geochemical features with Zr/Y between 4.7 and 6.9 (Belford, 2010). Therefore,

313    the calc-alkaline andesites are unlikely to be associated with the mineralization at the Jaguar

314    and have therefore been omitted from this study. Dacite is a major rock type within the

315    mineralized package at the Jaguar and is thought to be a differentiation product of the footwall

316    andesites (Belford, 2010). However, they only account for a small volume of the volcanic

317    successions in the Jaguar suite (Belford, 2010).

318      In Figure 3, the immobile trace element concentrations of the Teutonic Bore, Jaguar and

319    Bentley volcanic rocks are normalized to primitive mantle values (McDonough and Sun, 1995).

320    The patterns of volcanic rocks from three deposits are similar (Fig. 3). The basalt, andesite,

321    dacite, and rhyolites show similar fractionated patterns with marked negative Nb and Ti

322    anomalies (Fig. 3). The negative Ti anomalies become more pronounced with increasing Yb

323    contents (i.e., increasing fractionation) in the andesite, dacite, and rhyolite (Fig. 3a and b). The

324    trace element patterns of the andesite and rhyolite closely match those of Phanerozoic calc-

325    alkaline island arc andesite and rhyolite, respectively (Fig. 3a and b). The dolerite is distinct

326    from the other rock types, having flat trace element patterns with appreciably smaller negative

327    Nb and Ti anomalies (Fig. 3d).

328      Figure 4 compares the chondrite-normalized REE patterns of the Teutonic Bore, Jaguar, and

329    Bentley volcanic rocks analyzed for this study with Belford (2010). Belford (2010) documented

330    the geochemical features and the geometry of the volcanic rocks that host the Jaguar deposit

331    by logging of 24 km of drill core. The REE patterns of rhyolites from the Teutonic Bore, Jaguar

332    and Bentley are slightly to moderately fractionated with $La_N/Yb_N$ = 3.9 to 5.8, and marked

333    negative Eu anomalies (Fig. 4a). There is no systematic variation among the three localities.

334    Their patterns are similar to the dacites from the mineralized package from the Jaguar deposit

335    (Belford, 2010), which are considered to be less fractionated rhyolites.

336    The andesites from the mineralized package of the Jaguar deposit, analyzed for this study,

337    are moderately fractionated with $La_N/Yb_N$ ranging from 5.5 to 5.6 and small Eu anomaly (Fig.

338    4b). This trend differs from the patterns of typical footwall andesites from the Jaguar deposit

339    (Belford, 2010), but is similar to the hanging-wall andesite (Fig. 4b). The andesites from both

340    the hanging-wall and footwall of the Bentley deposit are characterized by slightly fractionated

341    REE patterns ($La_N/Yb_N$ = 3.3 to 4.2) with small negative Eu anomalies (Fig. 4b). Their patterns

342    are nearly identical to the footwall andesites from the Jaguar deposit in Belford et al. (2015).

343    The REE patterns of the basalts from the Jaguar and Bentley deposits in this study are

344    consistent with those of the footwall basalts reported in Belford (2010), despite higher REE

345    concentrations. They are slightly fractionated ($La_N/Yb_N$ = 2.9 to 3.6) and show both positive

346    and negative Eu anomalies (Fig. 4c). Belford et al. (2015) attributed the positive Eu anomaly

347    shown in some of the basalts to the inclusion of cumulative plagioclase. The REE compositions

348    of dolerites are consistent in both the Jaguar and Bentley. They are characterized by flat REE

349    patterns ($La_N/Yb_N$ = 1.1 to 1.6) with variable Eu anomalies (Fig. 4d).

350    Winchester and Floyd (1977) and Hallberg (1984) suggested $Zr/TiO_2$ and Ti/Zr as

351    fractionation indices for altered or metamorphosed volcanic rocks. However, the compatibility

352    of Ti and Zr can vary significantly during magma differentiation due to the crystallization of

353 Ti-bearing magnetite and zircon. Therefore, we use Yb as an index of fractional crystallization

354 in this study (e.g., Park et al., 2013). Ytterbium shows a clear positive correlation with other

355 immobile incompatible elements such as La, Y, Zr, and Nb (Fig. 5a and b; Table 2), and its

356 concentration increases through the overall fractionation sequence of basalt, andesite to

357 rhyolite. Note that basalt and andesite cannot be clearly distinguished by petrography due to

358 alteration, and classification of rock type is based on Ti/Zr ratios. Some basalt samples, with

359 Yb contents higher than andesite, may be misclassified probably due to local zircon saturation

360 or zircon inheritance from basement rocks (e.g., Hollis et al., 2015). They also contain very

361 low Cr (< 5 ppm) and Ni (< 11 ppm), suggesting they are the product of substantial magma

362 differentiation. Basalt and andesite form a continuum in most immobile trace element

363 variations (Fig. 5). Therefore, we will consider them as a single unit (basalt-andesite) in the

364 following discussion. Two andesite samples (JB44663 and JB44665) from the mineralized

365 package of the Jaguar deposit are slightly out of trend with higher La, Zr, and Nb than other

366 andesites at a given Yb, suggesting that they may be derived from a different parental magma

367 source or have undergone different evolutionary processes. The La and Zr contents of the

368 dolerites are significantly lower than those of other rock types over the same range of Yb (Fig.

369 5), implying that the dolerite originated from a different source that was depleted in La and Zr.

370 Chromium and Ni behave as compatible elements. Progressive depletion of Cr and Ni with

371 increasing Yb in the Jaguar and Bentley volcanic rocks (Fig. 5c and d) suggests olivine and Cr-

372 bearing clinopyroxene or chromite crystallization in the early stage of magma differentiation

373 (FC1). Titanium and V concentrations generally increase with increasing Yb in dolerite,

374 whereas their concentrations in basalt-andesite reach their maximum when Yb reaches about 4

375 ppm then decrease in the more fractionated samples (Fig. 5e and g). These trends suggest the

376 onset of magnetite crystallization at 4 ppm Yb in basalt-andesite (FC2). Note that the

377    geochemistry of andesite sample JB44906 is discordant to the trend of the majority of the

378    andesites with depleted Cr, Ni, Ti, and V over the same range of Yb as other rock types,

379    suggesting a different magma evolution history or an alteration effect. Note that the samples

380    JB44906 has the highest AI values among andesites (Fig. 8).

381

382    Platinum group elements and Re

383    The platinum group element concentrations are mostly below the method of determination

384    limit (m.d.l.) for rhyolites. Sample JB44699 is the least differentiated of the analyzed rhyolites

385    (i.e., the lowest Yb contents). It contains 0.333 ppb Pt, 0.001 ppb Rh and 0.005 ppb Ir, but the

386    other PGE concentrations, including Pd, are below the detection limits (Table 5). The PGE

387    concentrations in the basalt-andesite vary significantly between the samples with < 4 ppm Yb

388    and > 4 ppm Yb (Fig. 6). The basalt-andesite containing Yb < 4 ppm is enriched in PGE relative

389    to the latter. They contain 0.083 to 1.25 ppb Pd, 0.48 to 0.80 ppb Pt, 0.014 to 0.065 ppb Rh,

390    0.014 to 0.046 ppb Ru, and 0.008 to 0.014 ppb Ir. The PGE concentrations increase with

391    increasing Yb values in general, except for Ru, which shows a slight negative correlation with

392    Yb. Note that the basalt sample (JB44907) with Yb < 4 ppm contains PGE contents lower than

393    other basalt-andesite samples. It may have experienced some localized sulfide segregation.

394    Significantly lower PGE contents characterize the PGE contents in the most evolved basalt-

395    andesite (> 4 ppb Yb). The dolerites have the highest, but variable, PGE concentration among

396    all the rock types in the Jaguar and Bentley deposits. They contain < 0.008 to 5.03 ppb Pd, <

397    0.004 to 8.27 ppb Pt, < 0.0003 to 0.310 ppb Rh, < 0.001 to 0.028 Ru and < 0.0002 to 0.101 ppb

398    Ir. The PGE contents of the dolerite decrease with increasing Yb.

399    Copper contents of all the rock types show no clear trend with increasing Yb (Fig. 6f) and,

400    in this respect, differ from PGE. We attribute this difference to gain and loss of Cu during the

401    hydrothermal alteration associated with the mineralization as a consequence of the higher

402    mobility of Cu compared with the PGE in hydrothermal fluids (Crocket et al., 2000; Park et al.,

403    2016). There is no clear correlation between Cu and Pd. Rhenium concentrations range from

404    0.071 to 1.11 ppb in basalt-andesite, and 0.003 to 0.012 ppb in rhyolites. The dolerites have

405    high Re contents of 1.10 to 1.76 ppb.

406    Primitive mantle normalized PGE patterns of the Jaguar and Bentley volcanic rocks are

407    shown in Fig. 7. The basalt-andesite with > 4 ppb Yb is characterized by highly fractionated

408    patterns with a high Pd/Ir ratio ranging from 76 to 105, except for the basalt sample (JB44907).

409    These patterns are similar to those of the modern arc andesite, and their concentrations are at

410    the high end of the arc andesite range (Fig. 7a). The basalt-andesite with < 4 ppb Yb shows

411    similar PGE patterns but is substantially depleted in PGE concentrations. Two samples display

412    slightly negative Pd anomalies. The patterns of the Jaguar and Bentley basalt-andesite are

413    consistent with each other, which corresponds to their similar trace element geochemistry. One

414    rhyolite sample (JB44699) is enriched in Pt, Ir, and Rh compared to other rhyolites. The PGE

415    patterns of dolerite differ from those of the andesites. They are less fractionated with Pd/Ir

416    ranging from 38 to 50, and they have negative Ru anomalies. Although the absolute PGE

417    concentrations of three dolerite samples vary by more than an order of magnitude, the patterns

418    are sub-parallel to each other, indicating the same compatibility for all of the PGE (Fig. 7b).

419

420    **Discussion**

421    Effect of alteration

422    The whole-rock geochemistry of volcanic rocks associated with VMS deposits is often

423   affected by hydrothermal alteration. Large et al. (2001) proposed a graphical representation of

424   whole-rock geochemistry data, the alteration box plot, that provides information on alteration

425   mineralogy, and degree and type of alteration of the volcanic rocks. Most of the samples used

426   in this study plot within or close to the field of least altered volcanic rocks (Fig. 8), which

427   suggest they are likely to preserve magmatic compositions. Two exceptions are footwall

428   rhyolite samples of Jaguar and Bentley (Samples JB44681 and JB44922) that have an alteration

429   index larger than 80. They may have undergone intense chloritization and sericitization during

430   footwall alteration. Dolerite samples are characterized by a high CCP index (chlorite-

431   carbonate-pyrite; $100 \times (MgO + FeO) / (MgO + FeO + Na_2O + K_2O))$ of > ~80. This may be

432   due to their primitive nature (e.g., high MgO contents) because the CCP index is affected by

433   magma differentiation and tends to decrease with decreasing MgO (Large et al., 2001).

434

435   Magma differentiation

436      The coherent volcanic rocks from the Jaguar and Bentley are composed of basalt, andesite,

437   dacite, and rhyolite (This study; Belford, 2010). Belford et al. (2015) reported that the footwall

438   volcanic rocks in the Jaguar deposit, which include basalt, andesite, dacite, and rhyolite, have

439   similarities in geochemistry and suggested that they originated from a common source. The

440   geochemistry of the Jaguar footwall volcanic rocks analyzed in this study match well with those

441   of Belford et al. (2015). The hanging-wall and footwall andesites from the Bentley deposit

442   show surprisingly similar geochemistry to those of the Jaguar footwall volcanic rocks. Given

443   the close spatial and temporal relationship between two areas, together with similar

444   geochemical features, the hanging-wall and footwall units of the Bentley and the footwall units

445   of the Jaguar are likely to be comagmatic and to have experienced similar magma

446   differentiation process. Rayleigh fractional crystallization models were conducted with

447  published mineral-melt partition coefficients for basalt and andesite melts (ESM Table 3) and

448  assumed crystallizing mineral assemblages. The results show that the trace element

449  geochemical variations from basalt, andesite to rhyolite, including PGE, are best explained by

450  fractional crystallization models with two stages (Fig. 5 and 6): Stage 1 (FC1) can be modeled

451  by Rayleigh fractionation of plagioclase + clinopyroxene + Cr-spinel (50:49:1), and Stage 2

452  (FC2) by fractional crystallization of plagioclase + clinopyroxene + magnetite (50:35:15) with

453  0.1 wt.% of sulfide liquid fraction. These mineral assemblages are consistent with the

454  occurrence of phenocrysts in the Jaguar and Bentley volcanic rocks (Belford, 2010) and

455  experimental studies of basaltic systems (e.g., Toplis and Carroll, 1995). Formation of andesite,

456  with arc-like signatures, can also be produced by mixing between plume-related basalts and

457  crustal melts as suggested for Archean volcanic rocks from the Kurnalpi terrane by Barnes and

458  Kranendonk (2014). The Ni and Cr contents in the less-evolved andesite range up to 109 and

459  143 ppm, respectively, which are higher than those of modern island arc andesites (Barnes and

460  Kranendonk, 2014). This implies that the parental magma of the Jaguar and Bentley volcanic

461  rocks may have been produced by processes that differ from those that produce the modern arc

462  systems. However, the mixing model cannot be applied for the Jaguar and Bentley systems

463  because it does not account for the geochemical trends displayed by Ti, V, and PGE that reach

464  their maximum and abruptly decrease in andesite (Fig. 5 and 6).

465

466  Sulfide saturation

467    Recent PGE geochemistry studies of intermediate and felsic igneous rocks (Park et al., 2013,

468  2015) have shown that the PGE can be used as a sensitive sulfide saturation indicator in

469  evolving magmatic systems. Palladium, in particular, behaves incompatibly prior to sulfide

470  saturation, but its concentrations decrease rapidly once the magma becomes sulfide saturated,

471   and immiscible sulfide melts begin to segregate.

472   Pd, Pt, Rh, and Ir contents in the Jaguar and Bentley basalt and andesite increase slightly
473   with increasing Yb in the early stage magma differentiation, but their concentrations are
474   significantly depleted in samples with > 4 ppm Yb (Fig. 6). This suggests sulfide saturation
475   occurred at ~ 4 ppm Yb in the andesite magma. The fraction of sulfide melts in crystallizing
476   mineral assemblage is considered to be ~ 0.1 wt.% (Model FC2 in Fig. 6), assuming sulfide
477   saturation at ~ 4 ppm Yb. The sulfide fraction is consistent with those of sulfide melts
478   determined for other sulfide-saturated submarine volcanic systems (Jamais et al., 2008; Park et
479   al., 2013; 2015). The cause of the sulfide saturation can be partly ascribed to magnetite
480   crystallization. The Ti and V concentrations in the andesites increase with increasing Yb,
481   reaching their maximum at ~ 4 ppm Yb, and decrease in the sample with > 4 ppm Yb (Fig. 5e
482   and f). These trends indicate the onset of magnetite crystallization at 4 ppm Yb. Magnetite
483   crystallization has been suggested to be a trigger for sulfides saturation in evolving magmatic
484   systems (e.g., Jenner et al., 2010) by reducing $Fe_2O_3$ in the silicate melt and thereby lowering
485   its oxygen fugacity.

486   It should be noted that Ru behaves compatibly before sulfide saturation at 4 ppm Yb, which
487   is distinguished from the behavior of other Ir-group PGE (Ir and Ru) and Rh. This can be
488   attributed to the fractionation of Cr-spinel that has a higher affinity to Ru than Ir and Rh (Park
489   et al., 2017). Fractional crystallization model FC1 with 1 wt.% Cr-spinel fraction and $D_{Ru}^{Cr\text{-}spinel\text{-}melt}$
490   of 200 and $D_{Rh,Ir}^{Cr\text{-}spinel\text{-}melt}$ of 50 accounts for the variations in IPGE and Rh of sulfide-
491   undersaturated basalt and andesite (< 4 ppm Yb; Fig. 6).

492   The extremely low PGE content of rhyolites indicates that they were formed from a magma
493   that had experienced prolonged sulfide segregation. A spike in Pt-Ir-Rh in the least evolved
494   rhyolite sample, which is not accompanied by an increase in Pd, is considered to be a nugget

495    effect, rather than a magmatic signature. It cannot be a sulfide nugget because the presence of

496    a sulfide nugget would increase all of the PGE, particularly Pd. The sample may have included

497    a tiny Pt-rich alloy crystal as an inclusion in an early-formed mineral (e.g., Cocker et al., 2015)

498    although there is no sign of Pt alloy formation during the evolution of the Jaguar and Bentley

499    magma system.

500    The PGE concentrations in the limited number of analyzed dolerite samples (n = 5) decrease

501    as Yb contents increase (Fig. 6), which suggests early sulfide saturation in a differentiating

502    magma. They show sub-parallel PGE patterns despite more than an order of magnitude

503    variation in absolute abundances (Fig. 7b). This implies that their PGE concentrations are

504    controlled by the removal of immiscible sulfide melt because the partition coefficients of PGE

505    to the sulfide melts are similar to each other. The cause of sulfide saturation in the dolerites is

506    not clear, but magnetite crystallization can be excluded because Ti and V concentrations

507    increase continuously during magma differentiation (Fig. 5e and g).

508

509    Sources for Cu and Au

510    As noted in the introduction, two sources have been proposed for the ore metals in the VMS

511    deposit: the footwall strata to the VMS deposit and a direct contribution from magmatic-

512    hydrothermal fluids (Franklin et al. 2005). A recent S isotope study (Chen et al., 2015) of the

513    sulfides from the Teutonic Bore, Jaguar and Bentley deposits showed that the S isotopic

514    composition of ore sulfides are consistent with the S being mainly of mantle origin ($\delta^{34}$S = −

515    0.83 to +1.89‰; $\Delta^{33}$S = −0.46 to −0.05 ‰) and distinct from sedimentary sulfides ($\delta^{34}$S = +0.88

516    to +14.86‰; $\Delta^{33}$S = +0.19 to +6.20 ‰) both locally and regionally. Chen et al. (2015) suggested

517    the mantle S is likely to be derived from a magmatic-hydrothermal fluid, rather than from

518   magmatic sulfides in the footwall volcanic rocks by leaching based on several lines of evidence.

519   The sulfur contents of Archean marine sediments and Neoarchean shales are $< \sim10$ wt.%

520   (Lesher et al., 1981) and ~2.5 wt.% (Stüeken et al., 2012), respectively, whereas those of

521   unmineralized volcanic rocks from Teutonic Bore and Kambalda are significantly lower

522   $<< \sim0.1$ wt.% (Lesher et al., 1981; Chen et al., 2015), showing substantial sulfur enrichment in

523   metasedimentary rocks. Also, massive sulfide ore bodies of the Teutonic Bore, Jaguar and

524   Bentley are either hosted by and/or underlain by sedimentary rock units containing sulfur-rich

525   shale layers or lenses with thicknesses of up to 70 m (Hallberg and Thompson, 1985; Belford,

526   2010; Parker et al., 2017). Therefore, if the sulfur in the VMS ores dominantly came from the

527   footwall strata by leaching, $\Delta^{33}S$ values of the ores should be positive or at least trend toward

528   positive values, which is not shown by the Chen et al. (2015) study.

529   Recent studies of the PGE geochemistry of submarine basalt to rhyolite suites showed that

530   the PGE, particularly Pd, can represent chalcophile element fertilities in evolving magmatic

531   systems (Park et al., 2013; Park et al., 2015). The PGE geochemistry of the Jaguar and Bentley

532   volcanic rocks showed that the andesites, before sulfide saturation, are the most fertile (i.e.,

533   chalcophile element-rich) among the footwall volcanic rocks at Jaguar and Bentley.

534   Furthermore, the footwall andesites are typically amygdaloidal (Belford, 2010), suggesting

535   they are volatile-saturated. Therefore, it is likely that the Jaguar and Bentley ore is formed from

536   a Cu-bearing magmatic-hydrothermal fluid that is exsolved from an underlying magma

537   chamber that fed the andesite magma. The rhyolite is extremely depleted in PGE and, therefore,

538   an unlikely source for Cu. Some dolerites are fertile enough to produce Cu mineralization.

539   However, they postdate the mineralization at both Jaguar and Bentley (Belford et al., 2015).

540   It might be argued that the mantle-like sulfur isotope composition of the Jaguar and Bentley

541   ore sulfide were derived from the footwall volcanic rocks. The total Cu tonnages are 49,600

542    tons for Jaguar and 61,000 tons for Bentley (Hollis et al., 2017). A simple mass balance

543    calculation has been carried out to find the volume of the footwall andesite, the most Cu-rich

544    lithology in this system (average Cu = ~50 ppm), which must be leached by a hydrothermal

545    fluid to produce the observed Cu tonnages. If it is assumed that the leaching and precipitation

546    efficiencies are 40 % and 15 %, respectively, as suggested by Patten et al. (2016; 2017) for

547    SMS systems, the results show that ~ 3.5 km$^3$ and ~4.3 km$^3$ of andesite are required to form

548    the Jaguar and Bentley Cu ores. This shows that most of the footwall units of the Jaguar and

549    Bentley deposits would need to be composed of andesite, to produce a ~5 km$^3$ hydrothermal

550    cell similar in size to those that gave rise to the modern SMS deposits of the Eastern Pacific

551    Rise (Tolstoy et al., 2008). This is not possible for the Bentley. Although the andesites are one

552    of the major footwall units at the Bentley (Parker et al., 2017), the footwall lithology is

553    dominantly composed of Cu-depleted rhyolite (~17 ppm Cu; Table 2) with minor basalt in the

554    Bentley (Parker et al., 2017). Therefore, it is likely that additional Cu from a magmatic fluid

555    exsolved from an underlying magma chamber is necessary to form the Bentley Cu ores unless

556    abnormally efficient leaching and precipitation processes occurred in the source areas.

557

558    Chalcophile element fertility and implications for Au-rich VMS mineralization

559    Early studies of Archean VMS deposits showed that they are typically associated with felsic

560    volcanic rocks with specific geochemical characteristics (Lesher et al., 1986; Lentz, 1998).

561    Hart et al. (2004) reviewed all of the fertility models suggested previously and classified the

562    felsic volcanic rocks as FI, FII, FIII, and FIV types based on La/Yb and Yb concentrations.

563    They suggested that FIII and FIV types of rhyolites often host large VMS deposits (i.e., fertile),

564    FII type can hosts VMS deposits, but is commonly barren, and FI type rhyolites are usually

565    barren. Hart et al. (2004) suggested that the compositional variations between these types result

566    from the combined effects of differences in mineralogy, source composition, and the pressure

567    and temperature at which partial melting takes place. High-temperature melts, produced and

568    emplaced at shallow depths during extension (FIII affinity), are often associated with Archean

569    VMS deposits (Lesher et al., 1986; Hart et al., 2004). In a review of felsic and intermediate

570    volcanic rocks of the Yilgarn Craton, Hollis et al. (2015) found that the VMS-bearing volcanic

571    suites commonly display FII to dominantly FIII characteristics with high HFSE (Y, Zr, Sc)

572    concentrations, slight LREE enrichment ($La_N/Yb_N < 3$), and flat HREE patterns ($Dy_N/Yb_N \sim 1$).

573    Geochemistry of rhyolite and andesite from the Teutonic Bore, Jaguar and Bentley is in line

574    with other VMS-bearing volcanic rocks of the Yilgarn Craton, displaying FII and FIII affinities

575    (Fig. 9) and flattish REE profiles (Fig. 4). Although the magma fertility models based on

576    lithophile trace element geochemistry provide useful information on VMS ore genesis and

577    mineral exploration, they cannot account for variations in Cu and Au grades between different

578    VMS systems.

579    Recent studies on PGE geochemistry of porphyry deposits (Cocker et al., 2015; Hao et al.,

580    2017; 2019 Lowczak et al., 2018; Park et al., 2019) suggested that the PGE contents of volcanic

581    rocks can be used as a Cu and Au prospectivity indicator. They showed that the sub-volcanic

582    or volcanic suites associated with porphyry Cu and Cu-Au deposits are significantly enriched

583    in PGE at a given level of fractional crystallization compared to the barren suites. The PGE

584    contents of the felsic rocks also vary depending on the ore types (Cu-only vs. Cu-Au). The

585    rocks associated with Cu-Au porphyry deposits have higher PGE concentrations at a given

586    MgO content than those associated with Cu-only porphyry deposits. The PGE-depleted barren

587    rocks form from a magma that has undergone prolonged sulfide segregation and lost most of

588    its endowment of Cu, Au, and PGE in the solidifying magma chamber. In contrast, the PGE-

589    enriched fertile rocks crystallize from a magma that has either not experienced sulfide

590    saturation or precipitated a minimal amount of sulfide melt prior to volatile exsolution (Park et

591    al., 2019).

592        Figure 10 shows the volcanic rocks from Jaguar and Bentley plotted on the porphyry Cu±Au

593    fertility diagram proposed by Park et al. (2019) to show the difference between ore-bearing and

594    barren volcanic and intrusive magmatic suites. Pd is normalized by MgO to take into account

595    variations in fractionation, and Pd/Pt is a measure of the amount of fractional crystallization

596    before sulfide saturation (Park et al. 2019). We have also plotted PGE data for volcanic rocks

597    from two modern seafloor Cu-Au SMS deposits at arc-related settings: Pual Ridge

598    (PACMANUS hydrothermal field), Eastern Manus Basin, and the Niuatahi-Motutahi, Tonga

599    rear arc, for comparison (Binns and Scott, 1993; Kim et al., 2011; Berkenbosch et al., 2015;

600    Park et al. 2013b; 2015). The high Au contents in their ores were attributed to a large degree of

601    magmatic-hydrothermal fluid contributions (Moss et al., 2001; Kim et al., 2011; Berkenbosch

602    et al., 2015; Fuchs et al., 2019).

603        The pre-sulfide saturation andesites (< 4 ppm Yb) from the Jaguar and Bentley deposits

604    plot in the Cu-only porphyry field, but the remainder of the samples plot in the barren porphyry

605    field. The volcanic rocks from the Pual Ridge plot mostly in the Cu only field, whereas those

606    from Niuatahi-Motutahi plot mostly in the Cu-Au field but extend into the Cu only field. The

607    systematic depletion of chalcophile element fertility indicators, Pd/MgO and Pd/Pt, in the

608    Jaguar and Bentley rocks compared with the two modern Cu-Au SMS deposits suggests that

609    the Jaguar and Bentley magmas may have undergone sulfide saturation at an earlier stage of

610    differentiation than Pual Ridge and Niuatahi-Motutahi magmas, or that they have originated

611    from chalcophile element depleted sources. We suggest that sulfide saturation in the Jaguar and

612    Bentley magmas occurred before ore formation and that enough sulfide precipitated to deplete

613    the magma in Au but not Cu, because of the lower partition coefficient into immiscible sulfide

614   melts of the latter (Mungall and Brenan, 2014; Li and Audetat, 2015). As a consequence, the

615   Jaguar and Bentley deposits are Cu-rich but contain less Au than Pual Ridge and Niuatahi-

616   Motutahi. Bentley, for example, contains 0.7 g/t Au in the VMS ores (Hollis et al., 2017)

617   whereas Au grades are 10 g/t in Pual Ridge (PACMANUS; Fuchs et al., 2019) and 14 g/t in

618   Niuatahi-Motutahi (also known as Volcano O and MTJ; Fuchs et al., 2019). The Au grade of

619   0.7 g/t for the Bentley ore is at the lower end of the range of Au grades (0.24 to 6.2 g/t Au) for

620   the Archean VMS deposits in the Yilgarn Craton (Hollis et al., 2017).

621   Although the fertility diagram (Fig. 10), based on studies of porphyry deposits, generally

622   match well with the SMS and VMS systems, care needs to be taken for its application because,

623   unlike the porphyry system where metals are dominantly sourced from a magma, some portion

624   of the ore metals are thought to be leached from country rocks below the VMS deposits.

625   Furthermore, this method cannot be applied for Pb and Zn deposits because Pb and Zn are only

626   moderately chalcophile and not significantly influenced by sulfide saturation during magma

627   differentiation.

628

629   **Conclusions**

630   The trace element and PGE geochemistry of basalt, andesite, and rhyolites from the footwall

631   of the Jaguar and footwall and hanging-wall of the Bentley are similar to each other. Their

632   compositions are comparable to those of Phanerozoic calc-alkaline island arc volcanic rocks,

633   showing fractionated primitive mantle normalized trace element patterns with marked negative

634   Nb and Ti anomalies. Their geochemical similarity, together with the close temporal and spatial

635   relationship, suggests their comagmatic origin. The geochemical variations in trace elements

636   from basalt through andesite to rhyolite can be accounted for by fractional crystallization.

Sulfide saturation occurred late in the evolution of the andesite magma with magnetite crystallization as a likely trigger. The rhyolites are extremely depleted in all PGEs. The dolerites are geochemically distinct from the other rock types and show typical sulfide saturated magma differentiation from the early stage of magma evolution. The least evolved dolerites are fertile, but they cannot be related to the ore formation because they post-date the mineralization.

The PGE data of the Jaguar and Bentley volcanic rocks suggest that Cu in the ore sulfide was principally formed from a magmatic fluid exsolved from the andesite magma shortly after sulfide saturation. The chalcophile element fertility of the Jaguar and Bentley magma is significantly lower than that of volcanic rocks associated with Cu-Au SMS deposits, which is consistent with Cu-Zn mineralization in the Jaguar and Bentley VMS deposits. These results suggest chalcophile element fertility may play an important role in the formation of the ancient VMS and modern SMS deposits, particularly with respect to Au grade when the magmatic-hydrothermal component is the dominant source for metals in VMS systems.

Acknowledgment

665    Figure captions

666    Figure 1. a) Large scale tectonic segments of the Yilgarn craton with locations of Teutonic Bore,
667    Jaguar, and Bentley VMS deposits (modified from Belford, 2010). b) Regional geology map
668    of the Teutonic Bore volcanic complex, Western Australia produced by Max Frater and
669    geologists of Independence Group NL. Solid lines represent faults.

670    Figure 2. Simplified drill hole logs of Jaguar (13JUDD002, 12 JADD002) and Bentley
671    (09BTDD029, 09BTDD025) VMS deposits based on the core logs of Independence Group NL
672    geologists.

673    Figure 3. Primitive mantle normalized incompatible trace element diagrams for the Jaguar and
674    Bentley rhyolite/Dacite (a), andesite (b), basalt (c), and dolerite (d). Phanerozoic island arc
675    fields are from Barnes and Van Kranendonk (2014). Primitive mantle values are from
676    McDonough and Sun (1995).

677    Figure 4. Chondrite-normalized REE variation diagrams for a) rhyolite, b) andesite, c) basalt,
678    d) dolerite from Jaguar and Bentley. Dark and light gray fields represent the patterns of volcanic
679    rocks from Jaguar reported by Belford (2010).

680    Figure 5. Binary plots of a) La, b) Zr, c) Cr, d) Ni, e) Ti, and f) V against Yb concentrations for
681    the Jaguar and Bentley volcanic rocks. Yb concentration is a measure of the degree of
682    fractionation crystallization. Solid (FC1) and dashed lines (FC2) are fractional crystallization
683    models. FC1 represents fractional crystallization trends for plagioclase + clinopyroxene + Cr-
684    spinel (50:49:1) with the initial concentrations of a basalt (sample 44907). FC2 represents
685    trends for plagioclase + clinopyroxene + magnetite (50:35:15) with an immiscible sulfide liquid
686    fraction of 0.1 wt.%. The initial concentrations for FC2 are set as melt composition after 43%
687    fractional crystallization of FC1. Thin crosses on the model curves show 10% fractional
688    crystallization intervals. Partition coefficients used are given in ESM Table 3.

689    Figure 6. Binary plots of a) Pd, b) Rh, c) Pt, d) Ru, e) Ir, and f) Cu against Yb, as a fractionation
690    index. Solid (FC1) and dashed lines (FC2) are fractional crystallization models. FC1 displays
691    fractional crystallization trends for plagioclase + clinopyroxene + Cr-spinel (50:49:1). The
692    compositions of a basalt (sample 44907) are set as the initial concentrations for all elements
693    except Pd and Rh for which the compositions of andesite sample 44619 are used. FC2 shows
694    trends for plagioclase + clinopyroxene + magnetite (50:35:15) with an immiscible sulfide liquid
695    fraction of 0.1 wt.%. The melt compositions after 43% fractional crystallization of FC1 are
696    used as initial concentrations for FC2. Thin crosses on the curves show 10% fractional
697    crystallization intervals. Partition coefficients used are given in ESM Table 3. Dotted lines
698    represent the method detection limit for PGEs.

699    Figure 7. Primitive mantle normalized PGE and Re patterns. The arc andesite field is from Park
700    et al. (2013) (Sample MD53a, MD53b, MD7 with MgO ranging from 1.7 to 3.0 wt.%). Dotted
701    lines represent the method detection limit for PGEs.

702 Figure 8. An alteration box plot for Jaguar and Bentley volcanic rocks. Fields of least altered
703 felsic, intermediate, and mafic rocks are from the Rosebery, Que River, and Hellyer areas of
704 the Mount Read volcanics (Large et al., 2001 and references therein)

705 Figure 9. A chondrite-normalized plot of Yb vs. La/Yb. The fields of each rhyolite type are
706 from Hart et al. (2004). The data of volcanic rocks associated with Golden Grove, Hollandaire,
707 Quinns Archean VMS deposits in the Yuanmi terrane are from Hollis et al. (2015) and
708 references therein.

709 Figure 10. Binary plots of Pd/MgO vs. Pd/Pt. The fields for barren porphyries, Cu porphyries,
710 Cu-Au porphyries are from Park et al. (2019).

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Table

Table 1. Whole-rock major element composition of the Jaguar and Bentley volcanic rocks by XRF (wt.%)

| Samples | Core No. | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | FeO | MnO | $K_2O$ | CaO | $TiO_2$ | $P_2O_5$ | Total | LOI | $SO_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Recalculated compositions on a volatile-free basis* | | | | | | | | | | | | | | |
| *Rhyolite* | | | | | | | | | | | | | | |
| JB Rhy-02 | 13TRDD014 | 0.86 | 1.20 | 10.5 | 81.7 | 2.0 | 0.04 | 1.63 | 1.89 | 0.17 | 0.02 | 100 | 4.06 | 0.03 |
| JB 44681 | 13JUDD002 | 0.31 | 1.89 | 10.5 | 76.9 | 4.1 | 0.06 | 5.05 | 1.03 | 0.15 | 0.02 | 100 | 2.26 | b.d.l. |
| JB 44913 | 09BTDD025 | 0.30 | 2.10 | 10.9 | 76.5 | 4.6 | 0.11 | 2.33 | 2.86 | 0.22 | 0.02 | 100 | 5.48 | 0.47 |
| JB 44922 | 09BTDD025 | 0.18 | 2.88 | 10.9 | 78.0 | 5.5 | 0.05 | 2.23 | 0.04 | 0.17 | 0.02 | 100 | 4.13 | 0.22 |
| JB dac-01 | 12TRDD016 | 1.48 | 4.33 | 15.2 | 60.7 | 8.3 | 0.10 | 3.22 | 5.27 | 1.14 | 0.24 | 100 | 4.79 | b.d.l. |
| *Andesite* | | | | | | | | | | | | | | |
| JB 44663 | 13JUDD002 | 4.96 | 6.39 | 16.7 | 57.2 | 8.1 | 0.12 | 0.34 | 5.30 | 0.79 | 0.15 | 100 | 6.28 | 0.02 |
| JB 44665 | 13JUDD002 | 2.81 | 6.24 | 16.8 | 56.4 | 7.9 | 0.16 | 0.89 | 7.85 | 0.77 | 0.15 | 100 | 3.64 | 0.02 |
| JB 44640 | 09BTDD029 | 3.22 | 1.31 | 14.2 | 68.1 | 5.7 | 0.19 | 1.64 | 4.62 | 0.77 | 0.25 | 100 | 4.97 | 0.01 |
| JB 44904 | 09BTDD025 | 4.33 | 0.93 | 16.2 | 63.7 | 4.3 | 0.22 | 1.99 | 7.24 | 0.90 | 0.28 | 100 | 6.57 | 0.03 |
| JB 44906 | 09BTDD025 | 0.52 | 2.61 | 12.8 | 71.9 | 6.8 | 0.09 | 2.17 | 1.84 | 0.93 | 0.35 | 100 | 3.55 | 0.37 |
| JB 44613 | 09BTDD029 | 5.82 | 5.30 | 16.1 | 58.7 | 6.8 | 0.13 | 0.05 | 5.53 | 1.25 | 0.30 | 100 | 5.51 | 0.11 |
| JB 44616 | 09BTDD029 | 3.82 | 5.59 | 15.8 | 58.6 | 7.4 | 0.13 | 0.98 | 6.27 | 1.18 | 0.29 | 100 | 6.48 | 0.13 |
| JB and-01 | 12TRDD016 | 1.31 | 1.37 | 12.7 | 75.5 | 4.3 | 0.05 | 2.86 | 1.58 | 0.35 | 0.08 | 100 | 10.7 | 0.35 |
| JB and-02 | 13TRDD009 | 1.45 | 2.82 | 15.0 | 64.2 | 7.3 | 0.09 | 2.78 | 5.28 | 0.96 | 0.21 | 100 | 8.58 | 0.14 |
| JB and-03 | 13TRDD009 | 2.29 | 2.80 | 14.7 | 66.0 | 6.2 | 0.07 | 2.43 | 4.42 | 0.90 | 0.19 | 100 | 7.46 | 0.19 |
| *Basalt* | | | | | | | | | | | | | | |
| JB 44677 | 13JUDD002 | 0.05 | 1.73 | 13.6 | 63.2 | 10.2 | 0.43 | 3.33 | 5.47 | 1.67 | 0.28 | 100 | 6.11 | 0.39 |
| JB 44696 | 12JADD002 | 4.65 | 2.67 | 15.2 | 57.7 | 9.3 | 0.26 | 1.43 | 6.65 | 1.91 | 0.29 | 100 | 5.25 | 0.13 |
| JB 44907 | 09BTDD025 | 2.10 | 2.53 | 15.6 | 57.1 | 4.9 | 0.22 | 2.12 | 13.99 | 1.17 | 0.25 | 100 | 11.7 | 0.26 |
| *Dolerite* | | | | | | | | | | | | | | |
| JB 44672 | 13JUDD002 | 2.47 | 4.53 | 13.1 | 52.1 | 16.5 | 0.26 | 0.51 | 8.54 | 1.84 | 0.13 | 100 | 2.31 | 0.53 |
| JB 44673 | 13JUDD002 | 1.76 | 7.90 | 14.8 | 50.9 | 11.2 | 0.21 | 0.07 | 12.14 | 0.87 | 0.08 | 100 | 2.27 | 0.13 |
| JB 44605 | 09BTDD029 | 2.25 | 7.21 | 13.8 | 55.2 | 11.9 | 0.17 | 0.19 | 7.97 | 1.16 | 0.12 | 100 | 4.60 | 0.07 |
| JB Dol-01 | 09TRDD032 | 0.35 | 5.15 | 18.5 | 52.3 | 11.3 | 0.28 | 4.25 | 6.60 | 1.06 | 0.10 | 100 | 7.22 | 2.37 |
| JB Dol-02 | 13TRDD001 | 0.40 | 3.58 | 16.0 | 55.3 | 18.5 | 0.11 | 1.67 | 3.48 | 0.86 | 0.08 | 100 | 11.9 | 0.42 |

b.d.l., below detection limit

Table 2. Whole-rock trace element composition of the Jaguar and Bentley volcanic rocks by LA-ICP-MS (ppm)

| Lithology | Rhyolite | | | | | Dacite | Andesite | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | FW | FW | FW | MP | FW | FW | MP | MP | HW | HW | HW | HW | HW | HW | FW | FW | FW |
| Deposit | Teutonic Bore | Jaguar | Jaguar | Bentley | Bentley | Bentley | Jaguar | Jaguar | Bentley | Bentley | Bentley | Bentley | Bentley | Bentley | Bentley | Bentley | Bentley |
| Sample No. | JB Rhy-02 | JB 44681 | JB 44699 | JB 44913 | JB 44922 | JB dac-01 | JB 44663 | JB 44665 | JB 44640 | JB 44904 | JB 44906 | JB 44613 | JB 44619 | JB 44616 | JB And-01 | JB And-02 | JB And-03 |
| Sc | 7.9 | 8.3 | 6.3 | 11.4 | 8.8 | 12.2 | 28.5 | 27.9 | 18.7 | 20.4 | 16.2 | 33.2 | n.a. | 32.6 | 27.0 | 23.8 | 21.4 |
| Ti | 973 | 841 | 1063 | 1177 | 967 | 2385 | 4973 | 4580 | 4671 | 5409 | 5381 | 7257 | 6109 | 6617 | 7710 | 6531 | 6068 |
| V | 4.8 | 4.1 | 3.0 | 4.6 | 4.4 | 12.7 | 160 | 152 | 20.8 | 23.5 | 51.4 | 201 | n.a. | 197 | 169 | 150 | 118 |
| Cr | 4.9 | 4.8 | 7.0 | 5.7 | 4.3 | 9.0 | 142.9 | 143.1 | 7.8 | 6.2 | 5.2 | 91.6 | n.a. | 120.1 | 78.4 | 26.8 | 22.5 |
| Mn | 330 | 436 | 247 | 742 | 399 | 382 | 994 | 1157 | 1405 | 1592 | 695 | 936 | n.a. | 981 | 752 | 692 | 524 |
| Co | 8.1 | 12.8 | 0.4 | 10.6 | 15.3 | 1.5 | 38.8 | 36.9 | 13.9 | 11.6 | 16.1 | 35.8 | n.a. | 39.0 | 28.6 | 20.0 | 12.6 |
| Ni | 5.6 | 4.0 | 6.9 | 7.7 | 5.9 | 4.2 | 109.8 | 104.0 | 7.5 | 6.4 | 9.2 | 56.4 | n.a. | 84.9 | 46.4 | 35.6 | 21.7 |
| Cu | 14.6 | 5.2 | 24.8 | 12.0 | 34.1 | 14.5 | 55.3 | 52.9 | 15.1 | 75.7 | 55.2 | 42.9 | n.a. | 61.7 | 58.8 | 72.7 | 8.0 |
| Zn | 29 | 53 | 19 | 153 | 144 | 83 | 66 | 72 | 85 | 164 | 65 | 89 | n.a. | 87 | 83 | 64 | 49 |
| Rb | 44.5 | 52.3 | 63.3 | 38.6 | 50.7 | 66.3 | 13.7 | 24.4 | 34.3 | 38.8 | 64.6 | 0.9 | n.a. | 21.0 | 72.3 | 68.3 | 60.7 |
| Sr | 87.7 | 44.5 | 20.9 | 31.5 | 9.2 | 79.7 | 170.4 | 233.5 | 98.4 | 168.1 | 73.3 | 199.2 | n.a. | 149.2 | 153.5 | 103.7 | 92.7 |
| Y | 56.3 | 54.2 | 39.5 | 42.3 | 47.3 | 46.2 | 20.2 | 18.4 | 43.1 | 45.0 | 36.7 | 34.6 | 27.3 | 29.9 | 38.6 | 39.0 | 42.0 |
| Zr | 348 | 275 | 349 | 339 | 316 | 395 | 138 | 129 | 278 | 322 | 215 | 191 | 154 | 173 | 261 | 251 | 255 |
| Nb | 17.3 | 12.1 | 15.7 | 14.3 | 14.5 | 17.2 | 8.5 | 7.6 | 11.5 | 13.4 | 9.5 | 9.7 | 7.6 | 9.4 | 11.7 | 11.6 | 12.2 |
| Cs | 2.39 | 1.39 | 0.86 | 1.16 | 1.30 | 3.86 | 0.49 | 0.44 | 1.43 | 1.59 | 1.87 | 0.70 | n.a. | 3.49 | 3.61 | 6.32 | 6.20 |
| Ba | 289 | 1159 | 1496 | 218 | 280 | 346 | 165 | 210 | 183 | 301 | 519 | 88 | n.a. | 297 | 396 | 463 | 440 |
| La | 36.0 | 34.0 | 38.1 | 30.1 | 30.6 | 34.0 | 17.6 | 15.6 | 24.2 | 30.2 | 21.0 | 16.3 | 15.0 | 17.4 | 21.3 | 21.6 | 24.3 |
| Ce | 80.1 | 74.2 | 83.1 | 64.1 | 71.2 | 77.0 | 34.1 | 30.9 | 54.3 | 64.5 | 48.4 | 39.4 | 35.2 | 38.8 | 49.3 | 50.7 | 55.4 |
| Pr | 9.98 | 8.98 | 10.02 | 7.75 | 8.88 | 9.56 | 4.09 | 3.68 | 7.10 | 8.24 | 6.38 | 5.38 | 4.52 | 5.02 | 6.36 | 6.53 | 6.95 |
| Nd | 41.5 | 36.3 | 39.8 | 31.1 | 36.3 | 39.9 | 16.7 | 14.9 | 30.2 | 34.8 | 27.7 | 24.1 | 20.6 | 21.9 | 27.6 | 27.8 | 29.6 |
| Sm | 9.09 | 8.05 | 8.39 | 6.65 | 7.70 | 8.62 | 3.59 | 3.24 | 7.04 | 8.00 | 6.57 | 5.67 | 4.81 | 5.09 | 6.44 | 6.42 | 6.67 |
| Eu | 1.79 | 1.69 | 1.72 | 1.36 | 0.97 | 1.56 | 1.07 | 1.07 | 1.69 | 2.12 | 1.42 | 1.50 | 1.49 | 1.42 | 1.56 | 1.55 | 1.47 |
| Gd | 9.22 | 8.56 | 8.42 | 6.74 | 7.79 | 8.03 | 3.56 | 3.30 | 7.42 | 8.20 | 6.65 | 6.23 | 4.95 | 5.40 | 6.54 | 6.67 | 6.60 |
| Tb | 1.40 | 1.45 | 1.29 | 1.13 | 1.27 | 1.27 | 0.55 | 0.52 | 1.15 | 1.27 | 1.02 | 0.96 | 0.79 | 0.83 | 1.07 | 1.10 | 1.07 |
| Dy | 9.42 | 9.64 | 8.05 | 7.64 | 8.24 | 8.16 | 3.53 | 3.28 | 7.70 | 8.25 | 6.58 | 6.18 | 4.90 | 5.33 | 6.86 | 6.84 | 6.91 |
| Ho | 2.00 | 2.02 | 1.58 | 1.61 | 1.72 | 1.74 | 0.76 | 0.67 | 1.60 | 1.69 | 1.33 | 1.28 | 1.04 | 1.09 | 1.46 | 1.47 | 1.51 |
| Er | 6.27 | 6.04 | 4.68 | 5.02 | 5.16 | 5.21 | 2.22 | 2.06 | 4.71 | 5.04 | 3.85 | 3.77 | 2.75 | 3.21 | 4.25 | 4.29 | 4.36 |
| Tm | 0.92 | 0.88 | 0.67 | 0.71 | 0.77 | 0.77 | 0.31 | 0.28 | 0.68 | 0.73 | 0.56 | 0.52 | 0.41 | 0.47 | 0.61 | 0.63 | 0.64 |
| Yb | 6.35 | 5.69 | 4.46 | 5.04 | 5.37 | 5.45 | 2.19 | 1.90 | 4.59 | 4.91 | 3.61 | 3.41 | 2.80 | 3.16 | 4.30 | 4.32 | 4.37 |
| Lu | 0.96 | 0.87 | 0.66 | 0.76 | 0.83 | 0.82 | 0.33 | 0.31 | 0.73 | 0.72 | 0.56 | 0.52 | 0.42 | 0.47 | 0.62 | 0.66 | 0.64 |
| Hf | 9.61 | 7.64 | 9.66 | 9.14 | 8.78 | 10.84 | 3.58 | 3.26 | 7.36 | 8.32 | 5.71 | 4.62 | n.a. | 4.33 | 6.54 | 6.49 | 6.71 |
| Ta | 1.37 | 1.36 | 1.05 | 1.25 | 1.69 | 1.05 | 0.81 | 0.85 | 1.03 | 1.11 | 0.88 | 0.83 | n.a. | 0.76 | 0.67 | 0.75 | 0.76 |
| Pb | 3.49 | 3.12 | 2.95 | 68.95 | 82.08 | 4.38 | 1.80 | 2.33 | 3.80 | 3.48 | 3.71 | 1.25 | n.a. | 1.36 | 7.17 | 3.27 | 2.81 |
| Th | 5.26 | 5.21 | 6.06 | 5.15 | 5.67 | 4.97 | 2.03 | 1.89 | 3.63 | 4.20 | 2.87 | 1.23 | n.a. | 1.58 | 2.64 | 3.08 | 3.33 |
| U | 1.34 | 1.27 | 1.48 | 1.23 | 1.41 | 0.53 | 0.48 | 0.43 | 0.91 | 1.10 | 0.71 | 0.33 | n.a. | 0.40 | 0.67 | 0.85 | 0.78 |
| Ti/Zr | 3 | 3 | 3 | 3 | 3 | 6 | 36 | 36 | 17 | 17 | 25 | 38 | n.a. | 38 | 30 | 26 | 24 |
| Zr/Y | 6.2 | 5.1 | 8.8 | 8.0 | 6.7 | 8.6 | 6.9 | 7.0 | 6.5 | 7.2 | 5.9 | 5.5 | n.a. | 5.8 | 6.8 | 6.4 | 6.1 |

n.a. = not analyzed

Table 2. Continued.

| Lithology | Basalt | | | | Dolerite | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | FW | FW | FW | HW | FW | FW | FW | HW | FW | HW | HW | HW | HW | FW | FW | | | |
| | Jaguar | Jaguar | Jaguar | Bentley | Jaguar | Jaguar | Jaguar | Jaguar | Jaguar | Bentley | Bentley | Bentley | Bentley | Bentley | Bentley | | | |
| Elements | JB 44675 | JB 44677 | JB 44696 | JB 44907 | JB 44667 | JB 44672 | JB 44673 | JB 44686 | JB 44703 | JB 44605 | JB 44643 | JB 44908 | JB 44912 | JB Dol-01 | JB Dol-02 | BCR 2g (n=7) | σ | Jochum et al (2011) |
| Sc | 30.2 | 27.7 | 31.9 | 34.4 | n.a. | 50.6 | 55.4 | 50.2 | 52.5 | 44.0 | 50.7 | 41.2 | 52.1 | 61.9 | 53.3 | 35.0 | 0.8 | 33.0 |
| Ti | 10646 | 9632 | 11730 | 7175 | 6097 | 11966 | 5589 | 6916 | 7138 | 7139 | 6735 | 6683 | 6628 | 7209 | 5930 | 13290 | 259 | 14100 |
| V | 255 | 232 | 299 | 202 | n.a. | 595 | 306 | 302 | 329 | 299 | 286 | 280 | 317 | 368 | 312 | 418 | 8.2 | 425 |
| Cr | 5.3 | 5.3 | 4.7 | 190.9 | n.a. | 12.9 | 157.2 | 28.4 | 30.9 | 16.7 | 26.8 | 15.6 | 50.2 | 220.7 | 190.0 | 14.5 | 0.8 | 17 |
| Mn | 1956 | 3085 | 1953 | 1589 | n.a. | 2147 | 1609 | 1967 | 1825 | 1277 | 1236 | 1196 | 1575 | 2168 | 875 | 1478.4 | 14.6 | 1550 |
| Co | 38.2 | 40.0 | 41.1 | 32.2 | n.a. | 70.9 | 59.0 | 57.0 | 59.2 | 49.6 | 57.8 | 46.5 | 53.8 | 48.1 | 42.0 | 36.8 | 0.8 | 38 |
| Ni | 7.9 | 9.2 | 10.9 | 79.5 | n.a. | 41.7 | 104.3 | 60.2 | 64.4 | 41.3 | 60.8 | 38.7 | 69.5 | 68.7 | 75.5 | 11.6 | 0.8 | 13 |
| Cu | 46.1 | 157.0 | 131.6 | 68.0 | n.a. | 185.6 | 195.3 | 103.2 | 128.9 | 132.0 | 124.9 | 123.6 | 112.2 | 112.9 | 141.0 | 17.7 | 0.9 | 21 |
| Zn | 758 | 379 | 117 | 58 | n.a. | 143 | 88 | 76 | 200 | 76 | 77 | 71 | 86 | 95 | 355 | 157 | 3.2 | 125 |
| Rb | 15.5 | 58.6 | 26.8 | 46.2 | n.a. | 36.2 | 1.2 | 2.8 | 42.9 | 3.0 | 0.2 | 2.8 | 0.1 | 117.7 | 41.0 | 49 | 1.2 | 47 |
| Sr | 100.1 | 40.6 | 139.8 | 135.7 | n.a. | 159.5 | 174.1 | 150.2 | 141.4 | 236.1 | 276.0 | 221.0 | 206.0 | 72.2 | 74.8 | 341.4 | 7.3 | 342 |
| Y | 40.3 | 42.7 | 42.8 | 26.5 | 21.3 | 39.5 | 20.7 | 29.9 | 28.5 | 29.1 | 28.3 | 27.2 | 27.7 | 23.2 | 15.8 | 32.7 | 0.9 | 35.0 |
| Zr | 211 | 185 | 218 | 136 | 70 | 124 | 56 | 97 | 96 | 102 | 97 | 95 | 86 | 74 | 77 | 176 | 4 | 184 |
| Nb | 9.9 | 8.6 | 10.1 | 7.9 | 2.9 | 5.1 | 2.4 | 4.1 | 3.9 | 4.3 | 4.1 | 4.0 | 3.7 | 3.0 | 3.1 | 11.9 | 0.3 | 12.5 |
| Cs | 0.29 | 0.77 | 0.45 | 1.57 | n.a. | 16.87 | 0.23 | 0.16 | 7.05 | 1.21 | 0.28 | 1.13 | 0.16 | 3.05 | 1.08 | 1.15 | 0.1 | 1.16 |
| Ba | 492 | 489 | 568 | 321 | n.a. | 135 | 22 | 56 | 338 | 39 | 30 | 36 | 8 | 589 | 469 | 684 | 15 | 683 |
| La | 20.4 | 19.0 | 21.2 | 14.3 | 5.3 | 7.8 | 3.6 | 6.7 | 6.5 | 7.2 | 6.3 | 6.7 | 5.3 | 4.7 | 4.3 | 25.1 | 0.7 | 24.7 |
| Ce | 47.3 | 43.2 | 48.3 | 32.6 | 13.2 | 19.3 | 9.1 | 16.3 | 15.9 | 17.6 | 15.6 | 16.5 | 13.7 | 11.4 | 10.6 | 52.1 | 0.8 | 53.3 |
| Pr | 6.34 | 5.78 | 6.57 | 4.55 | 1.84 | 2.93 | 1.44 | 2.39 | 2.39 | 2.55 | 2.34 | 2.38 | 2.09 | 1.59 | 1.53 | 6.61 | 0.2 | 6.70 |
| Nd | 28.1 | 25.9 | 29.1 | 20.2 | 9.4 | 14.9 | 7.4 | 11.8 | 11.7 | 12.3 | 11.7 | 11.5 | 10.7 | 7.4 | 7.6 | 28.0 | 0.8 | 28.9 |
| Sm | 6.63 | 6.28 | 6.79 | 4.81 | 2.78 | 4.53 | 2.38 | 3.54 | 3.47 | 3.75 | 3.58 | 3.51 | 3.20 | 2.34 | 2.46 | 6.51 | 0.1 | 6.59 |
| Eu | 1.73 | 3.26 | 1.89 | 1.62 | 0.99 | 1.53 | 0.85 | 1.12 | 1.25 | 1.08 | 1.09 | 1.01 | 1.09 | 0.62 | 0.46 | 1.94 | 0.1 | 1.97 |
| Gd | 6.86 | 6.92 | 7.40 | 5.05 | 3.40 | 5.88 | 3.00 | 4.55 | 4.33 | 4.42 | 4.37 | 4.14 | 4.11 | 3.24 | 2.82 | 6.46 | 0.2 | 6.71 |
| Tb | 1.13 | 1.12 | 1.15 | 0.75 | 0.59 | 1.01 | 0.53 | 0.77 | 0.75 | 0.78 | 0.74 | 0.73 | 0.72 | 0.59 | 0.46 | 0.98 | 0.0 | 1.02 |
| Dy | 7.17 | 7.55 | 7.63 | 4.94 | 3.84 | 6.99 | 3.71 | 5.22 | 5.17 | 5.33 | 4.98 | 4.99 | 4.91 | 4.11 | 2.88 | 6.14 | 0.2 | 6.44 |
| Ho | 1.51 | 1.55 | 1.55 | 0.99 | 0.82 | 1.46 | 0.78 | 1.13 | 1.09 | 1.11 | 1.05 | 1.03 | 1.04 | 0.88 | 0.64 | 1.24 | 0.0 | 1.27 |
| Er | 4.51 | 4.58 | 4.72 | 2.87 | 2.36 | 4.47 | 2.41 | 3.41 | 3.23 | 3.33 | 3.23 | 3.12 | 3.19 | 2.62 | 1.95 | 3.54 | 0.1 | 3.70 |
| Tm | 0.65 | 0.65 | 0.65 | 0.38 | 0.34 | 0.63 | 0.33 | 0.48 | 0.46 | 0.45 | 0.45 | 0.42 | 0.46 | 0.39 | 0.30 | 0.49 | 0.0 | 0.51 |
| Yb | 4.19 | 4.48 | 4.41 | 2.68 | 2.46 | 4.26 | 2.21 | 3.19 | 3.14 | 3.11 | 3.06 | 2.91 | 2.97 | 2.73 | 2.19 | 3.23 | 0.1 | 3.39 |
| Lu | 0.64 | 0.66 | 0.65 | 0.39 | 0.36 | 0.64 | 0.34 | 0.50 | 0.49 | 0.48 | 0.47 | 0.45 | 0.47 | 0.41 | 0.33 | 0.48 | 0.0 | 0.50 |
| Hf | 5.70 | 4.96 | 5.84 | 3.42 | n.a. | 3.60 | 1.70 | 2.75 | 2.68 | 2.93 | 2.84 | 2.75 | 2.44 | 2.21 | 2.08 | 4.74 | 0.2 | 4.84 |
| Ta | 1.06 | 0.62 | 0.74 | 0.53 | n.a. | 0.61 | 0.43 | 0.46 | 0.40 | 0.41 | 0.52 | 0.39 | 0.38 | 0.18 | 0.19 | 0.73 | 0.0 | 0.78 |
| Pb | 6.73 | 3.46 | 3.15 | 3.63 | n.a. | 2.97 | 2.58 | 1.09 | 3.48 | 1.26 | 0.89 | 1.18 | 6.57 | 13.57 | 5.68 | 11.05 | 0.9 | 11.00 |
| Th | 2.48 | 2.17 | 2.56 | 0.92 | n.a. | 0.66 | 0.31 | 0.73 | 0.64 | 0.73 | 0.61 | 0.69 | 0.52 | 0.42 | 0.55 | 5.86 | 0.2 | 5.90 |
| U | 0.64 | 0.57 | 0.62 | 0.25 | n.a. | 0.15 | 0.07 | 0.19 | 0.15 | 0.19 | 0.17 | 0.18 | 0.12 | 0.12 | 0.14 | 1.68 | 0.0 | 1.69 |
| Ti/Zr | 50 | 52 | 54 | 53 | 88 | 97 | 99 | 72 | 75 | 70 | 70 | 70 | 77 | 97 | 77 | | | |
| Zr/Y | 5.2 | 4.3 | 5.1 | 5.1 | 3.3 | 3.1 | 2.7 | 3.2 | 3.4 | 3.5 | 3.4 | 3.5 | 3.1 | 3.2 | 4.9 | | | |

n.a. = not analyzed

Table 3. Platinum-group element composition of the Jaguar and Bentley volcanic rocks (ppb)

| Sample | Ir (ppb) | ρ | Ru (ppb) | ρ | Rh (ppb) | ρ | Pt (ppb) | ρ | Pd (ppb) | ρ | Re (ppb) | ρ | Pd/MgO x $10^9$ | Pd/Pt |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Rhyolite/Dacite* | | | | | | | | | | | | | | |
| JB 44699 | 0.005 | 0.0002 | <0.001 | | 0.001 | 0.0002 | 0.332 | 0.005 | <0.008 | | 0.01 | 0.00 | | |
| JB 44913 | <0.0002 | | <0.001 | | <0.0003 | | <0.004 | | <0.008 | | <0.008 | | | |
| JB 44922 | <0.0002 | | <0.001 | | <0.0003 | | 0.005 | 0.002 | <0.008 | | <0.008 | | <0.003 | <1.4 |
| JB Dac-01 | 0.0002 | 0.0001 | 0.001 | 0.000 | 0.001 | 0.0001 | 0.044 | 0.002 | 0.008 | 0.003 | 0.47 | 0.01 | 0.002 | 0.19 |
| *Andesite* | | | | | | | | | | | | | | |
| JB 44663 | 0.014 | 0.0006 | 0.026 | 0.001 | 0.037 | 0.001 | 0.698 | 0.010 | 1.04 | 0.02 | 0.29 | 0.01 | 0.16 | 1.5 |
| JB 44665 | 0.008 | 0.0002 | 0.046 | 0.002 | 0.036 | 0.0005 | 0.600 | 0.010 | 0.820 | 0.006 | 0.34 | 0.01 | 0.13 | 1.4 |
| JB 44640 | <0.0002 | | <0.001 | | <0.0003 | | <0.004 | 0.002 | 0.010 | 0.003 | 0.07 | 0.00 | | |
| JB 44904 | <0.0002 | | <0.001 | | <0.0003 | | <0.004 | 0.002 | <0.008 | | 0.12 | 0.01 | | |
| JB 44906 | <0.0002 | | <0.001 | | <0.0003 | | <0.004 | 0.002 | <0.008 | | 0.93 | 0.01 | | |
| JB 44613 | 0.012 | 0.0003 | 0.024 | 0.002 | 0.058 | 0.002 | 0.783 | 0.020 | 1.25 | 0.03 | 0.83 | 0.02 | 0.24 | 1.6 |
| JB 44616 | 0.011 | 0.0007 | 0.014 | 0.001 | 0.057 | 0.001 | 0.759 | 0.006 | 1.12 | 0.01 | 0.70 | 0.01 | | |
| JB 44619 | 0.012 | 0.0004 | 0.027 | 0.001 | 0.065 | 0.001 | 0.800 | 0.018 | 1.14 | 0.03 | 0.53 | 0.02 | 0.20 | 1.5 |
| JB And-01 | 0.000 | 0.0001 | 0.002 | 0.001 | 0.001 | 0.0001 | 0.011 | 0.002 | 0.003 | 0.003 | 0.00 | 0.00 | 0.006 | 0.72 |
| JB And-02 | 0.005 | 0.0001 | 0.012 | 0.001 | 0.012 | 0.0004 | 0.359 | 0.005 | 0.052 | 0.004 | 0.32 | 0.01 | 0.018 | 0.14 |
| JB And-03 | 0.004 | 0.0003 | 0.004 | 0.001 | 0.008 | 0.0003 | 0.274 | 0.008 | 0.058 | 0.004 | 0.20 | 0.01 | 0.021 | 0.21 |
| *Basalt* | | | | | | | | | | | | | | |
| JB 44677 | <0.0002 | | <0.001 | | <0.0003 | | 0.003 | 0.002 | <0.008 | | 0.87 | 0.01 | | |
| JB 44696 | <0.0002 | | <0.001 | | <0.0003 | | 0.012 | 0.002 | <0.008 | | 1.11 | 0.02 | <0.003 | <0.65 |
| JB 44907 | 0.010 | 0.0003 | 0.021 | 0.001 | 0.014 | 0.0005 | 0.476 | 0.005 | 0.083 | 0.004 | 0.56 | 0.01 | 0.033 | 0.17 |
| *Dolerite* | | | | | | | | | | | | | | |
| JB 44667 | 0.101 | 0.0021 | 0.028 | 0.002 | 0.310 | 0.007 | 8.27 | 0.192 | 5.029 | 0.074 | 1.11 | 0.03 | | |
| JB 44672 | <0.0002 | | <0.001 | | <0.0003 | | <0.004 | | <0.008 | | 1.68 | 0.02 | | |
| JB 44673 | 0.050 | 0.0012 | 0.018 | 0.001 | 0.065 | 0.001 | 5.78 | 0.061 | 1.92 | 0.02 | 1.10 | 0.01 | 0.24 | 0.3 |
| JB 44605 | 0.013 | 0.0005 | 0.002 | 0.001 | 0.028 | 0.001 | 1.82 | 0.029 | 0.55 | 0.01 | 1.76 | 0.02 | 0.08 | 0.3 |
| JB Dol-02 | 0.124 | 0.0011 | 0.034 | 0.001 | 0.630 | 0.009 | 9.76 | 0.109 | 12.5 | 0.2 | 0.29 | 0.01 | 3.50 | 1.3 |
| *TDB-1 (CANMET dolerite reference material)* | | | | | | | | | | | | | | |
| #1 | 0.098 | 0.001 | 0.183 | 0.005 | 0.445 | 0.003 | 4.99 | 0.02 | 22.1 | 0.2 | 0.729 | 0.006 | | |
| #2 | 0.070 | 0.001 | 0.161 | 0.003 | 0.417 | 0.003 | 4.25 | 0.02 | 22.3 | 0.2 | 0.721 | 0.007 | | |
| #3 | 0.071 | 0.003 | 0.175 | 0.008 | 0.427 | 0.012 | 4.42 | 0.15 | 22.2 | 0.6 | 0.717 | 0.023 | | |
| Average (n=3) | 0.079 | | 0.173 | | 0.429 | | 4.55 | | 22.2 | | 0.722 | | | |
| M&M [a] (n=7) | 0.075 | 0.009 | 0.198 | 0.008 | 0.471 | 0.039 | 5.01 | 0.17 | 24.3 | 1.7 | 0.790 | 0.020 | | |
| P [b] (n=8) | 0.078 | 0.003 | | | | | 4.40 | 0.15 | 24.8 | 0.7 | | | | |
| Certified [c] | 0.150 | | 0.300 | | 0.700 | | 5.80 | | 22.4 | | | | | |

[a] Meisel and Moser (2004), high pressure asher (HPA) digestion ID-ICP-MS.

[b] Peucker-Ehrenbrink et al. (2003), Ni-sulfide fire assay ID-ICP-MS.

[c] Govindaraju (2007), Note that Ir, Ru and Rh values are provisional values
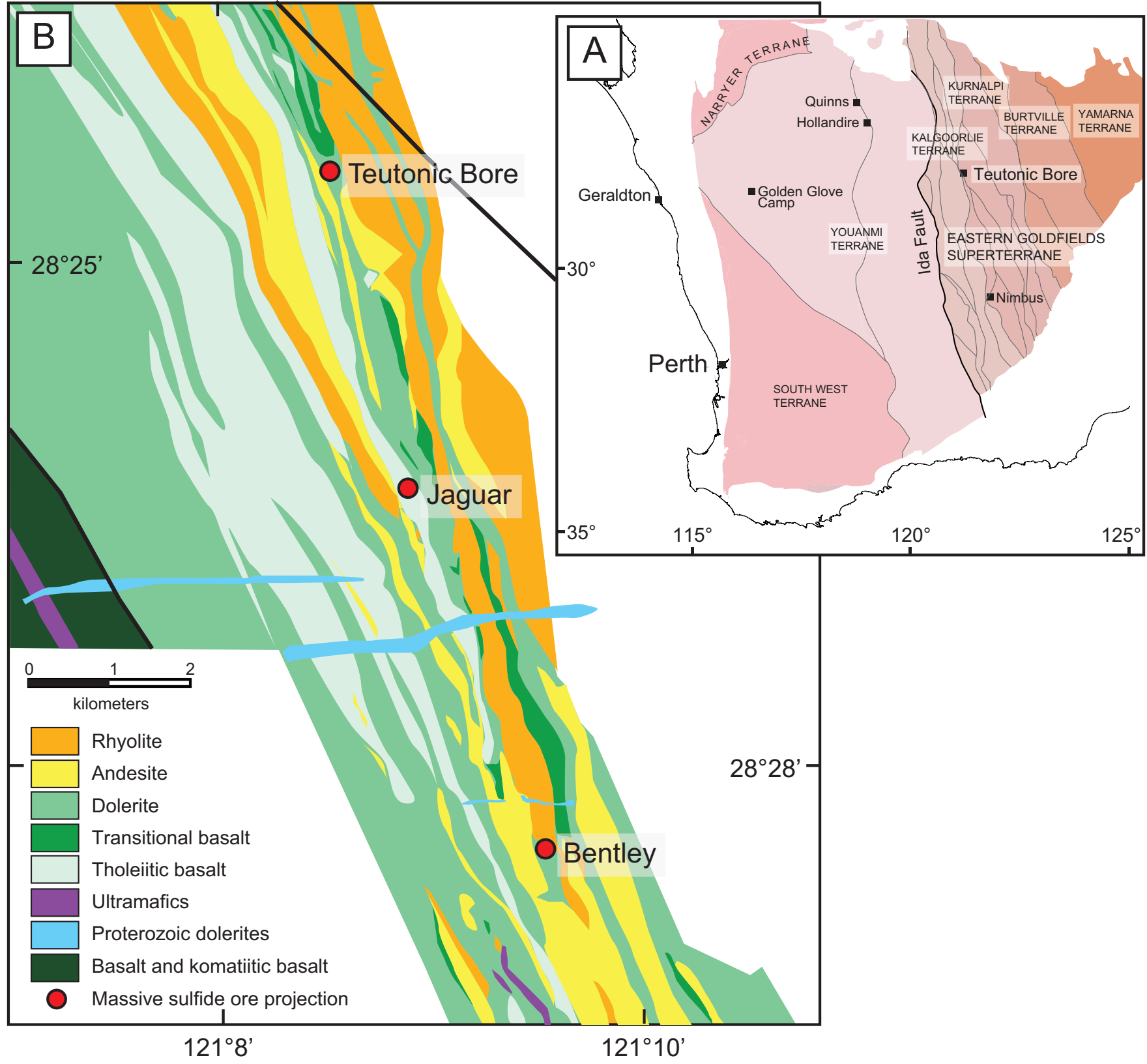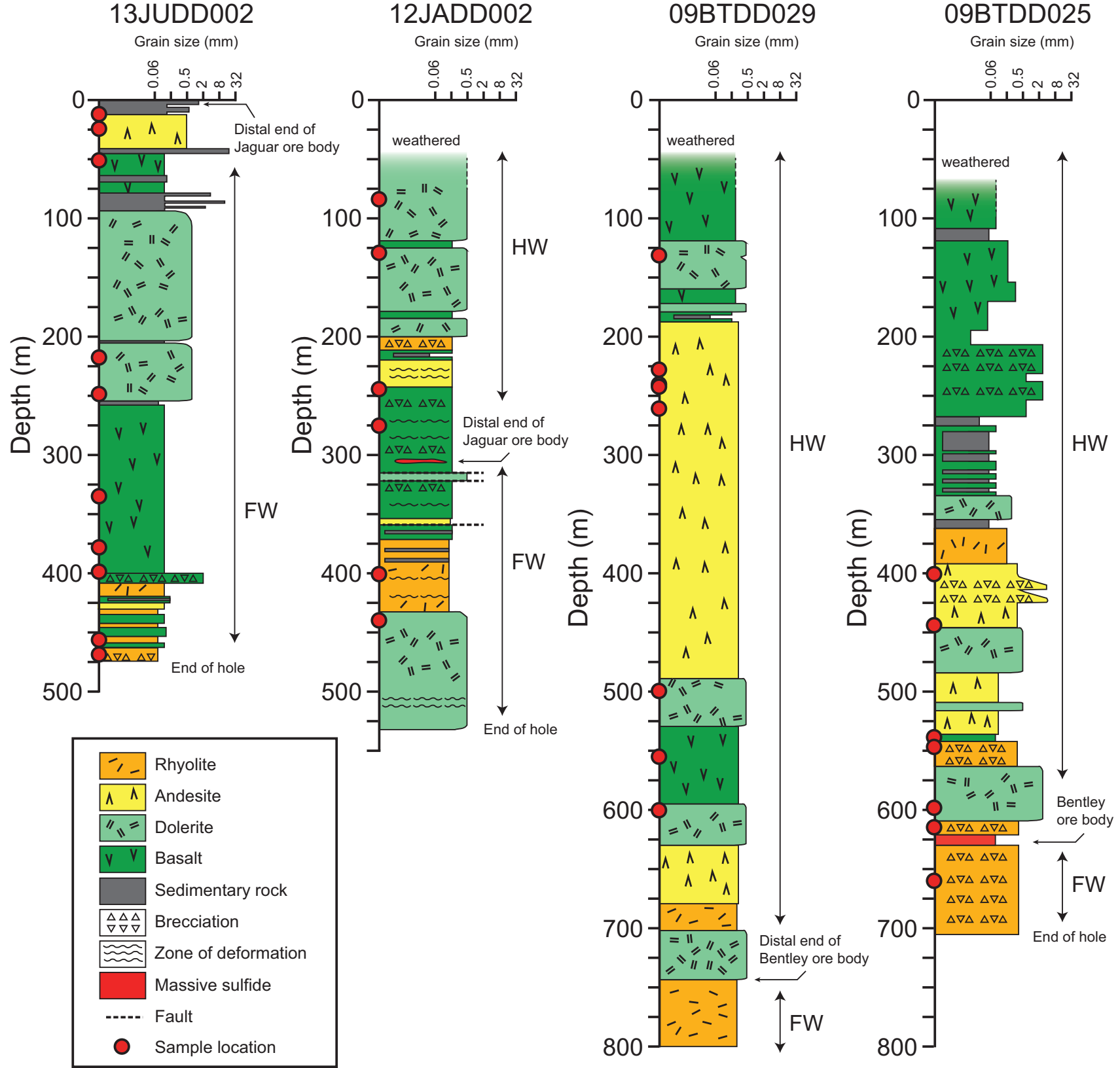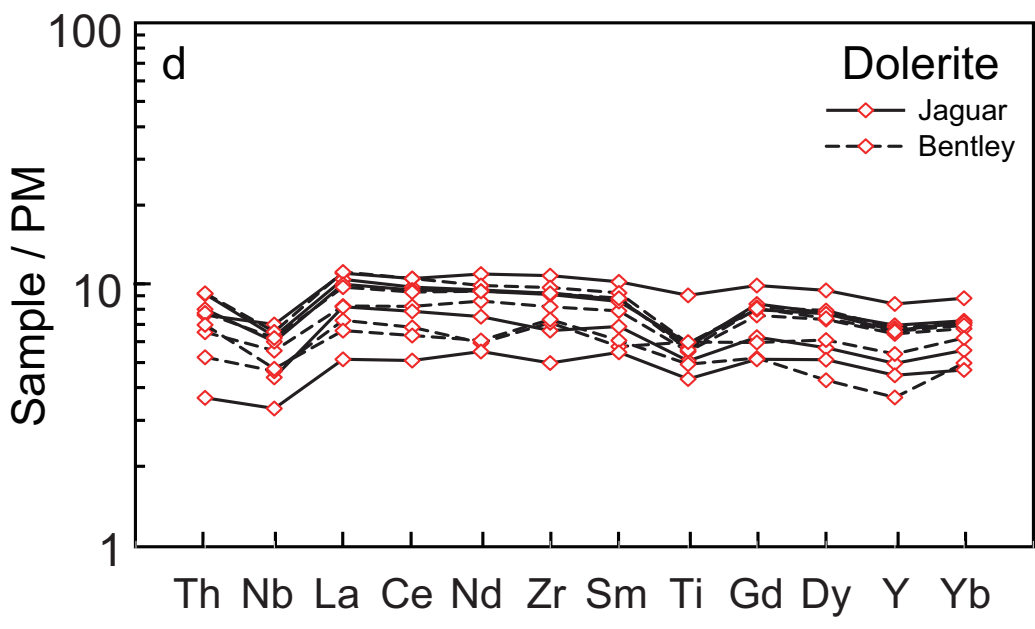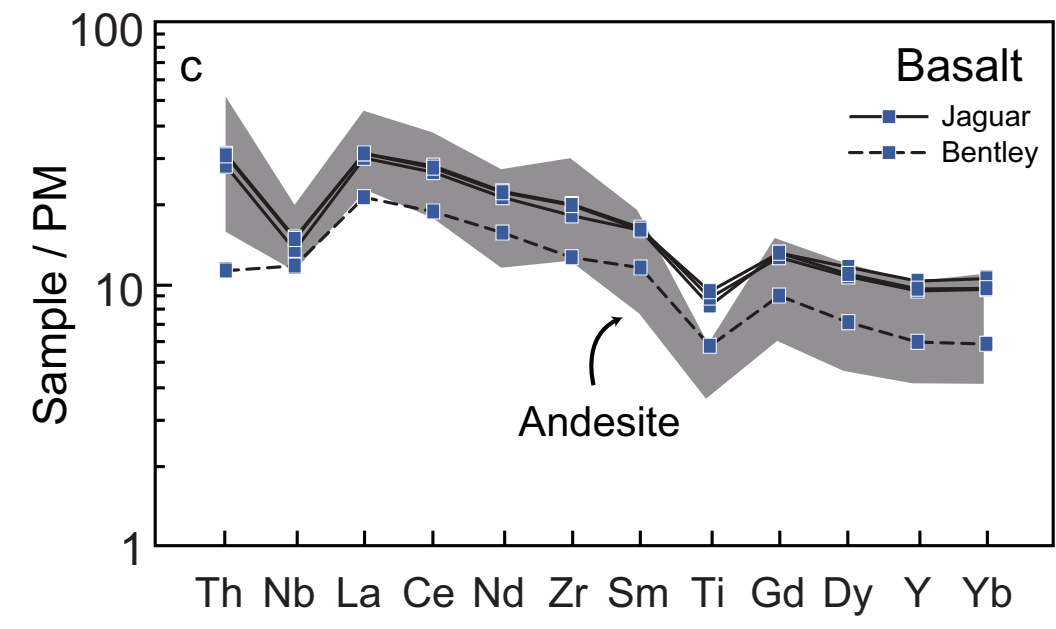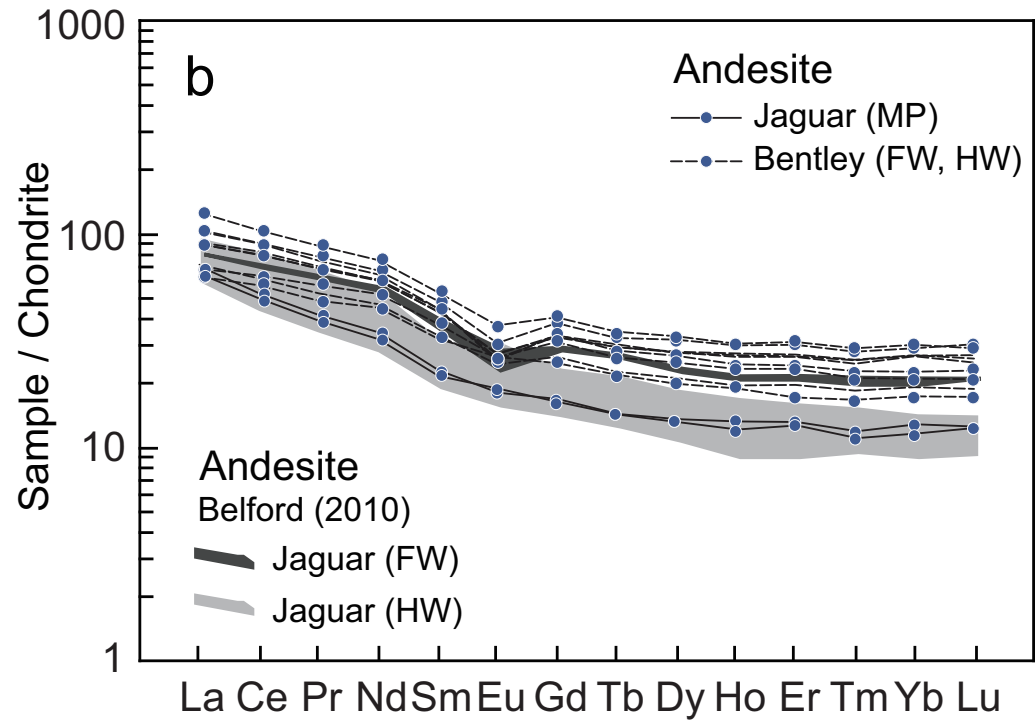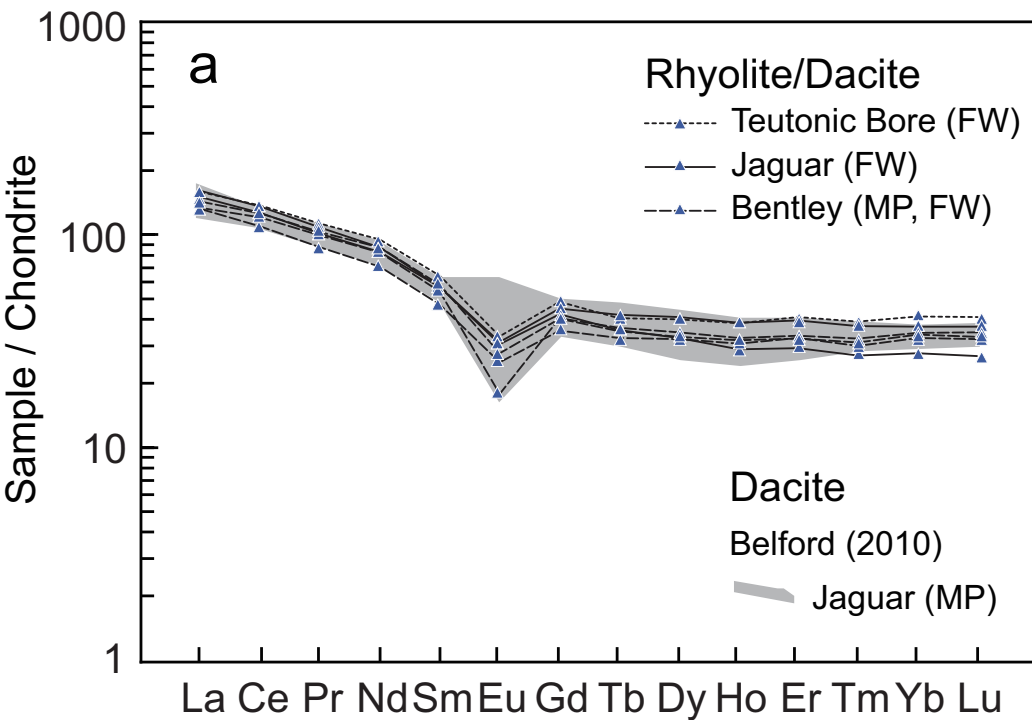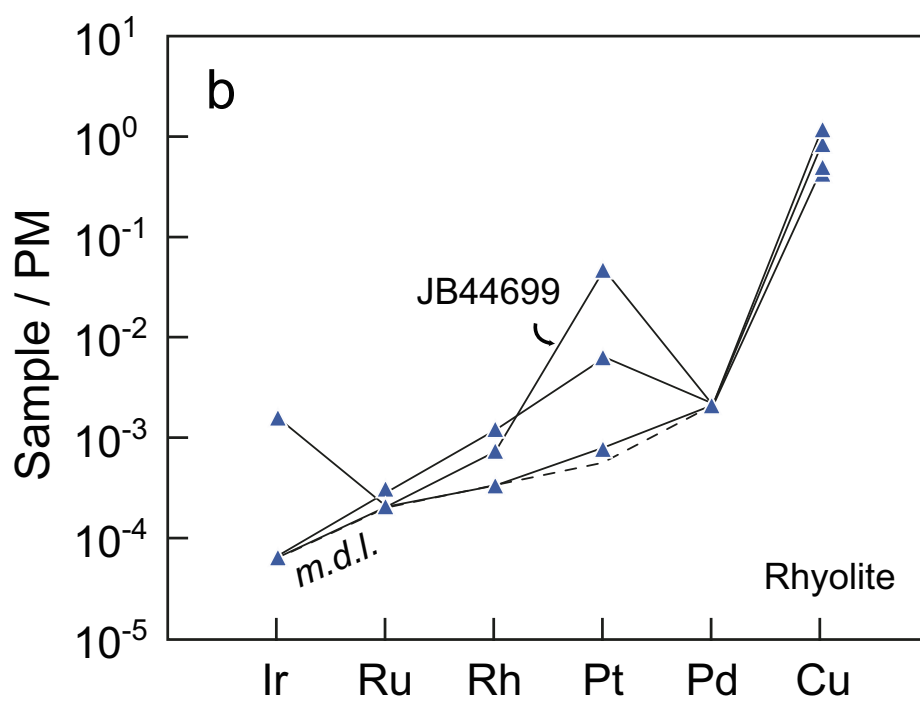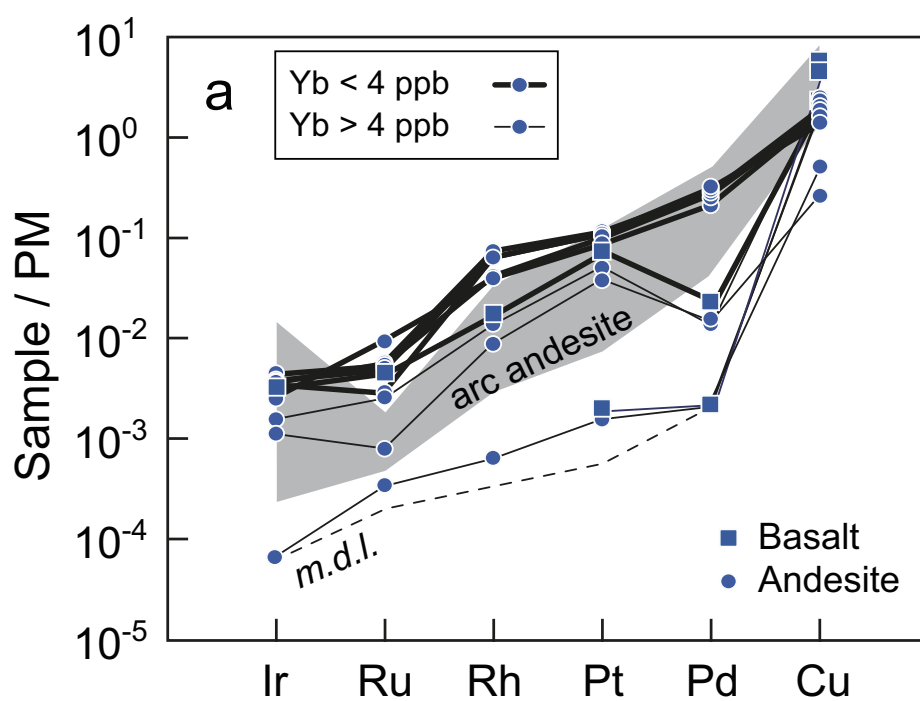
Figure 1

Figure 2

Figure 3
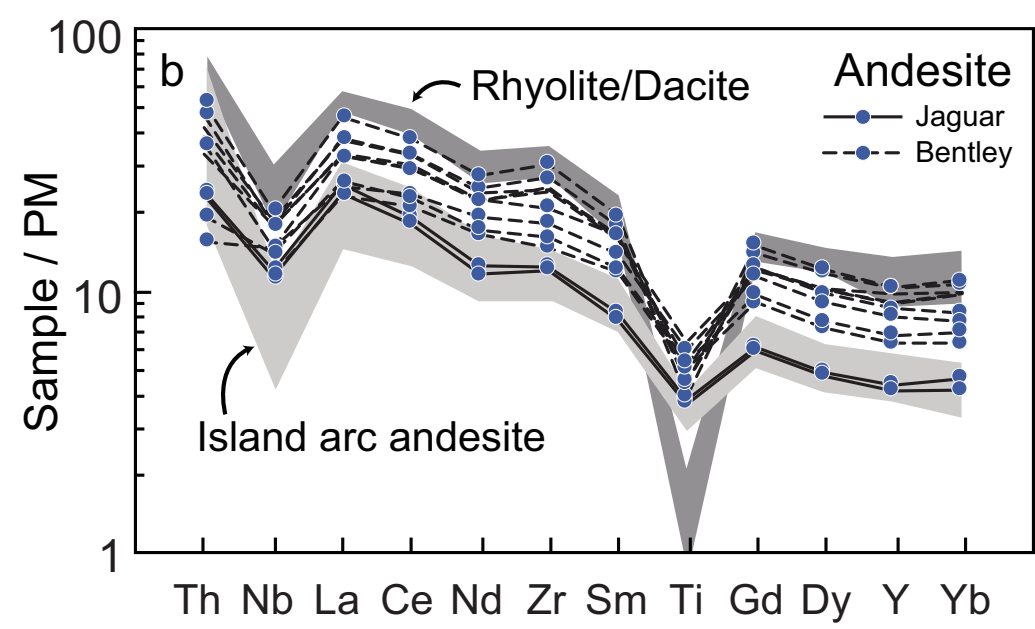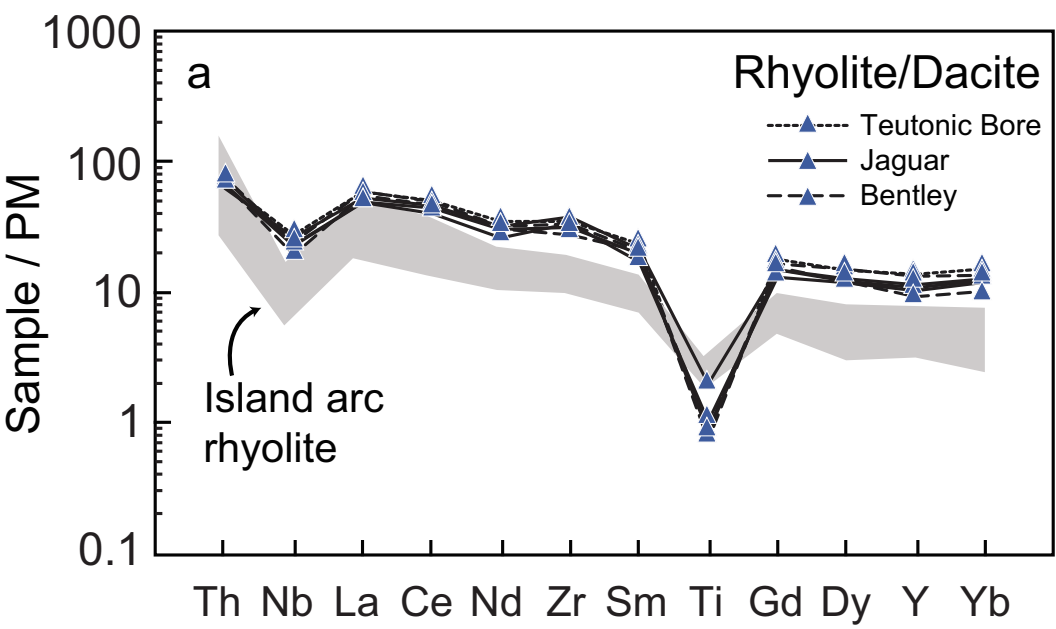
Figure 4
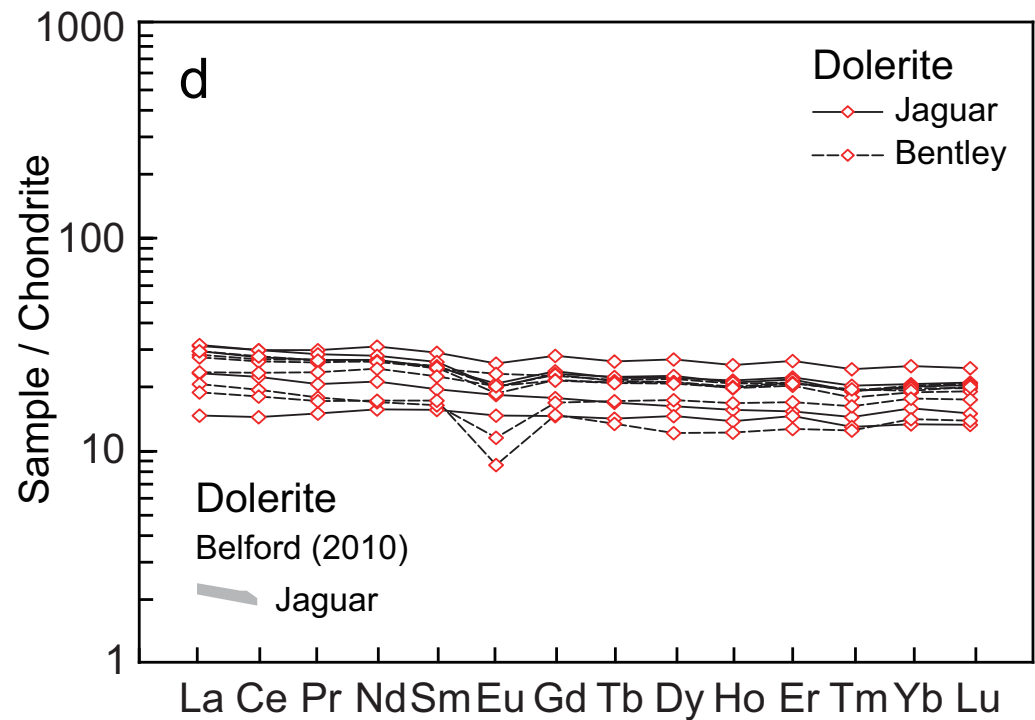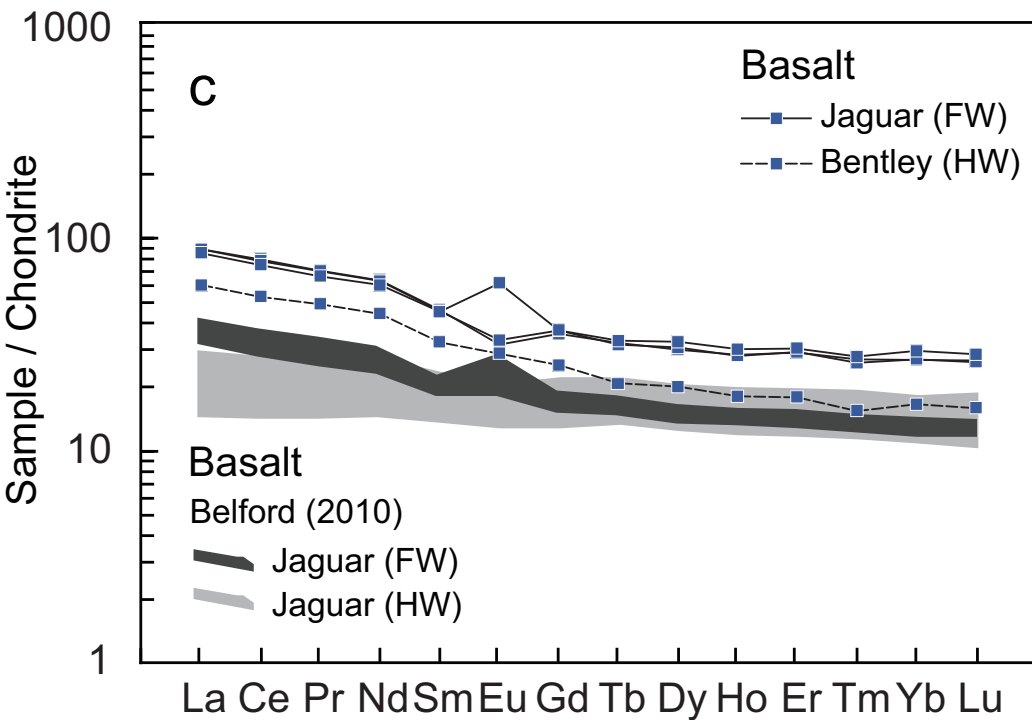
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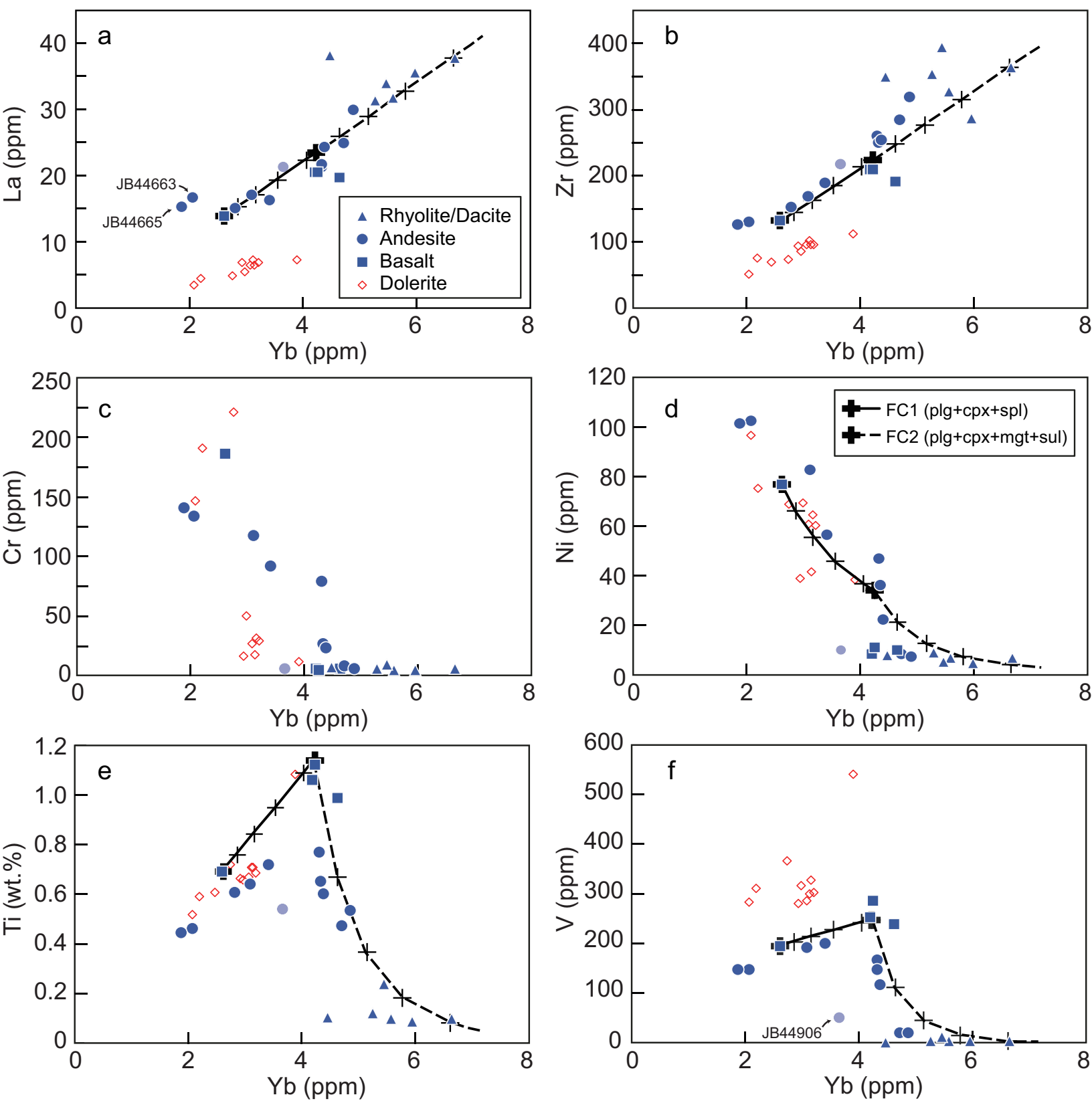
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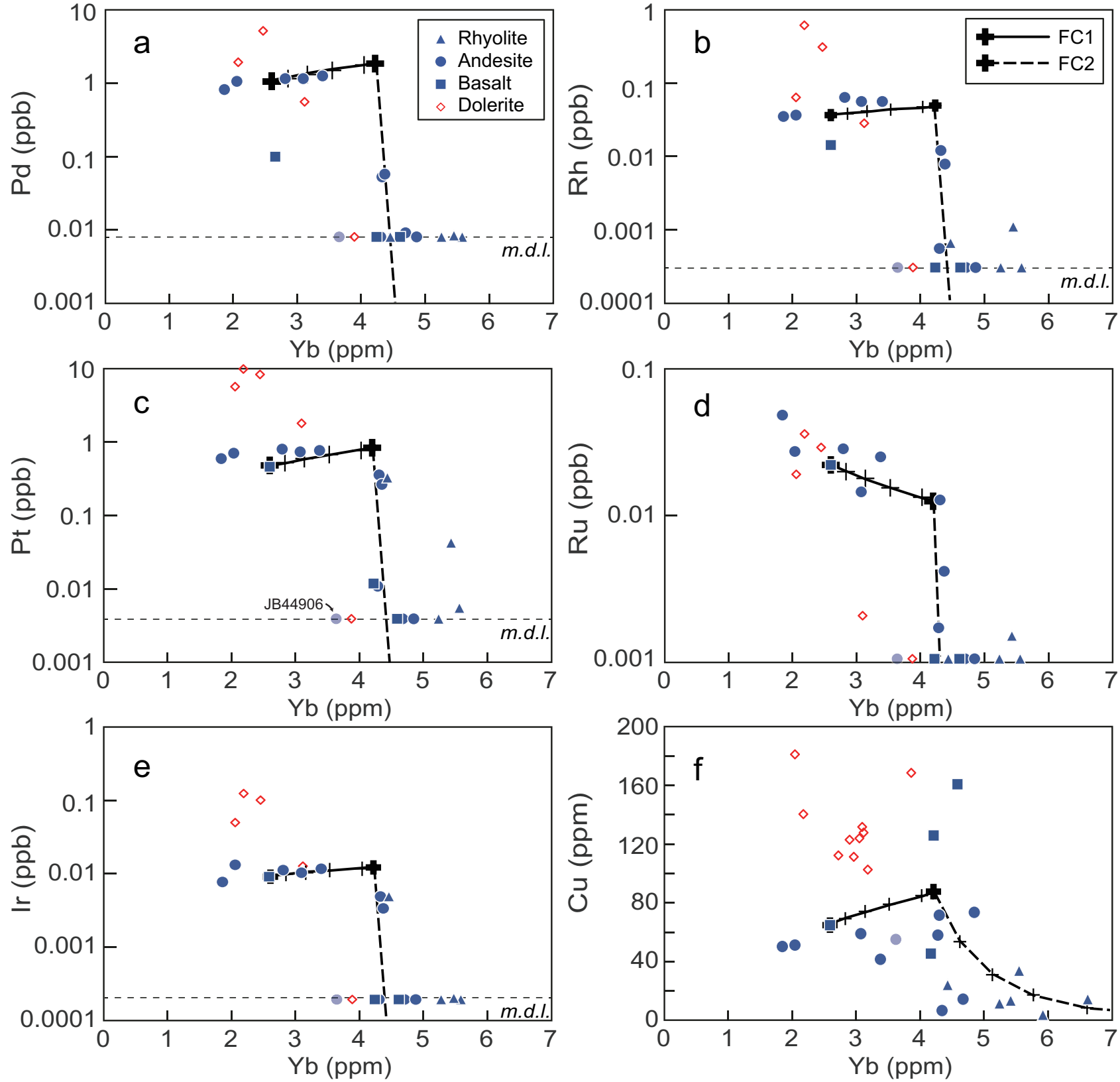
Figure 7
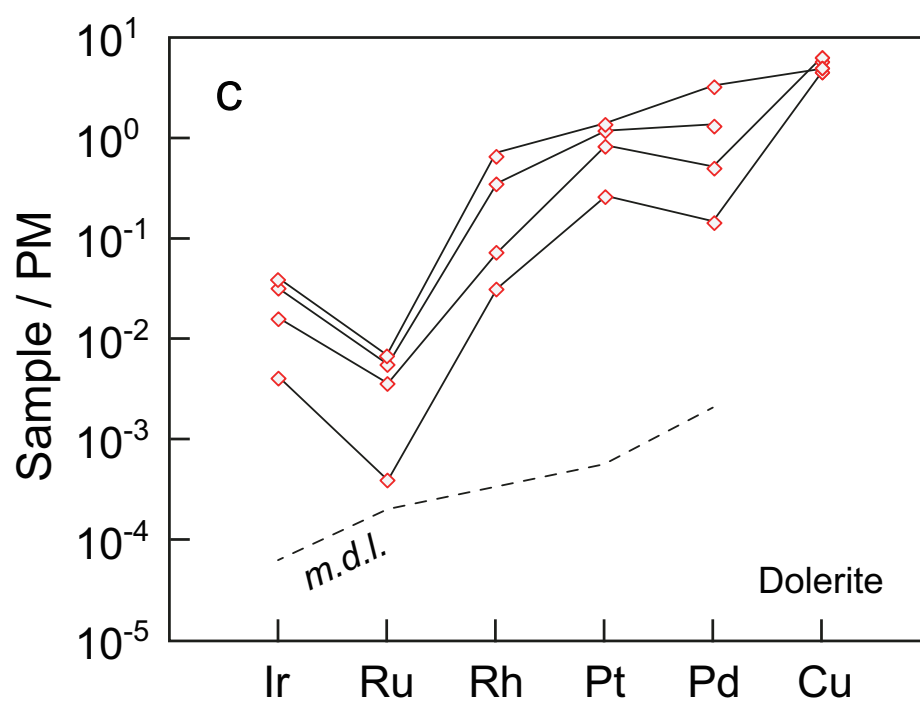
Figure 8

Figure 9

Figure 10