Evolution of the Tyrone ophiolite, Northern Ireland,
 during the Grampian-Taconic orogeny: A correlative of
 the Annieopsquotch Ophiolite Belt of central
 Newfoundland?

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23 ABSTRACT

24 The Tyrone Plutonic Group of Northern Ireland represents the upper portions of a tectonically 25 dissected suprasubduction zone ophiolite accreted to the composite Laurentian margin during 26 the Middle Ordovician. Understanding its development and relationship to the Tyrone 27 Central Inlier, an outboard fragment of relatively high-grade, peri-Laurentian continental 28 crust, is essential for reconstructing the closure of the Iapetus Ocean. The Tyrone Plutonic 29 Group is composed of tectonised layered, isotropic and pegmatitic gabbros, sheeted dolerite 30 dykes and rare pillow lavas. New U-Pb zircon TIMS geochronology has yielded an date of 31 483.68 ± 0.81 Ma from pegmatitic gabbro. Geochemical characteristics, Nd and Sr isotope 32 systematics, and zircon inheritance indicate the Tyrone Plutonic Group formed above a N-33 dipping subduction zone, by the propagation of a spreading centre into a microcontinental block. Syn-kinematic, calc-alkaline tonalitic to granitic material preserved in the contact 34 35 zone between the Tyrone Plutonic Group and the Tyrone Central Inlier has produced pressure estimates of 2.3-4.0 \pm 0.6 kbar and temperatures of 525-610 °C. Coeval arc-ophiolite 36 37 accretion at ca. 470 Ma may explain how sillimanite-grade metamorphic conditions were 38 reached locally in the underlying Tyrone Central Inlier. Strong temporal, geochemical and 39 lithological similarities exist with the Annieopsquotch Ophiolite Belt of Newfoundland.

41 **INTRODUCTION**

42 Ophiolites represent fragments of upper mantle and oceanic crust incorporated into 43 continental margins during continent-continent and arc-continent collisions, ridge-trench 44 interactions and/or subduction-accretion events (references in Dilek & Furnes 2011). 45 Following the Penrose definition (Anonymous 1972) and establishment of the plate tectonic 46 theory, a paradigm shift occurred for ophiolite genesis between the early 1970s and mid 47 1980s, when it was recognized that most have geochemical similarities to island-arcs (e.g. 48 Miyashiro 1973; Harper 1984). Consequently, the ophiolite concept moved toward a 49 magmatic origin in subduction zone settings (suprasubduction zone ophiolites; e.g. Pearce et 50 al. 1984). Suprasubduction zone ophiolites are interpreted to form in arc-forearc or backarc 51 settings at convergent margins shortly before orogenesis (Dilek & Furnes 2011). Common 52 within many Early Palaeozoic orogens, such as the Caledonian, Appalachian, and Uralian 53 belts, suprasubduction zone ophiolites often mark the location of subduction sutures within 54 short-lived collision zones and can therefore provide essential information on the closure of 55 ancient ocean basins and their temporal evolution (e.g. Dewey 2005).

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57 The Grampian-Taconic phase (ca. 475-465 Ma) of the Caledonian-Appalachian orogen (Fig. 58 1) resulted from the progressive accretion of a diverse set of arc terranes, ribbon-shaped 59 microcontinental blocks and oceanic tracts to the Laurentian margin during the Early 60 Palaeozoic closure of the Iapetus Ocean (Draut et al. 2004; van Staal et al. 2007; Cooper et 61 In the British and Irish Caledonides, deformed and metamorphosed al. 2011). 62 Neoproterozoic to Early Palaeozoic rocks of the Dalradian Supergroup represent cover sequences of the Laurentian margin (Chew 2009). Recent advances, including new 63 64 fieldwork, geochemistry, U-Pb zircon and Ar-Ar geochronology (e.g. Chew et al. 2008, 2010; 65 Flowerdew et al. 2009; Cooper et al. 2008, 2011; Hollis et al. 2012, companion publication), 66 revealed that the Grampian orogeny was more complex than previously thought. Three main episodes of arc-ophiolite emplacement are recognized within the Newfoundland 67 68 Appalachians, during the equivalent Taconic orogeny (van Staal et al. 2007). Although 69 potential correlatives to each of the ca. 510-500 Ma Lushs Bight Oceanic Tract, ca. 490-470 70 Ma Baie Verte Oceanic Tract/Snooks Arm arc, and ca. 480-460 Ma Annieopsquotch 71 Accretionary Tract of the Newfoundland Appalachians have been suggested in the British and 72 Irish Caledonides (e.g. van Staal et al. 1998; Chew et al. 2010; Cooper et al. 2011; Hollis et 73 al. 2012), a number of specific terrane correlations remain contentious.

75 In the Newfoundland Appalachians, the presence of outriding microcontinental blocks was 76 invoked to explain both: (i) discrepancies between the timing of syntectonic sedimentation 77 and tectonic loading on the passive continental margin at ca. 475 Ma and ophiolite 78 emplacement prior to ca. 488 Ma (see Waldron & van Staal 2001); and (ii) the range of ages 79 for Iapetan ophiolites accreted to the Laurentian margin (van Staal et al. 2007). Recent work 80 from the British and Irish Caledonides has similarly demonstrated that subduction and the 81 onset of obduction occurred at least ca. 15 Ma before the Grampian orogeny (Chew et al. 82 2010). Consequently, understanding the relationship between suprasubduction zone ophiolites 83 and any peri-Laurentian microcontinental blocks within the Caledonides (such as the Tyrone 84 Central Inlier and Slishwood Division; Flowerdew et al. 2009, Chew et al. 2010; Hollis et al. 85 2012) is vital for reconstructing the progressive closure of the Iapetus Ocean.

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87 The Tyrone Plutonic Group of Northern Ireland (Fig. 2) represents the upper parts of a 88 tectonically dissected ophiolite sequence (Hutton et al. 1985) accreted onto an outboard 89 segment of Laurentia, the Tyrone Central Inlier, during the Ordovician (Cooper & Mitchell 90 2004). Opinions on the timing of its formation, emplacement and relationship to both the 91 Tyrone Volcanic Group (a peri-Laurentian island arc) and the Tyrone Central Inlier (a peri-92 Laurentian microcontinental block; Chew et al. 2008, 2010) have varied (e.g. Angus 1970; 93 GSNI 1879; Hutton et al. 1985; Cooper & Mitchell 2004; Cooper et al. 2008; Chew et al. 94 2008; Draut et al. 2009; Cooper et al. 2011; Hollis et al. 2012). Recent U-Pb zircon 95 geochronology has dated LREE-depleted layered olivine gabbro from the Tyrone Plutonic 96 Group to 479.6 ± 1.1 Ma (Cooper *et al.* 2011), which is significantly younger than previous 97 geochronology from the ophiolite (493 \pm 2 Ma: Draut *et al.* 2009) and other ophiolites preserved in the British and Irish Caledonides. For example, the Deer Park Complex of 98 99 western Ireland, the Scottish Highland Border Ophiolite and the Shetland Ophiolite have 100 yielded considerably older ages of 514 ± 3 Ma, 499 ± 8 Ma and 492 ± 3 Ma respectively 101 (Spray & Dunning 1991; Chew et al. 2010). Only the Ballantrae Ophiolite Complex of 102 Scotland has produced a similar U-Pb zircon age of 483 ± 4 Ma (Bluck *et al.* 1980).

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Here we present the interpreted results of high-resolution airborne geophysics, whole rock and mineral geochemistry (including new Nd- and Sr-isotope constraints), and key field relationships across the region, in addition to a new U-Pb zircon age for a pegmatitic gabbro from the Tyrone Plutonic Group. These new data suggest that the *ca*. 484-479 Ma Tyrone Plutonic Group was emplaced relatively late in the Grampian orogeny at *ca*. 470 Ma, coeval 109 with the accretion of the Tyrone arc (=Tyrone Volcanic Group, see Cooper *et al.* 2011), and is 110 therefore broadly equivalent to the Annieopsquotch Ophiolite Belt of Newfoundland. The 111 relations between the accretion of oceanic rocks and sillimanite-grade metamorphism in the 112 underlying Tyrone Central Inlier will be discussed.

113

114 FIELD RELATIONSHIPS

The Tyrone Plutonic Group is exposed across approximately 95 km² of counties Tyrone and 115 116 Londonderry, Northern Ireland. It crops out predominantly SE of the Tyrone Central Inlier, 117 and to a lesser extent to the NW around Davagh Forest in faulted contact with the Tyrone 118 Volcanic Group (Fig 2). The Tyrone Plutonic Group consists mainly of variably tectonised 119 and metamorphosed, layered, isotropic and pegmatitic gabbros, sheeted dolerite dykes and 120 rare pillow lavas which were thrust over the Tyrone Central Inlier during the Middle 121 Ordovician (Hutton et al. 1985; Cooper & Mitchell 2004) (Fig. 2). Primary mineral 122 assemblages in the Tyrone Plutonic Group have been altered to epidote-amphibolite 123 metamorphic assemblages (Merriman & Hards 2000). Mafic minerals have been replaced by hornblende, epidote, actinolite and/or chlorite, with feldspars variably sericitised. 124 125 Groundmass often comprises a mixture of quartz, amphibole, actinolite, chlorite and epidote, 126 as well as less abundant zircon, titanite, sericite, biotite, and locally carbonate. Although the 127 Tyrone Plutonic Group is tectonically dissected and poorly exposed, several key localities 128 preserve a relatively complete upper crustal ophiolite sequence (Hutton et al. 1985). The 129 following zones have been recognised (adapted after GSNI 1879; Hutton et al. 1985).

130 Layered and isotropic gabbros: Layered and isotropic gabbros comprise the majority of the 131 Tyrone Plutonic Group and are best exposed at Scalp Hill and eastwards through 132 Cregganconroe and Craignagore (Fig. 2). Olivine gabbros at Scalp Hill display cumulate 133 layering, locally differentiated into compositionally distinct bands (cm to m scale) (Cobbing, 134 1969; GSNI 1879). Locally gabbro may be deformed to hornblende schist, with schistosity 135 parallel to mineral layering in surrounding rocks (Cooper & Mitchell 2004). Cooper et al. 136 (2011) reported a U-Pb zircon age of 479.6 ± 1.1 Ma for layered gabbro from Scalp Hill. 137 Layered magnetite gabbro is common around Scalp and immediately NW of the 138 Craigballyharky Complex (GSNI 1879).

139

Layered and isotropic gabbros at several localities appear to be younger than an early suite of
dolerites ('Early Dolerites and Gabbros': BGS 1986). At Craignagore, a central gabbro

intrudes early, fine to medium grained amphibolite-facies dolerite (Angus 1970). Exposures
of dolerite surrounding the gabbro are generally foliated or schistose amphibolites; with a
finely crystalline relic of pyroxene-hornfels exposed at one locality (Angus 1970). The
gabbro is largely uniform and porphyritic adjacent to its southern contact, and is itself cut by
a later series of dolerite dykes (equivalent to the 'Ophitic Dolerites of Carrickmore' of BGS
147 1986).

148

149 Transition Zone: At Black Rock (Fig. 2), coarse-grained hornblende gabbro intrudes, and 150 contains xenoliths of, an early-formed suite of dolerite (the 'Early Dolerites and Gabbros' of 151 BGS 1986). This sequence is in turn intruded by younger 1-2 m wide, basalt and dolerite 152 dykes (Cooper & Mitchell 2004) (Fig. 3a-b). Early basaltic and dolerite dykes are deformed, 153 locally schistose and extensively altered with fine stringers of epidote. Gabbro is extremely 154 coarse grained, ranging from equigranular in nature to pegmatitic. Irregular veins of 155 pegmatitic gabbro contain large hornblende and plagioclase crystals often exceeding 2 cm in 156 diameter (rarely > 8 cm). The youngest suite of basaltic and doleritic dykes at Black Rock 157 are relatively undeformed and less extensively altered. Porphyritic varieties contain 1-2 mm 158 rounded and angular laths of plagioclase in a fine-grained, ophitic or intergranular matrix.

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160 At Oritor (Fig. 2), dolerite dykes intrude gabbro, which contain xenoliths of an earlier foliated 161 dolerite. Dolerite dykes typically trend NW-SE and can be distinguished from Palaeogene 162 olivine-bearing dykes by their composition and state of alteration; the former always being 163 extensive uralitised (Hartley 1933). At Slaghtfreeden (Fig. 2), isotropic and pegmatitic 164 gabbro, microgabbro and dolerite also contain xenoliths of foliated basalt. These are intruded 165 by, and present as xenoliths in, late intrusive rocks of quartz and hornblende porphyritic 166 diorite (Fig. 3c). Late ophitic dolerite dykes are also present at Carrickmore, Cregganconroe 167 and Craignagore (Fig. 2) which cut olivine gabbro and/or poikiloblastic hornblende gabbro.

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Sheeted Dykes: Although the presence of ophitic dolerite at Carrickmore was recognized by Hartley (1933), it was Hutton *et al.* (1985) who first reported the presence of parallel sheeted dolerite dykes in Carrickmore Quarry (Fig. 2). The sheeted dykes typically average 1 m in thickness, intrude one another forming two-sided chilled margins and more commonly one sided chilled margins and can locally constitute 100 % of the exposure (Hutton *et al.* 1985). Dolerite at Carrickmore appears aphanitic in hand specimen, though may be either intergranular or ophitic in thin section. In Craigballyharky Quarry, dolerite dykes display rarechilled margins and are intruded by relatively undeformed plagiogranite and aplite (Fig. 3d).

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178 Pillow basalts and volcaniclastic rocks: Pillow lavas are scarce within the Tyrone Plutonic 179 Group, and are best exposed as a series of roof-pendants within the Craigballyharky complex 180 (Cobbing et al. 1965). Pillow structures at Craigballyharky typically range between 30 and 181 75 cm in diameter (Fig. 3e). These lavas are aphanitic, subalkaline, tholeiitic, LILE and 182 LREE-depleted and of suprasubduction affinity (Draut et al. 2009; Cooper et al. 2011, see 183 geochemistry). Intermediate and basic lavas have also been reported to occur at Scalp and 184 Oritor (Hartley 1933), with amygdaloidal lavas present SW of Scalp Hill. At Slaghtfreeden, 185 Hartley (1933) noted a sheet of gabbro intruding lavas overlain by coarse breccias and tuffs. 186 This sequence was subsequently intruded by a dolerite dyke that contains xenocrysts of 187 hornblende derived from the gabbro.

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189 Craigballyharky complex: The Craigballyharky complex (Cobbing et al. 1965; GSNI 1879) is exposed across approximately 3.5 km^2 (Fig. 2) and is composed of three major units: 190 191 an intrusion of tonalite representing the summit of Craigballyharky $(472^{+2})^{-4}$ Ma of Hutton et 192 al. 1985; 470.3 \pm 1.9 Ma of Cooper et al. 2011), an intrusion of biotite-granodiorite 193 representing the summit of Craigbardahessiagh (464.9 \pm 1.5 Ma of Cooper *et al.* 2011), and 194 quartz-diorite (see Angus 1962, 1977). A series of roof pendants exposed across the complex 195 include siliceous ironstone possibly derived from the Tyrone Volcanic Group, and isotropic 196 gabbros, dolerites and pillow lavas from the Tyrone Plutonic Group (Cobbing et al. 1965). 197 Siliceous ironstone xenoliths have been recorded in both the Craigbardahessiagh granodiorite 198 and Craigballyharky tonalite (GSNI 1879). Together, these roof pendants, coupled with 199 xenocrystic Proterozoic zircons, imply both the Tyrone Volcanic Group and Tyrone Plutonic 200 Group were in their present structural position above the Tyrone Central Inlier prior to ca. 201 470 Ma (Cooper et al. 2011). Occurrences of agglomerate, limestone and silicified 202 metasedimentary rocks have also been reported (Cobbing et al. 1965; GSNI 1879), though 203 were not observed during recent fieldwork.

204

Quartz diorite is widely regarded to be hybrid in origin (Angus 1962, 1977), produced by magma mixing and mingling between arc-related gabbro and *ca*. 470 Ma tonalite at Craigballyharky (Hutton *et al.* 1985; Cooper *et al.* 2011). Although recent dating reported an age of 493 ± 2 Ma for Craigballyharky gabbro (Draut *et al.* 2009), Cooper *et al.* (2011)

presented a recalculated mean ${}^{206}\text{Pb}/{}^{238}\text{U}$ age of 473.2 ±1.6 Ma for this unit, significantly 209 210 younger and in agreement with field-relations and its relatively unaltered and undeformed 211 nature. Consequently, the Craigballyharky gabbro is attributed to the younger ca. 470-464 212 Ma arc related intrusive suite (see following), consistent with its LILE and LREE-enriched 213 geochemical characteristics (figure 5 of Draut et al. 2009; Cooper et al. 2011). Late arc-214 related gabbro also intrudes the c. 475-469 Ma Tyrone Volcanic Group at Beaghbeg and 215 Mweenascallagh (Fig. 2), although the latter is of eMORB affinity (Hollis et al. 2012). At 216 Craigballyharky, magma mixing and mingling within a hybrid quartz diorite is seen in 217 outcrop where large quartz ocelli are observed to have migrated from the tonalite into gabbro. 218 Contacts are typically diffuse and irregular, though may locally be sharp (Fig. 3f).

219

220 Arc-related intrusive suite: The arc-related intrusive suite includes a series of high-level 221 plutons, sills and dykes of various compositions, which intrude all levels of the Tyrone 222 Igneous Complex (Fig. 2). Large intrusions of diorite, granodiorite, tonalite, biotite- and 223 hornblende-bearing granite, and quartz \pm feldspar porphyry are the most frequent; although 224 minor occurrences of arc-related gabbro and dolerite also occur (Hollis et al. 2012). Field 225 relationships and published U-Pb geochronology (Cooper et al. 2011) are consistent with the 226 intrusions being significantly younger than the Tyrone Plutonic Group (ca. 470-464 Ma). For 227 example, diorite at Lough Lily (Fig. 2) contains angular xenoliths of ophiolite-derived 228 dolerite and intrudes the latter as veins (Hartley 1933). At Scalp, coarsely crystalline, pink 229 and grey hornblende-rich tonalite (equivalent to the Golan Burn tonalite of Cooper et al. 230 2011: 469.9 ± 2.9 Ma) contains xenoliths of gabbro which show all stages of assimilation and 231 the development of hybrid granite (GSNI 1879). At Black Rock, xenoliths of amphibolite-232 facies gabbro are present within LREE-enriched arc-related quartz \pm biotite \pm hornblende 233 porphyry. Diorite at Crooked Bridge displays a magma mixing-mingling relationship with 234 hornblende-granite and has produced an age of 469.58 ± 0.77 Ma (see Hollis *et al.* companion 235 publication).

236

Tremoge Glen: Medium to coarse grained and pale-grey to pink granite exposed at Tremoge Glen is unusual within the Tyrone Igneous Complex as it is extensively altered, intensely sheared and muscovite-bearing. Geological mapping reveals the granite intrudes gabbros of the Tyrone Plutonic Group and is itself intruded by NE and NW trending late Fe-Ti enriched basaltic/doleritic dykes with ophitic textures (GSNI 1879; Fig. 2). The Tremoge Glen intrusion occurs as a NE-SW orientated wedge of granite bound on its eastern side by the Tempo – Sixmilecross Fault (Fig. 2). These dykes appear to be related to the younger *ca*.
475-469 Ma Tyrone Volcanic Group (see following).

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246 **OPHIOLITE CONTACT: BLAEBERRY ROCK**

247 A high strain zone of mylonitic metamorphosed igneous rocks E of Davagh Forest was 248 discovered at the mapped contact between the Tyrone Central Inlier and Tyrone Plutonic 249 Group (Fig. 2). The exposure, known locally as Blaeberry Rock, consists of a 7 x 6 x 3 m 250 block and several smaller boulders (Fig. 4a). The main exposure comprises cm- to dm-sized 251 blocks of amphibolite-facies gabbroic to doleritic material within an intimate mixture of mm-252 to cm- scale banded and isoclinally folded syn-kinematic tonalitic to granitic material, 253 amphibolite and possible Dalradian metasedimentary rocks (Fig. 4b-e). Nearby exposures 254 include smaller angular blocks of gabbro and dolerite which display preserved chilled 255 margins and patchy outcrops of quartzofeldspathic paragneisses of the Tyrone Central Inlier 256 invaded by tonalitic intrusive sheets, leucosomes and pegmatite. Younger moderately 257 deformed tonalitic to granitic veins cut the sheared rocks and are themselves often folded and 258 boudinaged.

259

Preferential localization of strain appears to be confined to the intrusive sheets, with gabbroic inclusions relatively undeformed except for some alignment of amphibole crystals. Large amphibole crystals up to 3.5cm in length occur within the melt network and appear to be derived from brecciated bodies of gabbro cut by thin veins. These crystals, along with minor drag folds, show evidence for sinistral shearing (Fig. 4f). Paler grey andesitic (?) clasts (~10 x 20 cm) also contain a well-developed mineral stretching lineation. Narrow shear zones and late veins of epidote cut the exposure.

267

268 Gabbroic and doleritic blocks exposed within the Blaeberry Rock contact are petrologically 269 and geochemically (see following) similar to those from the Tyrone Plutonic Group. These 270 ophiolite-derived lithologies have experienced amphibolite facies metamorphism and are 271 composed of actinolite (after pyroxene) and plagioclase replaced by white-mica, chlorite and 272 epidote (Supplementary Material: Fig. 4g-j). Syn-kinematic and late tonalitic to granitic veins 273 are composed of quartz, orthoclase, sericitised labradorite with minor muscovite, trace biotite 274 and accessory phases (fluorapatite and sphene). Plagioclase may be internally altered to 275 chlorite, epidote and muscovite (Supplementary Material: Fig. 4g-j).

277 TELLUS AIRBORNE GEOPHYSICS

278 During 2005-2006 the Tellus airborne geophysical survey, part of the Tellus Project (see 279 GSNI 2007), was flown across the entirety of Northern Ireland. Magnetic, radiometric and 280 electromagnetic (EM) data were acquired. Further detail on survey specification and 281 geophysical data processing are provided within Gunn et al. (2008). Interpreted EM and total 282 magnetic intensity (analytic signal) maps over the Tyrone Plutonic Group are shown in Figure 283 5. Lithologies of the Tyrone Plutonic Group are clearly distinguishable from the non-284 magnetic units of the Tyrone Central Inlier. Faulted contacts between the Tyrone Plutonic 285 Group, Tyrone Volcanic Group, Tyrone Central Inlier and post-Ordovician cover sequences 286 are best discriminated by EM imagery, (Fig. 5a) with boundaries corresponding well to 287 previous mapping (GSNI 1879, 1995). The Tyrone Plutonic Group is characterised by short-288 wavelength magnetic anomalies (Gunn et al. 2008), with magnetic highs corresponding to 289 areas of magnetite-bearing dolerite and gabbro. Magnetic imagery reveals the Tyrone 290 Plutonic Group to be dissected into thin slices by a series of NE-SW orientated Caledonian 291 faults (Fig. 5b). Magnetic lows within the Tyrone Plutonic Group are associated with deep 292 seated granitic plutons of the ca. 470-464 Ma arc-related intrusive suite (e.g. Pomerov 293 granite) and demagnetized zones associated with faulting (e.g. Tempo-Sixmilecross; Fig. 2). 294 Tonalitic and granodioritic plutons at Craigballyharky and Craigbardahessiagh, may represent 295 thin laccoliths underlain by highly magnetic material. Along the eastern side of the Tyrone 296 Central Inlier where gneissose psammites and semipelites crop out, highly-magnetic 297 lithologies appear to be present. Although it is possible a portion of the Tyrone Plutonic 298 Group structurally underlies the Tyrone Central Inlier, these magnetic rocks may also 299 represent mafic volcanics associated with the rifting of the Tyrone Central Inlier from the 300 Laurentian margin or buried basement material.

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302 WHOLE ROCK GEOCHEMISTRY

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304 Sampling and Analytical Techniques

Eighteen samples were collected from key localities across the Tyrone Plutonic Group and Blaeberry Rock for whole-rock geochemical analysis. Major-elements and trace-elements were determined for powdered whole-rock samples on fused glass beads and powder pellets by X-ray fluorescence at the University of Southampton. Rare earth-elements (plus Nb, Hf, Ta, Th, U) were determined by inductively coupled plasma mass spectrometry (ICP-MS) on the same samples using HF/HNO₃ digest. Further detail is provided in Hollis *et al.* (2012). 311 Geochemical analyses of Draut et al. (2009) and Cooper et al. (2011) are also included.

312 Results are presented as Supplementary Material (Table 1).

313

314 Two samples were analysed at Southampton for Sr isotopes (Supplementary Material Table 315 1). Strontium was separated using approximately 80µl columns containing Sr-Spec resin and 316 elution with 3M HNO₃ to remove interfering elements. The purified Sr samples were 317 collected with water and loaded onto a single Ta filament using a Ta activator solution. 318 Samples were run using a multi dynamic peak jumping routine on a VG Micromass Sector 54 319 thermal ionization mass spectrometer (TIMS) at the University of Southampton. Rb and Sr 320 concentrations were obtained by ICP-MS. The ratios were corrected using an exponential fractionation correction relative to ⁸⁶Sr/⁸⁸Sr of 0.1194. NIST-987 was run and its long term 321 average 87 Sr/ 86 Sr value was 0.710243 ± 18 (2sd n=93). An age correction was performed to 322 account for radioactive decay and ingrowth of ⁸⁷Sr; values for that time are reported as 323 ⁸⁷Sr/⁸⁶Sr_i. Modern CHUR was taken to be 0.7045 and 0.0827 for ⁸⁷Sr/⁸⁶Sr and ⁸⁷Rb/⁸⁶Sr 324 respectively. The decay constant of 87 Sr is 1.42 x 10⁻¹¹ yr⁻¹. 325

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327 Four samples were analysed for Sm-Nd and Rb-Sr by isotope dilution thermal ionisation mass 328 spectrometry at University College Dublin (Supplementary Material Table 1). Samples were 329 weighed and spiked prior to digestion in HF-NNO₃ in teflon bombs at temperatures up to 330 180°C, following initial treatment with cold, followed by hot, HCl, to remove any carbonates 331 present. Standard ion chromatography separation procedures used Eichrom ion specific 332 resins (Sr Resin for Sr, TRU Resin SPS for the REE as nitrates) and a Biorad cation exchange 333 resin (AG 50W-X12 for Rb as chloride). Sm and Nd were separated from one another as 334 chlorides using Eichrom Ln Resin SPS. Sm, Nd and Sr isotopic analyses were carried out on 335 a ThermoScientific Triton multiple collector thermal ionization mass spectrometer. Analyses 336 were carried out in static multicollection mode, with switching of amplifiers between Faraday collectors to correct for differential amplifier responses. All Nd peaks were measured, along 337 with ¹⁴⁹Sm and ¹⁵²Sm to correct for isobaric interference from Sm. In practice, this correction 338 was negligible (for example ≤ 2 ppm on 143 Nd/ 144 Nd ratios). The La Jolla standard yielded a 339 value of 143 Nd/ 144 Nd = 0.511842 ± 5 (2sd, n=24) during the period of this work. The 340 uncertainty in ¹⁴⁷Sm/¹⁴⁴Nd is estimated to be 0.1%. Sr aliquots were measured on single Ta 341 342 filaments using a Ta activator solution. At UCD, the SRM987 standard yielded a value of ${}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.710247 \pm 11$ (2sd, n= 25), indistinguishable from that obtained at Southampton. 343 ⁸⁷Rb/⁸⁵Rb ratios were measured on a ThermoScientific Neptune multiple collector inductively 344

coupled plasma mass spectrometer on solutions doped with zirconium and corrected for mass bias using the measured 90 Zr/ 91 Zr ratio, assuming a natural 90 Zr/ 91 Zr ratio of 4.588, following Nebel et al. (2005).

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349 **Element Mobility**

350 Various studies have demonstrated that most of the major elements (e.g. SiO₂, Na₂O, K₂O, 351 CaO, MgO) and the low field strength elements (LFSE: Cs, Rb, Ba, Sr, except Th) are mobile 352 during metamorphism and hydrothermal alteration (references in Dilek & Furnes 2011). As 353 primary mineral assemblages within the Tyrone Plutonic Group have been metamorphosed to 354 amphibolite facies conditions only elements demonstrated to be immobile are used to 355 elucidate petrogenesis and tectonic affinities. Comparison of the major and trace element 356 data from the Tyrone Plutonic Group to Zr (assumed immobile) confirms this mobility, with 357 considerable scatter for Na₂O, K₂O, Sr and Ba in particular (Hollis 2013). TiO₂, MgO, P₂O₅, Th, Nb, V, Cr, Co, Sc Y, U and the REEs appear to have remained immobile. SiO₂ appears 358 359 to have remained relatively immobile, apart from minor silicification in some samples. 360 Al₂O₃/Na₂O ratios vary between 2.3 and 23.9 (Fig. 6a). Sampled lithologies show carbonate-361 chlorite-pyrite index (CCPI: see Large et al. 2001) values typical of mafic volcanics (41.1-362 95.4, most >80 Fig. 6b) and Hashimoto alteration index (AI: Ishikawa et al. 1976) values (22.6-51.5) typical of weakly altered rocks. Sericite index values (Saeki & Date 1980; 363 364 K₂O/K₂O+Na₂O) vary between 0.07 and 0.49. Analyses show a weak negative correlation 365 between Na₂O and LOI, suggesting that lower Na₂O contents are due to losses associated 366 with alteration (e.g. sericitisation).

367

368 **Petrochemistry**

369 Tyrone Plutonic Group: Immobile element ratios within the Tyrone Plutonic Group are 370 predominantly subalkaline (Nb/Y <0.06) and tholeiitic (Zr/Y 0.7-3.8) (Fig. 6c). On multi-371 element variation diagrams sampled lithologies display slight LREE depletion (La/Sm 0.6-372 1.2, Fig. 7a) and flat HREE profiles (Gd/Lu 0.7-1.1, most 1.0-1.1). Th concentrations (i.e. 373 LILE) are similarly low (Th_{CN} 0.76-15.88; Fig. 6d). Aphanitic basaltic rocks classify as 374 island-arc tholeiitic basalts according to Pearce and Cann (1973), Pearce and Norry (1979), 375 Wood (1980), and Meschede (1986). Positive Pb, negative Nb and modest Ti anomalies 376 across the Tyrone Plutonic Group are consistent with formation in a suprasubduction environment (as in Draut et al. 2009; Cooper et al. 2011) (Fig. 6e-f; 7a). 377 Gabbro and 378 pegmatitic gabbro from Black Rock, Carrickmore and Bonnety Bush display slightly lower Th_{CN}, LREE and HREE concentrations than others sampled from the Tyrone Plutonic Group. Plagiogranite that cuts sheeted dykes at Craigballyharky Quarry is borderline calc-alkaline, and strongly LILE and LREE-enriched (Zr/Y 7.5, La/Yb 6.8, Th_{CN} 166.55) relative to the HREE (Fig. 7).

383

Initial ⁸⁷Sr/⁸⁶Sr ratios were calculated for five samples from the Tyrone Plutonic Group at an 384 age of 480 Ma (after Cooper *et al.* 2011). These vielded ⁸⁷Sr/⁸⁶Sr_i ratios ranging from 385 0.71064 to 0.70851, and included dolerite dykes from Craigballyharky Quarry (0.71019), 386 387 Black Rock (0.71064), Carrickmore Quarry (fine-grained dolerite = 0.70874 and coarse-388 grained dolerite = 0.70851) and a pillowed basalt at Craigballyharky (0.70908). Mobility of 389 Rb and Sr is well documented during seafloor hydrothermal alteration, metamorphism and subsequent weathering (e.g. Jacobsen & Wasserburg 1979). 87 Sr/ 86 Sr_i ratios obtained from 390 the Tyrone Plutonic Group are comparable to the ⁸⁷Sr/⁸⁶Sr isotopic composition of Lower to 391 392 Middle Ordovician seawater (0.7087-0.7090, Young et al. 2009), although they range up to slightly more radiogenic values. These slightly higher ⁸⁷Sr/⁸⁶Sr_i values may suggest the 393 394 incorporation of some continental material into the source region, which is supported by the 395 presence of inherited zircons in layered gabbros from Scalp (Cooper et al. 2011) and Sm-Nd 396 constraints (see following). By contrast, gabbro from Scalp (Fig. 2) has a less radiogenic ⁸⁷Sr/⁸⁶Sr_i value of 0.70391, suggesting somewhat lesser interaction with seawater, consistent 397 398 with its likely deeper original position within the ophiolite.

399

400 Previous Nd isotope geochemistry from the Tyrone Plutonic Group is restricted to three 401 samples of Draut et al. (2009). Recalculated ENdt values for an age of 480 Ma (Cooper et al. 402 2011) are: +4.40 (gabbro from Scalp), +5.85 (dolerite from Carrickmore) and +7.43 (gabbro 403 from Carrickmore). New analyses (Table 1) are consistent with these previously published 404 values, and include: +5.30 and +5.33 for fine-grained and coarse-grained dolerite respectively 405 from Carrickmore Quarry, +6.12 from gabbro at Scalp Hill; and +5.33 from pillowed basalt at 406 Craigballyharky. Most of these values are lower than calculated values from the depleted 407 mantle growth curve at 480 Ma (+7.0; DePaolo 1988), suggesting some contamination from 408 continentally-derived material occurred during the formation of the Tyrone Plutonic Group. 409

410 **Blaeberry Rock:** A fine to medium grained doleritic clast collected from Blaeberry Rock is 411 subalkaline (Nb/Y 0.27) and tholeiitic (Zr/Y 0.94; Fig. 6c), relatively LILE-depleted (Th_{CN} 412 15.8) and slightly LREE-depleted relative to the HREE (La/Yb_{CN} 0.93; Fig. 6d-e; 7b). These

- 413 geochemical characteristics, in addition to low Ti/V (1.2), and Zr/TiO₂ (91.9), moderate AI
- 414 (53.2), and high CCPI (94.5), Al_2O_3/Na_2O (12.9) and Gd/Lu ~1 are consistent with derivation
- 415 from the Tyrone Plutonic Group. Th/Yb-Nb/Yb systematics classifies the clast as similar to
- 416 eMORB (Fig. 6f). This sample displays a positive Nb anomaly relative to Th and La (Fig.
- 417 7b), and a higher Nb/Y ratio than samples typical from the Tyrone Plutonic Group (Fig. 6c).
- 418 Nb enrichment may be associated with increased alteration (e.g. CCPI).
- 419
- 420 Samples of tonalitic to granitic intrusive material collected from Blaeberry Rock (SiO₂ 59.6-421 64.4 wt%, Zr/TiO₂ 227.9-318.5) are calc-alkaline (Zr/Y 5.8-16.2), strongly LILE-enriched 422 (Th_{CN} 34.7-174.0, Fig. 8c), and display steep LREE profiles (La/Sm 3.3-6.5) relative to the 423 HREE (La/Yb 4.2-16.4) and strong negative Nb anomalies (0.11-0.48) on multi-element 424 variation diagrams (Fig. 7d). These samples geochemically resemble the ca. 470-465 Ma 425 tonalites of the Tyrone Igneous Complex (see Cooper et al. 2011) which are characterized by 426 high Zr/TiO₂ (154.5-583.8), Zr/Y (5.6-10.5) and La/Sm (4.5-6.8) ratios, Th_{CN} values (154.2-427 297.0) and pronounced negative Nb anomalies (0.17-0.27, Fig. 7c) (values from Cooper et al. 428 2011; Hollis et al. 2012; Hollis 2013). Sampled Dalradian-affinity metasedimentary rocks of 429 the Tyrone Central Inlier from Corvanaghan Quarry and Fir Mountain Quarry (adjacent to 430 Blaeberry Rock: Fig. 2) similarly have steep REE profiles (La/Sm to 7.2, La/Yb to 28.7) and 431 can display pronounced negative Nb anomalies (often due to the presence of melt), but have 432 significantly higher Zr, Rb, Ba, Th_{CN} and REE_{Total} concentrations, and higher Ti/V and Nb/Y 433 ratios (to 0.9) (Hollis 2013).
- 434

435 **Tremoge Glen:** S-type muscovite granite from Tremoge Glen shows calc-alkaline 436 characteristics (Zr/Y 13.3) is strongly LREE enriched relative to the HREE (La/Yb 18.2), and 437 strongly LILE enriched (Th_{CN} ~325). Samples analyzed have high K₂O/(K₂O+Na₂O) ratios 438 of ~0.6 and are strongly peraluminous (after Shand 1943). The S-type geochemical 439 characteristics suggest it may have been intruded shortly after the emplacement of the Tyrone 440 Plutonic Group from the melting of metasedimentary material of the Tyrone Central Inlier. 441 This is consistent with its high Th_{CN} and LREE enrichment.

442

443 A single sample (MRC129) was analysed from the basaltic-doleritic dykes at Tremoge Glen 444 which cut the S-type muscovite granite. This sample is Fe-Ti-enriched (Fe₂O_{3T} 15.4, TiO₂ 445 2.7), lacks a prominent negative Nb anomaly characteristic of island-arc tholeiites (Nb anom 446 0.82) and is of 'within-plate' or eMORB affinity (e.g. Wood, 1980, Fig. 6b). MRC129 is subalkaline, calc-alkalic, and LILE and LREE enriched (Nb/Y 0.55, Zr/Y 7.2, La/Yb 4.7, Th_{CN} 107.83). Low Cr (~50ppm) and Ni (~14ppm) confirms the relatively evolved nature of this sample. High LOI (7.06 wt.%), CCPI (87.4), SI (0.31) and AI (50.9) values are consistent with extensive alteration. The small negative Nb anomaly is indicative of a weak subduction signature or may reflect minor crustal contamination.

452

453 MINERAL CHEMISTRY

454 Electron microprobe analyses were completed at the Natural History Museum, London, to 455 determine mineral compositions and establish P-T conditions from the Tyrone Plutonic Group 456 and its contact with the underlying Tyrone Central Inlier. Three samples were analysed; one 457 from pegmatitic gabbro from Black Rock within the 'transition zone' of the Tyrone Plutonic 458 Group (SPH34); and two from Blaeberry Rock (SPH210: gabbroic clast; and SPH215: 459 tonalitic material in the contact). SPH34 from Black Rock is dominated by plagioclase and 460 amphibole (Fig. 4j). Plagioclase is extensively altered along grain boundaries to secondary 461 minerals: epidote, carbonate, white mica, chlorite and residual albite. Amphibole occurs as 462 large anhedral grains of hornblende intergrown with actinolite. Sample SPH210 (gabbroic 463 clast) is similar to SPH34 (collected from Black Rock) and contains amphibole closely 464 associated with epidote and muscovite, and is believed to represent ophiolite-derived material 465 based on mineral chemical and whole rock geochemistry. By contrast, sample SPH215 466 comprises a mixture of hornblende, quartz, orthoclase, plagioclase, chlorite, epidote and 467 accessory phases (sphene and fluorapatite) from tonalitic layers in the contact (Fig. 4g-h). 468 Spot analyses were performed on a Cameca SX-50 electron microprobe equipped with a 469 wavelength dispersive system, and were conducted at 20 keV and 20 nA. Counting times 470 ranged from 10 to 50 seconds for spot analysis. Data are presented as Supplementary 471 Material (Table 2).

472

473 Amphiboles analysed from SPH34 (Black Rock) and SPH210 (Blaeberry Rock clast) 474 chemically classify as tremolitic actinolite and magnesio-hornblende, whereas those analysed 475 from syn-kinematic tonalitic intrusive sheets at Blaeberry Rock (SPH215) classify as 476 magnesio-hornblende with significantly lower Mg/(Mg+Fe) ratios and Si contents, and higher 477 Ti, Fe and Mn concentrations (Fig. 8a). Low TiO_2 (0-0.45 wt.%) and Al_2O_3 (1.74-4.79 wt.%) 478 in amphiboles from Black Rock (SPH34) and from the ophiolite-derived clast at Blaeberry 479 rock (SPH210) plot predominantly just off the geothermometer of Ernst and Liu (1998), 480 producing temperature estimates of c. <500 to 570 °C. Spot analyses from SPH215

amphiboles (tonalite) contain higher TiO₂ (0.35-0.65 wt.%) and Al₂O₃ (6.51-8.54 wt.%) indicating slightly higher temperatures of 525-610 °C. Hammarstrom and Zen (1986) first proposed that solidus pressures of intermediate calc-alkaline plutons can be estimated from the Al content of hornblende. Rocks should be near-solidus with the magmatic assemblage: hornblende + biotite + plagioclase + quartz + sanidine + sphene + magnetite or ilmenite ± epidote. The Al-in-hornblende geobarometer experimentally calibrated by Schmidt (1992) produces pressure estimates of *ca*. 2.3 to 4.0 ± 0.6 kbar for tonalite from Blaeberry Rock.

488

Epidotes from the Tyrone Plutonic Group typically have lower Fe and Ca, and higher Al,
contents than those from Blaeberry Rock. Samples SPH210 and SPH215 are chemically
similar, except for higher Si content in SPH215.

492

493 Alkali feldspar compositions from Blaeberry Rock sample SPH215 are restricted to a 494 relatively narrow range between $Or_{82.6}Ab_{16.1}An_{1.3}$ and $Or_{96.7}Ab_{3.3}An_0$ (Fig. 8b). BaO and 495 Ce_2O_3 concentrations range between 0.46 and 1.4 wt% and 0.17 and 0.53 wt% respectively. 496 FeO_T concentrations vary between 0.03 and 0.43 wt%. The composition of plagioclase from 497 SPH215 varies from andesine to labradorite ($Or_{0.9}Ab_{59.6}An_{39.4}$ to $Or_{0.7}Ab_{48.0}An_{51.3}$) (Fig. 8b). 498 FeO_T concentrations range between 0.11 and 0.17 wt%.

499

500 Chlorites from the Tyrone Plutonic Group are relatively Mg-rich and classify as 501 pycnochlorite (SPH34), whereas those analysed from Blaeberry Rock (SPH215) classify as 502 both pycnochlore and ripidolite and have lower Mg# numbers (Fig. 8c-d). Si concentrations 503 are similar and range between 5.6 and 5.8 apfu (based on 22 oxygens). Fe/(Fe+Mg+Mn) 504 ratios are approximately 0.4 from Blaeberry Rock and 0.25 from the Tyrone Plutonic Group. 505 Al _{IV} concentrations vary between 2.15 and 2.41 apfu. Chlorite geothermometers of Zhang 506 and Fyfe (1995) and Kranidiotis and MacLean (1987) produce temperature estimates of ca. 261-274°C and 289-302°C respectively for chlorites from Blaeberry Rock sample SPH215. 507 508 Similar, temperature estimates were produced from chlorites of Black Rock (SPH34: 261-509 281°C and 265-288°C respectively). Chlorite temperature estimates most likely reflect 510 retrogression.

511

512 U-PB GEOCHRONOLOGY

514 **Analytical Methods:** A sample of pegmatitic gabbro from Black Rock was selected for U-Pb 515 zircon geochronology at the NERC Isotope Geosciences Laboratory (NIGL). Zircons were 516 isolated using conventional mineral separation techniques. Prior to isotope dilution thermal 517 ionization mass spectrometry (ID-TIMS) analyses zircons were subject to a modified version 518 of the chemical abrasion technique (Mattinson 2005). Methods are identical to those reported 519 in Hollis *et al.* (2012). Data are presented as Supplementary Material (Table 3). Errors for 520 U-Pb dates are reported in the following format: $\pm X(Y)[Z]$, where X is the internal or 521 analytical uncertainty in the absence of systematic errors (tracer calibration and decay 522 constants), Y includes the quadratic addition of tracer calibration error (using a conservative 523 estimate of the standard deviation of 0.1% for the Pb/U ratio in the tracer), and Z includes the quadratic addition of both the tracer calibration error and additional ²³⁸U decay constant 524 525 errors of Jaffey et al. (1971).

526

527 **Results:** Six fractions (single grains) were analyzed from the Black Rock sample MRC344 (pegmatitic gabbro). All six analyses are concordant when their systematic λ^{238} U and λ^{235} U 528 529 decay constant errors are considered with five analyses forming a coherent single population yielding a weighted mean ${}^{206}\text{Pb}/{}^{238}\text{U}$ date of $483.68 \pm 0.36 (0.60)[0.81]$ Ma (MSWD = 1.8) 530 (Fig. 9). We interpret this as being the best estimate for the age of this sample. This age is 531 532 slightly older than that produced for layered gabbro from Scalp (479.6 \pm 1.1 Ma: Cooper et 533 al. 2011). No inherited Proterozoic ages were derived from any of the dated zircon fractions, 534 although zircon selection was biased to avoid morphologies that may have contained 535 inherited cores.

536

537 **DISCUSSION**

538

539 **Evolution of the Tyrone Plutonic Group**

540 The Tyrone Plutonic Group is composed primarily of layered, isotropic and pegmatitic 541 gabbros, sheeted dolerite dykes and rare pillow lavas (Angus 1970; Hutton et al. 1985; 542 Cooper & Mitchell 2004). Geochemical evidence and field relations presented herein are 543 consistent with the Hutton et al. (1985) interpretation that the Tyrone Plutonic Group 544 represents the upper portions of a tectonically dissected ophiolite which was accreted to the 545 Laurentian margin during the Grampian orogeny. Multi-element profiles and Nd-isotope 546 compositions are consistent for basalts generated at an oceanic spreading centre above a 547 subduction zone (Draut et al. 2009). The new U-Pb zircon geochronology presented here

548 (483.68 \pm 0.81 Ma) is similar to that of Cooper *et al.* (2011: 479.6 \pm 1.1 Ma) constraining the 549 formation of the Tyrone Plutonic Group to *ca.* 484-479 Ma. The slightly older age presented 550 here for pegmatitic gabbro from Black Rock is in agreement with its more primitive 551 geochemical characteristics. Pegmatitic gabbro from Black Rock is more LILE, LREE and 552 HREE depleted than layered gabbro from Scalp. It is entirely possible that multiple slices of 553 Iapetan ocean floor of slightly varying age occur within the Tyrone Plutonic Group, as the 554 ophiolite is tectonically dissected.

555

556 Field relationships across the ophiolite are consistent with several phases of intrusive activity 557 typical of oceanic spreading centres. Poor preservation of the sheeted dyke complex is 558 typical of suprasubduction zone ophiolites in general; with large well-developed complexes 559 requiring an appropriate balance between spreading and magma supply rates (references in 560 Robinson et al. 2008). In contrast to fast-spreading Mid Ocean Ridges, where these 561 conditions are maintained, suprasubduction zone spreading rates are not directly controlled by 562 magma supply but are ultimately dependent on slab rollback, which is related to the angle of 563 subduction and the rate of convergence (Robinson et al. 2008). The absence of a thick 564 ultramafic section within the Tyrone Plutonic Group may be explained by post-tectonic 565 excision or more likely by delamination and subduction of the lower crust during ophiolite 566 emplacement (e.g. Annieopsquotch Ophiolite Belt; Zagorevski et al. 2009). Limited 567 occurrences of ultramafic material may be present around Davagh Forest, where "basic and 568 ultrabasic rocks, often pyroxenitic" have been described (see Gunn et al. 2008), closely 569 associated with elevated PGE, Cr and Ni soil anomalies.

570

571 Fe-Ti enriched basaltic dykes which intrude S-type muscovite granite at Tremoge Glen have a 572 within-plate affinity and lack a pronounced island-arc geochemical signature. High LILE and 573 LREE-enrichment, coupled with low Cr and Ni, is indicative of their more evolved nature 574 compared to other samples from the Tyrone Plutonic Group. Fe-Ti-enriched basalts are 575 defined by >12 wt% FeO_T and >2 wt% TiO₂ (e.g. Sinton *et al.* 1983), and typically display 576 lower concentrations of MgO, CaO and Al₂O₃ than normal MORB. Fe-Ti basalts are 577 common in propagating rifts, and occur at several stratigraphic horizons in the structurally 578 overlying ca. 475-469 Ma Tyrone Volcanic Group, a peri-Laurentian island arc/backarc 579 (Hollis et al. 2012). Geochemically identical Fe-Ti basalts of eMORB affinity with slight 580 negative Nb anomalies occur in the upper Tyrone Volcanic Group as the ca. 469 Ma 581 Mountfield Basalts of the Broughderg formation (see Hollis et al. 2012; companion publication). U-Pb zircon TIMS geochronology has also directly dated a geochemically similar unit from Sruhanleanantawey Burn (Fig. 2) to 469.36 ± 0.34 Ma (Hollis *et al.* companion publication). We suggest the Tremoge Glen Fe-Ti enriched dykes were emplaced at *ca.* 469 Ma, and may be part of an extensive swarm which fed the Mountfield Basalts (see Hollis *et al.* companion publication).

587

588 Incorporation of Palaeoproterozoic and Mesoproterozoic xenocrystic zircons (ca. 1015 and 589 2100 Ma) into the Scalp layered gabbros (Cooper et al. 2011) suggests that the Tyrone 590 Plutonic Group formed above a north-dipping subduction zone by the propagation of a 591 spreading centre into a microcontinental block (=Tyrone Central Inlier, see below) (Fig. 10). 592 A similar tectonic scenario was presented for the formation of the ca. 480 Ma 593 Annieopsquotch Ophiolite Belt of Newfoundland (Zagorevski et al. 2006; also see Cutts et al. 594 2012 and following section). The presence of propagating rifts is consistent with the 595 occurrence of: Fe-Ti-P enriched 'within-plate' basalt across the Tyrone Igneous Complex 596 from at least ca. 475 Ma to 469 Ma; minor continental contamination in the Tyrone Plutonic 597 Group according to Nd- and Sr-isotope systematics; and zircon inheritance at Scalp. This 598 tectonic scenario may also explain the strong LILE, LREE and negative εNd_t values in the *ca*. 599 475-469 Ma Tyrone Volcanic Group (Hollis et al. 2012). The Tyrone Volcanic Group is 600 believed to have formed above a north-dipping subduction zone immediately outboard of the 601 Tyrone Central Inlier (Hollis et al. 2012). These geochemical characteristics may be 602 explained if the arc was in part founded upon a fragment of microcontinental crust which was 603 rifted off the Tyrone Central Inlier during the formation of the Tyrone Plutonic Group (Fig. 604 10; Hollis et al. companion publication). A similar situation has been envisaged for the 605 evolution of the analogous Buchans-Robert's Arm arc of Newfoundland (Zagorevski et al. 606 2006; Zagorevski et al. 2012). In situ Hf isotope analysis of zircon rims from ca. 470 Ma 607 granitoid rocks that cut the Tyrone Central Inlier paragneisses yield negative εHf_{470} values of ca. -39 (Flowerdew et al. 2009). This isotopic signature requires an Archaean source, 608 609 suggesting that rocks similar to the Lewisian Complex of Scotland occur at depth beneath the 610 Tyrone Central Inlier (Flowerdew et al. 2009).

611

612 Accretion to the Tyrone Central Inlier

The Tyrone Central Inlier is composed of a thick sequence of psammitic and semi-pelitic paragneisses (Hartley 1933) exposed within the central regions of the Tyrone Igneous Complex (Fig. 2), and is cut by a variety of acidic intrusive rocks. A prograde assemblage of 616 biotite + plagioclase + sillimanite + quartz \pm muscovite \pm garnet is observed in pelitic 617 lithologies (Chew et al. 2010), with cordierite locally observed (Hartley 1933). The high-618 grade nature of the Tyrone Central Inlier (ca. 670 ± 113 °C, 6.8 ± 1.7 kbar; Chew et al. 2008) 619 and its position SE of the Fair Head - Clew Bay Line (Fig. 1) has led recent workers (e.g. 620 Chew et al. 2008; Flowerdew et al. 2009; Chew et al. 2010; Cooper et al. 2011) to suggest 621 the Tyrone Central Inlier may represent part of an outboard segment of Laurentia, which 622 detached as a microcontinent during the opening of Iapetus (ca. 570 Ma?) and subsequently 623 reattached during the Grampian orogeny (ca. 470 Ma). Geochronology of syn-tectonic leucosomes (207 Pb- 206 Pb zircon age of 467 ± 12 Ma; main fabric 40 Ar- 39 Ar biotite cooling age 624 of 468 \pm 11.4 Ma) and post-tectonic muscovite-bearing pegmatites (⁴⁰Ar-³⁹Ar step heating 625 626 plateaux ages of 466 and 468 \pm 1 Ma) suggest a Grampian age (ca. 475-465 Ma) for the 627 deformation and metamorphism of the Tyrone Central Inlier (Chew et al. 2008).

628

629 Obduction of the Tyrone Plutonic Group onto the Tyrone Central Inlier must have occurred 630 prior to the intrusion of the Craigballyharky tonalite (470.3 \pm 1.9 Ma) which contains 631 inherited Proterozoic zircons and roof pendants of ophiolitic and arc-related material (Cooper 632 et al. 2011). All rocks of the arc related intrusive suite are LILE and LREE-enriched with 633 strongly negative ENdt values (to -11.8: Hollis et al. 2012 and unpublished data) implying that 634 interaction with continental crust was an integral part of their petrogenesis (Draut et al. 2009). 635 Xenocrystic zircons are consistent with derivation from the structurally underlying Tyrone 636 Central Inlier (Cooper et al. 2011), although the source of the ca. 2100 Ma inheritance 637 remains elusive (Hutton et al. 1985; Cooper et al. 2011). Interestingly, plutons of the Notre 638 Dame Arc in Newfoundland, built on an along strike equivalent of the Tyrone Central Inlier, 639 termed the Dashwoods block (see following), have also yielded xenocrystic components of 640 Palaeoproterozoic age (e.g. upper intercept of 2090 ± 75 Ma: Whalen *et al.* 1987).

641

The muscovite granite which cuts layered gabbro at Tremoge Glen is unusual within the arc related intrusive suite; its S-type geochemical characteristics, high Th_{CN} and LREE enrichment suggest it may have been intruded shortly after the emplacement of the Tyrone Plutonic Group from the melting of underthrust peri-Laurentian metasedimentary material (i.e. Tyrone Central Inlier). Attempts to date the Tremoge Glen muscovite granite using U-Pb zircon were not successful and produced large errors (Noble *et al.* 2004). Although apparently core-free zircons were picked, two analyses showed very significant inheritance, with upper intercepts of *ca*. 1560 Ma and 2351 Ma (Noble *et al*. 2004). A second attempt todate this unit is in progress.

651

652 Although the Tyrone Plutonic Group was emplaced between ca. 479 and 470 Ma, the exact 653 timing of this event has remained elusive. At Blaeberry Rock the presence of ophiolite-654 derived blocks in abundant syn-kinematic tonalitic to granitic material and amphibolite 655 suggests the Tyrone ophiolite may have been accreted to the Tyrone Central Inlier at the same 656 time as the Tyrone Volcanic Group at ca. 470 Ma. Tonalite intrusions are abundant 657 throughout the Tyrone Igneous Complex and four occurrences have produced U-Pb zircon 658 ages: 470.3 ± 1.9 Ma at Craigballyharky (Cooper *et al.* 2011), 465.6 ± 1.1 . Ma from Laght 659 Hill (Cooper *et al.* 2011: also 475 ± 10 Ma: Draut *et al.* 2009), 469.9 ± 2.9 Ma from Golan 660 Burn (Cooper et al. 2011), and 469.29 ± 0.33 Ma from Cashel Rock (Hollis et al. 2012). 661 Emplacement at ca. 470 Ma, synchronous with the Tyrone arc (=Tyrone Volcanic Group), 662 may explain how the metamorphic conditions evident within the Tyrone Central Inlier (ca. 663 670 ± 113 °C, 6.8 ± 1.7 kbar; Chew *et al.* 2008) were generated prior to *ca.* 468 Ma. These 664 conditions cannot have been solely the result of the obduction of the Tyrone Plutonic Group, 665 as it is tectonically dissected, thin and lacks an ultramafic section. The coeval emplacement 666 of both the arc and the ophiolite would provide a >10-15 km thick, hot crustal sequence, 667 enough to produce the required P-T conditions in the Tyrone Central Inlier.

668

669 Amphiboles from syn-kinematic tonalitic material within the Blaeberry contact (SPH210; Fig. 670 8a) produced temperature estimates of 525-610 °C, slightly lower (but within error) than 671 those produced by Chew et al. (2008) from the Tyrone Central Inlier (670 ± 113 °C). 672 Pressure estimates (after Schmidt, 1992) up to 4.0 ± 0.6 kbar for tonalitic melt from Blaeberry 673 Rock (SPH210) are again lower than those produced by Chew et al. (2008), however Hartley 674 (1933) noted that the presence of sillimanite in the Tyrone Central Inlier is restricted to its SE 675 As the Tyrone Igneous Complex was emplaced from this direction, the higher side. 676 temperatures and pressures from Corvanaghan Quarry may simply be restricted to that region, 677 where the accreted succession was thickest. Sillimanite-bearing paragneisses are also 678 preserved across the Notre Dame and Dashwoods subzones of the equivalent Newfoundland 679 Appalachians associated with arc-ophiolite accretion (e.g. Brem et al. 2007; van Staal et al. 680 2007; 2009; Fig. 1b). In the Dashwoods subzone, large bodies and screens of variably 681 migmatized sillimanite-bearing paragneisses are exposed (see van Staal et al. 2007). Lesser exposures further north in the Notre Dame subzone (e.g. as screens in the Hungry Mountain
Complex: Waldron & van Staal 2001) is due to the level of denudation (van Staal *et al.* 2007).

684

685 Another possible fragment of microcontinental crust in the Irish Caledonides is the Slishwood 686 Division (Flowerdew et al. 2005; Chew et al. 2010) (Fig. 1a). This metasedimentary 687 sequence is exposed in three inliers of NW Ireland (NE Ox Mountains, Lough Derg and 688 Rosses Point) and is composed predominantly of migmatitic psammitic gneisses with minor 689 pelites, semipelites, calc-silicates, metabasites and serpentinites (Sanders 1979; Flowerdew & 690 Daly 2005; Daly 2009). All three inliers have been suggested on the basis of magnetic and 691 gravity data to form one basement block which acted as a rigid indenter during the Grampian 692 orogeny (Fig. 1a; references in Daly 2009). The Grampian histories of the Slishwood 693 Division and the Tyrone Central Inlier are very similar, both having undergone leucosome 694 generation during orogenesis, and subsequently intruded by pegmatites that cut the high level 695 fabrics (Flowerdew et al. 2005; Chew et al. 2008). The NE Ox Mountains Inlier was also 696 intruded by several tonalite and granite bodies between ca. 471-467 Ma (Flowerdew et al. 697 2005) with magmas contaminated by the host rocks. This is identical to the late-Grampian 698 evolution of the Tyrone Central Inlier (see Cooper et al. 2011). Final imbrication of the 699 Slishwood Division with the Central Ox Mountains Dalradian Supergroup occurred during 700 D3 regional thrusting (between c. 476-463 Ma: Flowerdew et al. 2005), equivalent in Country 701 Tyrone to the emplacement of the Dalradian Supergroup above the Tyrone Igneous Complex 702 and Tyrone Central Inlier (Omagh Thrust; Fig. 2).

703

704 Clear differences between the Slishwood Division and Tyrone Central Inlier are primarily 705 related to their pre-Grampian histories. These include the presence of calc-silicates, 706 metabasites serpentinites in the former (Daly and 2009). 707 although possible metabasites have been recognized in the Tyrone Central Inlier during GSNI 708 fieldwork. Metabasites in the Slishwood Division record pre-Grampian high-pressure 709 granulite- and earlier eclogite-facies metamorphic events (Sanders et al. 1987; Flowerdew & 710 Daly 2005) not observed within the Dalradian Supergroup or Tyrone Central Inlier. Sm-Nd 711 garnet-plagioclase whole rock isochrons from the granulite-facies assemblages have yielded 712 ages ranging between 605 ± 37 Ma and 539 ± 11 Ma; with P-T estimates of *ca*. 15 kbar and 713 860 °C (Saunders et al. 1987; Flowerdew & Daly 2005; see discussion in Daly 2009). 714 Although this early history is pre-Grampian, Daly (2009) has suggested the metamorphism 715 cannot be much older as: U-Pb detrital zircon ages (Daly et al. 2004) demonstrate a post716 Grenville age of deposition of the protolith; and a pre-tectonic metabasite body which 717 preserves original gabbroic textures has produced a Sm-Nd mineral isochron age of 580 ± 36 718 Ma. This Sm-Nd age is consistent with magmatism related to the opening of the lapetus 719 Ocean between ca. 570 and 535 Ma (Cawood et al. 2001). Detrital zircon analysis from the 720 Slishwood Division has also revealed differences compared with the Tyrone Central Inlier. A 721 significant population between ca. 2.5 and 2.7 Ga is present in the Appin, Argyll and 722 Southern Highland groups of the Dalradian Supergroup (Cawood et al. 2003) and Tyrone 723 Central Inlier (Chew et al. 2008), but is absent in the Slishwood Division (Daly et al. 2004) 724 cited by Flowerdew et al. 2005) and the Grampian Group of the Dalradian (Cawood et al. 2003). T_{DM} model ages are also significantly younger in the Tyrone Central Inlier than in the 725 726 Slishwood Division (references in Chew et al. 2008).

727

728 A correlative of the Annieopsquotch Ophiolite Belt of Newfoundland?

729 Recent fieldwork, U-Pb zircon geochronology and geochemistry from across the Tyrone Igneous Complex has highlighted the close similarities between: (i) the Tyrone Plutonic 730 731 Group and the Annieopsquotch Ophiolite Belt of Newfoundland (Cooper et al. 2011), (ii) 732 Tyrone Volcanic Group and the Buchans and Robert's Arm groups of central Newfoundland 733 (Hollis et al. 2012); and (iii) a late suite of ca. 470-464 Ma calc-alkaline intrusive rocks with 734 the second phase of the Notre Dame arc (van Staal et al. 2007), which also invade the 735 Annieopsquotch Accretionary Tract (Lissenberg et al. 2005; Lissenberg & van Staal 2006). 736 The work presented herein, adds further weight to these correlations, indicating that the 737 Tyrone Igneous Complex represents the third stage of arc-ophiolite emplacement in the peri-738 Laurentian British and Irish Caledonides at ca. 470 Ma, following the accretion of early ca. 739 510-500 Ma oceanic tracts (Chew et al. 2010), and the Lough Nafooey arc at ca. 480 Ma (see 740 Hollis et al. 2012).

741

742 The Annieopsquotch Ophiolite Belt of central Newfoundland comprises several 743 suprasubduction zone ophiolite complexes (e.g., King George IV, Annieopsquotch, Star 744 Lake), which formed during west-directed subduction outboard of the Dashwoods peri-745 Laurentian microcontinent (Dunning et al. 1987; Whalen et al. 1997; Lissenberg et al. 2005; 746 Zagorevski et al. 2006). Two U-Pb zircon ages from a pegmatitic and medium-grained trondhjemite (481.4 $^{+4.0}/_{-1.9}$ Ma and 477.5 $^{+2.6}/_{-2.0}$ Ma) constrain the age of the Annieopsquotch 747 Ophiolite Belt to ca. 481-478 Ma (Dunning & Krogh 1985). The Annieopsquotch Ophiolite 748 749 Complex is the largest and most studied ophiolite within the belt; and consists of suprasubduction zone affinity layered to isotropic gabbros, sheeted dykes and pillow basalts (Lissenberg *et al.* 2005). The lower gabbro zone contains enclaves of troctolite inferred to have formed from boninitic melts (Lissenberg *et al.* 2004). The youngest basalts are of MORB-type affinity and are cut by sheeted dykes with back-arc geochemical characteristics (Lissenberg *et al.* 2005). ϵ Ndt values within the Anniopsquotch Ophiolite Belt range from +7.6 to +8.4 (Zagorevski *et al.* 2006). The ophiolite lacks an upper mantle section apart from rare occurrences of dunite and pyroxenite (Lissenberg & van Staal 2006).

757

758 The age of formation for the Tyrone Plutonic Group between 484 and 479 Ma (including the 759 new date of 483.68 ± 0.81 Ma for the pegmatitic gabbro at Black Rock, Table 3), primitive 760 εNdt values ranging from +4.40 to +7.73 (Draut et al., 2009; Cooper et al., 2011; Table 1), 761 tholeiitic suprasubduction geochemical signatures (Table 1), preserved ophiolite sequences, 762 and development outboard of a possible microcontinental block (i.e. Tyrone Central Inlier) 763 support both a correlation with the Annieopsquotch Ophiolite Belt and formation at an 764 oceanic spreading centre above a subduction zone (see Draut et al. 2009; Cooper et al. 2011). 765 Xenocrystic Mesoproterozoic zircons present within the Tyrone Plutonic Group are consistent 766 with T_{DM} ages of 1200-1800 Ma from felsic intrusive rocks of the Moretons Harbour Group 767 (part of the Annieopsquotch Ophiolite Belt of Newfoundland; Cutts et al. 2012) indicating a 768 significant amount of contamination from Mesoproterozoic or older continental crust.

769

770 Furthermore, the Lloyds River Fault Zone which separates the Annieopsquotch Ophiolite Belt 771 from the Dashwoods microcontinental block bears a striking resemblance to Blaeberry Rock 772 (Lissenberg & van Staal 2002). The Lloyds River Fault at its type locality is a complex shear 773 zone having a central high-strain zone (mainly characterized by mafic and felsic tectonites), 774 which is bounded by less-strained moderately foliated amphibolite and orthogneiss dissected 775 by narrow shear zones (Lissenberg & van Staal 2002). The central high strain zone is 776 composed of an intimate mixture of banded amphibolite and metapyroxenite (probably of 777 ophiolitic origin) and strongly foliated quartz-diorite and tonalite. Moderately deformed, late-778 kinematic, folded and boudinaged tonalitic to granodioritic veins that cut sheared rocks 779 suggests that these arc magmas were intruded syn-kinematically (Lissenberg & van Staal 780 2006). The outer zone of the Lloyds River Fault consists of gabbro and diabase cut by diorite 781 and tonalite, with weakly deformed mafic rocks alternating with strongly sheared amphibolite 782 and orthogneiss. Preferential localization of shear zones occurs in intrusive sheets rather than 783 the ophiolite-derived gabbro, as at Blaeberry Rock. Shear sense indicators imply both the

784 Lloyds River Fault and Blaeberry Rock contacts accommodated oblique motion with a 785 sinistral component. Abundant metamorphic hornblende at both sites also suggests the fault 786 zones formed at amphibolite-facies conditions (with subsequent retrograde overprint) 787 (Lissenberg & van Staal 2006). Abundant syn-kinematic tonalitic material at Blaeberry 788 Rock implies that the Tyrone Plutonic Group was accreted at the same time as the Tyrone 789 Volcanic Group at ca. 470 Ma. This again is remarkably similar to that of the 790 Annieopsquotch Ophiolite Belt which occurred prior to ca. 468 Ma (Lissenberg et al. 2005; 791 Zagorevski et al. 2006).

792

793 In the Newfoundland Appalachians, three distinct phases of deformation and metamorphism 794 have been recognized during the Taconic orogeny, due to arc and ophiolite accretion (van 795 Staal et al. 2009). Early obduction of the Lushs Bight Oceanic Tract onto the peri-Laurentian 796 Dashwoods microcontinental block resulted in Taconic phase 1 at ca. 495 Ma (van Staal et al. 797 2009). Evidence for ductile deformation and metamorphism at this time is relatively cryptic (van Staal *et al.* 2009) as in the British and Irish Caledonides (e.g. 514 ± 3 Ma 40 Ar- 39 798 799 hornblende age from Deer Park ophiolitic mélange: Chew et al. 2010). Taconic phase 2 is 800 largely regarded as the main orogenic phase of the Appalachians, and is broadly equivalent to 801 the main episode of Grampian deformation in the British and Irish Caledonides (ca. 475-465 802 Ma) (e.g. van Staal et al. 2009). In the Newfoundland Appalachians this resulted from the 803 dextral oblique collision of an Early Ordovician west-facing peri-Laurentian arc (containing 804 ensimatic and ensialic segments) with the passive Laurentian margin, and the obduction of 805 suprasubduction affinity crust of the intervening seaways (van Staal et al. 2007, 2009). It has 806 been suggested that choking of the A-subduction channel during Taconic 2 may have been 807 the main cause for the initiation of subduction at ca. 480 Ma immediately outboard of the 808 accreted Notre Dame arc/Dashwoods Block, which led to the formation of the 809 Annieospquotch Accretionary Tract (van Staal et al. 2009). This timing is identical to that in 810 the Irish Caledonides where the Lough Nafooey arc collided with the Laurentian margin 811 between ca. 484 and 476 Ma (Draut et al. 2004), coeval with the early development of the 812 Tyrone Igneous Complex outboard of the Tyrone Central Inlier (Hollis et al. companion 813 publication). The rapid accretion of the Tyrone and Buchans-Robert's Arm arc systems to the 814 composite Laurentian margin occurred at ca. 470-468 Ma during the peak of Taconic phase 2 815 deformation (van Staal et al. 2009; Cooper et al. 2011). It is presently unclear why the 816 Tyrone Igneous Complex was obducted whereas the Annieopsquotch Accretionary Tract was 817 underplated (Hollis et al. 2012). Late orogenesis in Newfoundland (Taconic phase 3) is

818 related to the accretion of a late peri-Gondwanan arc system to the leading edge of Laurentia 819 along the Red Indian Line (Fig 1b) (van Staal et al. 2007).

820

821 **Other potential correlatives?**

822 The Ballantrae Ophiolite Complex of Scotland is a structurally imbricated assemblage of ophiolitic, ocean-island and island-arc rocks exposed over ca. 75km² immediately north of 823 the Southern Uplands Fault (Fig. 1). A U-Pb zircon date of 483 ± 4 Ma from trondhiemite 824 825 constrains the genesis of the ophiolite, and a K-Ar hornblende cooling age of 478 ± 4 Ma from its metamorphic sole constrains the timing of its emplacement (Bluck et al. 1980). 826 827 While it is possible that the Ballantrae Ophiolite Complex is an along strike equivalent of the 828 Tyrone Igneous Complex, current age constraints are not sufficient for reconstructing the 829 petrochemical evolution of the exposed sequences across tectonic blocks (discussed in Hollis 830 et al. 2012). Although graptolite-bearing sedimentary units are Early- to Late Arenig in age 831 (Stone & Strachan 1981; Stone & Rushton 1983; Rushton et al. 1986), considerably older 832 ages have also been produced from gabbro of within-plate affinity (K-Ar age of 487 ± 8 Ma: 833 Harris *et al.* 1965), and island-arc lavas (e.g. whole-rock Sm-Nd age of 501 ± 12 Ma: 834 Thirwall and Bluck, 1984). Post-obduction dykes of the Ballantrae Ophiolite Complex are 835 similarly divisible into those of island-arc and within-plate affinity (Holub et al. 1984).

836

837 The Norwegian (Scandinavian) Caledonides consist of four major allochthonous nappe 838 complexes, referred to as the Lower, Middle, Upper and Uppermost allochthons, which 839 overlie parautochthonous and autochthonous Baltican rocks (Roberts & Gee 1985). The 840 Uppermost Allochthon is of interest here as it is considered to represent an Ordovician 841 Taconic orogenic event on the Laurentian margin, similar to that preserved in the British and 842 Irish Caledonides (e.g. Slagstad et al. 2011). Although U-Pb ages similar to those from the 843 Tyrone Plutonic Group have been obtained in the Norwegian Caledonides from trondhjemite 844 of the Karmøy ophiolite (485 ± 2 Ma) and a cross-cutting arc related tonalite of the Gullfjellet ophiolite (482 ⁺⁶-4 Ma), both ophiolites also record earlier magmatism at *ca*. 490 Ma 845 846 (Dunning & Pedersen 1988). While it is clear ocean basin development occurred along the 847 Laurentian margin at this time (published U-Pb ages summarized in Slagstad et al. 2011), it is 848 not obvious how these units relate to those preserved in the Irish Caledonides.

849

850 CONCLUSIONS

852 The Tyrone Plutonic Group is composed of variably tectonised and metamorphosed, layered, 853 isotropic and pegmatitic gabbros, sheeted dolerite dykes and rare pillow lavas. New and 854 previously published geochronology constrains the formation of the Tyrone Plutonic Group to 855 ca. 484-479 Ma, within error of U-Pb zircon dating from the Annieopsquotch Ophiolite Belt 856 of Newfoundland. Whole rock Sr-isotopic constraints from the upper parts of the ophiolite are comparable to the ⁸⁷Sr/⁸⁶Sr composition of Lower to Middle Ordovician seawater and 857 range to slightly more radiogenic values. By contrast, gabbro from Scalp yielded a 858 significantly less radiogenic ⁸⁷Sr/⁸⁶Sr_i value suggesting somewhat lesser interaction with 859 860 seawater, consistent with its likely deeper original position within the ophiolite. High 87 Sr/ 86 Sr_i values in the upper ophiolite, Sm-Nd isotopic constraints (Nd_t +4.40 to +7.73) and 861 862 the presence of inherited zircons in layered gabbros are consistent with minor crustal 863 contamination into the source region. Together these data suggest that the Tyrone Plutonic 864 Group formed above a N-dipping subduction zone, by the propagation of a spreading centre 865 into a microcontinental block. S-type, peraluminous muscovite granite contains inherited 866 Proterozoic zircons, and appears to have been intruded shortly after ophiolite emplacement 867 generated from the partial melting of Laurentian-affinity metasedimentary material. 868 Ophiolite obduction onto the Tyrone Central Inlier must have occurred prior to the intrusion 869 of a ca. 470 Ma tonalite which contains roof pendants of ophiolitic and arc material and 870 xenocrystic Proterozoic zircons. Late Fe-Ti basaltic dykes of eMORB affinity are consistent 871 with formation at a propagating rift following obduction. Geochemically identical lavas are 872 present in the upper Tyrone Volcanic Group (Mountfield Basalts) and at Slieve Gallion 873 constrained by U-Pb zircon geochronology to ca. 469 Ma. The presence of syn-kinematic, 874 calc-alkaline tonalitic to granitic material within the contact between the Tyrone Central 875 Inlier and Tyrone Plutonic Group suggests that the latter may have been emplaced relatively 876 late within the orogen at ca. 470 Ma synchronous with the Tyrone arc. In the absence of an 877 ultramafic section, the coeval obduction of the ophiolite and volcanic arc may explain how 878 metamorphic conditions within the sillimanite-grade Tyrone Central Inlier were reached prior 879 to ca. 468 Ma.

880

881 Strong temporal, geochemical and lithological similarities to the Annieopsquotch Ophiolite 882 Belt of Newfoundland indicate that these ophiolites may have a shared origin and evolution. 883 This adds to a growing body of evidence that the Tyrone Igneous Complex represents the 884 third stage of arc-ophiolite emplacement in the peri-Laurentian British and Irish Caledonides at *ca.* 470 Ma, following the accretion of early *ca.* 510-500 Ma ophiolites (Highland Border
and Deer Park), and the Lough Nafooey arc at *ca.* 480 Ma.

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- 1199 FIGURES
- 1200

Fig. 1 (a) Setting of the Tyrone Igneous Complex and other comparable ophiolite and volcanic arc associations in Britain and Ireland. (b) Simplified regional geology of Newfoundland (c) Early Mesozoic restoration of North Atlantic region and Appalachian-Caledonian orogen. Figure after Cooper *et al.* (2001).

1205

Fig. 2. Geological map of the Tyrone Igneous Complex (after GSNI 1879, 1983, 1995;
Cooper *et al.* 2011; Hollis *et al.* 2012). For subdivision of the Tyrone Volcanic Group see
Hollis *et al.* (2012). Stars refer to localities discussed in the text.

1209

1210 Fig. 3. ***FIGURE IN COLOUR IN PRINT*** Field photographs from across the Tyrone 1211 Plutonic Group. (A) Pegmatitic gabbros (light coloured rock above hammer head) intruding, 1212 and intruded by, dolerite/basaltic dykes (dark coloured rock) at Black Rock, (B) Angular 1213 xenoliths (right of hammer) of early foliated dolerite/gabbro in hornblende gabbro at Black 1214 Rock, (C) Dolerite intruded by a dyke of quartz and hornblende porphyryitic diorite at 1215 Slaghtfreeden (D) Dolerite cut by veins of aplite at Craigballyharky Quarry, (E) Pillow basalts at Craigballyharky, (F) Quartz ocelli migrating from tonalite into gabbro at 1216 1217 Craigballyharky.

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Fig. 4. ***FIGURE IN COLOUR IN PRINT*** Field photographs and petrography from Blaeberry Rock and the Tyrone Plutonic Group. (A) Main Blaeberry Rock exposure, (B) Blocks of amphibolite facies gabbro (right) and andesite(?) (left), (C) Angular block of amphibolite-facies basalt in granitic-tonalitic intrusive material, (D) Late stage granitictonalitic veins crosscutting main fabrics, (E) Isoclinally folded tonalitic to granitic melt and amphibolite, (F) Sinistrally rotated amphibole crystals in melt network.

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Fig. 5. *******FIGURE IN COLOUR IN PRINT******* Results of the Tellus airborne geophysical survey of Northern Ireland. (a) EM low frequency (ApCond), (b) Total magnetic intensity, analytic signal (TMI-AS). All maps show original GSNI linework (GSNI 1879, 1983 and 1995). Grid references are according to Irish Grid. Dashed lines denote interpreted faults/unconformities. Heavier set lines show the boundaries between the Tyrone Volcanic Group, Tyrone Plutonic Group and Tyrone Central Inlier. Question marks show the position of magnetic material of unknown affinity underlying the Tyrone Central Inlier.

1234 Fig. 6. Geochemistry of the Tyrone Plutonic Group and associated rocks discussed herein. 1235 (A) Al₂O₃/Na₂O ratio of Spitz and Darling (1978) against SiO₂, (B) Carbonate-chlorite-pyrite Index of Large et al. (2001) against Zr/TiO₂, (C) Zr/Y against Nb/Y, (D) Th_{CN} against Ti/V, 1236 1237 (E) La/Sm_{CN} against Nb anomaly (calculated from Th and La), (F) Th/Yb against Nb/Yb 1238 (after Pearce, 1983). Data of Draut et al. (2009) and Cooper et al. (2011) also included. CN refers to chondrite normalized (after McDonough and Sun 1995). Shaded and dashed fields 1239 1240 reflect data for the Tyrone Plutonic Group and Annieopsquotch Ophiolite Belt respectively 1241 (from Lissenberg et al. 2004).

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Fig. 7. Multi-element variation diagrams for samples from the Tyrone Plutonic Group, Blaeberry Rock and arc-related intrusive suite. Chondrite normalization values after McDonough and Sun (1995). Analyses of Draut *et al.* (2009), Cooper *et al.* (2011), and Hollis *et al.* (2012, companion publication) are also included. Shaded field represents data from the Annieopsquotch Ophiolite Belt (from Lissenberg *et al.* 2004).

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Fig. 8. Mineral chemistry of samples from Black Rock (SPH34) and Blaeberry Rock
(SPH210 and SPH215). (A) Amphibole mineral chemistry; (B) Feldspar mineral chemistry
from Blaeberry Rock sample SPH215; (C) and (D) Chlorite mineral chemistry.

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Fig. 9. U-Pb zircon concordia and summary of interpreted U-Pb zircon date for pegmatiticgabbro from Black Rock.

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1256 Fig. 10. Tectonic model for the evolution of the Tyrone Plutonic Group. After model for the

1257 development of the Annieopsquotch Ophiolite Belt (Zagorevski et al. 2006). eMORB,

1258 enriched Mid Ocean Ridge basalt; IAT, island arc tholeiite; OIB, ocean island basalt.

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1260 SUPPLEMENTARY INFORMATION

- 1261
- Petrographic photographs, whole rock, isotopic and mineral geochemical data, and U-Th-Pb
 isotopic data.
- Petrography photographs: Figure 4g-h. SEM microphotographs of amphibolite-facies gabbroic material from Blaeberry Rock contact, (I) Thin section photograph of contact between amphibolite and tonalitic/granitic material at Blaeberry Rock (J) SEM microphotograph of Black Rock pegmatitic gabbro from the Tyrone Plutonic Group.
- Table 1. Whole rock geochemistry, and Sm-Nd and Rb-Sr isotope data. Samples with MRC
 prefixes from Cooper *et al.* 2011.

- Table 2(a-d). Mineral chemical data. (a) Chlorite (calculated after 28 oxygens). (b) Epidote
 (after 12.5 oxygens). All Fe calculated to Fe3+. (c) Amphibole (after 23 oxygens). (d)
 Feldspar.
- 1276
- 1277 Table 3. U-Th-Pb isotopic data for sample MRC344.























		Determined by (italics = isotope dilution):			XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF		
				Units:	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%		
Sample	Locality	Easting	Northing	Lithology (all meta-)	SiO2	TiO2	AI2O3	Fe2O3t	Mn3O4	MgO	CaO	K2O	Na2O	P2O5	LOI	Sample
JTP 207	Scalp Hill	263900	374400	Layered gabbro	48.31	0.37	21.97	6.15	0.12	5.53	12.91	0.59	1.95	0.03	1.75	JTP 207
JTP 211	Black Rock	268350	383810	Gabbro	47.69	0.24	15.92	10.12	0.20	9.54	11.38	0.46	1.09	0.01	3.23	JTP 211
MRC 129	Tremoge Glen	262800	371250	Basaltic dyke	49.61	2.69	12.76	15.37	0.26	4.80	3.51	0.91	1.99	0.39	7.06	MRC 129
MRC 340	Craigballyharky	273360	375660	Basalt	52.15	0.58	14.51	8.58	0.18	7.73	11.84	0.24	3.95	0.04	0.96	MRC 340
MRC 343	Craigballyharky Quarry	273320	375650	Dolerite	49.41	0.91	15.60	9.81	0.19	8.95	9.67	0.41	3.93	0.08	1.61	MRC 343
MRC 344	Black Rock	268360	383430	Pegmatitic gabro	47.88	0.12	16.47	7.21	0.16	10.33	14.47	0.62	0.69	0.01	2.93	MRC 344
SPH 030	Craigballyharky	273360	375660	Basalt	51.15	0.63	15.45	9.87	0.15	7.93	11.29	0.29	3.80	0.06	1.19	SPH 030
SPH 034	Black Rock	268360	383430	Pegmatitic gabro	48.63	0.13	16.73	8.04	0.16	10.29	15.24	0.51	0.80	0.01	2.91	SPH 034
SPH 041	Scalp Hill	263000	374000	Mafic dyke	62.99	0.65	16.01	7.33	0.13	2.25	5.13	1.52	3.72	0.24	1.61	SPH 041
SPH 059	Craigballyharky Quarry			Dolerite	52.13	0.48	17.75	7.05	0.24	6.15	12.04	0.60	4.05	0.04	1.11	SPH 059
SPH 063	Black Rock			Dolerite	50.39	0.73	15.62	9.58	0.25	8.75	10.96	0.38	3.99	0.10	1.16	SPH 063
SPH 185	Bonnety Bush	272636	387449	Pegmatitic gabro	50.72	0.11	17.02	6.49	0.11	10.44	12.88	0.97	1.74	0.01	2.28	SPH 185
SPH 186	Bonnety Bush	272636	387449	Pegmatitic gabro	49.61	0.17	13.35	6.51	0.16	10.67	14.51	0.70	1.11	0.02	2.99	SPH 186
SPH 209	Blaeberry Rock	272995	385210	Tonalitic material	59.68	0.17	18.68	5.74	0.12	4.64	8.05	1.83	3.26	0.03	2.17	SPH 209
SPH 212	Blaeberry Rock	272995	385210	Tonalitic material	64.40	0.41	17.30	5.73	0.10	3.29	5.78	1.53	3.13	0.13	1.99	SPH 212
SPH 214	Blaeberry Rock	272995	385210	Tonalitic material	59.55	0.18	17.70	6.06	0.13	4.72	8.05	1.69	2.79	0.03	3.21	SPH 214
SPH 215	Blaeberry Rock	272995	385210	Tonalitic material	61.61	0.29	12.74	6.52	0.16	5.34	6.65	2.45	2.07	0.07	1.11	SPH 215
SPH 459	Black Rock			Dolerite	52.48	0.50	14.22	9.89	0.16	9.17	10.61	0.27	2.40	0.12		SPH 459
SPH 464	Black Rock	268508	383838	Microgabbro	67.88	0.35	15.64	2.95	0.08	2.18	2.65	0.57	6.78	0.10		SPH 464
SPH 538	Craigballyharky Quarry			Plagiogranite	61.63	0.61	16.19	7.35	0.12	2.14	6.94	1.20	3.06	0.14		SPH 538
SPH 541	Craigballyharky			Basalt	51.10	0.55	14.74	8.96	0.20	6.28	14.14	0.39	3.19	0.06		SPH 541
SPH 552	Black Rock			Volcaniclastics?	79.22	0.17	10.51	1.97	0.03	0.40	2.57	0.28	4.26	0.03		SPH 552
SPH-BR	Black Rock			Pegmatitic gabro	61.96	0.66	14.93	6.83	0.08	3.82	6.49	2.07	2.52	0.12		SPH-BR
SPH-CONT	Blaeberry Rock	272995	385210	Clast	52.51	0.20	8.01	9.88	0.26	14.14	12.51	0.77	0.62	0.03		SPH-CONT
9/83-1A	Carrickmore Quarry		Fine grained dolerite													9/83-1A
9/83-1B	Carrickmore Quarry		Coarse grained dolerite													9/83-1B
9/83-3	Scalp			Gabbro												9/83-3

Note samples with MRC and JTP prefixes are from Cooper et al. (2011) Grid Reference is Irish Grid

Note samples Grid Referen

XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	XRF	ICP-MS	GICP-MS	SICP-N	I: ICP-MS	SICP-MS	SICP-M	SICP-MS	SICP-MS	ICP-M	S ICP-MS	S ICP-MS	
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	
Sc	Zr	v	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Ва	Pb	Y	Nb	Cs	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Sample
29	17	142	98	21	58	587	38	16	12	201	95	1	8.53				2.35	0.40	2.32	0.88	0.36	1.29	0.24	JTP 207
36	3	163	37	48	29	35	48	14	13	120	89	2	4.35				1.52	0.33	1.82	0.45	0.26	0.60	0.10	JTP 211
36	247	389	53	50	14	41	142	20	31	88	142	22	34.25	19.00		20.29	50.12	6.36	28.39	6.48	1.93	7.23	1.17	MRC 129
35	26	240	343	40	151	1	59	13	2	192	49	3	15.53	0.98		1.43	4.35	0.66	3.75	1.81	0.48	2.31	0.40	MRC 340
40	47	283	231	43	116	1	73	16	7	180	84	5	22.30	0.71		2.64	7.26	1.19	6.41	2.38	0.90	3.07	0.52	MRC 343
48	5	134	74	43	65	59	41	9	19	127	188	2	4.35	0.11		0.38	0.95	0.12	0.83	0.44	0.22	0.52	0.09	MRC 344
42	39	264	425	42	191	13	59	15	3	145	38	2	16.83	0.42	0.05	1.77	5.05	0.81	4.25	1.49	0.59	2.11	0.40	SPH 030
45	13	152	103	47	63	37	41	12	15	128	141	2	3.46	0.15	0.19	0.26	0.70	0.12	0.70	0.31	0.18	0.50	0.10	SPH 034
21	161	138	27	16	21	25	51	18	27	397	636	4												SPH 041
36	26	197	521	37	145	16	168	13	12	388	207	9	11.32	0.19	0.33	1.45	3.95	0.64	3.43	1.20	0.62	1.65	0.28	SPH 059
	40	257	306	39	93	16	124	13	5	308	49	4	18.14	0.35	0.08	1.86	5.27	0.88	4.80	1.68	0.62	2.37	0.42	SPH 063
20	17.7	96	296	34	85	12	31	9	31	219	331	3	3.43	0.12	0.65	0.22	0.64	0.11	0.66	0.29	0.09	0.51	0.09	SPH 185
46	15	115	97	36	51	59	36	10	22	135	107	3	5.49	0.07	0.42	0.37	0.82	0.13	0.75	0.35	0.15	0.62	0.12	SPH 186
	38	116	27	16	24	13	51	15	53	199	328	8	6.06	2.70	0.59	3.71	8.55	1.16	4.76	1.12	0.41	1.11	0.16	SPH 209
14	129	157	56	18	23	83	51	17	41	239	330	10	7.98	4.94	0.32	16.10	33.47	3.92	14.08	2.49	0.57	1.83	0.27	SPH 212
	54	122	63	19	35	12	61	15	53	213	313	8	7.18	2.78	0.44	4.70	10.40	1.35	5.58	1.27	0.45	1.26	0.19	SPH 214
	69	127	252	20	62	13	65	15	57	166	532	13	11.88	3.65	0.50	24.61	50.72	6.03	22.89	4.24	1.07	3.25	0.43	SPH 215
	75	227	479	124	122	28	53	15	4	307	34	3												SPH 459
	117	72	86	33	15	8	34	15	13	199	195	6												SPH 464
30	174	136	92	71	11	28	54	16	43	228	367	9	23.11	6.44	2.22	21.42	41.55	5.04	20.28	4.36	1.21	4.18	0.64	SPH 538
34	38	230	511	109	158	23	54	15	7.5	203.7	63	4	18.36	0.40	0.27	1.48	4.13	0.70	3.32	1.32	0.59	2.36	0.45	SPH 541
43	93	13	136	19	16	17	5	10	4	147	68	2	33.12	4.37	0.08	5.14	10.59	1.45	6.41	2.14	0.99	3.19	0.63	SPH 552
22	178	173	192	83	48	33	30	16	43	391	763	4	16.45	8.09	0.43	24.59	52.45	5.97	22.45	4.16	1.04	3.41	0.49	SPH-BR
64	18	165	1672	129	142	18	121	11	20	47	143	5	19.09	5.24	0.34	2.64	5.59	0.87	4.10	1.53	0.56	2.18	0.43	SPH-CONT
									39.6	276.3									3.42	1.27				9/83-1A
									36.8	282.7									3.43	1.29				9/83-1B
									1.6	99.3									3.06	0.97				9/83-3

s with MRC and JTP prefixes are from Cooper et al. (2011) ce is Irish Grid

Note samples Grid Referen ICP-MS ICP-MS ICP-MS ICP-MS ICP-MS ICP-MS ICP-MS ICP-MS ICP-MS

| ppm |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| | | | | | | | | | |

Dy	Но	Er	Tm	Yb	Lu	Hf	Та	Th	U	87Sr/86Sr (measured)	2SE	Initital Sr ratios	147Sm/ 144Nd	143Nd/144 Nd	2SE	Ep Ndt 480 Ma
1.61	0.35	1.04	0.15	0.99	0.15	0.57	0.50	0.20								
0.78	0.18	0.57	0.09	0.64	0.10	0.30	0.50	0.46								
7.22	1.42	3.76	0.50	3.12	0.47	5.81	1.03	3.13								
2.80	0.57	1.91	0.27	1.81	0.27	0.95	2.00	0.26								
3.94	0.86	2.77	0.36	2.35	0.36	1.71	2.00	0.23								
0.82	0.19	0.55	0.09	0.50	0.08	0.20	2.00	0.05								
2.68	0.61	1.82	0.28	1.86	0.29	0.89	0.04	0.27	0.10							
0.67	0.15	0.43	0.06	0.43	0.06	0.10	0.01	0.02	0.03							
1.88	0.40	1.17	0.17	1.18	0.18	0.51	0.04	0.19	0.14	0.710800	8	0.710192				
2.82	0.64	1.84	0.28	1.92	0.29	0.91	0.03	0.26	0.13	0.710958	7	0.710639				
0.63	0.14	0.42	0.07	0.43	0.07	0.20	0.02	0.03	0.02							
0.86	0.20	0.59	0.09	0.60	0.09	0.13	0.01	0.02	0.02							
0.94	0.19	0.54	0.09	0.61	0.09	0.52	0.41	1.01	0.46							
1.44	0.27	0.72	0.10	0.67	0.10	0.45	0.43	3.93	0.60							
1.11	0.22	0.63	0.10	0.67	0.10	0.47	0.43	1.27	0.74							
2.33	0.46	1.23	0.18	1.09	0.15	1.34	0.22	5.05	1.14							
3.89	0.82	2.32	0.35	2.27	0.34	2.11	0.13	4.71	1.78							
3.13	0.70	2.09	0.32	2.09	0.32	0.93	0.01	0.28	0.24	0.709807	5	0.709080	0.2400	0.513050	3	5.33
4.46	1.04	3.31	0.54	3.77	0.62	1.99	0.16	2.27	0.50							
2.81	0.56	1.60	0.24	1.61	0.24	3.97	0.22	7.28	1.59							
2.99	0.63	1.84	0.29	1.94	0.27	0.32	0.25	0.46	0.35							
										0.711583	4	0.708744	0.2257	0.513001	4	5.30
										0.711087	5	0.708507	0.2268	0.513006	4	5.33
										0.704223	5	0.703901	0.1910	0.512934	4	6.12

s with MRC and JTP prefixes are from Cooper et al. (2011) ce is Irish Grid

Supplementary Data Table 2: Mineral chemical data Chlorite

Wt.% oxide:

Sample	Analysis	SiO2	TiO2	AI2O3	FeO	MnO	MgO	CaO	Na2O	K2O	BaO	F
SPH34	PB-51	29.28	0.02	21.73	14.62	0.24	23.93	0.11	0.01	0.01	0.00	0.00
SPH34	PB-52	30.42	0.01	22.15	12.40	0.18	22.37	0.03	0.03	0.78	0.01	0.00
SPH34	PB-53	28.72	0.01	21.14	14.29	0.24	23.50	0.06	0.01	0.01	0.00	0.00
SPH215	PB-77	27.12	0.05	20.36	20.37	0.40	18.50	0.05	0.01	0.13	0.00	0.00
SPH215	PB-78	28.18	0.08	19.76	20.97	0.36	19.12	0.03	0.01	0.09	0.00	0.00

Atoms based on 28 oxygens:

Cr2O3	NiO	V2O3	P2O5	CoO	Si	AI(IV)	AI(VI)	Mg	Ca	Κ	Mn	Fe	Fe/Fe+Mg
0.01	0.04	0.00	0.00	0.02	5.63	2.37	2.57	6.86	0.02	0.00	0.04	2.35	0.26
0.00	0.03	0.00	0.00	0.01	5.84	2.16	2.90	6.40	0.01	0.38	0.03	1.99	0.24
0.00	0.06	0.02	0.00	0.03	5.65	2.35	2.55	6.89	0.01	0.01	0.04	2.35	0.25
0.15	0.08	0.04	0.01	0.04	5.59	2.41	2.54	5.68	0.01	0.07	0.07	3.51	0.38
0.02	0.04	0.06	0.02	0.00	5.71	2.29	2.44	5.77	0.01	0.05	0.06	3.55	0.38

Geothermometers:

Kranidiotis & MacLean (1987)
596.41
591.30
596.16
632.28
632.02

Epidote		Weight	% oxi	de									
Sample	Analysis number	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	К2О	P2O5	Cr2O3	CoO
SPH34	PB-84	38.64	0.00	28.42	6.25	0.14	0.02	23.81	0.02	0.00	0.01	0.00	0.00
SPH34	PB-89	40.83	0.00	31.29	2.12	0.06	0.03	22.95	0.60	0.04	0.02	0.00	0.00
SPH34	PB-91	39.15	0.03	29.39	5.17	0.03	0.01	23.98	0.02	0.04	0.02	0.00	0.00
SPH34	PB-79	39.07	0.01	28.69	5.95	0.04	0.03	24.07	0.06	0.05	0.01	0.00	0.00
SPH34	PB-81	38.78	0.09	26.22	9.07	0.15	0.03	23.49	0.01	0.00	0.03	0.00	0.00
SPH34	PB-90	39.51	0.04	29.00	5.55	0.05	0.02	23.47	0.19	0.08	0.06	0.01	0.00
SPH34	PB-82	39.20	0.00	29.33	5.64	0.03	0.01	24.14	0.00	0.01	0.03	0.01	0.00
SPH34	PB-85	38.95	0.01	29.46	5.19	0.06	0.03	24.38	0.00	0.02	0.03	0.00	0.00
SPH34	PB-88	41.78	0.01	31.16	1.78	0.10	0.03	22.40	0.96	0.01	0.02	0.00	0.00
SPH34	PB-80	38.09	0.16	24.98	10.09	0.09	0.03	23.65	0.03	0.00	0.01	0.00	0.02
SPH34	PB-83	38.76	0.02	26.19	9.29	0.07	0.02	23.78	0.00	0.01	0.02	0.00	0.00
SPH34	PB-86	34.53	0.04	25.64	8.30	0.08	3.49	18.97	0.03	0.00	0.00	0.01	0.00
SPH34	PB-87	39.09	0.01	29.99	4.64	0.09	0.04	24.05	0.00	0.00	0.04	0.00	0.00
SPH210	PB-109	38.26	0.06	24.38	11.18	0.10	0.08	23.67	0.00	0.00	0.01	0.02	0.00
SPH210	PB-110	38.15	0.04	24.75	10.85	0.14	0.03	23.64	0.01	0.00	0.02	0.02	0.01
SPH210	PB-111	37.63	0.23	22.94	12.49	0.27	0.04	23.30	0.02	0.01	0.03	0.01	0.00
SPH215	PB-112	42.16	0.06	25.89	8.61	0.10	0.53	18.94	0.04	1.95	0.01	0.07	0.01
SPH215	PB-115	36.62	0.11	23.10	10.98	0.11	0.01	23.00	0.00	0.00	0.02	0.26	0.00
SPH215	PB-117	38.15	1.67	22.08	12.65	0.08	0.03	23.31	0.02	0.02	0.03	0.05	0.00
SPH215	PB-113	38.24	0.04	25.40	9.72	0.11	0.03	23.38	0.00	0.00	0.05	0.03	0.00
SPH215	PB-114	38.00	0.04	23.51	11.89	0.18	0.16	22.72	0.01	0.00	0.03	0.10	0.01
SPH215	PB-116	37.91	0.04	23.75	11.56	0.15	0.08	22.94	0.01	0.00	0.01	0.10	0.01

Supplementary Data Table 2: Mineral chemical data

					Atoms	s (afte	(after 12.5 oxygens) Ti Al Fe3+ Mn Mg Ca Na								
NiO	F	Ce2O3	BaO	V2O3	Si	Ti	Al	Fe3+	Mn	Mg	Са	Na	К		
0.02	0.00	0.00	0.00	0.01	3.00	0.00	2.60	0.41	0.01	0.00	1.98	0.00	0.00		
0.00	0.00	0.02	0.01	0.00	3.09	0.00	2.79	0.13	0.00	0.00	1.86	0.09	0.00		
0.02	0.00	0.00	0.00	0.01	3.01	0.00	2.66	0.33	0.00	0.00	1.98	0.00	0.00		
0.02	0.00	0.00	0.00	0.00	3.01	0.00	2.60	0.38	0.00	0.00	1.99	0.01	0.00		
0.01	0.00	0.00	0.00	0.02	3.02	0.01	2.40	0.59	0.01	0.00	1.96	0.00	0.00		
0.00	0.00	0.00	0.00	0.02	3.03	0.00	2.62	0.36	0.00	0.00	1.93	0.03	0.01		
0.01	0.00	0.00	0.00	0.00	3.00	0.00	2.65	0.36	0.00	0.00	1.98	0.00	0.00		
0.01	0.00	0.00	0.00	0.00	2.99	0.00	2.67	0.33	0.00	0.00	2.01	0.00	0.00		
0.01	0.00	0.01	0.00	0.00	3.15	0.00	2.77	0.11	0.01	0.00	1.81	0.14	0.00		
0.01	0.00	0.00	0.00	0.01	3.00	0.01	2.32	0.66	0.01	0.00	2.00	0.00	0.00		
0.00	0.00	0.00	0.00	0.01	3.01	0.00	2.40	0.60	0.00	0.00	1.98	0.00	0.00		
0.03	0.00	0.00	0.00	0.03	2.87	0.00	2.51	0.58	0.01	0.43	1.69	0.00	0.00		
0.02	0.00	0.01	0.00	0.00	3.00	0.00	2.71	0.30	0.01	0.00	1.98	0.00	0.00		
0.00	0.00	0.00	0.00	0.05	3.00	0.00	2.25	0.73	0.01	0.01	1.99	0.00	0.00		
0.01	0.00	0.00	0.00	0.03	2.99	0.00	2.29	0.71	0.01	0.00	1.99	0.00	0.00		
0.03	0.00	0.00	0.00	0.04	2.99	0.01	2.15	0.83	0.02	0.00	1.99	0.00	0.00		
0.00	0.00	0.00	0.00	0.08	3.22	0.00	2.33	0.55	0.01	0.06	1.55	0.01	0.19		
0.02	0.00	0.00	0.00	0.03	3.00	0.01	2.23	0.75	0.01	0.00	2.02	0.00	0.00		
0.01	0.00	0.00	0.00	0.07	3.00	0.10	2.05	0.83	0.01	0.00	1.97	0.00	0.00		
0.01	0.00	0.00	0.00	0.06	3.01	0.00	2.36	0.64	0.01	0.00	1.97	0.00	0.00		
0.00	0.00	0.00	0.00	0.04	3.02	0.00	2.20	0.79	0.01	0.02	1.93	0.00	0.00		
0.00	0.00	0.00	0.00	0.04	3.01	0.00	2.23	0.77	0.01	0.01	1.95	0.00	0.00		

Supplementary Data Table 2: Mineral chemical data Amphibole Wt.% oxide

Amphibol	e	VVI. 70 O	xiue											
Sample	Analysis	SiO2	TiO2	AI2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	BaO	NiO	CoO
SPH34	PB-125	53.68	0.05	4.10	7.12	0.18	19.35	12.29	0.47	0.06	0.02	0.00	0.01	0.02
SPH34	PB-126	56.02	0.06	2.23	5.96	0.19	20.75	12.38	0.26	0.05	0.00	0.00	0.03	0.01
SPH34	PB-127	55.39	0.03	2.92	5.79	0.20	20.89	12.37	0.41	0.01	0.02	0.00	0.01	0.02
SPH34	PB-129	52.96	0.45	4.54	7.81	0.18	18.61	12.51	0.55	0.07	0.00	0.00	0.01	0.02
SPH34	PB-130	55.13	0.08	1.74	9.88	0.27	18.05	11.82	0.26	0.03	0.02	0.00	0.02	0.00
SPH210	PB-131	54.61	0.00	3.02	8.16	0.35	18.44	12.82	0.35	0.09	0.02	0.00	0.07	0.00
SPH210	PB-132	54.03	0.08	3.93	9.00	0.33	17.58	12.52	0.43	0.23	0.02	0.00	0.09	0.00
SPH210	PB-133	52.70	0.03	4.79	9.71	0.35	17.11	12.44	0.54	0.33	0.02	0.01	0.07	0.00
SPH215	PB-134	48.38	0.42	6.91	14.53	0.46	13.51	12.10	0.77	0.57	0.01	0.00	0.02	0.01
SPH215	PB-135	48.43	0.35	8.14	14.05	0.41	11.61	11.06	0.74	1.67	0.04	0.03	0.04	0.00
SPH215	PB-136	48.63	0.38	7.20	14.46	0.44	13.61	12.01	0.80	0.55	0.02	0.00	0.03	0.01
SPH215	PB-137	49.29	0.37	6.51	14.11	0.42	13.89	12.20	0.79	0.47	0.02	0.00	0.02	0.02
SPH215	PB-138	49.26	0.38	6.97	14.60	0.42	13.43	11.99	0.79	0.58	0.00	0.00	0.02	0.00
SPH215	PB-139	46.77	0.35	6.81	14.12	0.40	13.09	11.89	0.74	0.57	0.00	0.00	0.01	0.00
SPH215	PB-140	48.64	0.37	7.03	14.59	0.42	13.18	12.20	0.91	0.51	0.03	0.00	0.00	0.00
SPH215	PB-141	48.64	0.40	6.86	14.48	0.41	13.46	12.20	0.86	0.52	0.02	0.00	0.01	0.00
SPH215	PB-142	48.35	0.37	7.39	14.52	0.44	13.48	12.02	0.86	0.62	0.01	0.00	0.02	0.01
SPH215	PB-118	47.30	0.41	7.31	14.65	0.43	13.00	12.07	0.82	0.63	0.03	0.00	0.00	0.01
SPH215	PB-119	46.73	0.65	8.00	14.80	0.41	12.83	11.97	0.81	0.62	0.02	0.01	0.01	0.00
SPH215	PB-120	47.75	0.40	7.48	14.84	0.43	13.02	12.02	0.84	0.66	0.02	0.00	0.02	0.00
SPH215	PB-121	47.87	0.39	7.10	14.72	0.44	13.10	12.06	0.79	0.61	0.02	0.00	0.02	0.00
SPH215	PB-122	48.11	0.41	7.23	14.80	0.44	13.19	12.09	0.81	0.62	0.01	0.00	0.03	0.01
SPH215	PB-123	46.38	0.49	8.54	15.55	0.40	12.35	11.91	0.98	0.78	0.03	0.02	0.02	0.00

Atoms after 23 oxygens														
V2O3	Cr2O3	Ce2O3	F	Si	Al iv	Al vi	Ti	Cr	Fe3+	Fe2+	Mn	Mg	Ca	Na
0.02	0.01	0.00	0.00	7.46	0.54	0.13	0.01	0.00	0.60	0.23	0.02	4.01	1.83	0.13
0.01	0.01	0.00	0.03	7.68	0.32	0.04	0.01	0.00	0.55	0.14	0.02	4.24	1.82	0.07
0.01	0.00	0.02	0.00	7.58	0.42	0.05	0.00	0.00	0.63	0.03	0.02	4.26	1.81	0.11
0.03	0.02	0.00	0.02	7.40	0.60	0.14	0.05	0.00	0.46	0.45	0.02	3.87	1.87	0.15
0.05	0.01	0.00	0.01	7.73	0.27	0.02	0.01	0.00	0.60	0.56	0.03	3.77	1.78	0.07
0.00	0.00	0.00	0.07	7.65	0.35	0.15	0.00	0.00	0.25	0.71	0.04	3.85	1.92	0.10
0.02	0.00	0.00	0.14	7.57	0.43	0.22	0.01	0.00	0.28	0.77	0.04	3.67	1.88	0.12
0.01	0.03	0.00	0.12	7.42	0.58	0.21	0.00	0.00	0.40	0.74	0.04	3.59	1.88	0.15
0.08	0.03	0.00	0.07	7.02	0.98	0.20	0.05	0.00	0.59	1.17	0.06	2.92	1.88	0.22
0.04	0.01	0.00	0.01	7.18	0.82	0.60	0.04	0.00	0.10	1.64	0.05	2.56	1.76	0.21
0.05	0.01	0.01	0.07	7.01	0.99	0.23	0.04	0.00	0.64	1.10	0.05	2.92	1.85	0.22
0.05	0.08	0.00	0.04	7.11	0.89	0.21	0.04	0.01	0.52	1.18	0.05	2.98	1.88	0.22
0.06	0.13	0.00	0.07	7.08	0.92	0.26	0.04	0.01	0.55	1.21	0.05	2.88	1.85	0.22
0.06	0.14	0.00	0.07	7.00	1.00	0.20	0.04	0.02	0.56	1.20	0.05	2.92	1.91	0.21
0.06	0.13	0.00	0.07	7.06	0.94	0.27	0.04	0.01	0.43	1.34	0.05	2.85	1.90	0.26
0.06	0.06	0.01	0.05	7.06	0.94	0.23	0.04	0.01	0.49	1.27	0.05	2.91	1.90	0.24
0.06	0.03	0.00	0.07	6.98	1.02	0.24	0.04	0.00	0.61	1.14	0.05	2.90	1.86	0.24
0.05	0.14	0.00	0.07	6.96	1.04	0.23	0.05	0.02	0.55	1.26	0.05	2.85	1.90	0.23
0.05	0.02	0.01	0.10	6.86	1.14	0.25	0.07	0.00	0.63	1.19	0.05	2.81	1.88	0.23
0.06	0.11	0.00	0.03	6.96	1.04	0.25	0.04	0.01	0.58	1.23	0.05	2.83	1.88	0.24
0.06	0.07	0.01	0.05	7.01	0.99	0.23	0.04	0.01	0.55	1.25	0.05	2.86	1.89	0.22
0.05	0.12	0.00	0.09	6.99	1.01	0.23	0.04	0.01	0.57	1.23	0.05	2.86	1.88	0.23
0.05	0.06	0.00	0.07	6.80	1.20	0.28	0.05	0.01	0.63	1.27	0.05	2.70	1.87	0.28

Κ	K Ba		OH*	Total					
0.01	0.00	0.00	2.00	16.97					
0.01	0.00	0.01	1.99	16.90					
0.00	0.00	0.00	2.00	16.92					
0.01	0.00	0.01	1.99	17.03					
0.01	0.00	0.00	2.00	16.85					
0.02	0.00	0.03	1.97	17.03					
0.04	0.00	0.06	1.94	17.04					
0.06	0.00	0.05	1.95	17.08					
0.11	0.00	0.03	1.97	17.20					
0.32	0.00	0.00	2.00	17.29					
0.10	0.00	0.03	1.97	17.18					
0.09	0.00	0.02	1.98	17.19					
0.11	0.00	0.03	1.97	17.17					
0.11	0.00	0.03	1.97	17.23					
0.09	0.00	0.03	1.97	17.25					
0.10	0.00	0.02	1.98	17.23					
0.11	0.00	0.03	1.97	17.21					
0.12	0.00	0.03	1.97	17.25					
0.12	0.00	0.05	1.95	17.23					
0.12	0.00	0.01	1.99	17.24					
0.11	0.00	0.02	1.98	17.23					
0.11	0.00	0.04	1.96	17.23					
0.15	0.00	0.03	1.97	17.30					

Supplementary Data Table 2: Mineral chemical data

	Wt.% Oxide:												
Analysis	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	BaO	Na2O	К2О	Ce2O3	P2O5	
PB-153	64.79	0.00	18.74	0.20	0.01	0.02	0.00	0.46	0.46	16.57	0.17	0.00	
PB-154	64.30	0.01	18.58	0.06	0.01	0.00	0.00	0.61	0.38	16.63	0.21	0.00	
PB-155	64.45	0.00	19.18	0.06	0.00	0.00	0.25	0.71	1.76	13.73	0.25	0.00	
PB-156	63.76	0.02	19.09	0.07	0.00	0.00	0.00	1.42	0.57	16.04	0.53	0.00	
PB-157	64.27	0.00	18.76	0.06	0.01	0.01	0.02	0.65	0.61	16.33	0.21	0.00	
PB-158	64.50	0.00	18.70	0.03	0.00	0.00	0.00	0.68	0.64	16.36	0.26	0.00	
PB-159	62.99	0.03	19.98	0.43	0.01	0.37	0.00	0.58	0.35	15.74	0.22	0.00	
PB-160	64.06	0.01	18.47	0.05	0.00	0.00	0.00	0.49	0.40	16.59	0.18	0.01	
PB-161	64.81	0.00	18.92	0.05	0.01	0.00	0.00	0.71	0.78	16.05	0.23	0.03	
PB-162	64.15	0.02	19.07	0.03	0.00	0.01	0.00	1.25	0.65	15.80	0.47	0.00	
PB-163	64.66	0.00	18.63	0.06	0.00	0.00	0.00	0.50	0.43	16.44	0.20	0.00	
PB-164	64.74	0.00	18.69	0.16	0.00	0.00	0.00	0.55	0.43	16.64	0.19	0.00	
PB-165	64.55	0.00	18.76	0.04	0.00	0.01	0.00	0.80	0.37	16.43	0.27	0.01	
PB-166	64.82	0.00	18.82	0.04	0.00	0.00	0.00	0.55	0.64	16.36	0.18	0.01	
PB-167	63.86	0.01	18.88	0.07	0.00	0.00	0.01	1.23	0.58	16.08	0.44	0.01	
PB-168	65.10	0.00	18.88	0.06	0.00	0.01	0.00	0.62	0.41	16.30	0.20	0.01	
PB-169	63.28	0.02	18.44	0.07	0.00	0.01	0.00	0.47	0.46	16.44	0.19	0.00	
PB-170	64.79	0.01	18.75	0.04	0.01	0.00	0.00	0.51	0.48	16.48	0.17	0.02	
PB-242	54.71	0.00	29.05	0.14	0.00	0.00	10.85	0.00	5.61	0.12	0.00	0.03	
PB-243	58.18	0.00	27.08	0.17	0.00	0.00	8.53	0.00	7.13	0.17	0.00	0.04	
PB-244	55.73	0.01	28.50	0.16	0.00	0.00	10.24	0.02	5.87	0.21	0.00	0.01	
PB-245	57.43	0.00	26.69	0.14	0.00	0.01	8.44	0.01	6.99	0.19	0.00	0.02	
PB-246	57.60	0.00	26.89	0.16	0.01	0.00	8.75	0.00	6.67	0.30	0.02	0.01	
PB-247	58.26	0.00	26.95	0.11	0.00	0.00	8.46	0.00	6.97	0.15	0.00	0.00	
	Analysis PB-153 PB-154 PB-155 PB-156 PB-157 PB-158 PB-160 PB-161 PB-162 PB-163 PB-163 PB-164 PB-165 PB-166 PB-167 PB-168 PB-169 PB-170 PB-242 PB-243 PB-244 PB-245 PB-246 PB-247	Wt.%AnalysisSiO2PB-15364.79PB-15464.30PB-15564.45PB-15663.76PB-15764.27PB-15864.50PB-15962.99PB-16064.06PB-16164.81PB-16264.15PB-16364.66PB-16464.74PB-16564.55PB-16664.82PB-16763.86PB-16865.10PB-16963.28PB-17064.79PB-24254.71PB-24358.18PB-24455.73PB-24557.43PB-24657.60PB-24758.26	Wt.% OxideAnalysisSiO2TiO2PB-15364.790.00PB-15464.300.01PB-15564.450.00PB-15663.760.02PB-15764.270.00PB-15864.500.00PB-15962.990.03PB-16164.810.00PB-16264.150.02PB-16364.660.01PB-16464.740.00PB-16564.550.00PB-16664.820.00PB-16763.860.01PB-16865.100.00PB-16963.280.02PB-17064.790.01PB-24254.710.00PB-24455.730.01PB-24557.430.00PB-24657.600.00PB-24758.260.00	Wt.% Oxide:AnalysisSiO2TiO2Al2O3PB-15364.790.0018.74PB-15464.300.0118.58PB-15564.450.0019.18PB-15663.760.0219.09PB-15764.270.0018.76PB-15864.500.0018.70PB-15962.990.0319.98PB-16164.160.0118.47PB-16264.150.0219.07PB-16364.660.0018.63PB-16464.740.0018.63PB-16564.550.0018.76PB-16664.820.0018.88PB-16763.860.0118.88PB-16865.100.0018.88PB-16963.280.0218.44PB-16963.280.0118.75PB-16963.280.0218.44PB-17064.790.0118.75PB-24254.710.0029.05PB-24358.180.0027.08PB-24455.730.0128.50PB-24557.430.0026.89PB-24657.600.0026.89PB-24758.260.0026.95	Wt.% Oxide:AnalysisSiO2TiO2Al2O3FeOPB-15364.790.0018.740.20PB-15464.300.0118.580.06PB-15564.450.0019.180.06PB-15663.760.0219.090.07PB-15764.270.0018.700.03PB-15864.500.0018.700.03PB-15962.990.0319.980.43PB-16064.060.0118.470.05PB-16164.150.0219.070.03PB-16264.150.0219.070.03PB-16364.660.0018.630.06PB-16464.740.0018.690.16PB-16564.550.0018.760.04PB-16664.820.0018.880.07PB-16865.100.0018.880.07PB-16963.280.0218.440.07PB-16963.280.0218.440.07PB-17064.790.0118.750.04PB-24358.180.0027.080.17PB-24455.730.0128.500.14PB-24557.430.0026.890.16PB-24657.600.0026.890.16	Wt.% Oxide:AnalysisSiO2TiO2Al2O3FeOMnOPB-15364.790.0018.740.200.01PB-15464.300.0118.580.060.01PB-15564.450.0019.180.060.00PB-15663.760.0219.090.070.00PB-15764.270.0018.760.030.01PB-15864.500.0018.760.030.01PB-15962.990.0319.980.430.01PB-16064.060.0118.470.050.00PB-16164.810.0018.630.060.01PB-16264.150.0219.070.030.00PB-16364.660.0018.630.060.00PB-16464.740.0018.630.040.00PB-16564.820.0018.880.070.00PB-16664.820.0018.880.070.00PB-16763.860.0118.880.070.00PB-16865.100.0018.750.040.01PB-16963.280.0218.440.070.00PB-16963.280.0218.750.140.00PB-16963.280.0118.750.040.01PB-16963.280.0218.440.070.00PB-16963.280.0118.750.140.00	Wtt% Oxide:AnalysisSiO2TiO2Al2O3FeOMnOMgOPB-15364.790.0018.740.200.010.02PB-15464.300.0118.580.060.010.00PB-15564.450.0019.180.060.000.00PB-15663.760.0219.090.070.000.00PB-15764.270.0018.700.030.000.01PB-15864.500.0018.700.030.000.01PB-15962.990.0319.980.430.010.37PB-16064.060.0118.470.050.000.01PB-16164.810.0018.920.050.010.01PB-16264.150.0219.070.030.000.01PB-16364.660.0018.630.060.000.01PB-16464.740.0018.630.040.000.01PB-16564.820.0018.840.070.000.01PB-16664.820.0018.880.070.000.01PB-16865.100.0018.880.070.000.01PB-16963.280.0218.440.070.000.01PB-16963.780.0028.050.140.000.01PB-16963.780.0028.500.140.000.01PB-16963.78 <t< td=""><td>Mt.% Oxide:AnalysisSiO2TiO2Al2O3FeOMnOMgOCaOPB-15364.790.0018.740.200.010.020.00PB-15464.300.0118.580.060.010.000.25PB-15564.450.0019.180.060.000.000.00PB-15663.760.0219.090.070.000.000.00PB-15864.270.0018.760.030.000.000.00PB-15864.260.0018.700.030.000.000.00PB-15962.990.0319.980.430.010.010.00PB-16064.060.0118.470.050.000.000.00PB-16164.810.0018.820.050.010.000.00PB-16264.750.0018.690.160.000.000.00PB-16364.640.0018.820.040.000.000.00PB-16464.740.0018.820.040.000.000.00PB-16564.820.0018.880.070.000.010.00PB-16664.820.0018.880.040.000.010.00PB-16763.860.0118.880.040.000.010.00PB-16865.100.0018.880.040.000.000.01PB-169</td><td>Wt.% Oxide:AnalysisSiO2TiO2Al2O3FeOMnOMgOCaOBaOPB-15364.790.0018.740.200.010.020.000.46PB-15464.300.0118.580.060.010.000.000.010.11PB-15564.450.0019.180.060.000.000.020.71PB-15663.760.0219.090.070.000.000.001.42PB-15764.270.0018.760.000.010.010.020.58PB-15864.500.0018.700.030.000.000.000.49PB-15962.990.0319.980.430.010.370.000.49PB-16064.600.0118.470.050.000.000.000.49PB-16164.810.0018.920.050.010.000.000.17PB-16264.150.0219.070.030.000.000.000.17PB-16364.660.0018.630.000.000.000.55PB-16464.740.0018.820.040.000.000.55PB-16564.820.0018.880.070.000.010.000.55PB-16564.820.0018.880.070.000.010.000.55PB-16664.820.0018.880.07<td< td=""><td>Mut.% Oxide:AnalysisSiO2TiO2Al2O3FeOMnOMgOCaOBaONa2OPB-15364.790.0018.740.200.010.020.000.460.46PB-15464.300.0118.580.060.000.000.250.711.76PB-15564.450.0019.180.060.000.000.250.711.76PB-15663.760.0219.090.070.000.000.001.420.57PB-15764.270.0018.760.000.000.000.000.680.61PB-15864.500.0018.760.050.000.000.000.680.61PB-15962.990.0319.980.430.010.000.000.680.58PB-16064.610.0018.470.050.000.000.000.710.78PB-16264.150.0018.690.160.000.000.000.550.43PB-16364.640.0018.690.160.000.000.000.550.43PB-16464.740.0018.690.160.000.000.000.550.43PB-16564.550.0018.760.000.000.000.550.43PB-16664.790.0018.890.000.000.000.550.43PB-16763.86<td< td=""><td>MultikeVisionVisi</td><td>Wt.% Oxide:AnalysisSiO2TiO2Al2O3FeOMnOMgOCaOBaONa2OK2OCe2O3PB-15364.790.0018.740.200.010.020.000.610.3816.630.21PB-15464.300.0118.580.060.000.000.010.020.011.7613.730.25PB-15564.450.0019.080.070.000.000.001.420.5716.040.53PB-15764.270.0018.760.000.000.000.000.680.6116.330.21PB-15864.500.0018.700.030.000.000.000.680.6416.300.21PB-15962.990.0319.980.430.010.000.000.680.5815.740.22PB-16064.600.0118.470.050.000.000.000.011.6590.13PB-16164.810.0018.820.000.000.000.011.550.4316.490.23PB-16264.510.0018.620.000.000.000.000.550.4316.490.24PB-16364.660.0018.820.000.000.000.000.550.4416.940.24PB-16464.740.0018.820.000.000.000.050.4416.490</td></td<></td></td<></td></t<>	Mt.% Oxide:AnalysisSiO2TiO2Al2O3FeOMnOMgOCaOPB-15364.790.0018.740.200.010.020.00PB-15464.300.0118.580.060.010.000.25PB-15564.450.0019.180.060.000.000.00PB-15663.760.0219.090.070.000.000.00PB-15864.270.0018.760.030.000.000.00PB-15864.260.0018.700.030.000.000.00PB-15962.990.0319.980.430.010.010.00PB-16064.060.0118.470.050.000.000.00PB-16164.810.0018.820.050.010.000.00PB-16264.750.0018.690.160.000.000.00PB-16364.640.0018.820.040.000.000.00PB-16464.740.0018.820.040.000.000.00PB-16564.820.0018.880.070.000.010.00PB-16664.820.0018.880.040.000.010.00PB-16763.860.0118.880.040.000.010.00PB-16865.100.0018.880.040.000.000.01PB-169	Wt.% Oxide:AnalysisSiO2TiO2Al2O3FeOMnOMgOCaOBaOPB-15364.790.0018.740.200.010.020.000.46PB-15464.300.0118.580.060.010.000.000.010.11PB-15564.450.0019.180.060.000.000.020.71PB-15663.760.0219.090.070.000.000.001.42PB-15764.270.0018.760.000.010.010.020.58PB-15864.500.0018.700.030.000.000.000.49PB-15962.990.0319.980.430.010.370.000.49PB-16064.600.0118.470.050.000.000.000.49PB-16164.810.0018.920.050.010.000.000.17PB-16264.150.0219.070.030.000.000.000.17PB-16364.660.0018.630.000.000.000.55PB-16464.740.0018.820.040.000.000.55PB-16564.820.0018.880.070.000.010.000.55PB-16564.820.0018.880.070.000.010.000.55PB-16664.820.0018.880.07 <td< td=""><td>Mut.% Oxide:AnalysisSiO2TiO2Al2O3FeOMnOMgOCaOBaONa2OPB-15364.790.0018.740.200.010.020.000.460.46PB-15464.300.0118.580.060.000.000.250.711.76PB-15564.450.0019.180.060.000.000.250.711.76PB-15663.760.0219.090.070.000.000.001.420.57PB-15764.270.0018.760.000.000.000.000.680.61PB-15864.500.0018.760.050.000.000.000.680.61PB-15962.990.0319.980.430.010.000.000.680.58PB-16064.610.0018.470.050.000.000.000.710.78PB-16264.150.0018.690.160.000.000.000.550.43PB-16364.640.0018.690.160.000.000.000.550.43PB-16464.740.0018.690.160.000.000.000.550.43PB-16564.550.0018.760.000.000.000.550.43PB-16664.790.0018.890.000.000.000.550.43PB-16763.86<td< td=""><td>MultikeVisionVisi</td><td>Wt.% Oxide:AnalysisSiO2TiO2Al2O3FeOMnOMgOCaOBaONa2OK2OCe2O3PB-15364.790.0018.740.200.010.020.000.610.3816.630.21PB-15464.300.0118.580.060.000.000.010.020.011.7613.730.25PB-15564.450.0019.080.070.000.000.001.420.5716.040.53PB-15764.270.0018.760.000.000.000.000.680.6116.330.21PB-15864.500.0018.700.030.000.000.000.680.6416.300.21PB-15962.990.0319.980.430.010.000.000.680.5815.740.22PB-16064.600.0118.470.050.000.000.000.011.6590.13PB-16164.810.0018.820.000.000.000.011.550.4316.490.23PB-16264.510.0018.620.000.000.000.000.550.4316.490.24PB-16364.660.0018.820.000.000.000.000.550.4416.940.24PB-16464.740.0018.820.000.000.000.050.4416.490</td></td<></td></td<>	Mut.% Oxide:AnalysisSiO2TiO2Al2O3FeOMnOMgOCaOBaONa2OPB-15364.790.0018.740.200.010.020.000.460.46PB-15464.300.0118.580.060.000.000.250.711.76PB-15564.450.0019.180.060.000.000.250.711.76PB-15663.760.0219.090.070.000.000.001.420.57PB-15764.270.0018.760.000.000.000.000.680.61PB-15864.500.0018.760.050.000.000.000.680.61PB-15962.990.0319.980.430.010.000.000.680.58PB-16064.610.0018.470.050.000.000.000.710.78PB-16264.150.0018.690.160.000.000.000.550.43PB-16364.640.0018.690.160.000.000.000.550.43PB-16464.740.0018.690.160.000.000.000.550.43PB-16564.550.0018.760.000.000.000.550.43PB-16664.790.0018.890.000.000.000.550.43PB-16763.86 <td< td=""><td>MultikeVisionVisi</td><td>Wt.% Oxide:AnalysisSiO2TiO2Al2O3FeOMnOMgOCaOBaONa2OK2OCe2O3PB-15364.790.0018.740.200.010.020.000.610.3816.630.21PB-15464.300.0118.580.060.000.000.010.020.011.7613.730.25PB-15564.450.0019.080.070.000.000.001.420.5716.040.53PB-15764.270.0018.760.000.000.000.000.680.6116.330.21PB-15864.500.0018.700.030.000.000.000.680.6416.300.21PB-15962.990.0319.980.430.010.000.000.680.5815.740.22PB-16064.600.0118.470.050.000.000.000.011.6590.13PB-16164.810.0018.820.000.000.000.011.550.4316.490.23PB-16264.510.0018.620.000.000.000.000.550.4316.490.24PB-16364.660.0018.820.000.000.000.000.550.4416.940.24PB-16464.740.0018.820.000.000.000.050.4416.490</td></td<>	MultikeVisionVisi	Wt.% Oxide:AnalysisSiO2TiO2Al2O3FeOMnOMgOCaOBaONa2OK2OCe2O3PB-15364.790.0018.740.200.010.020.000.610.3816.630.21PB-15464.300.0118.580.060.000.000.010.020.011.7613.730.25PB-15564.450.0019.080.070.000.000.001.420.5716.040.53PB-15764.270.0018.760.000.000.000.000.680.6116.330.21PB-15864.500.0018.700.030.000.000.000.680.6416.300.21PB-15962.990.0319.980.430.010.000.000.680.5815.740.22PB-16064.600.0118.470.050.000.000.000.011.6590.13PB-16164.810.0018.820.000.000.000.011.550.4316.490.23PB-16264.510.0018.620.000.000.000.000.550.4316.490.24PB-16364.660.0018.820.000.000.000.000.550.4416.940.24PB-16464.740.0018.820.000.000.000.050.4416.490	

Atom	ıs:												End M	lember
Si	Ті	Al	Cr	Fe3	Fe2	Mn	Mg	Са	Ва	Na	К	Total Oxy	An	Ab
2.96	0.00	1.01	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.04	0.97	7.97	0.00	4.05
2.96	0.00	1.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.98	7.96	0.00	3.36
2.97	0.00	1.04	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.16	0.81	8.01	1.26	16.10
2.94	0.00	1.04	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.05	0.94	7.96	0.00	5.12
2.96	0.00	1.02	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.05	0.96	7.96	0.10	5.37
2.96	0.00	1.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.06	0.96	7.96	0.00	5.61
2.90	0.00	1.09	0.00	0.00	0.02	0.00	0.03	0.00	0.01	0.03	0.93	7.97	0.00	3.27
2.97	0.00	1.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.98	7.96	0.00	3.53
2.96	0.00	1.02	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.07	0.94	7.97	0.00	6.88
2.95	0.00	1.03	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.06	0.93	7.98	0.00	5.88
2.98	0.00	1.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.96	7.98	0.00	3.82
2.96	0.00	1.01	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.04	0.97	7.96	0.00	3.78
2.97	0.00	1.02	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.96	7.98	0.00	3.31
2.96	0.00	1.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.06	0.95	7.97	0.00	5.61
2.95	0.00	1.03	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.05	0.95	7.96	0.05	5.19
2.98	0.00	1.02	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.95	7.99	0.00	3.68
2.95	0.00	1.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.98	7.95	0.00	4.08
2.97	0.00	1.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.96	7.97	0.00	4.24
2.45	0.00	1.53	0.00	0.00	0.01	0.00	0.00	0.52	0.00	0.49	0.01	7.97	51.31	48.01
2.56	0.00	1.41	0.00	0.00	0.01	0.00	0.00	0.40	0.00	0.61	0.01	7.96	39.43	59.64
2.49	0.00	1.50	0.00	0.00	0.01	0.00	0.00	0.49	0.00	0.51	0.01	7.98	48.50	50.31
2.57	0.00	1.41	0.00	0.00	0.01	0.00	0.00	0.40	0.00	0.61	0.01	7.96	39.60	59.34
2.57	0.00	1.41	0.00	0.00	0.01	0.00	0.00	0.42	0.00	0.58	0.02	7.98	41.32	57.00
2.58	0.00	1.41	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.60	0.01	7.98	39.81	59.35

5:
Or
95.95
96.64
82.64
94.88
94.54
94.39
96.73
96.47
93.12
94.12
96.18
96.22
96.69
94.39
94.76
96.32
95.92
95.76
0.68
0.94
1.18
1.06
1.69
0.84

		Compo	sitional Pa	rameter	S			Radiogenic Isotope Ratios								Isotopic Ages						
Sample	Th U	²⁰⁶ Pb* x10-13 mol	mol % ²⁰⁶ Pb*	<u>Pb*</u> Pbc	Pbc (pg)	²⁰⁶ Pb ²⁰⁴ Pb	²⁰⁸ Pb ²⁰⁶ Pb	²⁰⁷ Pb ²⁰⁶ Pb	% err	²⁰⁷ Pb ²³⁵ U	% err	²⁰⁶ Pb ²³⁸ U	% err	corr. coef.	²⁰⁷ Pb ²⁰⁶ Pb	- ±	²⁰⁷ Pb ²³⁵ U	- ±	²⁰⁶ Pb ²³⁸ U	±		
*	†	§	§	§	§	#	**	**	<u>††</u>	**	<u>†</u> †	**	<u>††</u>		§§	<u>††</u>	§§	<u>††</u>	§§	<u>††</u>		
z1	0.627	8.4572	99.92%	380	0.58	22342	0.197	0.05689	0.17	0.6108	0.22	0.077865	0.100	0.694	486.91	3.76	484.05	0.86	483.44	0.47		
z2	0.353	2.8468	99.76%	120	0.57	7597	0.111	0.05683	0.11	0.6100	0.19	0.077845	0.090	0.932	484.54	2.41	483.55	0.72	483.34	0.42		
z3	0.407	2.0402	99.71%	103	0.48	6432	0.127	0.05683	0.12	0.6109	0.20	0.077961	0.088	0.909	484.52	2.70	484.12	0.76	484.03	0.41		
z5	0.423	1.8008	98.47%	19	2.38	1118	0.133	0.05692	0.21	0.6116	0.30	0.077926	0.117	0.852	488.01	4.62	484.55	1.16	483.82	0.54		
z6	0.787	3.7671	99.63%	88	1.15	4969	0.246	0.05685	0.14	0.6126	0.34	0.078162	0.277	0.915	485.25	3.06	485.22	1.30	485.22	1.30		
z7	0.416	3.1163	99.92%	388	0.20	24071	0.130	0.05681	0.09	0.6103	0.17	0.077916	0.087	0.959	483.75	2.00	483.76	0.66	483.76	0.40		

Table 3. U-Th-Pb isotopic data for sample MRC344.

* z1, z2 etc. are labels for fractions composed of single zircon grains or fragments; all fractions annealed and chemically abraded after Mattinson (2005). + Model Th/U ratio calculated from radiogenic 208 Pb/ 206 Pb ratio and 207 Pb/ 235 U age.

§ Pb* and Pbc represent radiogenic and common Pb, respectively; mol % ²⁰⁶Pb* with respect to radiogenic, blank and initial common Pb.

Measured ratio corrected for spike and fractionation only.

** Corrected for fractionation, spike, and common Pb; up to 2 pg of common Pb was assumed to be procedural blank: ${}^{206}Pb/{}^{204}Pb = 18.60 \pm 0.80\%$; ${}^{207}Pb/{}^{204}Pb = 15.69 \pm 0.32\%$; ${}^{208}Pb/{}^{204}Pb = 38.51 \pm 0.74\%$ (all uncertainties 1-sigma). Excess over blank was assigned to initial common Pb.

⁺⁺ Errors are 2-sigma, propagated using the algorithms of Schmitz and Schoene (2007). $S_{\rm S}$ Calculations are based on the decay constants of Jaffey et al. (1971). ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²⁰⁶Pb ages corrected for initial disequilibrium in ²³⁰Th/²³⁸U using Th/U [magma] = 3 using the algorithms of Schärer (1984).

Dates in bold are those included in weighted mean calculations. See text for discussion.