1	The slab-mantle wedge interface of an incipient subduction zone: Insights from the <i>P-T-D</i>										
2	evolution and petrological characteristics of the Dalrymple Amphibolite, Palawan Ophiolite,										
3	Philippines										
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Abstract

11

In this contribution, we present the petrological characteristics and pressure-temperaturedeformation (*P-T-D*) history of the Dalrymple Amphibolite in Palawan Island, Philippines. This unit occurs below the residual mantle peridotites of the Palawan Ophiolite composed of interlayered dunite and harzburgite. The Dalrymple Amphibolite is predominantly comprised of high-grade metamafic blocks with minor metasedimentary units surrounded by a highly sheared hybridized matrix (kyanite + Ca-amphibole + biotite + ilmenite  $\pm$  garnet).

18 Zr-in-rutile geothermometry and quartz-in-garnet geobarometry of the garnet amphibolite 19 block reveals the P-T conditions of the prograde metamorphism from ~625 °C, 11.5 kbar to ~700 °C, 20 13 kbar. Zr-in-rutile geothermometer and the TZARS geobarometer (clinozoisite + rutile + quartz = 21 anorthite + titanite + H<sub>2</sub>O) further indicate comparable peak metamorphic conditions for the 22 amphibolite and epidote amphibolite (~605-710 °C, 10-13 kbar) blocks. Geothermobarometry of the 23 matrix surrounding the blocks reveals similar peak metamorphic conditions of ~700 °C and 13 kbar 24 to the garnet amphibolite blocks. The paleogeothermal gradient preserved in the Dalrymple 25 Amphibolite (~16 °C/km) and its block-in-matrix structure are atypical of metamorphic soles, and are more akin to high-T mélange complexes interpreted to have formed during incipient subduction. These 26 27 *P-T* estimates and its block-in-matrix structure suggest that the Dalrymple Amphibolite likely 28 represents the slab-mantle wedge interface of a young arc complex already transitioning from the 29 much warmer paleogeothermal gradients of the slab-mantle wedge interface when subduction was first 30 initiated.

The similar peak metamorphic conditions constrained in the matrix and the metamafic blocks in the Dalrymple Amphibolite indicate that the matrix-forming deformation started before the sequence reached peak metamorphic conditions at depths of around 45 km. Furthermore, the petrological and geochemical characteristics of this block-in-matrix sequence and the multiple generation of cross-cutting veins reveal the complex processes that occur in the slab-mantle wedge interface of an arc in its infancy. Our results highlight the prevalence of Ca-amphibole and kyanite over phyllosilicates (e.g. chlorite and serpentine) in the mélange matrix, mixing of crustal components

along the slab-mantle wedge interface promoted by multiple deformation events and the ubiquity of
fluids throughout its history. Subduction zones with similar geothermal gradients (e.g. warm
subduction zones) possibly share these petrological characteristics.

41 Keywords: Dalrymple Amphibolite, slab-mantle wedge interface, incipient subduction zone, mélange
42 complex

43 1. Introduction

44 The boundary between the subducting oceanic lithosphere and the mantle wedge, i.e. slab-45 mantle wedge interface (also termed subduction channel by Bebout, 2013 and plate interface by Agard 46 et al., 2016, 2018), is a dynamically evolving component of intraoceanic subduction zones. Processes 47 that occur in this interface are thought to control arc magma chemistry (Marschall and Schumacher, 48 2012; Codillo et al., 2018). Much of the information on the slab-mantle wedge interface beneath a 49 mature arc comes from studies of high P/T type metamorphic terranes (e.g. Locatelli et al., 2019). 50 These studies reveal chaotic mélange complexes that preserve paleogeothermal gradients of 4-51 10 °C/km (e.g. Guillot et al., 2009; Bebout and Penniston-Dorland, 2016). These complexes are 52 composed of blocks derived from the underthrusting slab and the overlying serpentinized mantle 53 surrounded by a highly sheared, fluid-rich matrix (e.g. Guillot et al., 2009; Bebout, 2013). This matrix 54 represents the mixture of end-member lithologies (sediment, basalt/gabbro, and peridotite) in the slab-55 mantle wedge interface (e.g. Bebout and Barton, 2002; Marschall and Schumacher, 2012).

56 The slab-mantle wedge interface during the earliest stages of intraoceanic subduction on the 57 other hand, is sometimes preserved as relatively intact sheets of metamorphic soles that underlie the mantle section of ophiolites. Ophiolites, which are fragments of fossil oceanic lithosphere, allow direct 58 59 observation of the spatial, temporal and structural relationships of the different sections comprising an oceanic crust and mantle. Studies of metamorphic soles (e.g. Semail Ophiolite, Oman) reveal that 60 61 these thin sheets of amphibolite- and granulite-facies grade metamorphic rocks preserve much higher 62 geothermal gradients of >20 °C/km and are typically formed within the first 2 Myr of subduction 63 inception (e.g. Soret et al., 2017; Agard et al., 2018).

64 Less information is however available on the petrological characteristics and metamorphic 65 evolution of the slab-mantle wedge interface as it transitions from a young and hot subduction zone to 66 a mature arc with more hydrous minerals (e.g. chlorite and serpentine) stabilized at depth and marked 67 by cold geothermal gradients (e.g. Guillot et al., 2009). A potential candidate for understanding 68 relatively young island arcs is the Philippine island arc system which preserves a complex history of 69 subduction, rifting, and arc-continent collision (e.g. Yumul et al., 2003). In its western margin, the 70 collision between a nascent arc and the southward drifting North Palawan Continental Terrane (NPCT) 71 led to the emplacement of the Palawan Ophiolite. The Dalrymple Amphibolite, a relatively well 72 preserved high-grade metamorphic block-in-matrix complex, is located at the base of this ophiolite. 73 Earlier works interpret these metamafic blocks as the slab-mantle wedge interface (i.e. metamorphic 74 sole) of the Palawan Ophiolite (e.g. Encarnacion et al., 1995; Keenan et al., 2016).

In this contribution, detailed field characteristics of the metamafic blocks coupled with trace element geothermometry (i.e. Zr-in-rutile geothermometer) and elastic geobarometry (i.e. quartz-ingarnet Raman geobarometer) are used to constrain the pressure-temperature-deformation (*P-T-D*) history of the blocks and the matrix which comprise the Dalrymple Amphibolite. Additional constraints are obtained from conventional geothermobarometry, thermodynamic modelling and fluid inclusion microthermometry. Mineral abbreviations are after Whitney and Evans (2010) except for Ca-amphibole (Camp).

#### 82 2. Geological Setting

Palawan island is located in western Philippines and forms part of the Palawan 83 84 Microcontinental Block (PCB). It is divided into two terranes, the North Palawan Continental Terrane (NPCT) and the oceanic South Palawan Terrane (SPT, Fig. 1a). The NPCT was part of the Southeast 85 86 Asian continental margin from Paleozoic through Mesozoic (Padrones et al., 2017; Cao et al., 2020). 87 During the Eocene to Oligocene, rifting in the Southeast Asian margin resulted to the southward drift 88 of the NPCT and ultimately led to the opening of the South China Sea marginal basin (Yumul et al., 89 2003; Keenan et al., 2016). The compression due to the southward drift of the NPCT was 90 accommodated by subduction on its southeastern front forming a nascent arc. Some authors argue that

91 the Cagayan de Sulu Ridge (CR in Fig. 1a) is the remnant of this nascent arc (Rangin and Silver, 1991). 92 There is however, a significant difference in the proposed age of subduction initiation based on the 93 igneous crystallization age of the ophiolite (~34 Ma; Encarnacion et al., 1995) and the cooling age of 94 the metamorphic sole (~34 Ma; Keenan et al., 2016) compared to the age of arc magmatism in the CR (~18-16 Ma; Rangin and Silver, 1991). During the Late Oligocene to Early Miocene, the NPCT 95 96 collided with this nascent arc and segments of the overlying plate were thrusted on top of the continent-97 derived turbidites as the Palawan Ophiolite (e.g. Keenan et al., 2016). Slivers of this fossil oceanic 98 lithosphere crops out extensively in the central and southern segments of the island and is referred to 99 as the South Palawan Terrane. Questions remain with regard to the presence of another Mesozoic 100 ophiolite exposed in south Palawan and underthrusting the Eocene Palawan Ophiolite in central 101 Palawan (e.g. Muller, 1991; Labis et al., 2020). This work focuses on the Eocene ophiolite exposed 102 in central Palawan (e.g. Encarnacion et al., 1995; Keenan et al., 2016).

103 The Palawan Ophiolite represents a complete ophiolite sequence with basaltic pillow lava flows, 104 isotropic and layered gabbroic and ultramafic cumulates comprising the crustal section and the residual mantle peridotites below (e.g. Dilek and Furnes, 2014). U-Pb geochronology of zircon separates from 105 106 a plagiogranite associated with the ophiolite revealed the igneous crystallization age of the ophiolite 107 to be  $34.1 \pm 0.1$  Ma (Encarnacion et al., 1995). A thin block-in-matrix complex composed of high-108 grade metamorphic rocks underlie the interlayers of mostly fresh to moderately serpentinized dunite 109 and harzburgite in the localities of Botoon, Nanad and Dalrymple points (Fig. 1b). This unit is 110 collectively referred to as the Dalrymple Amphibolite (Fig. 1b). Less extensive metamafic exposures 111 also occur further south along Malatgao river in Dumangueña, Aborlan (Fig. 1a; Raschka et al., 1985). 112 The Dalrymple Amphibolite, along with the other ophiolitic lithologies, are thrusted on top of 113 deformed Eocene turbidites referred to either as Panas-Pandian Formation or the Barton Metamorphics 114 (Fig. 1a; Aurelio et al., 2014).

Earlier studies on the Dalrymple Amphibolite exposed in Ulugan Bay in central Palawan,
estimated the peak *P-T* conditions of its formation at 700–760 °C at a minimum pressure of 9 kbar

117 using conventional geothermobarometry, i.e. Grt-Camp-Pl-Qz geobarometer and Grt-Bt and Grt-118 Camp geothermometers (cf. Encarnacion et al., 1995).  ${}^{40}$ Ar/ ${}^{39}$ Ar ages of  $34.2 \pm 0.5$  Ma,  $34.2 \pm 0.6$  Ma 119 and  $34.3 \pm 0.3$  Ma were obtained from two amphibole samples in metamafic blocks and one muscovite 120 from kyanite-chlorite-muscovite schists, respectively (Encarnacion et al., 1995; Keenan et al., 2016). 121 These were interpreted as metamorphic cooling age of the Dalrymple Amphibolite (Encarnacion et al., 122 1995). Chemical Abrasion Thermal Ionization Mass spectrometry (CA-TIMS) U-Pb dating of 123 oscillatory-zoned zircons from competent pods in the Dalrymple Amphibolite yielded weighted mean 124 ages of  $35.242 \pm 0.062$  Ma,  $35.862 \pm 0.048$  Ma and  $35.25 \pm 0.15$  Ma (Keenan et al., 2016). This was 125 interpreted as the igneous crystallization age of the mafic protolith of the metamafic blocks.

126

### 2.1 Field Occurrence

127 The Dalrymple Amphibolite occurs as a mélange complex with blocks surrounded by a highly 128 sheared matrix in contrast to the relatively coherent sheets that characterize most metamorphic soles 129 (Agard et al., 2016; 2020). Earlier works, based on kinked quartz and kyanite in the metamafic blocks, 130 attributed the mélange-like appearance to a later, 'cold' deformation event that transformed a more 131 coherent metamafic and schist unit (Encarnacion et al., 1995). Several stages of deformation are 132 however possible in these shear zones as described below.

133 In Botoon point (10.1353°N 118.8133°E; Fig. 1b), the Dalrymple Amphibolite consists of 134 tabular, angular to subrounded blocks up to 15 m in length (Fig. 2a, b). Most blocks are metamafic, 135 with variable amounts of garnet and epidote. Randomly-oriented epidote-veins are locally developed 136 in an amphibolite block but do not continue to the surrounding matrix (Fig. 2c, d). Minor 137 metasedimentary blocks are also observed, including metacherts (i.e. Camp-Czo quartzites) and 138 metacarbonates replaced by Ep amphibolite. The foliation in some blocks is marked by the 139 arrangement of elongate minerals (e.g. amphibole) or the interlayers of quartz-rich and mafic domains dipping gently  $(\sim 30^\circ)$  to the SE. The foliation in the blocks is denoted as S1 (e.g. Fig. 2e). 140

141 The blocks in Botoon are surrounded by a sheared matrix material occupying the low-lying142 portions of the exposure (Fig. 2a-d). Two generations of matrix formation defined by the same

143 assemblage (Ky+Camp+Bt+Grt+Ilm) but distinguished by cross-cutting pervasive foliation directions 144 are observed (matrix 2a and 2b in Fig. 2). In some parts of the exposure, the foliation of the earlier 145 matrix 2a denoted as S2a (e.g. Fig. 2e) are generally subparallel to those of the blocks. Elongate 146 minerals such as kyanite and Ca-amphibole exhibit foliation S2a and a WNW-ESE mineral lineation 147 is observed locally in the kyanite and quartz. In other parts of the exposure, coarse kyanite grains are 148 surrounded by accumulations of ilmenite (Fig. 2f, g). Quartz and Qz-Ky-rich domains occur as 149 deformed lenses (Fig. 2e) arranged subparallel to the foliation of the matrix2a (S2a) and as veins cross-150 cutting the matrix (Fig. 2h) and the blocks. In some parts of the exposure, the matrix2a is cut by a 151 subsequent melanocratic matrix2b which transformed the earlier formed matrix2a into small 152 autochthonous blocks (Fig. 2i, j). The matrix2b in Botoon have the same mineralogy as the earlier 153 matrix2a but elongate minerals (e.g. Ca-amphibole and kyanite) exhibit distinct foliation, denoted as 154 S2b.

Some of the blocks (e.g. metacarbonates) in Botoon are surrounded by rinds (Ep amphibolite) with concentric foliation and separating the blocks from the matrix. In other blocks, a distinct rind is not observed but progressive changes in mineralogy (e.g. increasing garnet in some metamafic blocks) can be noted towards the contact with the matrix (Fig. 2d). The overlying interlayers of dunite and harzburgite are exposed in the NE side of the exposure.

160 The contact between the Dalrymple Amphibolite and the mantle section of the ophiolite is best 161 exposed in Nanad (Figs. 1b, 3a). Shear-sense indicators suggest a top-to-the-NW sense of movement 162 (Fig. 3b). Shearing is also more pervasive in Nanad than Botoon. The blocks in Nanad are smaller and 163 have rounded to subrounded corners compared to those in Botoon (Fig. 3c). The matrix2a with 164 Ky+Camp+Bt+Grt assemblage in Botoon is also found as randomly-oriented blocks in this locality 165 (Fig. 3d-e). Amphibolite cut by Qz-Ky veins, also observed in Botoon, occur as blocks in Nanad. 166 These veins abruptly end and do not continue towards the surrounding matrix2b (Fig. 3f, g). In Botoon 167 matrix2b occurs locally, cross-cutting the predominant matrix2a. In Nanad, matrix2b is the dominant 168 matrix type. This matrix2b (Grt+Ky+Camp+Bt+Qz) surrounds metamafic and matrix2a blocks as well as garnet (0.5–5 mm), peapod-shaped Ca-amphibole (0.5–7 mm) and altered kyanite porphyroclasts.

- 170 Local S-C fabrics are also exhibited by matrix2b in Nanad.

171 The metamorphic rocks are most extensively exposed in Dalrymple point (Figs. 1b, 4a). The 172 exposure can be divided to a block-dominated zone in the northwest which occurs proximal to dunite-173 harzburgite interlayers and a more homogenous amphibolite zone to the southeast (cf. Encarnacion et 174 al., 1995; Keenan et al., 2016). The NW zone consists of interlayered blocks of garnet amphibolites 175 (Fig. 4b, c), metachert quartzite (Fig. 4d) and biotite schists (Fig. 4e) with schistosity dipping 176 moderately (53°) towards the SE. In the northwestern section of the exposure, a resistant quartzite 177 block sits on top of the surrounding Camp-Ky-dominated matrix2a similar to the exposure in Botoon 178 (Fig. 4f). The schistosity of the matrix2a dips gently towards the SE while stretching lineation on S2a 179 (L2 in Fig. 4g) defined by hornblende is N-S. Kyanite crystals are also more extensively replaced by 180 pseudomorphic muscovite compared to other localities (Fig. 4g-h).

181 Further southeast of the block-dominated zone is a more homogenous, foliated and folded 182 amphibolite, Ep amphibolite sequence (Fig. 4a). The Ep amphibolites are highly sheared (i.e. fine to 183 very fine grained; 0.10–0.25 mm) and generally dip gently towards the SE (Fig. 4i-k). Epidote-rich 184 domains appear as subparallel veins rather than distinct, continuous layers (Fig. 4j, k). The 185 amphibolites commonly occur as elongated pods surrounded by Ep amphibolite and are coarse-grained 186 (Fig. 41). The sequence is crosscut by quartz veins that are subparallel and in places crosscut the S1 187 foliation of the Ep amphibolites (Fig. 4j, k). Encarnacion et al. (1995) interpreted the prevalence of Ep 188 amphibolites farther away from the metamorphic-ultramafic contact to signify decreasing 189 metamorphic grade southward although peak P-T estimates for the Ep amphibolites are lacking.

190 The information on samples used in this study are summarized in Table 1 while the deformation 191 stages (D1–D3), veining stages (V1–V3), mineral paragenesis and mineral occurrence based on the 192 field characteristics of the Dalrymple Amphibolite are summarized in Table 2. The timing of matrix 193 formation which surround the blocks relative to the *P-T-D* history of the blocks cannot be constrained 194 solely on field characteristics. In the metamorphic sole of the Semail (Oman) Ophiolite for example, 195 shearing which isolated and emplaced high-grade metamafic blocks against lower P-T metamorphic 196 rocks, occurred late in its P-T-D history (e.g. Soret et al., 2017). In the Catalina schists on the other 197 hand, petrological and field characteristics reveal that matrix formation started early at lower grades 198 and the mélange sequence as a whole was subsequently exposed to higher P-T conditions along the 199 subduction channel (e.g. Penniston-Dorland et al., 2014; 2018). In the case of the Dalrymple 190 Amphibolite, constraining the P-T-D history of the blocks and the surrounding matrix is needed to 201 elucidate the origin of the block-in-matrix sequence as a whole.

202 The information for the metamafic and metasedimentary blocks are therefore recorded as Stage 203 1 while those of the matrix are regarded as Stage 2 in Table 2. In the exposures in Botoon and northwest 204 Dalrymple, the first stage of deformation (D1) is preserved as foliation (S1) in the blocks. Deformation 205 events related to the formation of schistosity (S2a) and stretching lineation (L2) in matrix2a is marked 206 as D2a. In Botoon, the start of a subsequent deformation event (D2b) is hinted by the formation of 207 matrix2b which crosscuts the matrix2a (Fig. 2i, j) and follows a distinct foliation direction (S2b). The 208 exposure in Nanad exhibits a more pervasive D2b deformation. Matrix2a occurs exclusively as 209 rounded blocks (Fig. 3d, e) along with the blocks of other rock types which preserve the earliest stage 210 (Stage 1, D1). The surrounding matrix2b is finer-grained (~0.05 mm) than matrix2a, highly foliated 211 (S2b) and locally preserves S-C fabric (S2b and C2b).

Lastly, coarser Stage 1 and Stage 2 minerals comprising both the blocks and the matrix respectively, are partially to completely replaced by finer hydrous minerals in most samples, e.g. kyanite to muscovite and ferromagnesian minerals to chlorite, epidote and actinolite. These replacement minerals also occur as veins which cut through the foliation of the blocks and both matrix2a and 2b. This indicates a final retrograde stage (Stage 3) where the planar veins associated with Stage 3 indicate a late stage deformation event (D3) during Stage 3.

# 218 **3.** Analytical methods

Quantitative analysis of rock-forming minerals and X-ray elemental mapping of thin section
 samples were conducted using a JEOL JXA-8105 electron probe microanalyzer. Analytical conditions

221 for quantitative analyses were 15.0 kV acceleration voltage, 10 nA beam current, and 3 µm beam 222 diameter. The counting time for the peak and backgrounds were 30 s and 15 s for Cl, 60 s and 30 s for 223 F, and 10 s and 5 s for other elements. Natural and synthetic minerals were used as standards and ZAF 224 correction was applied. Representative mineral analyses are given in Tables 3 and 4. Estimation of Fe<sup>3+</sup> in garnet and Ca-amphibole followed Droop (1987) and Schumacher (1991). Analytical 225 226 conditions for the Zr-in-rutile geothermometry followed that of Zack et al. (2004). Acceleration 227 voltage used was 20.0 kV, 120 nA probe current and a probe diameter of 5 µm to determine both major 228 and trace element concentration of the rutile grains. Elemental mapping was conducted using an 229 acceleration voltage of 15.0 kV, probe current of 60 nA, with either a focused beam or a beam diameter 230 of 3-5 µm. Panchromatic cathodoluminescence (CL) mapping of quartz for Stage 3 was performed at 231 15.0 kV, 1 nA. All of the analyses in this study except whole-rock geochemical analysis were done at 232 Department of Geology and Mineralogy, Kyoto University.

233 Elastic geobarometry utilizing shifts in the Raman bands of quartz inclusions in garnet host was 234 employed by determining remnant inclusion pressures  $(P_{inc})$ . The Raman shifts were obtained using a 235 laser Raman spectroscopy (JASCO NRS 3100). Pinc can be calculated using room temperature (20 236 ±1 °C) measurements of the shift from the 128, 206, and 464 cm<sup>-1</sup> Raman bands of quartz inclusions  $(\Delta v_{128}, \Delta v_{206}, \text{and } \Delta v_{464} \text{ respectively})$  and a hydrostatic pressure calibration (Schmidt and Ziemann, 237 238 2000; Thomas and Spear, 2018). Spectral interference from the 170–215 cm<sup>-1</sup> Raman bands of the 239 garnet host can however result in linewidth broadening of the 206 cm<sup>-1</sup> band while the 128 cm<sup>-1</sup> band 240 is relatively weak and is not observed in some inclusions (e.g. Thomas and Spear, 2018). The shift of 241 the 464 cm<sup>-1</sup> band ( $\Delta v_{464}$ ) was therefore used to calculate the entrapment isomeke consistent with the 242 method employed in other related studies (e.g. Thomas and Spear 2018). The isomeke represents the 243 *P-T* curve along which fractional volume changes of the host and inclusion are the same and whose 244 instantaneous slope is determined by the ratio of the difference in volume thermal expansion 245 coefficients and compressibility of quartz and garnet (e.g. Angel et al., 2017a, b). The entrapment 246 isomeke was calculated using the freeware EoSFit-Pinc module (e.g. Angel et al., 2017a) applying the

equation of state parameters for the curved α-β quartz phase boundary of Angel et al. (2017b) and the
Tait equation of state and parameters for garnet from Holland and Powell (2011).

249 Fluid inclusion assemblages associated with Stage 3, were identified by petrography and CL-250 imaging. Microthermometry was performed using a LINKAM, LK-600 heating and cooling stage. The 251 calibration was performed on synthetic fluid inclusion standards, 10 wt% NaCl solution and pure water. 252 Final ice-melting temperature and total homogenization temperature of the two-phase aqueous fluid 253 inclusions were determined by heating and cooling the fluid inclusions respectively at a rate of 1 °C 254 min<sup>-1</sup> close to the final temperature. Precision of the microthermometric measurements are  $\pm$  0.1 °C 255 for melting and homogenization temperatures. During our heating experiments, no decrepitation was 256 observed.

Representative matrix sample B214-10 used for thermodynamic modelling was powdered in a
tungsten-carbide mill at Kyoto University and whole-rock geochemical analysis was performed at
Bureau Veritas, Perth, Australia. Major-element concentrations were obtained by fused glass bead XRay fluorescence (XRF) analysis. Analytical precision based on replicate sample is within 1 % for all
elements.

262 4. Results

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# 4.1 Petrography and mineral chemistry of blocks

264 4.1.1 Garnet amphibolites

The earliest stage of metamorphism and deformation (Stage 1a in Table 2) is preserved in the Grt amphibolite blocks (Fig. 5a, b; Botoon: B213-8, B214-21; Dalrymple: D113-14, D113-15, D113-18). The Grt amphibolite blocks consist mainly of Grt+Camp+Ep(Czo)+Qz with accessory minerals Rt+IIm+Bt (Table 1). Plagioclase is absent in Grt amphibolite samples from Botoon while it occurs as a major matrix mineral (P11b in Table 2) in one block from Dalrymple point (D113-15), and in minor amounts (< 5 vol%) in two Dalrymple point samples (D113-14 and D113-18; Table 1). Secondary minerals such as epidote and chlorite occur as veins and along grain boundaries. 272 The Grt porphyroblasts in these samples exhibit pronounced concentric compositional zoning 273 marked by increasing pyrope content and Mg#  $[=Mg/(Mg+Fe^{2+})]$  and decreasing spessartine content 274 from core (e.g. B214-21 =  $Alm_{46-51}Prp_{10-19}Grs_{15-20}Sps_{15-25}$ ) to rim (=  $Alm_{38-41}Prp_{30-35}Grs_{13-15}Sps_{13-17}$ ; 275 Fig. 5a–d). Stage 1 is therefore subdivided in the garnet core and its inclusion assemblage (Stage 1a) 276 and the garnet rim and matrix assemblage (Stage 1b). Multiphase solid inclusions (MSI) composed of 277 Chl+Ep+Qz+Grt+Rt+Ilm (B213-9; Fig. 5d) occur in the Sps-rich, low Mg# core of some garnet 278 porphyroblasts (Grt1a). The Sps-poor, Mg-rich rim of the garnet porphyroblasts (Stage 1b in Table 2) 279 exhibit textural equilibrium, i.e. sharp boundaries, with the surrounding Ca-amphibole (Camp1b), 280 epidote (clinozoisite), quartz, rutile and ilmenite.

281 The Grt amphibolite block B214-21 used for geothermobarometry (Tables 1.1 and 1.2) contains 282 garnet porphyroblasts distributed parallel to the arrangement of the long axis of hornblende in the 283 matrix. This arrangement defines the foliation (S1) in the Grt amphibolite blocks (Fig. 5a). S1 foliation 284 is attributed to the deformation (D1) that affected the blocks prior to the block-in-matrix structure 285 formation (Table 2). A quartz-kyanite vein (V1) cuts B214-21 and includes garnet and Ca-amphibole 286 derived from the block. These minerals incorporated in the vein have the same composition and zoning 287 pattern (in the case of garnet) as those in the block (Fig. 5a). There is no reaction zone between the 288 vein and block. Furthermore, local Al-rich domains are observed in this sample where minor amounts of (< 5%) kyanite (Ky1b) and epidote (Czo1b) are in textural equilibrium with the garnet 289 290 porphyroblasts (Table 2).

291 The Ca-amphibole (Camp1b) in the Grt amphibolite blocks range from ferrotschermakite to 292 tschermakite with minor magnesiohornblende (Fig. 6a, b). Some Ca-amphibole in the matrix of these 293 blocks show increasing Si, Al and Mg# from the core to the rim (Fig. 6a, b). Other Stage1b Ca-294 amphibole (Camp1b) grains are replaced along grain boundaries by either actinolite (Camp3) or chlorite (Chl3). Chlorite (Chl1a) inclusions in the garnet core generally have lower Si (= 5.3-5.4 295 a.p.f.u.) and higher Mg# (= 0.46–0.53) than replacive chlorite (Chl3 in Table 2; Si = 5.9–6.7 a.p.f.u., 296 297 Mg# = 0.38-0.53) and epidote (Ep3 in Table 2). These replacive chlorite (Chl3) occurs as veins and 298 as secondary minerals surrounding garnet and Ca-amphibole rims (Fig. 5a-c). Muscovite hosted by 299 garnet in the Grt amphibolite blocks (Ms1a; Table 2) have moderate phengite component (Ms1; Si = 300 3.13-3.28 a.p.f.u.) whereas fine mica aggregates (Ms3) are classified as aluminoceladonite (Fig. 6j, 301 k). Plagioclase in some Grt amphibolite blocks have low Ca-content (D113-14 = An<sub>10-16</sub>, D113-18 = 302 An<sub>10-18</sub>) and some are rimmed by albite (Pl3 = An<sub><5</sub>; Fig. 6l). An exception to this is the Grt 303 amphibolite block D113-15 composed mostly of Ca-rich plagioclase (An<sub>15-24</sub>). Whole-rock data 304 reveals a gabbroic protolith for this sample (cf. Part 2).

Rutile grains in the Grt amphibolite block D113-14 have low Nb and Cr content while those in B214-21 exhibit systematic variability in their chemistry. Rutile grains included in the garnet core (Rt1a in Table 2) of B214-21 have low Zr (Fig. 7) and Nb contents (175–266 ppm; Fig. 6 m). Those enclosed in the garnet mantle and rim have higher Nb concentration, 161–6664 ppm and 720–5606 ppm, respectively (Fig. 6 m). These values are comparable to the Nb content of rutile in the matrix (1692-5082 ppm) and those included in Camp1b (587–4760 ppm). These high Nb rutile grains are grouped as Rt1b in Table 2.

#### 312

#### 4.1.2 Amphibolites

313 The amphibolite lenses (D113-9; D113-11) hosted in Ep amphibolites in Dalrymple point are 314 composed almost exclusively (~90 %) of coarse Ca-amphibole along with minor amounts of Ep+Pl+Qz+Rt+Ttn (Table 1; Fig. 5e, f). The absence of garnet porphyroblasts in the amphibolite 315 316 blocks limits the use of mode of occurrence in discriminating between garnet inclusion assemblage 317 (Stage 1a) and the matrix assemblage (Stage 1b). Some of the Ca-amphiboles (Camp1b) in the 318 amphibolites show optical zonation (Fig. 5f) and have dark (low  $Al_T = 1.55$  a.p.f.u., high Mg# = 0.77) 319 cores and brighter (high  $Al_T = 1.78 - 1.83$  a.p.f.u., low Mg# = 0.72 - 0.75) rims in BSE images (Fig. 5g). 320 Compared to Camp1b in the Grt amphibolites, the amphiboles in amphibolites are mostly 321 magnesiohornblende and have lower total Al content  $(Al_T)$  and higher Si and Mg# (Fig. 6a, b). 322 Actinolite (Camp3 in Table 2) replacing Camp1b is also more common in the amphibolite blocks (Fig. 323 6a, b). The plagioclase (Pl1b) in the amphibolite blocks are  $An_{2-17}$  in composition, while epidote (Ep1b) are clinozoisite (= Ps<sub>20-22</sub>). Rutile (Rt1b in Table 2) occurs in small quantities in the 324 amphibolites and is sometimes partially surrounded by titanite (Fig 1.5i inset). Some rutile grains in 325

the matrix show increasing Zr content towards the rim (Fig. 5i). Rutile in these blocks generally have
low Nb content (748–1782 ppm) although some grains in D113-9 have higher Nb concentration (Fig.
6 m).

329

# 4.1.3 Epidote amphibolites

330 The Ep amphibolites in Dalrymple point (D113-2, D113-5; Fig. 5j-n) are fine-grained (~0.2 331 mm) and consist mainly of Camp1b, Pl1b, Qz1b, and Ep1b (Czo; core =  $Ps_{20-29}$ ; rim =  $Ps_{22-27}$ ) with 332 Rt+Ttn+Bt as accessory minerals (Table 1). Like the Grt amphibolite in Botoon point, the Ep 333 amphibolite blocks in Dalrymple are highly foliated. The foliation (S1), marked by the arrangement 334 of Ca-amphibole (Camp1b), epidote (Ep1b) and biotite (Bt1b) (Fig. 5j-l), is associated to the 335 deformation of the blocks (D1). The Ca-amphibole are mostly tschermarkite-magnesiohornblende and 336 show similar chemical zonation pattern as those in the amphibolite blocks. Ca-amphibole has higher 337 Mg# and lower Al content at the core than the rim (Fig. 6a). Replacement of Camp1b by actinolite 338 (Camp3) is more common in the Ep amphibolites compared to the Grt amphibolites (Fig. 6a-b). The 339 growth of actinolite in some Ep amphibolite samples are linked to late stage quartz veins (V3). In the 340 sample D113-1, replacement of hornblende (Camp1b) by actinolite (Camp3) is more pervasive closer 341 to a V3 Qz-vein (Act zone) which crosscuts its foliation (cf. Section 1.5.3.3). Plagioclase (Pl1) in the 342 Ep amphibolite have low An content (e.g.  $D113-2 = An_{7-15}$ ,  $D113-5 = An_{1-12}$ ) although those in D113-343 8 are more anorthitic (An<sub>16-27</sub>, Fig. 61). Similar to the Grt amphibolite sample D113-15, whole-rock 344 data also show a gabbroic protolith for this Ep amphibolite block with An-rich plagioclase (cf. Part 2). 345 Minor biotite (Bt1 in Table 2) in the Ep amphibolites occurs as anhedral interstitial grains (Fig. 5k-l). 346 The Mg# (0.53–0.56) and Ti (0.05–0.11 a.p.f.u.) of Bt1b in the Ep amphibolites are comparable to 347 those in the Grt amphibolite block D113-18 (Mg# = 0.50-0.58; Ti = 0.01-0.11 a.p.f.u.; Fig. 6g). 348 Titanite is also more common in this lithology. Rutile (Rt1b) in the Ep amphibolite records the lowest 349 Nb concentration (<958 ppm; Fig. 6m). Lastly, rutile in the Ep-Bt-Ms schist block sample 215-7 have 350 the highest Nb concentrations ranging from 1.5-6.2 wt.% (Fig. 6m, n).

### 4.2 Petrography and mineral chemistry of matrix2a and matrix2b

353 Stage 2 in Table 2 is assigned to the two generations of matrix (2a and 2b) surrounding the 354 blocks of the Dalrymple Amphibolite. The mineral assemblage of matrix2a is highly variable but 355 always includes kyanite (Ky2a) and ilmenite (Ilm2a; Fig. 8a-d). Hornblende (Camp2a), biotite (Bt2a), 356 quartz (Qtz2a) and garnet (Grt2a) are present in most matrix samples but are sometimes absent in other 357 samples (Table 1). Minor chlorite (Chl2a) occurs as local inclusions in kyanite and Ca-amphibole in 358 B214-8 and B214-2G (Table 2). Orthoamphibole is also present in some matrix2a samples (e.g. 359 Oam2a in B214-29; Table 1) coexisting with Ca-amphibole (Camp2a). Accessory minerals include 360 Ap+Rt while secondary minerals, muscovite (Ms3), chlorite (Chl3) and epidote (Ep3), are similar to 361 those in the blocks (Fig. 8).

The foliation trend of the matrix2a (S2a) is typically identifiable from the arrangement of elongate minerals Ky2a and Camp2a as well as Bt2a when present (e.g. B214-2G; Fig. 8e, j). Garnets in matrix2a are typically euhedral, fine-grained (Grt2a, < 50 μm) and are often included in larger matrix2a minerals (e.g. Ky2a in B214-14; Fig. 8h, i). The matrix2a sample B214-2G from Botoon preserves a unique mineral assemblage of coarser Grt2a (~5 mm), staurolite (St2a), kyanite (Ky2a), Ca-amphibole (Camp2a) and biotite (Bt2a) (Fig. 8j, k). The foliation (S2a) marked by the elongate minerals in this sample is a clear evidence of the D2a deformation that affected the matrix2a.

369 Matrix2b in Botoon point is associated with thin shear zones that cut earlier matrix2a (e.g. Fig. 370 8a-c). In this locality they consist of the same minerals (Ky2b, Camp2b, Oam2b in Table 2) as the 371 matrix2a that they transect but follow a distinct foliation direction (S2b). Their cross-cutting 372 relationship and the different foliation trend of matrix2b corresponds to a later deformation event 373 (D2b) during Stage 2. In Nanad point, matrix2b is more dominant and D2b is apparently more 374 pervasive. Matrix2b is largely composed of biotite (Bt2b) and quartz which surround garnet (Grt2a) 375 and hornblende (Camp2a) porphyroclasts. Thin overgrowths of Ca-amphibole (Camp2b) and garnet 376 (Grt2b) surround the margins of some Camp2a and Grt2a porphyroclasts, respectively (Fig. 8o, p; 377 Table 2).

S-C fabrics are observed in this sample (Fig. 81). The S-plane (S2b) is marked by the arrangement of Ca-amphibole (Camp2a) and kyanite (Ky2a) porphyroclasts and the surrounding biotite (Bt2b in Fig. 8m–p). The C-plane (C2b, Fig. 8l–n), which still contains minor biotite, is largely composed of replacive chlorite (Chl3) and muscovite (Ms3; Fig. 8n). Some of the Chl3 and Ms3 in the C-plane (C2b) are arranged parallel to its direction while others are oriented randomly. Both chlorite and muscovite also replaces the Bt2b in the S-plane in matrix2b (Fig. 8 m, n).

384 Garnet (Grt2a in Table 2) in the matrix2a (Fig. 6c) lack the pronounced chemical zonation 385 observed in the garnet porphyroblasts in the blocks (Fig. 5c, d). The Grt2a that do exhibit subtle 386 zonation, preserve increasing Prp and Mg# (e.g. B214-6) from the core (Alm<sub>36</sub>Prp<sub>28</sub>Grs<sub>17</sub>Sps<sub>19</sub>; Mg# 387 = 0.44) to the rim (Alm<sub>36</sub>Prp<sub>32</sub>Grs<sub>16</sub>Sps<sub>16</sub>; Mg#= 0.47). The Grt2a garnet grains also generally record 388 higher Mg# (e.g. B214-2G, Mg# = 0.44-0.47) and slightly lower Ca content (e.g. B214-2G = Grs<sub>16-</sub> 389  $_{19}$ ) compared to the garnet porphyroblasts in the Grt amphibolite blocks (e.g. Grt1a-b in D113-18, Mg# 390 = 0.30-0.38; Grs<sub>18-23</sub>). An exemption to this general distinction between garnet in the blocks (Grt1) 391 and in matrix2a (Grt2a) is the rim stage (Grt1b) of the Grt amphibolite blocks in Botoon. These Grt1b 392 in Botoon blocks (e.g. B214-21) also record comparably high Mg# (Grt1b in B214-21, Mg# =  $\sim 0.41$ ; 393 Grt1b in B213-8, Mg# = 0.40-0.47) and low Ca content (Grt1b in B214-21, Grs<sub>13-15</sub>; Grt1b in B213-394  $8 = \text{Grs}_{8-16}$ ) as the Grt2a.

395 Calcic amphibole in matrix2a (Camp2a in Table 2) is classified as tschermakite to 396 magnesiohornblende (Fig. 6d, e). Ca-amphibole (Camp2a) exhibits a generally narrow range of Mg# 397 (0.72–0.78) which is comparably higher than Ca-amphibole in the blocks (Camp1) at a given Si 398 content. Amphibole in samples with two matrix generations, i.e. matrix2a and matrix2b such as B214-399 29 (Fig. 8a-c) and N215-3 (Fig. 8l-n), exhibit comparable compositions in terms of Al<sub>T</sub>, Mg# and Si 400 (Fig. 6d, e). In sample B214-29, the hornblende (Camp2a) are relatively Cr-rich (matrix2a = 0.12 - 1.3wt.%  $Cr_2O_3$ ; matrix2b = 0.12-0.37 wt.%  $Cr_2O_3$ ) compared to those in blocks (Camp1 < 0.1% wt.% 401 402  $Cr_2O_3$ ). Orthoamphibole is found exclusively in the matrix surrounding the blocks and mostly ranges 403 from gedrite to anthophyllite (Leake et al., 1997). Like the Ca-amphiboles, the orthoamphiboles in 404 matrix 2a and 2b have the same composition (Mg# and Si; Fig. 6f). Kyanite (Ky2) in the matrix sample 405 B214-29 is also relatively Cr-rich (matrix2a = 0.710 - 2.17 wt.% Cr<sub>2</sub>O<sub>3</sub>; matrix2b = 0.01-0.67 wt.% 406 Cr<sub>2</sub>O<sub>3</sub>) compared to other samples. The matrix2a sample B214-5 contains kyanite (Ky2a) grains which 407 are surrounded by fine-grained muscovite (Ms3) connected by radially-oriented healed fractures. 408 These fluid-inclusion bearing fractures will be utilized to estimate the *P*-*T* conditions for the growth 409 of replacive minerals (i.e. Ms3) during Stage 3. Biotite (Bt2a, b; Fig. 6g) and chlorite (Chl2a; Fig. 6h) 410 in the matrix are also generally more Mg-rich compared to the blocks.

411

## Geothermobarometry

## 412 4.3.1 *P-T* estimate for Stage 1

4.3

413 The Zr-in-rutile geothermometry which utilizes rutile grains coexisting with quartz and zircon 414 (Tomkins et al., 2007) was employed on the metamafic blocks of the Dalrymple Amphibolite and the 415 surrounding Ky+Camp+Bt+Ep+Grt matrix2a. Rutile grains included along with zircon and quartz in 416 the core (Stage 1a) and rim (Stage 1b) of garnet porphyroblasts in sample B214-21 (Fig. 5a-c) were 417 used to estimate T condition preserved in the Grt amphibolite blocks (Fig. 9) (e.g. Suzuki and 418 Kawakami, 2019). Rutile grains in the garnet core (Stage 1a) have lower Zr concentrations (170-266 419 ppm) compared to inclusions in the garnet rim (422-540 ppm Zr; Stage 2b; Fig. 5c). Those included 420 in Ca-amphibole (281-540 ppm Zr) and in the matrix (266-540 ppm Zr) exhibit the same maximum 421 Zr concentrations as the rutile grains included in the garnet rim. Rutile grains in the Grt amphibolite 422 blocks from Dalrymple point (D113-14 = 311-551 ppm Zr, D113-18 = 329-689 ppm Zr) record a 423 similar range of Zr concentration (Fig. 7).

424 Several factors may result to lower Zr concentration in rutile which may cause the 425 underestimation of peak T conditions. These range from primary processes (e.g. timing of rutile 426 formation relative to P-T path) to secondary processes such as retrograde rutile growth and diffusive 427 loss of Zr from rutile during cooling (Penniston-Dorland et al., 2018). In contrast, conditions such as 428 absence of quartz in equilibrium with rutile observed in B214-2G garnet inclusions could result to 429 higher Zr concentration in rutile (Tomkins et al., 2007). Penniston-Dorland et al. (2018) suggested the 430 use of "Mean Maximum Zr-in-rutile" along with textural constraints in interpreting and estimating 431 peak metamorphic conditions. This method was adopted in this study in selecting rutile analysis used 432 for geothermometry. The rutile grains in the metasedimentary sample D215-7 have very high Nb 433 content (>17,000 ppm) which may have possibly affected its crystal structure (Zack et al., 2004). The 434 Zr content of these rutile grains were therefore not used to estimate T conditions.

435 In the Dalrymple Amphibolite blocks, rutile grains in the matrix (e.g. D113-5 = 348-415 ppm) 436 show maximum Zr concentrations similar to or slightly higher than those which occur as inclusions (e.g. D113-5 = 237–311 ppm). There is no significant difference in the Zr concentration between rutile 437 438 surrounded by titanite and those without titanite (e.g. D113-8; D113-5). Rutile grains in the Ep 439 amphibolites and amphibolites in Dalrymple show slightly lower Zr concentration than those in the 440 Grt amphibolites but the corresponding difference in peak T are small ( $\leq 25$  °C). The Ep amphibolites 441 in Botoon also have the same Zr concentration as the Grt amphibolites, indicating the stability of 442 epidote at peak P-T conditions.

443 The three Raman bands of quartz inclusions in garnet, i.e. 128, 206 and 464 cm<sup>-1</sup>, are all shifted 444 towards higher wavenumbers compared to the quartz crystal standard. Replicate analysis showed that 445 the broad 206 cm<sup>-1</sup> Raman band ( $\Delta v_{206}$ ) has the highest variation (n = 84;  $2\sigma = 8$  cm<sup>-1</sup>) while readings 446 of the shifted 464 cm<sup>-1</sup> ( $\Delta v_{464}$ ) band are more precise (n = 84;  $2\sigma = 1.8$  cm<sup>-1</sup>). Quartz inclusions are 447 more abundant at the garnet core (Stage 1a) compared to the rim (Stage 1b). Those at the core have  $\Delta v_{464} = 2.94 \pm 0.58$  cm<sup>-1</sup> (n = 16;  $P_{inc} = 3.29 \pm 0.7$  kbar using Schmidt and Ziemann, 2000) while the 448 464 cm<sup>-1</sup> band of the quartz inclusions at the rim are shifted  $\Delta v_{464} = 2.8 \pm 0.65$  (n = 8;  $P_{inc} = 3.14 \pm 0.7$ 449 450 kbar using Schmidt and Ziemann, 2000). Other quartz inclusions are either near fractures resulting to 451 lower Raman shifts or are adjacent to other inclusions.

The combined results of Zr-in-rutile geothermometer (Tomkins et al., 2007) and quartz-ingarnet geobarometer (Schmidt and Ziemann, 2000; Angel et al., 2017a, b) applied to inclusions in the garnet porphyroblasts constrain the *P*-*T* conditions preserved at the garnet core (Stage 1a: ~625 ± 25 °C, 11.5 ± 1.0 kbar) and the garnet rim (Stage 1b: ~700 ± 13 °C, 13 ± 0.5 kbar) of the Grt amphibolite block B214-21 (Fig. 9). The peak *P*-*T* conditions of other Grt amphibolite blocks from Dalrymple point were constrained by applying the Grt+Camp+Pl+Qz geobarometer (Kohn and Spear, 458 1990) using the garnet rim and matrix assemblage (Grt1b+Camp1b+Pl1b+Qz1b) coupled with Zr-in-459 rutile geothermometry of rutile grains in the matrix (Rt1b) and included in Ca-amphibole (Camp1b) 460 and garnet rim (Grt1b). The obtained *P-T* condition of ~700  $\pm$  45 °C at 13.2  $\pm$  0.9 kbar (D113-14) and 461 710  $\pm$  40 °C at 11.9  $\pm$  1.3 kbar (D113-18) are comparable to the Stage 1b of B214-21. Note that the *P* 462 obtained for the Grt amphibolite block D113-14 are slightly above the pressure range (2.8–13 kbar) to 463 which the geobarometer of Kohn and Spear (1990) are calibrated.

464 Zr-in-rutile geothermometer was also applied to rutile grains in the matrix and included in Ca-465 amphibole in representative Ep amphibolite (D113-2) and amphibolite blocks (D113-9). The Zr 466 concentration of these rutile grains, 237-415 ppm for D113-2 and 174-525 ppm for D113-9, are 467 comparable to the range of values in the Grt amphibolites. There are also no systematic differences in 468 the Zr concentration of rutile grains of different texture, i.e. matrix vs inclusion and with or without 469 titanite envelop (Fig. 7) although some coarse rutile grains show increasing Zr concentration towards 470 the rim (Fig. 5i). Peak P was estimated for the Ep amphibolites and amphibolites by calculating the 471 position of the equilibria:  $3 \text{ An}+2 \text{ Czo} + \text{Rt} + \text{Qz} = 3 \text{ An} + \text{Ttn} + \text{H}_2\text{O}$  (TZARS; Kapp et al., 2009) 472 using the prograde rim of the corresponding minerals, i.e. albitic rims of plagioclase were not 473 considered. The  $aH_2O$  was assumed to be high (= 0.95) based on the absence of calcite in the samples 474 which contain Pl+Czo+Ttn and on the results of previous works (Kapp et al., 2009; Picazo et al., 2019). 475 If the actual  $aH_2O$  is less than assumed, the calculated position of TZARS equilibria represent the 476 minimum pressure value for these samples. A decrease in the  $aH_2O$  of 0.1 (= 0.85) for example 477 increases the P by 0.15 kbar whereas a value of  $aH_2O = 1$  lowers the calculated P by 0.07 kbar. The 478 constrained P-T conditions for the Ep amphibolite (D113-2: ~660  $\pm$  42 °C at 11.4  $\pm$  1.1 kbar) and 479 amphibolite (D113-9:  $\sim$ 616 ± 29 °C at 10.4 ± 0.9 kbar) blocks are within the range of those obtained 480 for the Grt amphibolite blocks albeit slightly lower with respect to T and P (Fig. 9).

481

#### 4.3.2 *P-T* estimate for Stage 2

Zr-in-rutile geothermometer and quartz-in-garnet geobarometer were also applied to the
matrix2a sample B214-14. Rutile inclusions in kyanite (Ky2a), and quartz hosted in garnet (Grt2a)
which are in turn included in Ky2a were used (Fig. 8e–i). The Grt2a (= Alm<sub>35-36</sub>Prp<sub>28-32</sub>Grs<sub>16-19</sub>Sps<sub>16-</sub>

485 <sub>19</sub>) in this sample are fine-grained and do not preserve clear zonation (Figs. 6c; 8i). The rutile grains 486 have high Zr concentrations (400–614 ppm). The 464 cm<sup>-1</sup> Raman band of quartz inclusions in the 487 garnet are also shifted  $\Delta v_{464} = 3.04 \pm 0.53$  (n = 12;  $P_{inc} = 3.41 \pm 0.6$  kbar). Using these values, the *P*-*T* 488 condition preserved in this matrix2a sample (= ~700 ± 16°C, 13 ± 0.9 kbar) are obtained, which is 489 comparable to the rim stage of the metamafic blocks (Fig. 9).

490

#### 4.4 Microthermometry of secondary fluid inclusions and *P-T* estimate for Stage 3

491 Low-T retrograde overprint is observed in blocks and matrix samples of the Dalrymple 492 Amphibolite. In the matrix2a in sample B214-5, kyanite (Ky2a) grains surrounded by fine-grained 493 muscovite (Ms3) are connected by radially oriented healed fractures (Fig. 10a-c). These fractures 494 appear as thin nonluminescent lines compared to the host quartz in CL maps (Fig. 10c). The healed 495 fractures contain two-phase aqueous fluid inclusions apparently related to the formation of the fine-496 grained muscovite pseudomorphing kyanite (Fig. 10b). Variation in the homogenization temperatures 497 of the retrograde, secondary fluid inclusions are relatively narrow ( $T_H$  = 151.8 ± 17 °C; Fig. 10d). The 498 salinity of these fluid inclusions range from 1.82-6.95 wt.% NaCl equivalent using the formula of 499 Bodnar (1993). Bulk density (= 0.94-0.96 g/cm<sup>3</sup>) was calculated for these H<sub>2</sub>O-NaCl fluid inclusions 500 following Steele-MacInnis et al. (2012). These earlier fractures are transected by later stage fractures 501 which appear as thin subparallel non-luminescent features in the CL maps (Fig. 10c).

502 The subparallel quartz-veins cutting the Ep amphibolite exposure in Dalrymple point (Fig. 4f, 503 g) appear related to hornblende replacement by actinolite (Camp3 in Table 2). In sample D113-1, 504 compositional maps reveal progressively increasing Si, Ca, Mg# and decreasing Na, K and Al towards 505 the quartz vein, i.e. increasing actinolite component (Fig. 10f, g). Hornblende grains closest to the 506 veins (0-10 mm; Act zone in Fig. 10f-g) are completely to almost completely replaced by actinolite 507 (Fig. 10h) whereas farther from the vein (Camp zone in Fig. 10f, g), actinolite occur only along grain 508 boundaries forming irregular networks (Fig. 10i). Later discordant potassium feldspar-veins transect 509 both Act and Camp zones.

## 4.5 Pseudosection modeling

The pseudosection modeling for matrix2a (B214-10; Fig. 11) was done in the Na<sub>2</sub>O-MnO-CaO-K<sub>2</sub>O-FeO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O-TiO<sub>2</sub> (NMnCKFMASHTO) system using Theriak-Domino (ver 4.2.2017; de Capitani and Brown, 1987, de Capitani and Petrakakis, 2010). The sample shows low degree of Stage 3-related metamorphism, and the peak metamorphism assemblage is largely preserved. The updated database of Holland and Powell (2011) and the activity-composition (*a*-*x*) relations of Green et al. (2016) for metamafic rocks were used following Jørgensen et al. (2019). H<sub>2</sub>O-fluid was included in all assemblages.

519 The pseudosection for the matrix2a sample B214-10 (Fig. 11) well reproduced the observed 520 Stage 2a mineral assemblage (Camp+Grt+Ky+Ilm+Bt+Mag) within the red P-T field (Table 1): 521 Absence of chlorite is predicted over ~650 °C, which constrains the lower T limit of the observed stage 522 2a mineral assemblage. Hornblende is predicted to be stable from ~550-750 °C coexisting with garnet 523 and kyanite among others. Absence of evidence for partial melting in B214-10 constrains the higher-524 T limit. Kyanite limits the minimum P recorded in this matrix2a sample. The peak P-T conditions 525 modelled through pseudosection is comparable to that obtained using geothermobarometric techniques 526 (Fig. 9).

527 5. Discussion

528

#### 5.1 *P-T-D* history of the Dalrymple Amphibolite

Application of Zr-in-rutile geothermometer (Tomkins et al., 2007) and quartz-in-garnet Raman geobarometer (Schmidt and Ziemann, 2000; Angel et al., 2017a, b) to the Grt amphibolite block, B214-21, successfully determined the prograde *P-T* path (~625°C, 11.5 kbar to ~700°C, 13 kbar) that the blocks experienced (Fig. 9). This prograde path is consistent with the garnet zonation, i.e. increasing pyrope and decreasing spessartine content (Fig. 5c, d). The Chl+Ep+Qz+Ms MSI preserved in the core of some garnet porphyroblasts in the blocks (Fig. 5d) also reflect the transition from Ep amphibolite facies to high-pressure amphibolite facies. Considering the high variance of these 536 lithologies, the use of trace element geothermometry and elastic geobarometry as successful ways of537 constraining *P*-*T* conditions is highlighted in this study.

538 The net-transfer reaction geobarometer, TZARS equilibria (Kapp et al., 2009), provided 539 additional P-T constraints on the Ep amphibolites (Fig. 9). This revealed comparable peak 540 metamorphic conditions with the Grt amphibolites in contrast to previous hypothesis (Fig. 9; cf. 541 Encarnacion et al., 1995). Earlier works inferred a mid-oceanic ridge basalt (MORB) protolith for 542 much of the metamafic blocks of Dalrymple point (Keenan et al., 2016). Considering the same MORB 543 protolith and since the peak P-T conditions are similar for the Grt amphibolites and Ep amphibolite, 544 the prevalence of epidote in the latter type can possibly be attributed to earlier modification of the 545 basaltic protolith (i.e. Ca metasomatism) relative to typical MORB (Wei and Duan, 2018). The 546 randomly-oriented epidote veins cutting the amphibolite block in Botoon (Fig. 2c) and Dalrymple 547 further support Ca metasomatism of some metamafic blocks. Modifications in the chemistry of 548 basaltic rocks formed in spreading centers, especially in terms of Ca, Na and Mg, is prevalent during 549 hydrothermal alteration (e.g. Seyfried et al. 1988). Whole-rock data also reveal the CaO content of Ep 550 amphibolites to be higher at a given FeO/MgO ratio than the Palawan Ophiolite basalts (Part 2). The 551 same scenario has been documented in other ophiolites (e.g. epidosites in Semail; Gilgen et al., 2016) 552 and greenstone belts (Starr and Pattison, 2019). The pre-D1 modification of the Ep amphibolites is 553 suggested by the similar fine-grained texture and foliation trend shared by the epidote-rich and 554 epidote-poor domains of the amphibolites in Dalrymple (Fig. 4j-k). The random orientation of epidote 555 veins cutting the metamafic blocks in Botoon furthermore suggest that Ca-metasomatism of the 556 metamafic blocks persisted during prograde metamorphism, i.e. subduction of the slab (Fig. 2c).

557 Compared to Grt amphibolite blocks, garnet in the matrix2a (Grt2a) does not exhibit 558 pronounced zonation. The single *P-T* condition constrained on matrix2a ( $\sim$ 700°C, 13 kbar) is 559 essentially the same as the peak conditions preserved in the blocks. This indicate that the matrix-560 forming deformation (Stage 2, D2a) likely started *en route* towards peak *P-T* conditions at depths of 561 around ~45 km using the density values of Jagoutz and Behn (2013). Pseudosection modelling further 562 supports that the dominant mineral assemblage which comprise the matrix2a, i.e. Ca-amphibole, 563 garnet, biotite, kyanite, and ilmenite, were stable at relatively high P-T conditions (Fig. 11) comparable 564 to the peak metamorphic conditions of the blocks determined by geothermobarometry (Fig. 9). This 565 suggests that the unique bulk composition of the matrix2a was largely fixed prior to reaching peak 566 metamorphic conditions. Consequently, the deformation of the blocks (D1) and matrix2a (D2a; Table 567 2) may have occurred continuously as the whole mélange complex was being transported towards 568 greater depths (i.e. prograde path in Fig. 9). In the Catalina Schist, California, the formation of the block-in-matrix structure is considered to have also started at lower P-T (i.e. blueschist facies) and the 569 570 block-in-matrix complex was metamorphosed together towards higher grades, i.e. amphibolite facies 571 (e.g. Penniston-Dorland et al., 2014; 2018).

572 Subsequent deformations (D2b) possibly took place in the mechanically-weak shear zone. 573 Although the specific P-T conditions of D2b stage cannot be constrained, matrix2b has similar 574 mineralogy as matrix2a (Camp + Ky + Oam + Bt) in Botoon where development of matrix2b is still 575 weak. Hornblende in matrix 2a and 2b are also chemically identical including in Al<sub>T</sub>, Mg# and Ti 576 content which are often used as proxies for P and T (Fig. 6d-e; Garcia-Casco et al., 2008). Therefore, 577 it is likely that D2b started at similar *P*-*T* condition as D2a. In Nanad matrix2b is more dominant and 578 consist of finer-grained matrix assemblage of Bt-Qz and thin overgrowths surrounding some garnet 579 and Ca-amphibole porphyroclasts (Fig. 81-p). Both the matrix2a and 2b are further replaced by chlorite 580 (Chl3) and muscovite (Ms3) assemblage with some grains oriented parallel to the C-plane (C2b) in 581 sample N215-3 (Fig. 81-p). The prevalence of Ms3, Chl3 and albite (Pl3) during Stage 3 suggests that 582 these replacive minerals grew at lower P-T conditions within the Ms+Qz stability field, compared to 583 the other stages (Stages 1, 2) and is likely promoted by fluid migration as the sequence was being 584 exhumed towards lower P-T conditions (Figs.10, 12). These fluids possibly utilized pre-existing 585 foliations (S2b and C2b) as their pathways.

The *P-T* conditions constrained for the Stage 3 retrograde metamorphism (~600 °C, 8 kbar) using fluid inclusion microthermometry is the final step in the *P-T-D* history of the Dalrymple Amphibolite. Considering that the Ms+Qz-in curve of the matrix2a sample is used, its intersection with the isochore of the fluid inclusions correspond to the maximum *P-T* of Stage 3 (Fig. 12a). The 590 growth of hydrous replacement minerals may have happened at lower T within the Ms+Qz stability 591 field and along the isochore line depending on the timing of the infiltration of saline fluids. 592 Nonetheless, the location of the calculated isochore with its low dP/dT slope clearly support a 593 clockwise P-T path for the Dalrymple Amphibolite (Fig. 12). This is consistent with the observation 594 that actinolite, not glaucophane, replaced the hornblende both in the blocks (Camp1) and in the matrix 595 (Camp2). The veins associated with Stage 3 (V3; Fig. 10e-i) suggest that this low P and T retrograde 596 metamorphism and deformation event (Stage 3, D3) postdating peak metamorphic conditions are 597 likely related to the exhumation of the metamorphic sole together with the ophiolite. Similar clockwise *P-T* path and deformation sequences have been reported from the Semail ophiolite (e.g. Soret et al., 598 599 2017).

600

## 5.2 The Dalrymple Amphibolite: slab-mantle wedge interface of an infant arc

601 Different models have been invoked to explain the higher T/P gradients in the slab-mantle 602 wedge interface during incipient subduction compared to mature arcs. These warmer conditions are 603 typically recorded in metamorphic soles with their inverted thermal gradients. Current models to 604 explain these characteristics of metamorphic soles are as follows: 1. Sequential underplating of rocks 605 metamorphosed at different grades and different times being juxtaposed together to result in an 606 apparent inverted temperature gradient (e.g. Wakabayashi, 2017); 2. Post metamorphic flattening and 607 lateral attenuation resulting to a condensed metamorphic gradient (e.g. Cowan et al., 2014); 3. Shear 608 heating producing high-grade tectonites in major shear zones documented in the Tsiknias Ophiolite, 609 Greece (Lamont et al., 2020); 4. Flow of hotter asthenospheric mantle during forearc rifting; and 5. 610 The thermal conduction between a warm overriding mantle and the uppermost section of the 611 subducting slab (e.g. Hacker 1990; Agard et al., 2018).

Radiometric dating of plagiogranites associated with the Palawan Ophiolite reveals an Early
Oligocene (~34.1 Ma; Encarnacion et al., 1995) to Late Eocene age (~40.01 Ma; Dycoco et al., 2021).
This is similar to the reported cooling age of the Dalrymple Amphibolite from Ar-Ar dating of
amphibole and mica separates (~34.2 Ma; Encarnacion et al., 1995). The synchronous age of the
ophiolite and Dalrymple Amphibolite, the comparable peak *P-T* conditions preserved in different

617 blocks and matrix units, and its block-in-matrix occurrence are distinct from typical metamorphic soles 618 which generally consist of relatively intact sheets recording inverted thermal gradient (van Hinsbergen 619 et al., 2015). Such distinct characteristics rule out sequential underplating of diachronously 620 metamorphosed units and post-metamorphic flattening and lateral attenuation for the Dalrymple 621 Amphibolite. Shear heating has been invoked to explain the high T/P preserved in the metamorphic 622 sole of the Tsiknias Ophiolite whose cooling age is ~90 Myr younger than the overlying ophiolite 623 (Lamont et al., 2020). In contrast to the Tsiknias Ophiolite, the similar age of the Palawan Ophiolite 624 and Dalrymple Amphibolite supports a spreading center-turned-subduction zone model similar to the 625 Semail Ophiolite (e.g. Rioux et al., 2016). The extensive block-in-matrix structure of the Dalrymple 626 Amphibolite furthermore indicates that deformation was likely not restricted in a single shear zone 627 between the subducting slab and the hanging wall as in the Tsiknias Ophiolite (Lamont et al., 2020). 628 The thermal conduction model wherein the heat from the young and hot overlying mantle, possibly 629 coupled by upwelling asthesnospheric mantle during forearc rifting, may have caused the metamorphism of the slab-mantle wedge interface now preserved as the Dalrymple Amphibolite. 630

631 Compared to a developed subduction zone, the residual heat of the overlying mantle peridotites 632 during early subduction is significantly warmer (Hacker, 1990; Agard et al., 2018). This heat bakes 633 the crustal lithologies of the subducting slab and prevent the stabilization of serpentine in the overlying 634 mantle. Deformation in incipient subduction is accommodated by weaker lithologies, i.e. sediments 635 (e.g. Agard et al., 2016). Unlike most metamorphic soles however, the *P*-*T*-*D* history of the Dalrymple 636 Amphibolite reflects the petrological characteristics of a cooler slab-mantle wedge interface (Fig. 12a). 637 Due to its close association with the ultramafic section of the Palawan Ophiolite and its limited 638 exposure, the Dalrymple Amphibolite has been regarded as a typical metamorphic sole formed during 639 the first million year of subduction initiation (Encarnacion et al., 1995; Keenan et al., 2016). The 640 comprehensive investigation on the P-T-D history of its lithologies in this study suggest key 641 differences with typical metamorphic soles.

642 The peak *T* obtained for the block and matrix by Zr-in-rutile geothermometery are generally643 comparable to that obtained by conventional geothermometers for the Dalrymple Amphibolite (cf.

644 Encarnacion et al., 1995). These values are lower than the peak T of other ophiolites (e.g. Semail 645 ophiolite; Soret et al., 2017). The peak P values are however significantly higher than other 646 metamorphic soles (e.g. Semail ophiolite; Figs. 9; 12a). The paleogeothermal gradient preserved in 647 the Dalrymple Amphibolite (~16 °C/km) and its block-in-matrix structure are atypical of metamorphic soles but are also warmer than a developed subduction channel underlying a mature arc (Fig. 12a). 648 649 This intermediate gradient preserved in the Dalrymple Amphibolite and its block-in-matrix occurrence 650 are more comparable to early subduction high T mélanges or the high T eclogites of Agard et al. (2018). 651 This suggest that the Dalrymple Amphibolite may correspond to the slab-mantle wedge interface of a 652 young subduction complex already transitioning from the much warmer conditions when subduction 653 was first initiated. Compared to metamorphic soles which are interpreted to have formed within 2 Myr 654 from subduction initiation (e.g. Soret et al., 2017), the cooler conditions of this transitional period may 655 be reached within 2–5 Myr (Agard et al., 2018). We can therefore use the characteristics of this 656 mélange complex, that is the Dalrymple Amphibolite, to investigate the petrological characteristics of 657 the slab-mantle wedge interface in transition from its incipient stages into a mature subduction zone. 658 Other intraoceanic arc settings with similar geothermal gradients (e.g. hot subduction zones) may also 659 exhibit similar petrological characteristics.

# 660

661

5.3

# *P/T* gradient

662 The slab-mantle wedge interface of a cold mature subduction zone is typically composed of 663 juxtaposed blocks which preserve highly variable peak metamorphic P-T conditions, i.e. blueschists 664 and eclogites (Fig. 12a; Guillot et al., 2009). These are attributed to the flow of blocks from different 665 depths along the subduction channel (e.g. Gerva et al., 2002; Guillot et al., 2009). This flow is thought 666 to be enabled by the soft and mechanically weak matrix surrounding the blocks typically dominated 667 by phyllosilicates (e.g. chlorite and serpentine). One notable characteristic of the matrix surrounding 668 the Dalrymple Amphibolite blocks is the predominance of Ca-amphibole and kyanite (e.g. Fig. 8). The 669 strength of these minerals are thought to increase the mechanical strength of the matrix and impede 670 flow of materials along the subduction channel (Penniston-Dorland et al., 2018). Considering that the

Insights on the nature of the slab-mantle wedge interface of arcs with intermediate

671 weaker matrix started forming before the complex reached peak metamorphic conditions, the 672 relatively narrow range of peak *P-T* conditions preserved in the blocks ( $\sim$ 600–720 °C; 10–13 kbar) 673 supports this limited flow and the viscous nature of this matrix. Thermodynamic modelling also 674 predicts the prevalence of Ca-amphibole over weaker minerals (e.g. chlorite) in the Stage 2 matrix 675 beyond ~550 °C (Fig. 10c).

676 Processes that lead to the hybrid composition of the matrix in slab-mantle wedge interface 677 mélanges subsequently control the chemistry of arc magmas (e.g. Marschall and Schumacher, 2012). 678 Although the petrogenesis of the matrix in the Dalrymple Amphibolite is investigated in more detail 679 using whole-rock data in Part 2, the chemistry of constituent minerals already provides insights into 680 processes that are possibly at work in this slab-mantle wedge interface. Rutile, a sink for trace elements 681 in the subducting slab, can be used to distinguish the mafic (Cr-rich) and pelitic (Nb-rich) character of 682 a metamorphic rock's protolith (e.g. Meinhold et al., 2008). Rutile in the metamafic blocks from 683 Dalrymple generally fall in the metamafic field (Fig. 6m) while the very high Nb content of those in 684 the Ep-Bt-Ms schist block sample 215-7 fall well into the metapelite field (Fig. 6n). The metamafic 685 block B214-21 from Botoon exhibits interesting Nb content variability tied to its mode of occurrence. 686 Rutile grains in the garnet core have low Nb content (Rt1a = 175–266 ppm) and fall into the metamafic 687 field (Fig. 6). In contrast, those included in garnet mantle and rim and rutile grains in the matrix and 688 included in Camp (Rt1b) have significantly higher Nb content and falls in the metapelite field along 689 with the matrix2a samples (Fig. 6n, B214-2G and B214-14).

690 Nb and Cr contents of rutile do not show any correlation with increasing Zr concentration (i.e. 691 increasing T). We interpret the variations in the Nb-Cr contents of rutile in the blocks and matrix (Fig. 692 6m, n) as reflective of the mixing (in a broad sense) of crustal components, i.e. mafic basalts and 693 sediments, during the development of this mélange complex. More detailed investigation of the 694 geochemical characteristics of the matrix is needed to discriminate between the processes which may 695 have controlled its bulk composition, i.e. mechanical mixing, fluid/melt induced advective mixing and 696 diffusion (Marschall and Schumacher, 2012). We therefore only argue that the Nb-Cr variations in the 697 rutile grains indicate the variable involvement of the mafic basalt and sedimentary components. More importantly, the chemical change in rutile inclusions at the garnet mantle and rim with respect to those
at the garnet core suggests that such processes started prior to the blocks reaching peak metamorphic
conditions (Fig. 6m). This is consistent with the *P*-*T*-*D* history of the surrounding matrix 2a outlined
in the previous section.

702 The involvement of mantle-derived components during this mixing process is less apparent in 703 the Dalrymple Amphibolite. The high T condition maintained during the deformation history of the 704 block-in-matrix complex is beyond the serpentine-stability field (Fig. 12a) and the scarce fluid supply 705 at greater depths during incipient subduction due to early devolatilization at shallower regions (e.g. 706 Agard et al., 2018) likely prevented the formation of serpentine. Orthoamphibole-rich blocks in 707 Botoon and the chemical characteristics of some constituent minerals in the matrix2a sample B214-708 29 however suggest the involvement of mantle components. Kyanite ( $Cr_2O_3 = 0.71-2.17$  wt.%) in 709 B214-29 are relatively Cr-rich while Ca-amphibole grains are both Mg- and Cr-rich (Mg# = 0.72-710 0.78; Cr<sub>2</sub>O<sub>3</sub> = 0.12–1.3 wt.%). Some rutile grains N215-3 also has high Cr<sub>2</sub>O<sub>3</sub> content (= 0.16–1.93 711 wt.%).

712 The presence of fluids in this shear zone throughout its history is also apparent from the multiple 713 generation of veins cross-cutting the block-in-matrix complex. The earlier stage fluids appear to be in 714 equilibrium with the blocks (i.e. internally sourced; cf. Locatelli et al., 2019) as suggested by the 715 absence of any reaction zone between the vein and the block (e.g. Qz-Ky vein, Figs. 2h, 5a). 716 Monomineralic epidote veins possibly represent Ca-rich fluids. The Oz-Ky veins in particular are 717 interesting since they suggest either a change in the behavior of some immobile elements like Al in 718 this environment similar to what has been described for orogenic belts (e.g. Alpe Sponda, Central 719 Alps; Beitter et al., 2008), or the extreme leaching of the other components which left behind relatively 720 immobile elements. The latter is apparently favored by the occurrence of ilmenite-kyanite 721 accumulations in some sections of matrix2a in Botoon (B214-10; Fig. 8d).

722 Evidence for migration of externally-derived fluids is also preserved in the latest stage (Stage723 3). Microthermometry of fluid inclusions related to the replacement of kyanite by muscovite reveals

724 the involvement of saline fluids (1.8-6.9 wt.% NaCl equivalent; Fig. 10d). Such aqueous fluids with 725 relatively low salinity dominate the shallow regions (< 80 km) of the subduction zone (e.g. Kawamoto 726 et al., 2013; Manning and Frezzotti, 2020). In D113-1, the quartz vein is linked to the replacement of 727 hornblende by actinolite. Compositional maps and line analysis reveal replacive actinolite with 728 progressively higher Si, Ca and Mg# and lower Al, Na and K towards the vein (Fig. 10f, g). The degree 729 of hornblende replacement by actinolite also increases towards the vein. Farther from the vein, 730 actinolite formation is limited along grain boundaries which maps out the pathway of the percolating 731 fluids (Fig. 10h, i). These greenschist-facies fluids were likely derived from the lower-grade 732 lithologies underthrusted below the ophiolite during its exhumation. These observations in the 733 Dalrymple Amphibolite highlight the importance of fluids in element mobility and material transfer 734 through the slab-mantle wedge interface from initiation to its exhumation. Future studies on the 735 chemical signatures of these different generations of fluids may provide further insights on the nature 736 of fluids and fluid-rock interaction along the slab-mantle wedge interface.

737

#### 5.4 Tectonic implications on the NPCT

The Late Eocene Palawan Ophiolite exposed in central Palawan is argued to have formed as a back-arc basin hosted within the Cretaceous proto-South China Sea (SCS) Plate (Labis et al., 2020; Dycoco et al., 2021). In the Eocene, rifting in the Southeast Asian margin was initiated and the NPCT started drifting toward the southeast (e.g. Yumul et al., 2003; Cao et al., 2020). The shift from a tensional regime to compressional, forced the initiation of subduction at/or near the spreading center of this Eocene proto-SCS (Fig. 12b; Keenan et al., 2016). This convergence resulted in an intraoceanic arc. Slivers of this arc were then emplaced during its collision with the NPCT as the Palawan Ophiolite.

The degree to which subduction proceeded in this intraoceanic arc before the underplating of the NPCT and subsequently the emplacement of the ophiolite is largely unknown. The volcanic section of the ophiolite only records its mid-oceanic ridge history (e.g. Keenan et al., 2016; Gibaga et al., 2020) and products of arc magmatism is undetected. Earlier models linked a small volume of calcalkaline lavas (~17 Ma) in the Cagayan de Sulu ridge to the Eocene subduction initiation (Encarnacion et al., 1995) but the connection remain contentious (e.g. Dycoco et al., 2021). 751 The P-T-D evolution of the Dalrymple Amphibolite outlined here however, suggests that 752 subduction along this plate interface did progress, enough to shift its P-T gradients towards cooler 753 conditions (Fig. 12a; cf. Agard et al., 2020). Based on the compilation study of Agard et al. (2018), 754 such conditions (~16 °C/km) are usually reached around 2-5 Myr since subduction is initiated (Fig. 755 12b). In contrast, the hot thermal gradients of metamorphic soles are thought to dominate the first  $\sim 2$ 756 Ma since subduction is first initiated. Radiometric dating of the peak metamorphism of the metamafic 757 blocks and the surrounding matrix in the future can further constrain the duration of subduction in the 758 Palawan Ophiolite. Exhumation of the ophiolite with the Dalrymple amphibolite at its base is linked 759 with the complete consumption of the oceanic lithosphere at the leading edge of the NPCT and 760 continental material underplating beneath the arc.

## 761 6. Conclusions

762 The P-T-D history of the Dalrymple Amphibolite underlying the Palawan Ophiolite are discussed in Part 1 of this thesis. The prograde P-T path preserved in the metamafic blocks indicate cooler 763 764 paleogeothermal gradients (~16 °C/km) compared to typical metamorphic soles (>20 °C/km). The 765 peak P-T conditions of the metamafic blocks, i.e. amphibolites, Ep amphibolites and Grt amphibolites, 766 and the surrounding matrix are also shown to be similar (~700 °C, 13 kbar). The block-in-matrix 767 structure of the Dalrymple Amphibolite indicates that this complex likely represents the slab-mantle 768 wedge interface of a subduction zone already in its infancy. Field characteristics, matrix2a P-T 769 conditions and Cr and Nb contents of rutile grains indicate that the matrix-forming deformation likely 770 started prior to the rock sequence reaching peak metamorphic conditions at depths of approximately 771 ~45 km. Deformation events accompanying each metamorphic stage also affected the textural and 772 petrological characteristics of this block-in-matrix sequence. Multiple generation of veins and lenses 773 of veins cross-cutting the block-in-matrix sequence reveal the important role of fluids in material 774 transfer along the slab-mantle wedge interface throughout its history. The petrological characteristics 775 and *P-T-D* history of the Dalrymple Amphibolite therefore provide important insights on the nature 776 of the slab-mantle wedge interface of an arc with intermediate P/T geothermal gradients which is 777 prevalent during incipient subduction and in warm subduction complexes.

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Fig. 1. a) Map showing the distribution of lithologies in central Palawan. The metamorphic sole is exposed in Ulugan Bay, Puerto Princesa and Dumangueña, Aborlan. Inset map shows tectonic map of the Philippines, the surrounding marginal basins and trenches. NPCT-North Palawan Continental Terrane, SPT-South Palawan Terrane, CR-Cagayan de Sulu Ridge. Modified from Labis et al. (2020); b) Distribution of Dalrymple Amphibolite and sampling points in Ulugan Bay modified from Encarnacion et al. (1995). The localities discussed in the text are marked as diamonds.



Fig. 2. Field photos of the exposure in Botoon point. a) Panoramic photo of the block and matrix sequence. Inset shows a schematic representation of the area enclosed in red box showing the blocks (white solid lines) and the matrix in the low lying portions of the exposure. b–d) Melanocratic metamafic block surrounded by lighter matrix2a and cut by epidote veins. e) Foliation (S1) parallel quartz lenses. f) Matrix2a below the Ep amphibolite block which shows g) Coarse kyanite crystals surrounded by ilmenite. h) Qz-Ky veins in the surrounding matrix2a. i,j) Matrix2a transected by later matrix2b.



Fig. 3. Field photos of the exposure in Nanad. a) Panoramic photo showing the thrust boundary between the metamorphic sole and the overlying peridotites. b) Shear sense indicator suggests a top to NW movement. c) Rounded metamafic blocks surrounded by the lighter-colored and highly sheared matrix2b. d–e) Matrix2a lenses transformed into small rounded blocks. f, g) Metamafic block transected by Qz-Ky vein which terminates in the surrounding matrix2b. h) Dunite-harzburgite interlayers which comprise the hanging wall in Nanad.



Fig. 4. Field photos in Dalrymple point. a) Schematic representation of the exposure showing the blockdominated NW section and the more coherent Ep amphibolite sequence in the SE side. The boxes indicate the relative position of the field photos. b–e) Interlayers of Grt amphibolite, quartzite and Bt schist blocks. f) Quartzite block surrounded by matrix2a. g–h) Kyanite pseudomorphed by muscovite, and Ca-amphibole in matrix2a. i) Relatively coherent Ep amphibolite block cut by later stage j–k) Quartz veins (v3) which transect the foliation of the blocks (S1). In Fig. 1.4 j, k, epidote-rich domains are the yellowish portions while the darker parts are the epidote-poor domains. l) Amphibolite lens surrounded by Ep amphibolite.



Fig. 5. Photomicrographs, BSE images and X-ray elemental map of the blocks. a) Grt amphibolite block showing foliation direction delineated by the linear arrangement of garnet porphyroblasts and long axis direction of Ca-amphibole. An earlier epidote-vein (V1) is transected by a discordant Qz-Ky vein (V1). Garnet porphyroblasts in plane polarized light (PPL; 1.5b) and back-scattered electron image (BSE; 1.5c) showing inclusion assemblage at the core (C), mantle (M) and rim (R) delineated in the line analysis (A-A'). d) X-ray elemental map showing distribution of Mn in the garnet porphyroblast and the multiphase solid inclusion (MSI) composed of Rt+IIm+Chl+Qz+Ep+Qz at the garnet core identified by line analysis (B-B'). e) PPL; Amphibolite block composed of f) PPL; Coarse Ca-amphibole with optical zonation. g) BSE image of one Ca-amphibole showing difference in Al<sub>T</sub>, Mg# and Ti content of the core (C) compared to the rim (R). h) in cross-polarized light (XPL), plagioclase (P11) in the amphibolite blocks are mostly interstitial while i) in PPL; Rutile grains are sometimes partially replaced by titanite. j, k) in PPL; l) in XPL; Epidote amphibolite are fine-grained and composed of foliated Camp+Bt+Pl+Ep+Qz+Ttn. m) in PPL; Rt+Zrn+Qz assemblage included in the Ca-amphibole and n) BSE; In the matrix surrounded by titanite.



Fig. 6. Mineral chemistry of blocks and matrix from the Dalrymple Amphibolite. Legends are the same for a and b, and d and e. a, b) Amphibole in the blocks. c) Garnet composition and d, e) Amphiboles in the matrix2a samples. f) Point analysis of orthoamphiboles in the matrix and g) Biotite and h) Chlorite in the Ep amphibolite (triangle), Grt amphibolite (circles) blocks and matrix samples. i) Histogram showing pistacite content of epidote in the Dalrymple Amphibolites. j, k) Point analysis of muscovite in the Grt amphibolite blocks compared to Stage 3 alteration. l) Histogram of the anorthite content of plagioclases. m, n) Cr vs Nb concentration of rutile grains in the blocks and the matrix. Note the change in scale in Fig. 1.6 m, n to accommodate the high-Nb rutile grains. The metamafic and metapelite fields are from Meinhold et al. (2008).



Fig. 7. Zr content of rutile grains in blocks and matrix2a samples of Dalrymple Amphibolite and their modes of occurrence. Several factors may result to lower Zr concentration in rutile which may cause the underestimation of peak *T* conditions. These range from primary processes (e.g. timing of formation relative to *P*-*T* path) to secondary processes such as retrograde growth and diffusive loss during cooling (Penniston-Dorland et al., 2018). In contrast, conditions such as the absence of quartz in equilibrium with rutile observed in B214-2G garnet inclusions could result to higher Zr concentration in rutile (Tomkins et al., 2007). Penniston-Dorland et al. (2018) suggested the use of "Mean Maximum Zr-in-rutile" along with textural constraints in interpreting and estimating peak metamorphic conditions. This method was adopted in this study in selecting rutile analysis used for geothermometry. The rutile grains used for geothermobarmetry in Fig. 1.9 are bordered by rectangles with dashed borders. The rutile grains in the metasedimentary sample D215-7 have very high Nb content (>17,000 ppm) which may have possibly affected its crystal structure (Zack et al., 2004). The Zr content of these rutile grains were therefore not used to estimate *P*-*T* conditions.



Fig. 8. Photomicrographs (in XPL and PPL) and BSE images of matrix samples. a) in PPL; Matrix2a block with foliation (S2a) surrounded by matrix2b which exhibit a distinct foliation (S2b). b) in PPL; The matrix2a has the same mineralogy as c) Matrix2b (in XPL). d) in PPL; Ilm2a accumulations surrounding coarse Ky2a grains. e, f) in PPL; Matrix2a sample B214-14. g) in PPL; Kyanite porphyroblasts include Zrn-Rt-Qz assemblage used for h) Zr-in-rutile geothermometry (BSE). i) in PPL; Quartz inclusion in garnet (Grt2a) in turn hosted by kyanite used for elastic geobarometry. j, k) in PPL; Grt+St+Bt+Camp+Ky bearing matrix2a. l) in PPL; Matrix2a block surrounded by matrix2b showing crenulations and multiple deformation stages marked by different foliation planes. m, n) BSE images of the matrix2a clast and the matrix2b. o) BSE image of Camp2a porphyroclast with the thin overgrowth of Camp2b equilibrated with Bt2b. p) X-ray elemental map showing distribution of Ca in Grt2a porphyroclast which is also surrounded in some parts by a thin overgrowth of Grt2b.



Fig. 9. *P*-*T* estimates for the blocks and matrix2a samples of the Dalrymple Amphibolite. The prograde *P*-*T* path for the Grt amphibolite block B214-21 was obtained using the inclusion assemblage (Zr-inrutile geothermometry and quartz-in-garnet geobarometry) at the core (C) and rim (R) of garnet. The estimates for the amphibolite D113-9 and Ep amphibolite blocks D113-2 were determined using Zr-inrutile geothermometry and the TZARS equilibria. *P*-*T* conditions of the matrix2a sample B214-14 utilized the same technique as in B214-21. See text for details. The peak *P*-*T* estimates for the Catalina Schist (Grove and Bebout, 1995) and the Semail Ophiolite (Soret et al., 2017) are also indicated. The petrogenetic grid for metabasalts in the NCKFMASH system (Vielzeuf and Schmidt, 2001) is also shown.



Fig. 10. a, b) Photomicrographs of Qz-Ky (B214-5) lens in matrix2a. The Ky2a grains replaced by Ms3 are interconnected by radial fractures (red arrows) that contain fluid inclusion (blue arrows). c) SEM-CL map of Qz-Ky lens. The fractures interconnecting the altered kyanite appear as thin nonluminescent lines marked by red arrows. Inset shows the fluid inclusions contained in these healed fractures. d) Homogenization ( $T_H$ ) and melting ( $T_M$ ) temperatures of the fluid inclusions. Histogram shows the salinity of these fluid inclusions calculated using Bodnar (1993). e) Scanned thin section of the Ep amphibolite sample in Dalrymple cut by a Stage 3 (v3) quartz vein. X-ray elemental maps reveal increasing f) Si and decreasing g) Al in the amphiboles towards the vein. BSE images show h) pervasive replacement of Camp1 (hornblende) by actinolite closer to the vein while replacement is limited i) along grain boundaries farther from the vein.



Fig. 11. Pseudosection calculated for the representative matrix2a sample B214-10 in the NMnCKFMASHTO system using Theriak-Domino (de Capitani and Brown, 1987; de Capitani and Petrakakis, 2010). Bulk rock composition used for the calculation is in molar percentages (%). Red field corresponds to the peak P-T assemblage observed in the samples while the solid red line is the calculated solidus. Isopleths of pyrope content (XPrp) of garnet are shown as blue dash lines.



Fig. 12. a) P-T estimates for the Grt amphibolite block (Stage 1) and matrix2a (Stage2). The green diamond corresponds to the intersection of the isochore of the Stage 3 fluid inclusions and the calculated Ms+Qz-in curve for the matrix2a. Geothermal gradients of hot (SW Japan) and cold (NE Japan) subduction zones are from Peacock and Wang (1999). Metamorphic facies are from Guillot et al. (2009): LB-lawsonite blueschist, EB-epidote blueschist, EC-eclogite, GS-greenschist, EA-epidote amphibolite, AM-amphibolite, GR-granulite. Srp-out curve is from Ulmer and Trommsdorff (1995). Compilation of P-T conditions of metamorphic soles (met sole sheet) are from Agard et al. (2016) and other slab-mantle wedge interface lithologies (sheets and mélanges) are from Agard et al. (2018). The rock types that comprise each deposit are labelled M-mafic, UM-ultramafic, S-sedimentary. b) Schematic representation of the subduction initiation of the proto-South China Sea (SCS) promoted by the rifting of the North Palawan Continental Terrane (NPCT) from the southeast (SE) Asian Margin in the Eocene. The cooler paleogeothermal gradient preserved in the Dalrymple Amphibolite and its mélange occurrence resemble the transitional stage of subduction zones compared to metamorphic soles (e.g. Semail; Soret et al., 2017) and mature arcs (e.g. Guillot et al., 2009) as discussed in Agard et al. (2018). Blue arrows correspond to fluids released from the slab.

Sample		Locality		Field		Major mineral assemblage	Accessory	EPMA	
No.	Area	Latitude (N)	Longitude (E)	occurrence	Lithology	[+secondary]	minerals	analysis	Notes
B213-8	Botoon	10°8'7.1"	118°48'47.7"	Block	Grt amphibolite	Camp + Grt + Qz + Ep [+Chl +Ep]	Rt + Ilm + Zrn + Ap + Ky	$\bigcirc$	
B214-2G	Botoon	10°7'44.2"	118°48'40.2"	Matrix2a	Grt amphibolite	Camp + Grt + Ky + St + Bt [+Chl]	Rt + Ilm + Zrn + Ap + Chl	$\bigcirc$	
B214-5	Botoon	10°7'44.8"	118°48'40.6"	Qz-Ky lens in Matrix2a	Ky-Camp-Bt schist	$\begin{array}{c} Camp + Ky + St + Bt \\ [+Chl + Ms] \end{array}$	Ilm	$\bigcirc$	Stage 3 <i>P</i> - <i>T</i> estimation
B214-6	Botoon	10°7'44.8"	118°48'40.4"	Matrix2a	Ky-Grt-Bt schist	Grt + Ky + Ilm + Bt [+Chl +Ms]	Ар	$\bigcirc$	
B214-8	Botoon	10°7'44.4"	118°48'40.6"	Matrix2a and 2b	Ky-Camp-Bt schist	$\begin{array}{l} Matrix2a: Camp + Oam + \\ Grt + Ilm + Ky + Chl + Bt \\ [+Chl] \\ Matrix2b: Camp + Oam + \\ Ilm + Ky + Bt [+Ms + Chl] \end{array}$	Both 2a and 2b: Ap	0	
B214-9	Botoon	10°7'44.4"	118°48'40.6"	Matrix2a	Ky-Grt-Bt schist	Grt + Ky + Ilm + Bt [+Ms +Chl]	Ар	$\bigcirc$	
B214-10	Botoon	10°7'44.7"	118°48'41"	Matrix2a	Ky-Camp-Bt schist	Camp + Grt + Ky + Ilm + Bt [+Ms +Chl]	Mag + Ap + Tur	$\bigcirc$	Pseudosection
B214-14	Botoon	10°7'45.8"	118°48'41"	Matrix2a	Ky-Ep-Grt schist	Ky + Grt + Ep + Ilm + Bt [+Ms +Ep +Chl]	Rt + Ap + Zrn + Chl	0	Geothermobarometry
B214-21	Botoon	10°7'45.0"	118°48'40.1"	Block	Grt amphibolite	$\begin{array}{c} Camp+Grt+Ep+Qz\\ [+Act+Ep+Chl] \end{array}$	$\begin{array}{l}Ky+Bt+Ap+\\Rt+Ilm+Zrn\end{array}$	$\bigcirc$	Geothermobarometry cut by Qz-Ky vein
B214-29	Botoon	10°7'44.6"	118°48'40.8"	Matrix2a and 2b	Ky-Hbl schist	$\begin{array}{c} Matrix2a: Camp + Oam + \\ Qz + Ky + Chl [+Chl \\ +Ms] \\ Matrix2b: Camp + Oam + \\ Qz + Ky [+Ms] \end{array}$	Both 2a and 2b: Ilm	0	
N215-3	Nanad	10°7'24.3"	118°48'26.1"	Matrix2a and 2b	Grt-Hbl-Bt schist	Matrix2a and 2b: Camp + Grt + Ky + Bt + Qz [+Ms +Chl]	Ilm + Rt + Zrn + Ap	0	

Table 1 Summary of samples used in this study

Table 1 co	ntinued								
Sample No.	Locality Area Latitude Longitude		Field occurrence	Lithology	Major mineral assemblage [+secondary]	Accessory minerals	EPMA analysis	Notes	
D113-1	Dalrymple	10°6'39.4"	118°48'41.1"	Block	Ep amphibolite	Camp + Ep + Pl + Qz $[+Act + Chl + Ab]$	Ttn + Ap	0	cut by Qz vein
D113-2	Dalrymple	10°6'39.4"	118°48'41.1"	Block	Ep amphibolite	$Camp + Ep + Pl (An_{8-14}) + Qz [+Act +Ab]$	Rt + Zrn + Ttn + Ap + Bt	0	Geothermobarometry
D113-5	Dalrymple	10°6'39.4"	118°48'41.1"	Block	Ep amphibolite	$Camp + Ep + Pl (An_{1-14}) + Qz [+Act +Ab]$	Rt + Zrn + Ttn + Ap + Bt	$\bigcirc$	
D113-8	Dalrymple	10°6'41.6"	118°48'36.7"	Block	Ep amphibolite	$\begin{array}{l} Camp + Ep + Pl (An_{16-27}) \\ + Qz [+Act + Ab] \end{array}$	Rt + Zrn + Ttn + Ap + Bt	$\bigcirc$	
D113-9	Dalrymple	10°6'41.6"	118°48'36.7"	Block	Amphibolite	$\begin{array}{l} Camp + Ep + Pl (An_{8-17}) + \\ Qz \left[ +Act + Chl + Ab \right] \end{array}$	Rt + Zrn + Ttn	$\bigcirc$	Geothermobarometry
D113-10	Dalrymple	10°6'41.6"	118°48'36.7"	Block	Ep amphibolite	$\begin{array}{c} Camp + Ep + Pl (An_{1-14}) + \\ Qz [+Chl + Ab] \end{array}$	Rt + Zrn + Ttn + Ap + Bt	0	
D113-11	Dalrymple	10°6'41.6"	118°48'36.7"	Block	Amphibolite	$Camp + Ep + Pl (An_{1-11}) + Qz [+Act +Ab]$	Rt + Zrn	0	
D113-14	Dalrymple	10°6'42.5"	118°48'36.1"	Block	Grt amphibolite	$\begin{array}{l} Camp + Grt + Pl (An_{7-16}) \\ + Qz + Ep [+Act + Chl \\ + Ep] \end{array}$	Rt + Zrn + Ap + Ms	$\bigcirc$	Geothermobarometry
D113-15	Dalrymple	10°6'42.5"	118°48'36.1"	Block	Grt amphibolite	$Camp + Grt + Pl (An_{15-24}) + Qz + Ep [+Chl + Ep +Ab]$	$\begin{array}{c} Rt + Ap + Ms + \\ Ccp + Py \end{array}$	0	
D113-18	Dalrymple	10°6'43.3"	118°48'36.3"	Block	Grt amphibolite	$\begin{array}{c} Camp+Grt+Pl \left(An_{8\text{-}18}\right)\\ + Qz+Ep+Bt \left[+Act\right.\\ + Chl+Ep +Ab \right] \end{array}$	Rt + Zrn + Ap	0	Geothermobarometry
D215-7	Dalrymple	10°6'43.3"	118°48'36.3"	Block	Ep-Bt-Ms schist	Bt + Ms + Pl + Ep + Qz [+Chl]	Rt + Ilm + Zrn + Ap	$\bigcirc$	

Phase	Block (Sta	age 1)*	Matrix (St	Retrograde (Stage 3)	
	Stage 1a	Stage 1b	Matrix 2a	Matrix 2b	· · · · · · · · · · · · · · · · · · ·
		01 (V1	D2a	- D2b	
Grt	Alm <sub>46-51</sub> Prp <sub>10-19</sub> Grs <sub>15-20</sub> Sps <sub>15-25</sub>	Alm <sub>38-41</sub> Prp <sub>30-35</sub> Grs <sub>13-15</sub> Sps <sub>13-17</sub>	Alm <sub>35-36</sub> Prp <sub>28-32</sub> Grs <sub>16-19</sub> Sps <sub>16-19</sub>		
Amp		Camp1b: Mg# = 0.64-0.80	Oam2a/Camp2a: Mg# = 0.72-0.76	Oam2b/Camp2b: Mg# = 0.72-0.74	Camp3: Mg# = 0.45-0.83
Ep	Czo1a: Ps <sub>20-29</sub>		Czo2a:Ps <sub>18-29</sub> / Aln2a		Czo3: Ps <sub>30-39</sub>
PI		**An <sub>10-18</sub>			An <sub>0-10</sub>
Bt			Mg# = 0.80-0.86	Mg# = 0.75-0.81	
Rt	Nb = 175-266 ppm; Zr = 170-466 ppm	Nb = 720-5606 ppm; Zr = 222-562 ppm	Nb = 748-1782 ppm; Zr = 281-533 ppm		
Qz					
Ар					
llm					
Ку			Cr <sub>2</sub> O <sub>3</sub> = 0.71-2.17 wt.%	Cr <sub>2</sub> O <sub>3</sub> = 0.01-0.67 wt.%	
Chl			Mg# = 0.83-0.84		Mg# = 0.38-0.53
Ms					Si = 3.71-3.95 a.p.f.u.
Mag					
St					
Tur					

# 994 Table 2. Summary of the mineral paragenesis, their representative mineral chemistry and the deformation (D) and veining (V) stages of the Dalrymple Amphibolite.

- abundant - accessory mineral ----- - minor minerals with special occurrence (see text for details)

\*Mineral paragenesis of the Grt amphibolite block B214-21 used for geothermobarometry

\*\*PI1b is absent in Grt amphibolite block B214-21 but occurs in other Dalrymple Point blocks; Mineral chemistry data from D113-18

Sample No. (area) B214-21 (Botoon)					D113-15 (Dalrymple)				
Lithology	gy Grt amphibolite			Grt amphibolite					
Mineral	Grt1		Hbl1		Grt1	Hbl1	Pl1	Ms1	Ep1
Occurrence	Matrix	Matrix	Matrix	Matrix	Matrix	Matrix	Matrix	Matrix	Matrix
Core/Mantle/Rim	Core	Rim	Core	Rim	Rim	Rim	Rim		
$SiO_2$	38.27	38.95	43.46	43.92	38.87	43.02	64.20	47.78	38.36
TiO <sub>2</sub>	0.16	0.10	0.52	0.96	0.20	0.33	0.04	0.58	b.d.
$Al_2O_3$	20.94	21.60	15.13	14.94	21.31	14.80	22.83	30.94	23.62
$Cr_2O_3$	b.d.	0.03	0.02	0.04	0.02	b.d.	b.d.	b.d.	b.d.
FeO	22.46	19.55	12.03	11.11	26.74	17.47	b.d.	3.29	
Fe <sub>2</sub> O <sub>3</sub>									12.691
MnO	8.99	7.27	0.60	0.62	3.38	0.22	b.d.	0.04	0.10
MgO	3.17	7.71	12.22	12.44	4.28	8.82	b.d.	1.35	b.d.
CaO	6.53	5.07	10.57	10.92	6.84	10.34	4.36	0.03	23.72
BaO	n.d.	n.d.	0.01	0.09	0.04	0.02	0.04	0.24	b.d.
Na <sub>2</sub> O	b.d.	0.07	1.80	1.71	0.06	2.69	9.06	1.33	b.d.
K <sub>2</sub> O	0.02	b.d.	0.48	0.46	0.02	0.45	0.08	9.51	b.d.
F	n.d.	n.d.	0.09	0.08	b.d.	0.07	n.d.	b.d.	b.d.
Cl	n.d.	n.d.	b.d.	b.d.	b.d.	b.d.	n.d.	b.d.	b.d.
-O≡F			0.04	0.03		0.03			
-O≡Cl									
Total	100.53	100.36	96.92	97.30	101.75	98.21	100.62	95.10	98.49
Number of O	12	12	23	23	12	23	8	11	12.5
Si	3.02	3.00	6.32	6.37	3.01	6.39	2.82	3.22	3.03
Ti	0.01	0.01	0.06	0.10	0.01	0.04	< 0.01	0.03	b.d.
Al	1.95	1.96	2.60	2.55	1.95	2.59	1.18	2.45	2.20
Cr	b.d.	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	b.d.	b.d.	b.d.
$\mathrm{Fe}^{2+}$	1.48	1.22	1.46	1.35	1.73	2.10	b.d.	0.19	
Fe <sup>3+</sup>	< 0.01	0.04	0.41	0.24	< 0.01	0.07			0.75
Mn	0.60	0.47	0.07	0.08	0.22	0.03	b.d.	< 0.01	0.01
Mg	0.37	0.89	2.65	2.69	0.49	1.95	b.d.	0.14	b.d.
Ca	0.55	0.42	1.65	1.70	0.57	1.65	0.21	< 0.01	2.01
Ba			< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	b.d.
Na	b.d.	0.01	0.51	0.48	< 0.01	0.77	0.77	0.17	b.d.
К	< 0.01	b.d.	0.09	0.09	< 0.01	0.09	< 0.01	0.82	b.d.
F			0.04	0.04	b.d.	0.03		b.d.	b.d.
Cl			b.d.	b.d.	b.d.	b.d.		b.d.	b.d.
Total cation	7.99	8.01	15.86	15.69	8.00	15.71	4.98	7.02	7.99
$Mg/(Mg+Fe^{2+})$	0.20	0.42	0.64	0.67	0.22	0.48			
Prn	12.4	29.5			16.4				
Grs	18.4	13.9			18.8				
Sns	20.0	15.8			7.4				
Alm	49.3	40.7			57.4				
An							20.9		
Ps							,		25.5
10									

Table 3 Representative analyses of rock-forming minerals in the blocks

b.d.=below detection limit; n.d.=not determined

Sample No. (area) D113-9 (Dalrymple)					D113-2 (Dalrymple)			
Lithology Amphibolite			)			Ep Aı	nphibolite	1 /
Mineral	Hbl1	Hbl3	P11	Ep1	Chl3	Hb11	P11	Ep1
Occurrence	Matrix	Hbl alt	Matrix	Matrix	Hbl alt	Matrix	Matrix	Matrix
Core/Mantle/Rim	Rim	Rim	Rim	Rim		Rim	Rim	Rim
SiO <sub>2</sub>	47.68	51.54	64.97	38.62	27.33	45.08	65.03	38.17
TiO <sub>2</sub>	0.43	0.07	b.d.	b.d.	0.03	0.82	b.d.	0.17
$Al_2O_3$	11.91	2.95	22.23	25.58	22.07	11.64	22.14	23.94
$Cr_2O_3$	0.11	0.05	b.d.	0.05	0.13	0.07	0.01	b.d.
FeO	10.28	20.31	b.d.		12.65	14.28	0.13	
$Fe_2O_3$				10.355				12.618
MnO	0.37	0.40	b.d.	0.17	0.23	0.21	b.d.	0.10
MgO	13.96	9.22	0.02	0.05	23.17	12.11	0.03	0.06
CaO	11.24	11.94	3.01	23.66	b.d.	10.22	3.05	23.34
BaO	0.03	b.d.	b.d.	0.06	b.d.	0.18	0.06	0.08
Na <sub>2</sub> O	1.90	0.52	10.31	b.d.	0.02	2.58	10.34	b.d.
K <sub>2</sub> O	0.21	0.28	0.10	b.d.	0.01	1.27	0.09	b.d.
F	b.d.	0.01	n.d.	0.04	0.01	0.14	n.d.	0.01
Cl	0.01	0.01	n.d.	b.d.	0.01	b.d.	n.d.	< 0.01
-O≡F		0.00		0.01	0.00	0.06		0.01
-O≡Cl	0.00	0.00			0.00			0.00
Total	98.14	97.28	100.64	98.57	85.65	98.61	100.86	98.50
Number of O	23	23	8	12.5	28	23	8	12.5
Si	6.81	7.75	2.85	3.02	5.50	6.62	2.85	3.01
Ti	0.05	0.01	b.d.	b.d.	< 0.01	0.09	b.d.	0.01
Al	2.01	0.52	1.15	2.36	5.23	2.02	1.14	2.23
Cr	0.01	< 0.01	b.d.	< 0.01	0.01	< 0.01	< 0.01	b.d.
$\mathrm{Fe}^{2+}$	1.23	2.55	b.d.		2.13	1.75	< 0.01	
Fe <sup>3+</sup>	< 0.01	< 0.01		0.61		< 0.01		0.75
Mn	0.05	0.05	b.d.	0.01	0.04	0.03	b.d.	0.01
Mg	2.97	2.07	< 0.01	0.01	6.95	2.65	< 0.01	0.01
Ca	1.72	1.92	0.14	1.98	b.d.	1.61	0.14	1.97
Ba	< 0.01	b.d.	b.d.	< 0.01	b.d.	0.01	< 0.01	< 0.01
Na	0.53	0.15	0.88	b.d.	0.01	0.74	0.88	b.d.
Κ	0.04	0.05	0.01	b.d.	< 0.01	0.24	< 0.01	b.d.
F	b.d.	< 0.01		0.01	0.01	0.07		< 0.01
Cl	< 0.01	< 0.01		b.d.	< 0.01	b.d.		< 0.01
Total cation	15.41	15.08	5.02	8.00	19.87	15.82	5.02	7.99
$Mg/(Mg+Fe^{2+})$	0.71	0.45			0.77	0.60		
Prp								
Grs								
Sps								
Alm								
An			13.8				13.9	
Ps				20.5				25.2

Table 3 continued

b.d.=below detection limit; n.d.=not determined

Table 4 continued										
Sample No. (area)	ea) B214-14 (Botoon)			B214-29 (Botoon)						
Lithology	Ky-Ep-	Grt schist		Ky-Hbl schist						
Mineral	Grt2a		Ep2a	Hbl2a	Oam2a	Ky2a	Hbl2b	Oam2b	Ky2b	
Occurrence	Ky inclu	usion	Matrix	Matrix	Matrix	Matrix	Matrix	Matrix	Matrix	
Core/Mantle/Rim	Core	Rim	Rim	Rim		Rim	Rim			
SiO <sub>2</sub>	39.50	39.91	30.38	44.88	47.66	36.85	45.11	48.57	37.10	
TiO <sub>2</sub>	0.35	0.10	35.23	0.22	b.d.	0.14	0.37	0.11	b.d.	
$Al_2O_3$	21.22	21.79	1.95	13.55	13.98	59.91	14.34	13.06	60.87	
$Cr_2O_3$	b.d.	b.d.	b.d.	0.98	0.64	1.85	0.05	b.d.	0.67	
FeO	17.35	16.58		9.59	11.39		8.85	11.73		
Fe <sub>2</sub> O <sub>3</sub>			1.19			1.98			1.39	
MnO	7.34	6.93	0.18	0.62	1.03	0.04	0.56	1.09	0.05	
MgO	8.12	8.07	b.d.	14.39	19.86	0.02	14.69	21.38	0.02	
CaO	6.26	6.84	28.98	9.95	0.69	0.02	10.12	0.68	b.d.	
BaO	n.d.	n.d.	0.08	0.09	b.d.	0.09	b.d.	b.d.	b.d.	
Na <sub>2</sub> O	n.d.	n.d.	0.05	1.81	1.19	b.d.	2.04	1.37	0.01	
K <sub>2</sub> O	n.d.	n.d.	0.03	0.27	b.d.	b.d.	0.26	b.d.	0.01	
F	n.d.	n.d.	0.03	0.04	0.12	0.03	0.10	b.d.	b.d.	
Cl	n.d.	n.d.	b.d.	< 0.01	b.d.	b.d.	0.01	b.d.	b.d.	
-O≡F			0.01	0.02	0.05	0.01	0.04			
-O≡Cl				0.00			0.00			
Total	100.14	100.21	98.10	96.38	96.55	100.93	96.48	97.99	100.10	
Number of O	12	12	12.5	23	23	20	23	23	20	
Si	3.03	3.04	2.53	6.49	6.74	4.00	6.47	6.77	4.03	
11	0.02	0.01	2.21	0.02	< 0.01	0.01	0.04	0.01	b.d.	
Al	1.92	1.96	0.19	2.31	2.33	/.66	2.42	2.14	/./9	
Cr	b.d.	b.a.	b.a.	0.06	0.04	0.08	<0.01	b.a.	0.03	
Fe <sup>2+</sup>	1.11	1.06		1.16	1.35		1.06	1.37		
Fe <sup>3+</sup>	< 0.01	< 0.01	0.07	0.36	< 0.01	0.16	0.40	< 0.01	0.11	
Mn	0.48	0.45	0.01	0.08	0.12	< 0.01	0.07	0.13	< 0.01	
Mg	0.93	0.92	b.d.	3.10	4.19	< 0.01	3.14	4.44	< 0.01	
Ca	0.51	0.56	2.59	1.54	0.10	< 0.01	1.56	0.10	b.d.	
Ba			< 0.01	0.01	b.d.	< 0.01	b.d.	b.d.	b.d.	
Na			0.01	0.51	0.33	b.d.	0.57	0.37	< 0.01	
K			< 0.01	0.05	b.d.	b.d.	0.05	b.d.	< 0.01	
F			0.01	0.02	0.05	0.01	0.05	b.d.	b.d.	
CI	- 00	- 00	b.d.	< 0.01	b.d.	b.d.	< 0.01	b.d.	b.d.	
Total cation	7 <b>.99</b>	7.98	7.64	15.70	15.24	11.93	15.82	15.33	11.97	
$Mg/(Mg+Fe^{2+})$	0.45	0.46	<b>2</b> 0.0	0.73	0.76		0.75	0.76		
Ps			28.0							

b.d.=below detection limit; n.d.=not determined

Sample No. (area)	N215-3 (Nanac	1)				
Lithology	Grt-Hbl-Bt sch	ist				
Mineral	Hbl2a	Bt2a	Bt2b	Bt3	Ms3	Chl3
Occurrence	Porphyroclast		Matrix	Matrix	Matrix	Matrix
Core/Mantle/Rim	Rim					
SiO <sub>2</sub>	45.96	40.97	40.45	40.55	49.37	28.16
TiO <sub>2</sub>	0.30	0.87	1.06	1.03	0.66	0.18
$Al_2O_3$	13.67	17.51	16.91	16.52	30.40	21.45
$Cr_2O_3$	0.13	b.d.	0.27	0.13	0.05	0.19
FeO	10.39	9.55	9.74	9.42	3.89	9.77
$Fe_2O_3$						
MnO	0.63	0.27	0.32	0.36	0.03	0.41
MgO	14.13	17.03	17.04	17.27	2.52	25.44
CaO	9.02	0.10	0.03	0.03	0.03	b.d.
BaO	b.d.	0.14	0.23	0.03	0.19	0.06
Na <sub>2</sub> O	3.23	0.38	0.15	0.14	0.73	b.d.
K <sub>2</sub> O	0.23	7.85	8.58	8.45	6.07	b.d.
F	b.d.	0.15	b.d.	0.16	0.12	0.01
Cl	b.d.	b.d.	b.d.	0.01	< 0.01	0.01
-O≡F		0.06		0.07	0.05	0.00
-O=Cl				0.00	0.00	0.00
Total	97.68	94.82	94.77	94.10	94.06	85.67
Number of O	23	11	11	11	11	28
Si	6.59	2.94	2.92	2.94	3.29	5.58
Ti	0.03	0.05	0.06	0.06	0.03	0.03
Al	2.31	1.48	1.44	1.41	2.38	5.01
Cr	0.01	< 0.01	0.01	< 0.01	< 0.01	0.01
Fe <sup>2+</sup>	1.25	0.57	0.59	0.57	0.22	1.62
Fe <sup>3+</sup>	0.11					
Mn	0.08	0.02	0.02	0.02	< 0.01	0.07
Mg	3.02	1.82	1.84	1.87	0.25	7.52
Ca	1.39	0.01	< 0.01	< 0.01	< 0.01	b.d.
Ba	b.d.	< 0.01	0.01	< 0.01	< 0.01	< 0.01
Na	0.90	0.05	0.02	0.02	0.09	b.d.
Κ	0.04	0.72	0.79	0.78	0.52	b.d.
F	b.d.	0.03	b.d.	0.04	0.03	< 0.01
Cl	b.d.	b.d.	b.d.	< 0.01	< 0.01	< 0.01
Total cation	15.73	7.69	7.69	7.73	6.82	19.86
Mg/(Mg+Fe <sup>2+</sup> )	0.71	0.76	0.76	0.77		0.82
Ps						

 Table 4 Representative analyses of rock-forming minerals in the matrix

 Sample No. (area)
 N215-3 (Nanad)

b.d.=below detection limit; n.d.=not determined