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1 Blueschist from the Mariana forearc
2 records long-lived residence of material in the
3 subduction channel

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13

14 **Highlights**

- 15 • Blueschist from serpentine mud volcano in Mariana forearc is ca. 50 Ma old
- 16 • The mineral assemblage records warm metamorphic conditions during IBM subduction
17 initiation
- 18 • Blueschist rocks have resided in the subduction channel for at least 46 Ma

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Abstract

From ca. 50 Ma to present, the western Pacific plate has been subducting under the Philippine Sea plate, forming the oceanic Izu-Bonin-Mariana (IBM) subduction system. It is the only known location where subduction zone products are presently being transported to the surface by serpentinite-mud volcanoes. A large serpentinite mud “volcano” forms the South Chamorro Seamount and was successfully drilled by ODP during Leg 195. This returned mostly partially serpentinitized harzburgites enclosed in serpentinite muds. In addition, limited numbers of small (1 mm–1 cm) fragments of rare blueschists were also discovered. U–Pb dating of zircon and rutile from one of these blueschist clasts give ages of 51.1 ± 1.2 Ma and 47.5 ± 2.0 Ma, respectively. These are interpreted to date prograde high-pressure metamorphism. Mineral equilibria modelling of the blueschist clast suggests the mineral assemblage formed at conditions of ~ 1.6 GPa and ~ 590 °C. We interpret that this high-pressure assemblage formed at a depth of ~ 50 km within the subduction channel and was subsequently exhumed and entrained into the South Chamorro serpentinite volcano system at depths of ~ 27 km. Consequently, we propose that the material erupted from the South Chamorro Seamount may be sampling far greater depths within the Mariana subduction system than previously thought. The apparent thermal gradient implied by the pressure–temperature modelling (~ 370 °C/GPa) is slightly warmer than that predicted by typical subduction channel numerical models and other blueschists worldwide. The age of the blueschist suggests it formed during the arc initiation stages of the proto-Izu-Bonin-Mariana arc, with the P – T conditions recording thermally elevated conditions during initial stages of western Pacific plate subduction. This indicates the blueschist had prolonged residence time in the stable forearc as the system underwent east-directed rollback. The Mariana blueschist shows that subduction products can remain entrained in subduction channels for many millions of years prior to exhumation.

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1. Introduction

From ca. 50 Ma until present, the Western Pacific plate has been subducting under the Philippine Sea plate, forming the oceanic Izu-Bonin-Mariana (IBM) arc-basin system (Figure 1; Stern and Bloomer, 1992; Ishizuka et al., 2011, 2018). This system provides an opportunity to study active processes within convergent intra-oceanic settings such as magmatism, seismicity, element recycling and hydrothermal transport. It is also the only known location on Earth where subduction zone products are actively transported to the surface by serpentinite-mud volcanoes (e.g. Fryer, 2012; Pabst et al., 2012). These serpentinite-mud volcanoes occur up to 90 km away from the trench axis in the forearc region (Figure 1; Fryer et al., 2006). In the southern Mariana segment, these volcanoes are interpreted to currently sample slab-generated fluids from a depth of up to 27 km (Fryer, 2012), offering a unique window into processes operating at shallow depths during subduction and in the mantle wedge above.

Previous studies on the variety of hard rock clasts “erupted” from these serpentinite-mud volcanoes have used them to infer the chemical and physical conditions of the subducting slab surface at shallow depths under the Mariana forearc (Savov et al., 2005; Fryer et al., 2006; Pabst et al., 2012). A major assumption from all previous studies is that the clasts and muds are derived from recently subducted products and hence are representative of the modern subduction system, however this assumption has never been tested. Additionally, there has been no in-depth and detailed metamorphic work done on the clasts to constrain the metamorphic conditions of formation and therefore the depth they sample within the subduction system. A high-pressure origin for blueschist clasts from the Mariana serpentinite-mud volcanoes has been suggested

81 before, but never quantified (Maekawa et al., 1993; Fryer et al., 2006; Yamamoto et al., 1995).
82 Because these metamorphic clasts contain a wealth of information about the thermal conditions
83 within the slab, as well as potentially providing avenues to determine the age of metamorphic
84 recrystallization, they can provide unique insights into the residence times of material within
85 subduction channels formed by ocean-ocean plate convergence.

86

87 This study is focused on one mafic clast (195-1200E-1H-3-4b), recovered from serpentinite mud
88 drilled during ODP Leg 195 at Site 1200 at the summit of the active South Chamorro Seamount
89 (Figure 1; see Pabst et al. (2012) for further description on this sample). Clasts recovered from the
90 drilling were predominately serpentinite fragments, however rare blueschist-facies metamafic
91 fragments were also recovered. While multiple clasts contained blueschist-facies mineral
92 assemblages (including amphibole, chlorite, epidote and phengite), one rare sample contained
93 rutile and zircon which could be targeted for geochronology. We derive constraints on the
94 thermobarometric conditions recorded by this sample, and the age of metamorphism. The results
95 provide insight into the depth of material return to the surface, and the subduction channel P - T
96 conditions during the very beginning of Mariana subduction.

97

98 **2. Background**

99 *2.1 Geology and geometry of the IBM system*

100

101 The IBM system is generated by the westward directed subduction of the Pacific oceanic plate
102 under the Philippine Sea, which initiated at ca. 51 Ma (Figure 1; Reagan et al., 2010; Ishizuka et
103 al., 2018). The northern IBM trench segment (Izu-Bonin) shows an increasing dip of the Wadati-
104 Benioff zone from $\sim 40^\circ$ in the north to $\sim 80^\circ$ in the south, with intermediate-depth seismicity
105 occurring between depths of ~ 150 to ~ 300 km (Gvirtzman and Stern, 2004). In contrast, the
106 southern IBM segment (Mariana) has a subvertical Wadati-Benioff zone, with deep (>300 km)
107 seismic events (Gvirtzman and Stern, 2004). As such, the width of the subduction zone interface

108 between the overriding and subducting plates increases along the IBM from north to south
109 (Gvirtzman and Stern, 2004). While this only delineates the current subduction zone structure
110 under the IBM, it is useful for interpretations of subduction channel dynamics which presently
111 operate. Currently, the slab in the Mariana segment is in a state of rollback, as the Pacific and
112 Philippine plates are both advancing westwards, with the latter at a slightly faster rate (Gvirtzman
113 and Stern, 2004). Complex geometries involving slab tearing and steepening in the southern
114 segment of the IBM have led to the extreme dip and hence depth of the trench in this area
115 (Gvirtzman and Stern, 2004). The Mariana forearc is extensively faulted, due to oblique
116 convergence as well as the curvature produced by back-arc extension, resulting in it being
117 dominated by sinistral shear (Stern et al., 2003). This structural architecture is probably a crucial
118 factor in allowing serpentinitized mantle to exhume and rise to the surface, driving serpentinite-mud
119 volcanism. The Mariana forearc is the only place on modern Earth where this occurs (Fryer et al.,
120 1992, 1999, 2000, 2006; Fryer, 2012;).

121

122 The recent history of the IBM is well studied. However, the cause for subduction inception in the
123 IBM is the source of much debate, due to lack of access to the earliest subduction-generated rocks
124 (e.g. Arculus et al., 2015; 2016). However, the Jurassic oceanic crust to the east formed a west-
125 dipping subduction zone under the Philippine Sea or Pacific crust. The timing of this is estimated
126 to be ca. 51–47 Ma (Ishizuka et al, 2011, 2018). Ar–Ar whole rock ages for initial construction of
127 the Mariana arc match those for the Izu-Bonin arc at ca. 49–47 Ma, while forearc basement from
128 the IBM has been dated by Ar–Ar to have formed by at least ca. 47–45 Ma (Cosca et al., 1998).
129 More recently, the basement of the IBM arc was dated by Ar–Ar geochronology at 48.7 ± 0.3 Ma
130 (Ishizuka et al., 2018). This age is further supported by nano and microfossils in the overlying
131 volcanoclastic sediments (Arculus et al., 2015). A ca. 51 Ma age is reported based on stratigraphic
132 relationships for tholeiitic fore-arc basalts interpreted to be the first lavas to erupt when the Pacific
133 plate initially sunk under the Philippine plate (Reagan et al., 2010; 2017). This has been further
134 supported by a U–Pb zircon age of 51.1 ± 1.5 from gabbro underlying the fore-arc basalts

135 (Ishizuka et al., 2011). Regardless of the exact timing of initiation, it seems that subduction
136 initiation along the 2800 km IBM system occurred over 51–47 Ma (Stern et al., 2003; Arculus et
137 al., 2015). The Kyushu-Palau Ridge (Figure 1) was active from ca. 48 Ma to ca. 25 Ma, and is the
138 result of a stable magmatic arc during which the IBM subduction system was essentially immobile
139 (Ishizuka et al., 2011). Spreading in the mid-southern Parece Vela Basin began after this (Figure
140 1a), and further spreading in the northern Izu-Bonin segment commenced at ca. 25 Ma with both
141 terminating around 15 Ma due to collision of the northern IBM with Honshu (Stern et al., 2003).
142 In the southern segment, eastwards rollback resulted in extension to form the Mariana Trough (~6
143 Ma back-arc basin), with the onset of seafloor spreading at ca. 3–4 Ma (Yamazaki and Stern,
144 1997). As such, the inception of the currently active Mariana Arc (Figure 1b; the West Mariana
145 Ridge) is interpreted to be 3–4 Ma old (Stern et al., 2003), and the remnant arc was left behind.
146 Over this Eocene–Pleistocene evolution, the relative slab rollback to the east has resulted in two
147 former oceanic arcs younging from the Palau-Kyushu Ridge (active from the onset of subduction
148 to ca. 25 Ma), to the current Mariana Ridge (Figure 1a).

149

150 2.2 *Previous studies of blueschists from the Mariana forearc drill sites*

151

152 A series of active mud volcanoes occur on the upper plate between the arc (the Mariana Ridge)
153 and the Mariana Trough (current trench; Figure 1a). The two most intensely studied active
154 seamounts are the South Chamorro Seamount and the Conical Seamount, which occur 85 and 90
155 km from the trench respectively (Fryer et al., 1999; Savov et al., 2005). Deep sea drilling of these
156 serpentinite seamounts (ODP Legs 125 and 195) returned predominantly serpentinitized harzburgite
157 and dunite clasts, but also rare metabasic blueschist clasts (~5% of clasts) in a matrix of fine
158 serpentinite muds (Savov et al., 2004; Fryer and Salisbury, 2006; Fryer et al., 2006). These clasts
159 have been divided into amphibole-talc-chlorite-schists, chlorite-epidote-schists, amphibole-
160 chlorite-phengite-schists and mono-mineralic aggregates of talc or amphibole (Pabst et al., 2012).

161

162 A variety of metamafic clasts as well as matrix serpentinite muds have been studied to make
163 inferences about the pressure–temperature (P – T) conditions within and below the Conical and
164 South Chamorro seamounts. Blueschist clasts were discovered during drilling of the Conical
165 Seamount in the northern Mariana forearc (east of Asuncion; Figure 1b) by Maekawa et al. (1993),
166 who reported the first direct evidence for low temperature and relatively high-pressure
167 metamorphism in a subduction zone. These blueschists were estimated to have formed at
168 temperatures of 150–250 °C and pressures of 5–6 kbar (potentially corresponding to depths of 16–
169 20 km), based on the presence of aragonite, the compositions of sodic pyroxenes and temperature
170 dependence of inferred metamorphic reactions (Maekawa et al., 1993). Maekawa et al. (1995) also
171 noted the existence of lawsonite-bearing blueschist clasts, and indicated that higher grade
172 metamorphic rocks may be sourced from below the seamount. Numerous blueschist clasts were
173 recovered from Conical Seamount drilled during ODP Leg 125. These were analysed for their
174 whole rock geochemistry by Yamamoto et al. (1995), who concluded the volcano was returning
175 clasts derived from a MORB source.

176

177 Blueschist clasts drilled from the summit of the South Chamorro Seamount to the east of Guam
178 were recovered only recently (Figure 1b; Shipboard Scientific Party, 2000). Due to similar jadeitic
179 (Jd) compositions of their pyroxenes, Pabst et al. (2012) estimated that blueschists from the South
180 Chamorro Seamount had reached similar P – T conditions as those from Conical Seamount, studied
181 by Maekawa et al. (1993; 1995). Further comparisons of the metamorphic mineral assemblages of
182 the blueschists from South Chamorro Seamount with those of the Franciscan Complex have been
183 used to infer conditions of 250–300 °C and 7 kbar for the late-stage blueschist facies assemblage
184 (Pabst et al., 2012). Fryer et al. (2006) estimated conditions of ~250–300 °C and 4–5 kbar based
185 on assumed equilibrium of epidote with magnesioriebeckite/barroisite from a different metabasite
186 schist from South Chamorro Seamount. Higher grade conditions for metamorphic products have
187 also been suggested by Murata et al. (2009) from the existence of antigorite in serpentinitized
188 peridotites. Antigorite coexisting with clinopyroxene and olivine indicates high-temperature
189 serpentinitization between ~450–550 °C, leading Murata et al., (2009) to suggest possible tectonic

190 cycling of mantle wedge material. Additionally, temperatures and pressures of 350 °C and 8 kbar
191 have been estimated for the source of serpentinite muds of the South Chamorro Seamount (Fryer et
192 al., 2000), corresponding to depths of ~25–27 km. Fryer (1992) and Fryer et al. (2006) suggested
193 that blueschists record higher grade conditions than those of the slab interface directly below the
194 seamount, however no quantitative P – T estimates have been made. Geochemical and seismic
195 studies, as well as earthquake locations on the subducting Pacific plate, have been used to suggest
196 the mud volcanoes are sampling the slab interface at depth of 27–29 km (Oakley et al., 2008;
197 Savov et al., 2005; Fryer et al., 2000). This is also generally supported by temperatures of ~200–
198 300 °C estimated from chrysolite, lizardite and brucite-bearing serpentinitized peridotites
199 (D’Antonio and Kristensen, 2004). Fryer et al. (2006) suggested that MORB and OIB samples
200 must have been derived from subducted oceanic plate buried to a depth of up to 30 km. This would
201 suggest that the variety of clasts erupted from the South Chamorro Seamount and by inference
202 other serpentinite volcanos in the Marianas forearc are being sampled from the slab interface
203 beneath the volcano. While some of the geochemical signature of the fluid released from the South
204 Chamorro Seamount appears to be originating from the currently subducting Pacific slab surface at
205 a depth of ~27 km (Mottl et al., 2004), studies on the metamorphic conditions of the blueschist
206 fragments span a range of P – T conditions.

207

208 In addition to the only limited constraints on the P – T conditions recorded by the metamorphic
209 clasts, there is also lack of age data. While not overtly stated, existing studies on the mud hosted
210 clasts assume they record modern conditions on the slab interface. However studies (Krebs et al.,
211 2008; Lázaro et al., 2009; Blanco-Quintero et al., 2011) from high-pressure rocks in ancient
212 serpentinite mélanges show that they may contain a range of metamorphic ages, indicating that
213 material can reside within subduction zone channels for potentially tens of millions of years.

214

215 **3. Methods**

216

217 The ~ 2×2 mm blueschist clast recovered from ODP Site 1200 was mounted in epoxy resin and
218 polished. It was primarily mapped in BSE using a Quanta 600 SEM at Adelaide Microscopy,
219 University of Adelaide, using Mineral Liberation Analysis software, to determine petrological
220 relationships and mineral modal proportions in the clast.

221

222 Quantitative Electron probe microanalysis (EPMA) elemental mapping used a CAMECA SXFive
223 equipped with 5 wavelength-dispersive spectrometers (WDS) and X-Ray detectors, running the
224 PeakSite software. Beam conditions were set at an accelerating voltage of 15 kV and 100 nA,
225 utilising a focussed beam. Compositional mapping was done at a 4 µm pixel resolution. Pixel
226 dwell time in all maps was set to 40 ms. Calibration and quantitative data reduction of maps was
227 carried out with the “Probe for EPMA” software, distributed by Probe Software Inc. Calibration
228 was performed on certified natural and synthetic standards from Astimex Ltd and P&H Associates.
229 The clast was mapped for 10 elements using their K α lines, thus requiring two mapping passes on
230 the five spectrometers (Pass 1: Ca, Na, P, Mg, Fe; Pass 2: Ti, Si, Al, Mn, K). Potentially mobile
231 elements were analysed in the first pass. The average minimum detection limits (at the 99%
232 confidence interval) in wt.% for the quantitative maps were: Ca (0.06), Na (0.12), Ti (0.07), Mg
233 (0.08), Fe (0.17), K (0.06), Si (0.01), P (0.08), Al (0.08), Mn (0.16).

234

235 The X-ray maps were then used to identify the metamorphic mineral assemblages and mineral
236 modal proportions were determined by pixel counting using image analysis software. Although the
237 blueschist clast contains some coarse-grained minerals, is generally medium-grained. As such,
238 these modal proportions are reasonably representative of the local equilibrium volume. The modal
239 proportion and electron microprobe compositions of mineral assemblages was used to compute a
240 bulk chemical composition for petrological modelling (Supplementary Data Table 1). We chose
241 this approach to determine a bulk composition as the sample was considered too valuable to be
242 consumed for conventional-style geochemical analysis. Ti-magnetite was omitted from the bulk
243 rock chemistry calculations, based on textural evidence it is magmatic. Allanite and zircon were
244 also omitted as they contain elements that cannot be modelled. Results of pixel counting and

245 associated calculations to construct the bulk composition are shown in Supplementary Data Table
246 2.

247

248 Mineral equilibria forward modelling was undertaken using THERMOCALC v 3.4 in the
249 NCFMASHTO system, using the internally consistent thermodynamic dataset 'ds55' (filename tc-
250 ds55.txt; November 2003 updated version of the Holland and Powell 1998 dataset) and activity-
251 composition models in Diener et al. (2012) and references within. The calculated K and Mn
252 concentrations in the calculated bulk rock composition are near zero, therefore K and Mn were
253 excluded from the model system. Pumpellyite was not predicted in the modelling, possibly due to
254 lack of a pumpellyite activity-composition model that allows solid solution. Calculations to test
255 the sensitivity of modelled mineral equilibria to H₂O content using P-M_{H₂O} models demonstrated
256 the mineral assemblage, modal proportions and compositions recorded by the sample are stable
257 over a large range of H₂O contents (from 9 mol% to more than 13 mol %, Supplementary Figure
258 1). As a specific value could not be pinpointed, and the sample evidently formed under water-rich
259 conditions as indicated by abundant chlorite, amphibole and epidote, modelling was done with
260 water in excess, i.e. defining H₂O as a saturating phase. Oxidation state (Fe₂O₃, or O in the bulk
261 rock chemistry) was constrained from a P-M_O model (Supplementary Figure 2), where mineral
262 modal proportions and compositions overlapped in the interpreted peak field at approximately
263 M(O) = 0.55, or O = 1.97 mol%. This value directly overlaps with recalculated mineral
264 microprobe chemical analyses used to calculate the bulk rock chemistry by assuming perfect
265 mineral stoichiometry in the calculation of cations from the wt% oxide data (Droop, 1987; Leake
266 et al., 1997). Contouring of the mineral equilibria model for the normalised abundances (mode) of
267 minerals was calculated using the software TCInvestigator v1.0 (Pearce et al., 2015).

268

269 Secondary ionization mass spectrometry (SIMS) U-Pb geochronology was carried out using a
270 CAMECA ims 1270 ion microprobe at the University of California of Los Angeles
271 (Supplementary Data Table 3). In-situ analyses targeted zircon in the polished blueschist block
272 using methods for analysis of small grains in their matrix as described in Schmitt et al. (2010).

273 Rutile analyses were also performed in situ on the same mount, but due to the larger grain size of
274 rutile compared to zircon, nearly full transmission was reached in the ion microprobe's field
275 aperture. Instrumental set-up for rutile analysis is summarized in Schmitt and Zack (2012); all ages
276 are reported relative to AS3 reference zircon (1099 Ma; Paces and Miller, 1993) and R10b
277 reference rutile (1090 Ma; Luvizotto et al., 2009).

278

279 **4. Results**

280

281 *4.1 Petrography*

282 The blueschist clast (E1H3-4b) is dominated by an amphibole and chlorite-bearing matrix, with
283 less abundant epidote, rutile, titanite and allanite, and very rare pumpellyite, phengite and
284 clinopyroxene (Figure 2). Amphibole is typically ~10–200 μm in size and zoned (Figure 3; 4),
285 with patchy magnesio-hornblende cores, surrounded by volumetrically dominant edenite/pargasite,
286 and then a sharply-defined thin rim of magnesiokatophorite (Figure 5a, nomenclature follows
287 Leake et al., 1997). This zonation can be seen in element maps (Figure 4a), with a marked increase
288 in Na and Fe from core to rim, a decrease in Mg and Ca from core to rim, and high SiO_2 cores and
289 rims and corresponding low alumina cores and rims. Small needle-like grains of actinolite also
290 occur within the amphibole. Chlorite is commonly usually less than 50 μm , but rare grains are up
291 to 300 μm in size. It is weakly zoned with thin rims that are comparatively poor in Fe and Al but
292 rich in Si and Mg (Figure 3b, Figure 5b). It forms irregular grains intergrown with amphibole and
293 epidote as well as narrow veins which cross-cut or occur along amphibole cleavage planes.
294 Epidote occurs as smaller (occasionally up to ~250 μm) grains within amphibole or chlorite. It
295 regularly overgrows texturally early allanite (Figure 2), and is unzoned, except for a thin rim of
296 elevated Fe (Figure 5c, increase of ~1.65 wt% Fe_2O_3 ; Supplementary Data Table 1). Allanite is up
297 to 80 μm in size and oscillatory zoned in rare earth elements (Figure 2), consistent with
298 metamorphic allanite grown in the presence of fluid. Ti-magnetite (~10–100 μm) is overgrown by
299 rims of rutile (up to ~100 μm across). Titanite forms discontinuous overgrowths on the rutile and

300 Ti-magnetite which are up to 40 μm wide (Figure 2), and also occurs as euhedral crystals with
301 amphibole and chlorite. Minor (<1%) fine-grained (5–20 μm) pumpellyite is associated with
302 retrograde titanite and chlorite. Rare fine-grained clinopyroxene (<10 μm) occurs in the chlorite-
303 amphibole matrix, and contains 7–26 mol% jadeite (Figure 5d, Pabst et al., 2012). Very fine-
304 grained rare phengite occurs as needles in amphibole, and fine-grained zircon up to 10 μm also
305 occurs in amphibole and epidote. The main mineral assemblages are: 1) early Na-rich amphibole
306 core, chlorite, epidote, clinopyroxene and rutile, and 2) late Na-Fe rich amphibole rims, actinolite,
307 titanite, and pumpellyite. Quartz is absent, and is typically absent from most blueschists from
308 South Chamorro (Pabst et al., 2012).

309

310 *4.2 Zircon and rutile geochronology*

311 Textually resolved in-situ SIMS U–Pb geochronology (Figure 6) yields concordia ages of $47.5 \pm$
312 2.0 Ma (mean square of weighted deviates MSWD of concordance = 0.00052; $n = 9$) for rutile, and
313 51.1 ± 1.2 Ma (MSWD = 0.16; $n = 4$) for zircon (Figure 7; Supplementary Data Table 3). U
314 abundances in rutile range between 11 and 30 ppm, and corresponding radiogenic ^{206}Pb yields are
315 between 42 and 95%. U abundances in zircon range from ~180 to ~1300 ppm, with high
316 radiogenic ^{206}Pb yields of >97% in favourable cases. Zirconium in rutile has on average 380 ppm,
317 which corresponds in the presence of zircon and absence of quartz to a maximum temperature of
318 650 $^{\circ}\text{C}$ using the Tomkins et al. (2007) calibration at pressures 1.5 GPa derived from mineral
319 equilibria modelling (see below).

320

321 *4.3 Mineral equilibria modelling*

322

323 A peak to retrograde P – T evolution can be inferred from the compositional isopleths of amphibole
324 as well as the modal proportions of metamorphic minerals for the modelled mineral equilibria
325 (Supplementary Data Table 2; Figure 8; in one-oxide-normalized %, compliant with the modes
326 computed by THERMOCALC). Uncertainties on the calculations in the mineral equilibria model
327 are 2 sigma and are shown in Supplementary Figure 3. The peak assemblage consists of chlorite +

328 amphibole + epidote + clinopyroxene (diopside) + rutile, and is bound by the disappearance of
329 clinopyroxene and the addition of hematite to higher temperatures, and the solid-solution transition
330 of diopside to omphacite (across the clinopyroxene solvus) at lower temperatures and higher
331 pressures. The peak assemblage occurs over a large range of conditions, from 1.1 ± 0.07 GPa and
332 515 ± 9 °C to 1.8 ± 0.06 GPa and 600 ± 21 °C. The retrograde evolution is characterized by the
333 formation of titanite and calcic amphibole, evidenced by the presence of titanite coronas on rutile
334 and small, late actinolite needles within amphibole. Clinopyroxene is interpreted to be relict from
335 the peak assemblage, and therefore the retrograde path also involves the loss of clinopyroxene. The
336 *P–T* path can be further constrained using amphibole compositional isopleths. Compositional
337 parameters A (xNa on the A site), C (xCa on the M4 site) and Z (xNa on the M4 sites) were
338 calculated from amphibole microprobe data and plotted on the mineral equilibria model (grey
339 dashed lines). Compositional isopleths of the amphibole cores plot over a wide range of pressures
340 and temperatures, from 1.2–1.7 GPa and 540–600 °C, with average errors on each compositional
341 range of ± 0.07 GPa and 12 °C. Corresponding model proportions of the amphibole cores from
342 1.5–1.7 (± 0.06) GPa and 575–600 (± 12) °C. Although not definitive, it is likely the compositions
343 and modal proportions of the magnesio-hornblende cores point to a high-pressure history that
344 predated the formation of the texturally dominant assemblage in the rock. Modal proportion
345 isopleths of chlorite, total amphibole and epidote within the modelled peak field span from 1.1–
346 1.45 GPa and 540–590 °C with average errors of 0.07 GPa and 10 °C, and also occur in retrograde
347 *P–T* space with the addition of titanite. The compositions of amphibole rims
348 (magnesiokatophorite) plot within the field of the retrograde mineral assemblage from 0.7–0.9
349 GPa and 470–495 °C, with average errors of 0.06 GPa and 9 °C.

350

351 *4.4 Protolith constraints*

352 The investigated sample has an unusual whole rock composition, with 44.2 mol% SiO₂ and 22
353 mol% MgO (Supplementary Data Table 2). Technically it can be labelled a picrite, which is not
354 typically observed in likely protoliths such as MORB, OIB or former arc basement. A more

355 realistic scenario to explain the bulk rock composition is the formation of a hybrid rock
356 composition derived from MORB with a metasomatic imprint from surrounding hydrated mantle,
357 similar to that observed on Catalina Island (e.g. Bebout and Barton 2002; Pabst et al., 2012). The
358 implication is that the investigated sample was not part of a coherent subducting slab at the time of
359 zircon and rutile formation.

360

361

362 **5. Discussion**

363

364 Texturally, rutile in blueschist clast E1H3-4b forms part of a typical high-pressure metamorphic
365 assemblage (Zack & Kooijman, 2017). Furthermore rutile is extremely rare as an igneous mineral
366 in mafic rocks, and the chance that the erupted clast sampled a metamorphosed mafic rock with
367 relic igneous rutile would appear negligible. Zircon is relatively common in mafic subvolcanic
368 and plutonic rocks as a late-crystallizing igneous mineral, however in general it is not abundant in
369 MORB. A magmatic zircon age from crystallisation of the subducting slab for the zircon can
370 probably be dismissed as the age of oceanic crust being subducted into the IBM system is Jurassic
371 (Stern et al., 2003). Moreover, the similarity in age to the rutile also strongly implies a
372 metamorphic origin. Hence, the U–Pb ages from rutile and zircon are interpreted to record the
373 high-pressure metamorphism.

374

375 Texturally, rutile rims early magmatic Ti-magnetite (Figure 6a). Regardless of the P – T path taken
376 by the clast, rutile growth would have occurred on the prograde path (Figure 8), and continued to
377 be stable to the peak conditions. To demonstrate this, black dashed lines on the mineral equilibria
378 model indicate the stabilization of rutile (rutile in) and the maximum rutile mode reached (Figure
379 8a), after this mode line rutile abundance is unchanging as it does not continue to grow. As the
380 closure temperature of U–Pb diffusion in rutile is estimated to be ca. 600–640 °C (Zack &
381 Kooijman 2017), the age of ca. 47.5 Ma most likely represents the growth of rutile during prograde
382 metamorphism.

383

384 The mechanism of metamorphic zircon formation in low-temperature metamorphic rocks is still
385 not well understood. Zircon occurs in the clast as small (5–50 μm) euhedral grains within matrix
386 amphibole and epidote/allanite (Figure 6b,c). Metamorphic zircon in blueschist-facies mafic rocks
387 is thought to grow as a result of either dissolution-precipitation of inherited zircon, or release of
388 zirconium through the breakdown of higher temperature minerals such as magmatic pyroxene (e.g.
389 Rubatto and Hermann, 2007) and granulite-facies rutile (Zack & Kooijman 2017). There is no
390 evidence for relic inherited zircon or textural features suggesting dissolution-precipitation (Rubatto
391 and Hermann, 2007; Rubatto et al., 2008). Possible mechanisms of zircon growth in the sample are
392 the breakdown of Zr-bearing magmatic minerals which persisted to high pressures (Rubatto and
393 Hermann, 2007). Breakdown of Ti-magnetite to form zircon (+ rutile + Fe-phase) on the prograde
394 path would result in both minerals producing similar ages as they were formed in the same
395 reaction. Alternatively, breakdown of magmatic clinopyroxene to amphibole also may release
396 zirconium, and may have been the source during prograde metamorphism (Rubatto et al., 2008).
397 While the exact prograde reaction that formed zircon is unclear, the closure temperature of U–Pb
398 diffusion in zircon is estimated to be $>900\text{ }^{\circ}\text{C}$ (Cherniak and Watson, 2001). Therefore, the Eocene
399 age is interpreted to record growth of zircon during metamorphism that occurred very soon after
400 subduction initiation.

401

402 The mineral equilibria modelling results indicate a peak to retrograde evolution from $\sim 1.6\text{ GPa}$ to
403 0.8 GPa . Although the exact P – T points are poorly constrained, the path is strongly supported by
404 textural relationships within the sample, mineral modal proportions, and the compositions of zoned
405 amphibole. It is possible to suggest a higher-pressure peak assemblage at approximately 1.6 ± 0.2
406 GPa and $585 \pm 20\text{ }^{\circ}\text{C}$, followed by a retrograde evolution towards $\sim 0.8 \pm 0.15\text{ GPa}$ and 485 ± 30
407 $^{\circ}\text{C}$. These conditions range in approximate apparent thermal gradients from $\sim 370\text{ }^{\circ}\text{C}/\text{GPa}$ at peak,
408 and $\sim 600\text{ }^{\circ}\text{C}/\text{GPa}$ during the retrograde evolution, with an average of around $470\text{ }^{\circ}\text{C}/\text{GPa}$. These
409 approximations could be within error of uncertainties within the mineral equilibria model

410 (Supplementary Figure 1), and the geochronology from the clast only constrains the prograde part
411 of this evolution. However, if it is not within error of the mineral equilibria model uncertainties,
412 the change in thermal gradient may reflect changes in subducting slab geometry, as the slab
413 becomes steeper at greater depth, resulting in lower thermal gradients at depth (Peacock, 2003;
414 Syracuse et al., 2010; Penniston-Dorland et al., 2015). Alternatively, the change in thermal
415 gradient could be due to the advection of heat within the rising serpentinite melange that carried
416 the blueschist clast to comparatively shallow depths within the subduction channel (Gerya et al.,
417 2002). These pressure-temperature conditions are in line with measured global subduction zone
418 data (Figure 9a,b,c; Penniston-Dorland et al., 2015; Brown and Johnson, 2017; Agard et al., 2018),
419 albeit slightly above the global average. When compared to numerical models (Figure 9d; Gerya et
420 al., 2002; Syracuse et al., 2010; van Keken et al., 2011; Ruh et al., 2018), the pressure-conditions
421 remain slightly above average, all though this may be due to the exclusion of shear heating as a
422 model parameter (e.g. Kohn et al., 2018). Combined with the U–Pb rutile and zircon
423 geochronology, the P – T data suggests the blueschist clast records initially warm conditions
424 relative to global norms during the early initiation of subduction of the Pacific plate (ca. 52 Ma;
425 Ishizuka et al., 2011; 2018; Agard et al., 2018). During the early stages of subduction, conditions
426 are generally warmer, as the plate subducts at a shallower angle, and the ‘dragging down’ of
427 geotherms at the base of the overlying mantle wedge has not yet been significantly achieved
428 (Gerya et al., 2002). ‘Warm’ pressure-temperature estimates from newly initiated subduction zones
429 have also been recorded by high-pressure mafic rocks (Figure 9c; Agard et al., 2018).

430

431 Forearc and reararc basalts mark the initiation of subduction in the Mariana system, and are
432 immediately followed by forearc boninite magmatism from 48.2–45.1 Ma (Reagan et al., 2008;
433 Ishizuka et al., 2011; Arculus et al., 2015; Reagan et al., 2017). The eruption of these boninites
434 necessitates the interaction of very depleted mantle wedge with slab-derived fluids at shallow
435 depths during subduction, and was coeval with blueschist metamorphism (this study). The
436 similarity between the metamorphic ages obtained in this study and the age of boninitic
437 magmatism, as well as the higher than usual thermal gradients recorded by the mineral

438 assemblage, supports the existence of a hot mantle wedge above a warm subduction channel
439 during early stages of subduction initiation in the Marianas.
440
441 If only lithostatic pressure is assumed, then the pressure estimates correspond to depths ranging
442 from ~46 km to ~25 km. Therefore, it appears the retrograde P - T path essentially ends at
443 conditions corresponding to the slab depth below the South Chamorro Seamount (~27 km; Pabst et
444 al., 2012; Fryer et al., 2006). ODP Site 1200 is on the summit of the seamount (Figure 1b;
445 Shipboard Scientific Party, 2000), and therefore it can be assumed that the drill core represents
446 most recent mud extrusions from the serpentinite-mud volcano (Fryer et al., 2006). The oldest
447 magmatic volcanism in the current Mariana arc (or Mariana ridge, Figure 1b) is interpreted to be
448 ca. 3–4 Ma (Stern et al., 2003), and as such the position of the subduction zone and the maximum
449 age of the serpentinite volcanoes is reasonably inferred as being similar. However, the rutile and
450 zircon ages record metamorphism at ca. 50 Ma. This suggests that the clast was trapped
451 somewhere within the subduction channel for at least ca. 46 Ma. The preservation of mineral
452 assemblages that record ‘warm’ peak metamorphic conditions, as well as metamorphic rutile and
453 zircon with Eocene ages, can be explained by either residence at peak depths for a significant
454 portion of the metamorphic history of the clast, or that this clast was exhumed to shallower depths
455 under the forearc and resided at cool conditions where recrystallization of minerals to lower
456 pressure-temperature assemblages was not achieved. Unfortunately, there are no geochronologic
457 constraints on when the blueschist was exhumed from depth to distinguish between these
458 possibilities. The lack of retrograde recrystallisation may suggest that the small clast was protected
459 from fluids and may have been armoured within a larger blueschist boudin or ‘knocker’, as
460 commonly occur in high-pressure metamorphic and serpentinite mélanges such as the Franciscan
461 Complex and Carribean (cf. Becker and Cloos, 1985; Lázaro et al., 2009; Blanco-Quintero et al.,
462 2011). While the lack of geochronology on the retrograde history of the rock precludes definite
463 explanation, it seems likely that the clast was exhumed to a shallow refrigerated region under the
464 forearc in the Mariana subduction channel some time between ca 49 and 3 Ma, prior to its eruption
465 in the mud volcano (Figure 10). However, the exact mechanism of this exhumation from ca. 50 km

466 deep remains unknown. It could have occurred as return flow of the hydrated serpentinite mantle
467 wedge cycled high-pressure material as the Mariana subduction system matured and steepened
468 (Gerya et al., 2002). Alternatively, detachment and slicing of oceanic crust within the subduction
469 channel could have allowed partial exhumation of the blueschist-facies material (Ruh et al., 2015;
470 Agard et al., 2018). Regardless, given that the clast is erupted in a serpentinite-mud volcano,
471 serpentinite-driven buoyancy appears to have been an important part of the exhumation
472 mechanism.

473

474 Implicit in the above scenario is that the blueschist must have formed during the early stages of
475 subduction under the proto-IBM arc. A number of workers (e.g. Cosca et al., 1988; Reagan et al.,
476 2008; 2010; Ishizuka et al., 2018), have argued that subduction initiated at around 51–47 Ma ago.
477 High-pressure metamorphism at ca. 50 Ma supports the upper scale of those scenarios. The current
478 location of the trench is ~ 1300 km to the east of the ridge (Figure 1a), as slab rollback has resulted
479 in extension of the Philippine Sea Plate. This means that the forearc not only entrapped and
480 preserved the blueschist clast, but it also survived at least partly intact in its ~1300 km long
481 eastward journey transported by slab rollback. A similar scenario has been suggested for long-
482 lived (>40 Ma) entrapment of high-pressure metamorphic rocks in serpentinite mélangé in other
483 oceanic subduction systems such as the Caribbean and the Franciscan Complex (Krebs et al.,
484 2008; Lázaro et al., 2009; Blanco-Quintero et al., 2011).

485

486 The age and source region of the blueschist clast sampled from the South Chamorro seamount has
487 implications for interpretations and future models regarding subduction zone conditions inferred
488 from past studies on erupted clasts and muds from these seamounts. Some authors (Fryer et al.,
489 1992; Savov et al., 2005; Fryer et al., 2006; Murato et al., 2009), have indicated that subduction
490 products from serpentinite volcanoes may be sampled from greater depths than the slab
491 immediately below the mud volcano and therefore have more complex source regions. However,
492 they have been unable to quantify those depths. These authors have also assumed that the material
493 exhumed in the mud volcanism was recently subducted. As such, the data has been used to

494 describe ongoing Mariana trench subduction systematics, when in fact the subduction zone retains
495 an integration of material from its inception until recently. The inferred depth from the modelled
496 metamorphic assemblage in the blueschist clast indicates that the ‘plumbing system’ of the
497 Marianas mud volcanoes is much more temporally and spatially complex than previously thought,
498 meaning the metamorphic clasts in the IBM mud volcanoes capture a long history of the chemical
499 and thermal evolution of the western Pacific slab. This temporally and spatially complex range of
500 sources for material from the mud volcanoes means that caution should be exercised when
501 interpreting data from clasts or muds erupted from seamounts in the Mariana forearc.

502

503 **6. Conclusions**

504

505 Detailed petrographic analyses and mineral equilibria forward modelling of a blueschist clast from
506 the South Chamorro Seamount in the Mariana forearc indicates the mud volcano samples material
507 from depths of ca. 50 km, which is well below the current depth of the slab directly below the
508 volcano. The modelled P – T conditions (ca. 1.6 GPa and 590 °C) of the blueschist clast indicate the
509 thermal regime was warmer than typical oceanic subduction, suggesting the modelled mineral
510 assemblage formed in the initial stages of the IBM subduction system. This is consistent with
511 concordant U–Pb ages of ca. 50 Ma from rutile and zircon within the blueschist assemblage,
512 confirming the mineral assemblage formed soon after the Pacific plate began subducting under the
513 Philippine Sea plate. Maturation of the subduction zone and formation of serpentinite within the
514 subduction channel then facilitated return flow, driving exhumation of the blueschist clast to a
515 refrigerated region under the forearc for at least ca. 46 Ma, before it was erupted in the South
516 Chamorro mud volcano in the Mariana forearc. During this period of time there was ~1300 km of
517 east-directed slab rollback, which transported the blueschist and other early subduction products
518 with it. Therefore the South Chamorro Seamount, and by inference other volcanoes in the Mariana
519 forearc, are probably sampling a temporally and spatially diverse range of lithologies and P – T – t
520 histories that document the thermal evolution of the surface of the subducting plate over time. The
521 data from the Mariana system suggests that potential serpentinite hosted blueschist and eclogite

522 blocks in ancient subduction product complexes (e.g. Franciscan and Caribbean) may hold
523 extensive records of the thermal evolution of subducting slabs.

524

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531

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695

696 *Figure captions*

697

698 **Figure 1.** a) Bathymetric map of the Mariana segment of the IBM system, showing the tectonic
699 plates and ridges. Cross section is marked a' to b'. Location of South Chamorro Seamount is
700 indicated in black arrow. Modified from Fryer et al. (2002). b) 3D bathymetric image of South
701 Chamorro Seamount, indicated ODP drill site location after Savov et al (2005). c) Interpreted
702 cross section (a'–b') of the Mariana trench and forearc. Vertical exaggeration is 2:1. Plate
703 location and structure of the Philippine and Pacific plates after Fryer et al. (1999), Oakley et al.
704 (2008) and Pabst et al. (2012). Schematic representation of serpentinisation after Ruh et al.
705 (2015).

706

707 **Figure 2:** Mineralogical map of blueschist chip sample E1H3-4b, based on BSE imaging and
708 X-ray derived elemental maps. C and R correspond to examples of amphibole cores and rims.
709 Fine-grained minerals such as pumpellyite, clinopyroxene and zircon are not visible at this
710 scale.

711

712 **Figure 3:** Electron microprobe X-ray element maps of blueschist chip E1H3-4b. Black and
713 cooler colours indicate lower concentrations, whereas warmer colours indicates higher
714 concentrations. The maps are not quantitative and the colours scales from different maps do not
715 indicate the same numerical concentrations.

716

717 **Figure 4:** a) BSE and X-ray elemental maps of an amphibole grain from the blueschist clast.
718 Dotted white lines indicate the boundary of the core, main grain volume and sharp rim. b) BSE
719 and X-ray elemental maps of a chlorite grain that includes epidote (white core). Dotted line
720 indicates thin outer rim. The maps are not quantitative and the colours scales from different
721 maps do not indicate the same numerical concentrations.

722

723 **Figure 5:** Mineral composition plots. a) Amphibole compositions. b) Chlorite compositions. c)
724 Epidote compositions. d) Clinopyroxene compositions.

725

726 **Figure 6:** BSE images of locations of rutile and zircon targeted for U–Pb dating by Zack et al.
727 (2013). a) Metamorphic rutile rimming Ti-magnetite, further rimmed by retrograde titanite. b)
728 Zircon in the amphibole matrix. c) Zircon associated with metamorphic allanite/epidote. Ti-
729 mag: Ti-magnetite, Ru: Rutile, Ttn: Titanite, Ep: Epidote, Chl: Chlorite, Amph: Amphibole,
730 Zrc: Zircon, All: Allanite.

731

732 **Figure 7:** U–Pb Concordia for a) rutile and b) zircon analyses conducted on blueschist clast
733 sample E1H3-4b. Individual error ellipses (open) and error-weighted averages (filled) are
734 plotted at 95% confidence. Ages are calculated as concordia ages with probabilities of
735 concordance of 0.98 (rutile) and 0.69 (zircon) using Isoplot v.4.15 (Ludwig, 2012).

736

737 **Figure 8:** *P–T* mineral equilibria model for the blueschist chip, bulk composition used is in
738 upper left corner in mol %. a) Mineral equilibria model with inferred *P–T* path as a grey arrow,
739 dashed line represents unconstrained evolution. Fine black dotted line indicates rutile in and
740 maximum rutile modes. Variance is coloured where $v = 6$ is the darkest shade and variance
741 decreases as the shade lightens. Purple dashed lines indicate the locations of the omphacite-
742 diopside and actinolite-hornblende solvi. b) Mineral equilibria model with ranges of amphibole
743 compositions A (xNa on the A site), C (xCa on the M4 site) and Z (xNa on the M4 sites) are
744 shown as shaded grey areas, and mineral modes as coloured solid lines. Chl: chlorite, Amph:
745 Amphibole, O: Omphacite, Di: Diopside, Ep: Epidote, Ru: Rutile, Ttn: Titanite, Act: Actinolite,
746 Gl: Glaucophane, Q: Quartz, Ilm: Ilmenite, Hem: Hematite, Law: Lawsonite, G: Garnet.

747

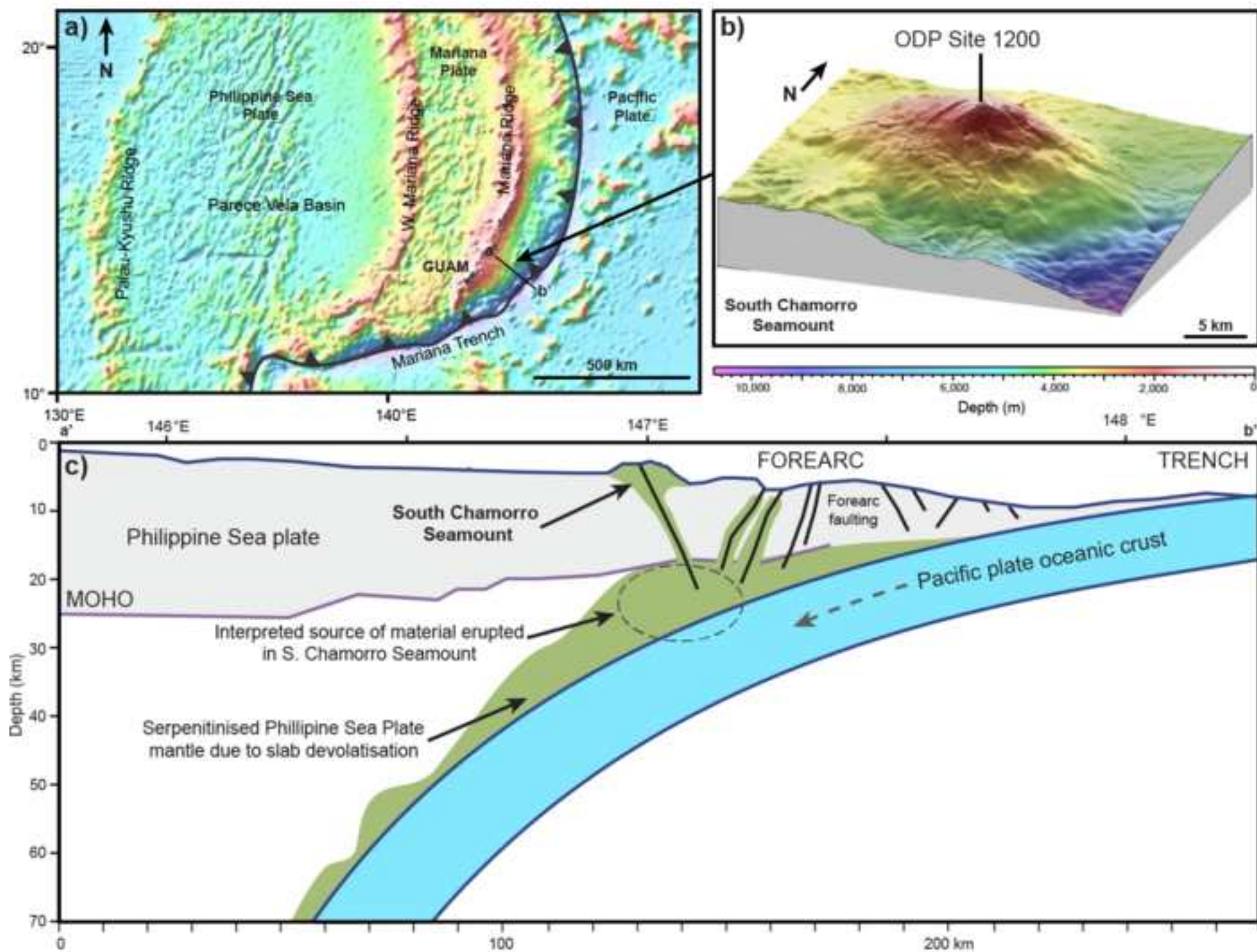
748 **Figure 9:** Pressure–temperature estimates from real subducted rocks and numerical models.
749 Grey arrow indicates the P–T path of this study. a) Real rock dataset of Penniston-Dorland et
750 al. (2015). b) Real rock dataset of Brown and Johnson (2018), including all low temperature-
751 high pressure datasets. c) Real rock dataset of Agard et al. (2018), data from mélanges is
752 indicated as circles. d) Prograde pressure-temperature paths taken from the top of subducting
753 slabs from numerical models of Gerya et al. (2002), Syracuse et al. (2010), van Keken et al.
754 (2011) and Ruh et al (2015).

755
756 **Figure 10:** Schematic model for formation and exhumation of the blueschist chip. Structure of
757 subduction zone after Fryer et al. (1999), Oakley et al. (2008) and Pabst et al. (2012).
758 Schematic serpentinitisation after Ruh et al (2015). Blueschist clast indicated as purple star. The
759 mechanism of exhumation of the blueschist clast from ca. 50 km ca. 49 Ma ago to the shallow
760 region under the forearc before the last 3 Ma is unknown.

761

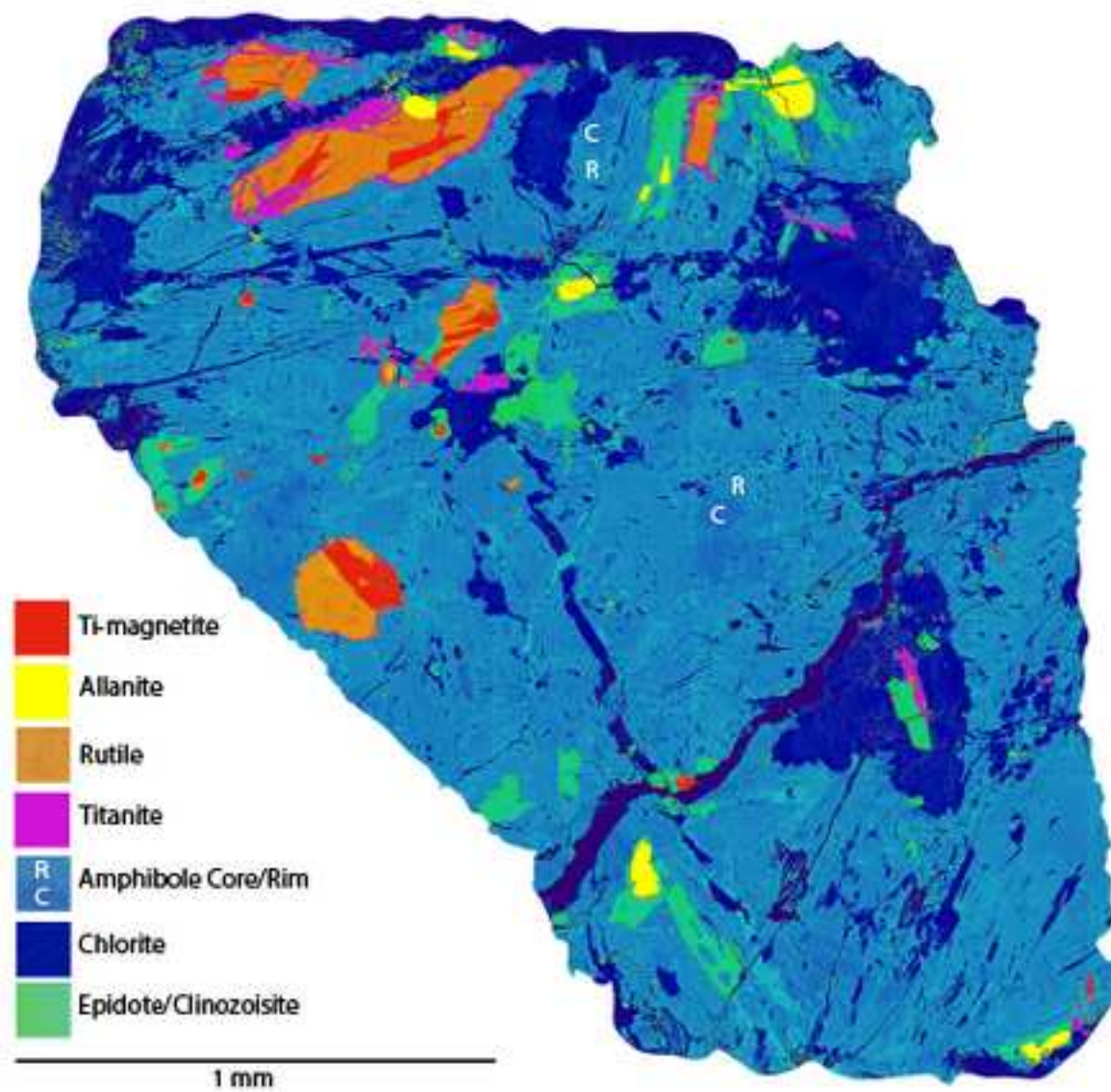
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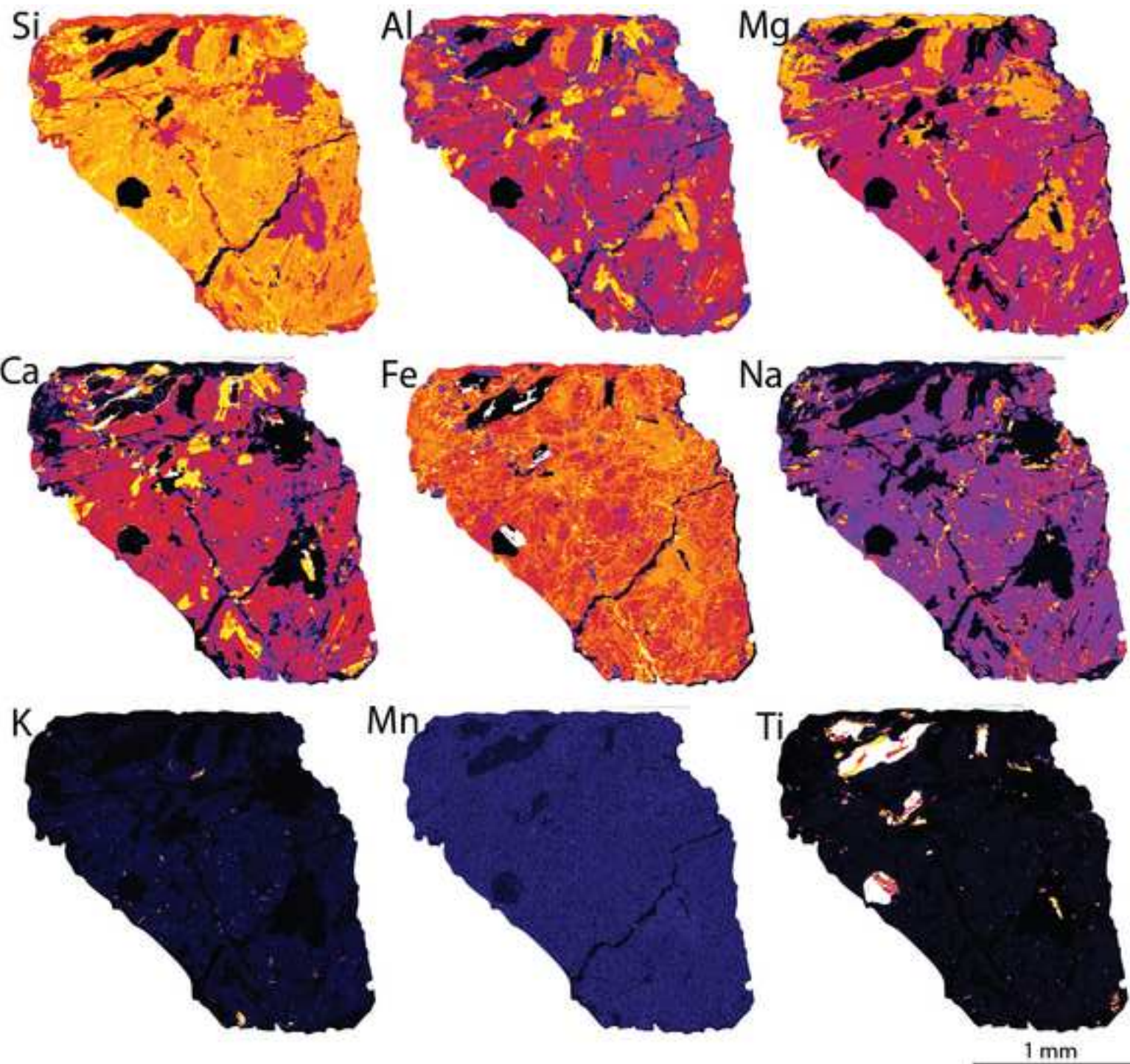
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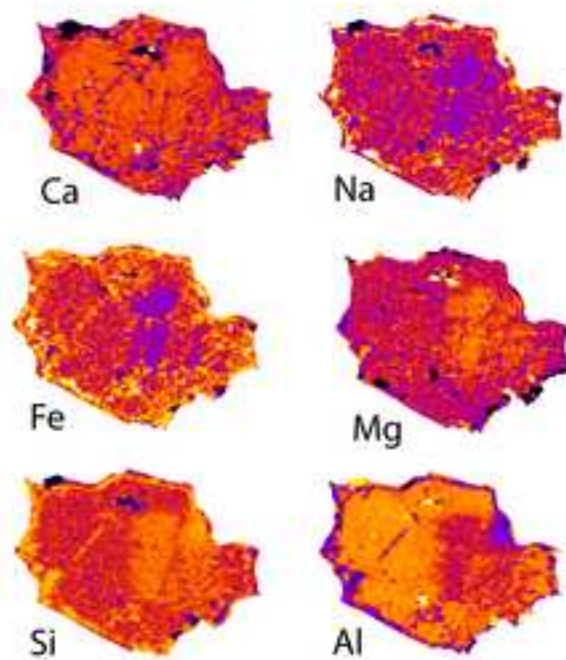
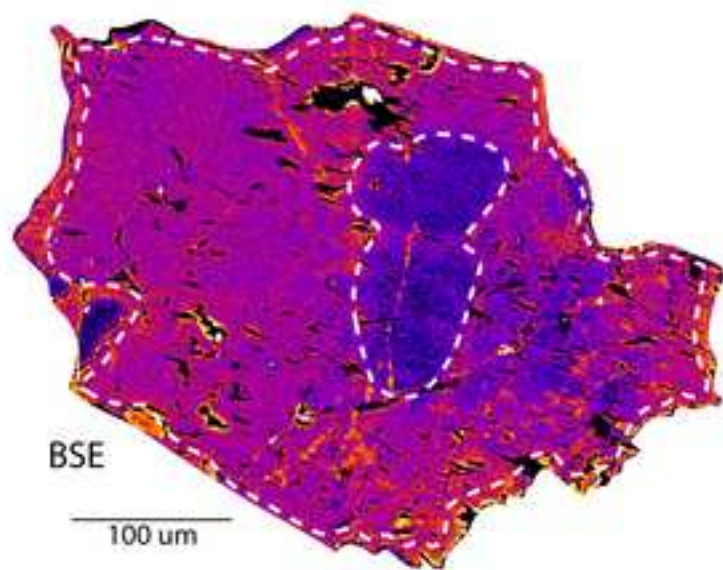


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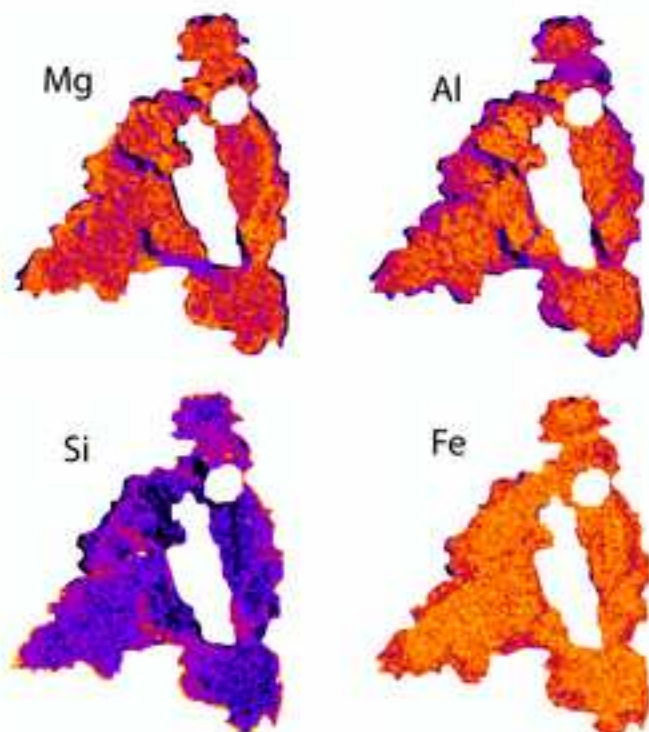
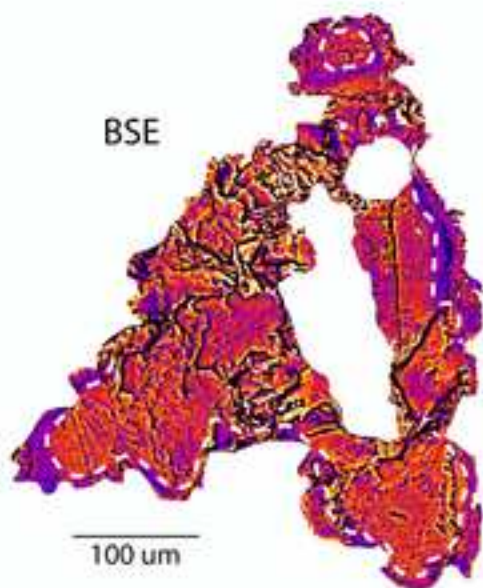
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a) Amphibole



b) Chlorite



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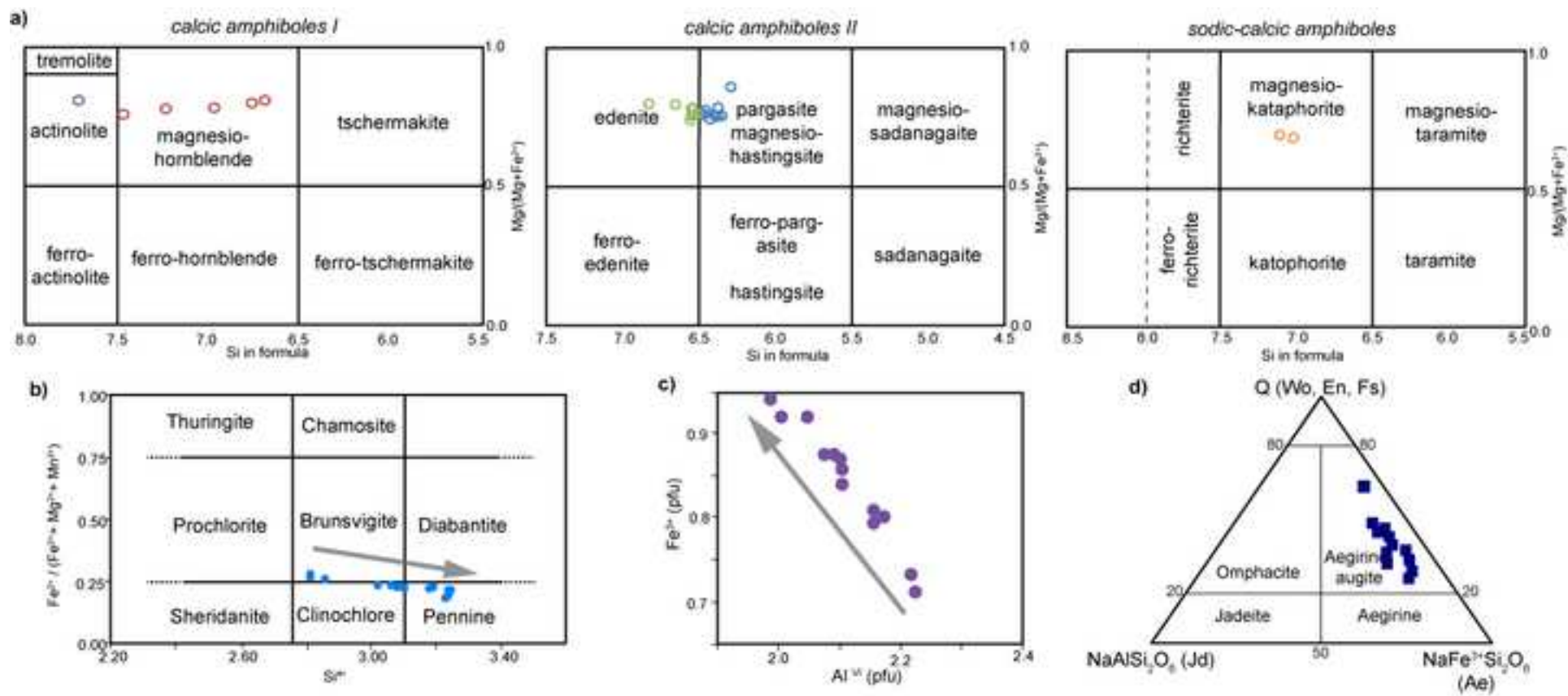
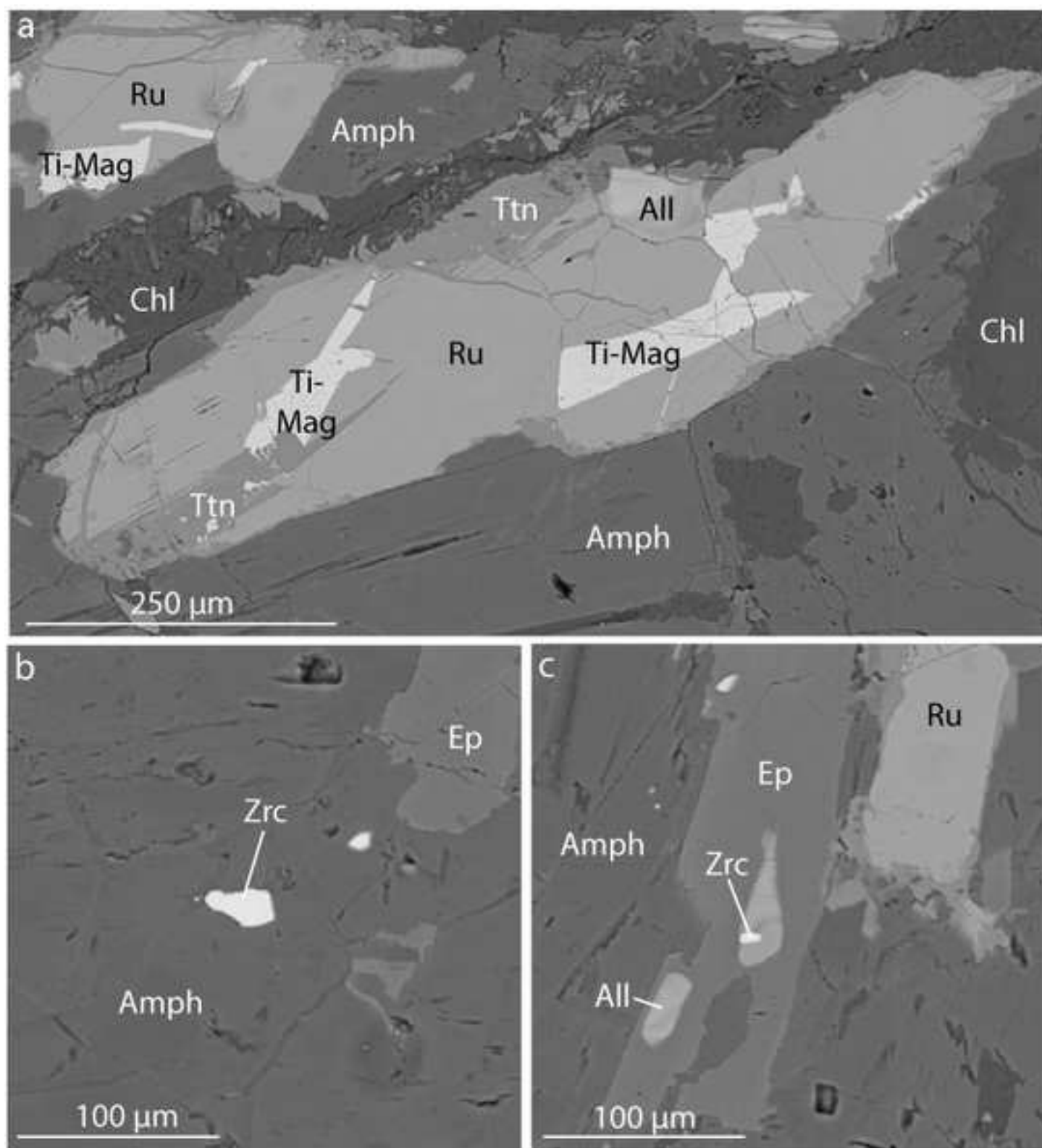
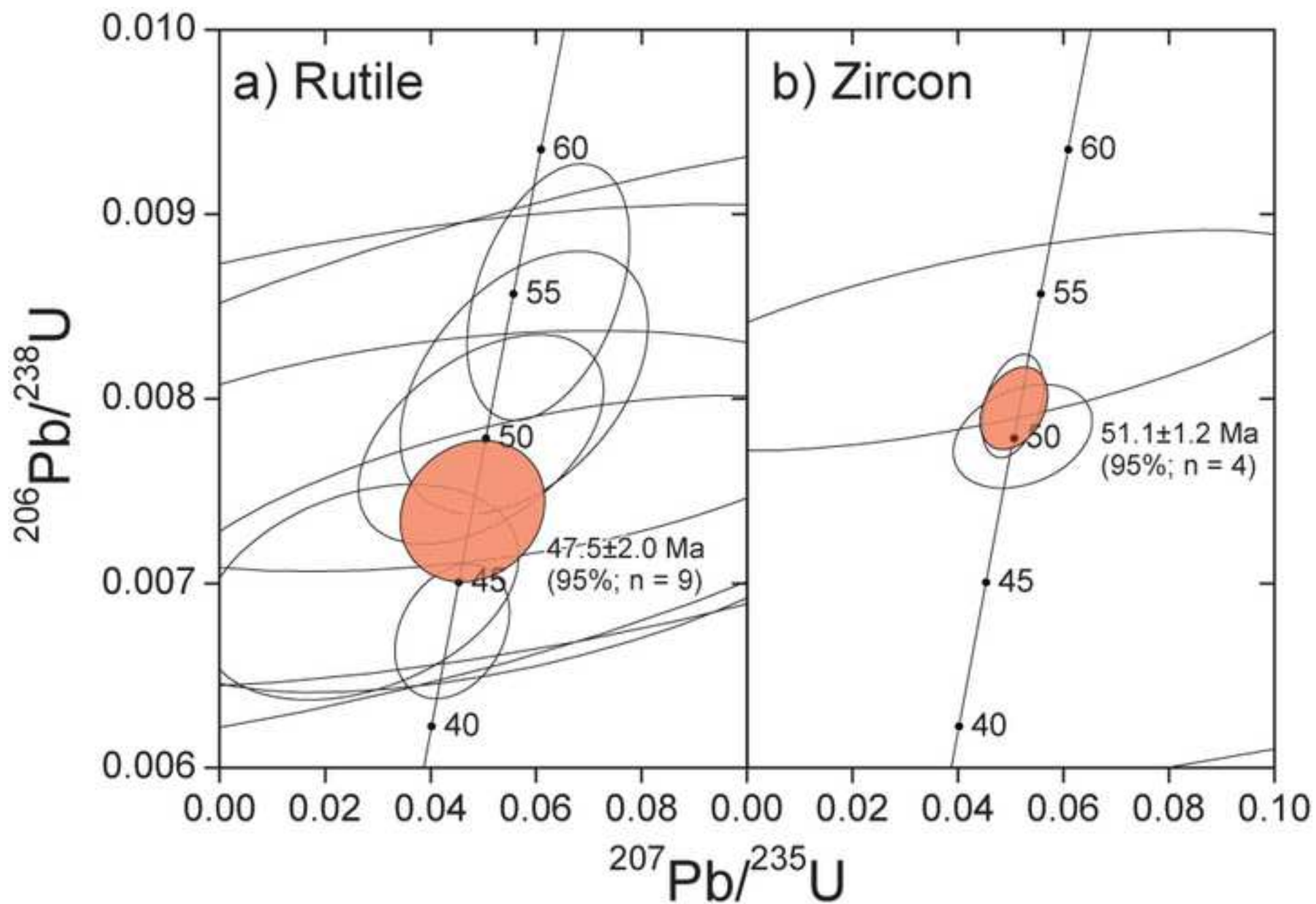


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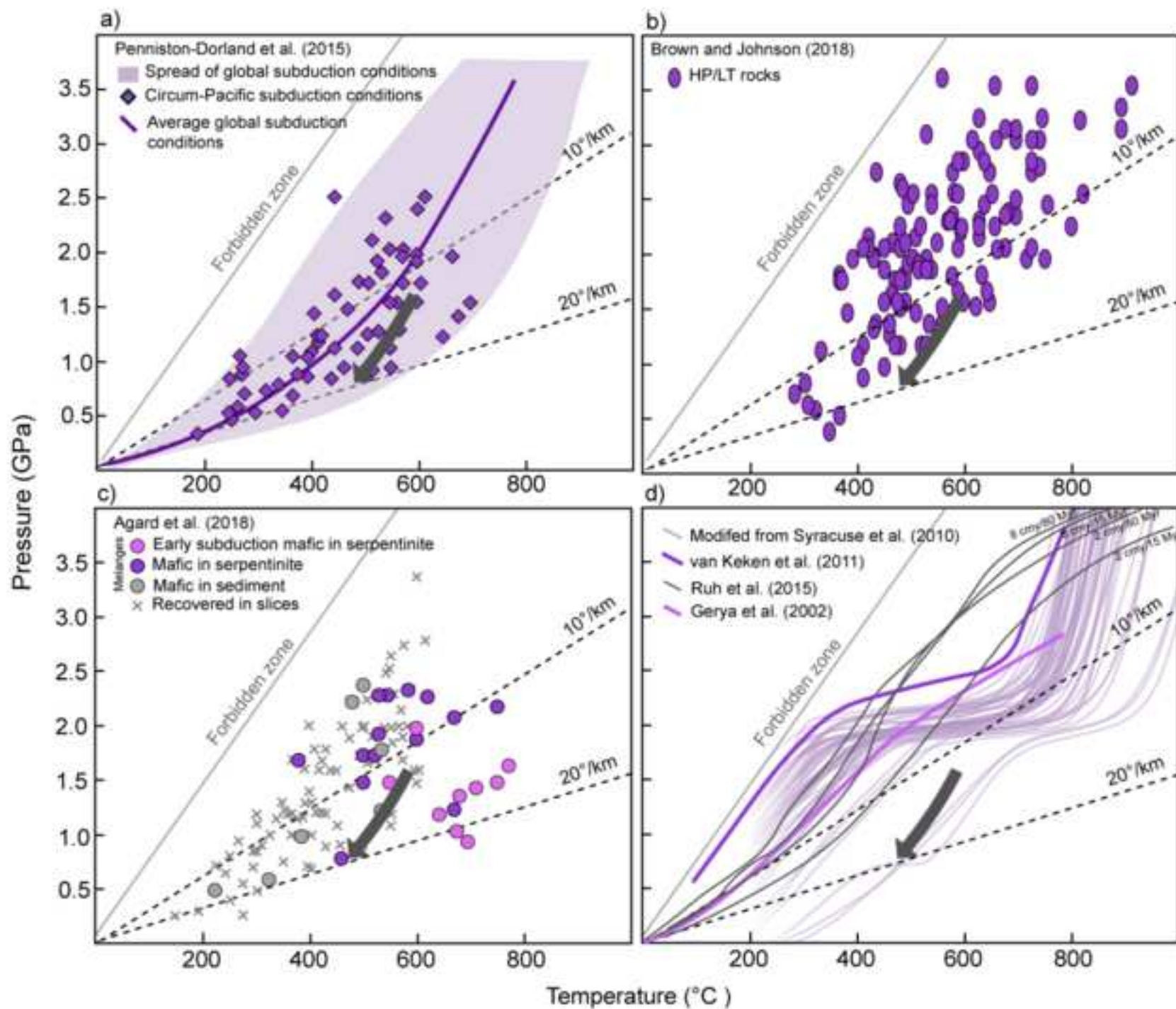


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