

**Stratigraphic, geochemical and U-Pb zircon constraints
from Slieve Gallion, Northern Ireland: A correlation of
the Irish Caledonian arcs**

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ABSTRACT

Recent Ar-Ar and U-Pb zircon geochronology from across the British and Irish Caledonides has revealed a prolonged period of arc/ophiolite formation (c. 514-464 Ma) and accretion (c. 490-470 Ma) to the Laurentian margin during the Grampian orogeny. The Slieve Gallion Inlier of Northern Ireland, an isolated occurrence of the Tyrone Volcanic Group, records the development of a peri-Laurentian island-arc/backarc and its obduction to an outboard microcontinental block. Although a previous biostratigraphic age constraint provides a firm correlation of at least part of the volcanic succession to the Ca1 Stage of the Arenig (c. 475-474 Ma), there is uncertainty on its exact stratigraphic position in the Tyrone Volcanic Group. Earliest magmatism is characterized by light rare earth element (LREE) depleted island-arc tholeiite. Overlying deposits are dominated by large ion lithophile and LREE-enriched, hornblende-phyric and feldspathic calc-alkaline basaltic andesites and andesitic tuffs with strongly-negative ϵNd_t values. Previously published biostratigraphic age constraints, combined with recent U-Pb zircon geochronology and new petrochemical correlations, suggest the Slieve Gallion Inlier is equivalent to the lower Tyrone Volcanic Group. Temporal and petrochemical correlations between the Slieve Gallion Inlier and Charlestown Group of Ireland suggest they may be part of the same arc-system which was accreted at a late stage (c. 470 Ma) in the Grampian orogeny. A switch from tholeiitic volcanism to calc-alkaline dominated activity within the Lough Nafooeey Group of western Ireland occurred prior to c. 490 Ma, approximately 15 to 20 Myr earlier than at Tyrone and Charlestown.

Keywords: Tyrone Igneous Complex, arc-continent collision, Caledonian - Appalachian.

INTRODUCTION

The Caledonian-Appalachian orogen provides a rare window through the mid to lower crustal levels of an evolving orogenic belt. Early Paleozoic closure of the Iapetus Ocean resulted in extensive arc-ophiolite accretion to the Laurentian margin (=Grampian-Taconic orogeny) prior to continent-continent collision (=Acadian orogeny) (Dewey 2005; van Staal *et al.* 2007; Chew 2009; Cooper *et al.* 2013). Modern subduction systems, such as the W and SW Pacific, reveal complexities during episodes of large-scale ocean closure, including: diachronous and/or oblique arc-continent collision, arc-arc collisions, subduction polarity reversals, subduction rollback, triple junctions, arc-interactions with propagating rifts and spreading centres, and the presence of microcontinental blocks and oceanic plateaus. Despite these complexities, forward modeling of collision between Australia and the Asian continent has produced remarkably linear orogenic belts when associated with sinistral oblique convergence (see van Staal *et al.* 1998). Pseudo-simplistic linear orogenic zones can conceal complex histories and geometries, especially if poorly exposed and subjected to terrane excision and strike-slip duplication (van Staal *et al.* 1998). It is only through detailed study of individual terranes, and their inter-relationships, that orogens may be understood

The Grampian-Taconic orogeny resulted from widespread and episodic arc-ophiolite accretion to the Laurentian margin between the Late Cambrian and Middle Ordovician (Dewey & Shackleton 1984; van Staal *et al.* 2007; Chew *et al.* 2010). Western Ireland, although not representative of the Grampian orogen as a whole, was a focus for establishing many of the fundamental processes of arc-continent collision due to its abundant exposure, low metamorphic grade and limited deformation (e.g. Dewey & Shackleton 1984; Dewey & Ryan 1990; Draut *et al.* 2004; Dewey 2005; Ryan & Dewey 2011). Collision between the Lough Nafooe arc of western Ireland and the passive Laurentian margin was associated with polyphase deformation and metamorphism of thick Neoproterozoic cover sequences such as the Dalradian Supergroup between c. 475-465 Ma. The South Mayo Trough, a thick and relatively undeformed accumulation of lavas and volcanoclastic sedimentary rocks, represents the pre-collisional fore-arc and syn- to post-collisional successor basin to the Lough Nafooe arc (Draut *et al.* 2004) (Fig. 1). Within its sedimentary record, the South Mayo Trough preserves the progressive evolution of the Lough Nafooe arc system, its collision with the Laurentian margin, and the unroofing of the orogen (reviewed in Ryan & Dewey 2011). A younger c. 464 Ma continental arc founded upon the Laurentian margin was associated with subduction polarity reversal following arc-continent collision (Dewey 2005).

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79 Arc-ophiolite formation is now recognized to span c. 514-464 Ma within the peri-Laurentian
80 British and Irish Caledonides (e.g. Chew *et al.* 2008, 2010; Cooper *et al.* 2011; Hollis *et al.*
81 2012). Early obduction of some ophiolites onto outboard microcontinental blocks (c. 510-
82 490 Ma) may explain discrepancies in the timing between the termination of Laurentian
83 passive margin sedimentation and ophiolite emplacement (Chew *et al.* 2010). Remnant slices
84 of the accreted volcanic arcs are exposed across the Midland Valley terrane, and include the
85 Bohaun Volcanic Formation, Lough Nafooe Group, Tourmakeady Group and Charlestown
86 Group of Ireland, the Tyrone Volcanic Group of Northern Ireland (Fig. 1), and probably the
87 Games Lough and Mains Hill successions of the Ballantrae Ophiolite Complex, Scotland.
88 Abundant arc-related and ophiolitic detritus in sediments of the Southern Uplands terrane and
89 Middle Ordovician sediments of Girvan also indicate the presence of an extensive arc-
90 ophiolite complex(s) buried within the Midland Valley Terrane (Midland Valley arc) (see
91 Oliver *et al.* 2002).

92

93 The Tyrone Volcanic Group of Northern Ireland occupies an important position in the
94 Caledonides between the well documented sectors of western Ireland and Scotland (Fig. 1).
95 It records the formation of a peri-Laurentian island arc/backarc during the Middle Ordovician
96 and its accretion to an outboard microcontinental block at c. 470 Ma (see Cooper *et al.* 2011;
97 Hollis *et al.* 2012). However, despite its importance, geochronology from the Tyrone arc is
98 limited to three high resolution U-Pb zircon dates from one formation (Cooper *et al.* 2008;
99 Hollis *et al.* 2012). Furthermore, the volcanic succession exposed at Slieve Gallion (herein
100 termed the Slieve Gallion Inlier) provides the only biostratigraphic age constraint for the
101 entire Tyrone Volcanic Group (Cooper *et al.* 2008). Although the Slieve Gallion Inlier was
102 initially suggested to be within the upper Tyrone Volcanic Group (Cooper *et al.* 2008), this
103 appears to be unfounded as similar lithologies are now known to occur in the Loughmacrory
104 Formation towards the base of the Tyrone Volcanic Group (Hollis *et al.* 2012).

105

106 Here we present the results of new field mapping, complemented by high-resolution airborne
107 geophysics, the first detailed geochemical study of the volcanic succession, and two new U-
108 Pb zircon dates that shed further light on this enigmatic arc-system and the orogen as a
109 whole. Herein we demonstrate that the Tyrone and Lough Nafooe arcs differ significantly
110 in the timing of their geochemical evolution and accretion. Either arc evolution and accretion
111 was diachronous in the Irish Caledonides, or perhaps more likely the Tyrone and Lough

Nafooeey arcs represent distinct arc systems accreted to the Laurentian margin during the Grampian orogeny (after Hollis *et al.* 2012).

PREVIOUS WORK

The Slieve Gallion Inlier of Northern Ireland is exposed over ~15km² directly NE of the c. 484-479 Ma ophiolitic Tyrone Plutonic Group (Cooper *et al.* 2011; Hollis *et al.* companion publication), which separates this package of rocks from the main occurrence of the c. 475-469 Ma Tyrone Volcanic Group to the SW (Fig. 2). The Slieve Gallion Inlier is bounded to the north and east by post-Silurian cover and along its southern margin has been intruded by a large body of biotite/hornblende-bearing granite (Slieve Gallion granite: 466.5 ± 3.3 Ma; Cooper *et al.* 2011) (Fig. 2). The first comprehensive study of the inlier was presented within Hartley's (1933) seminal work on the "Tyrone Igneous Series" (now Tyrone Igneous Complex). Although no stratigraphy was attempted, Hartley's map for the complex divided the volcanic succession at Slieve Gallion into (i) andesites, (ii) tuffs, and (iii) phyllites and chloritic schists. The volcanic rocks have since been resurveyed for the 2nd edition Cookstown and Draperstown sheets (Geological Survey of Northern Ireland: GSNI 1983 & 1995; also see Cameron & Old 1997), which provided the most up to date map of the inlier. No division within the volcanic succession was presented at 1:50,000, although GSNI field-slips record a variety of lithologies in detail.

Fragmentary graptolites from one locality at Sruhanleanantawey Burn [IGR 27905-38790] have been variably interpreted since their initial discovery by Hartley (1936). A late Llandeilo to early Caradoc age was originally favoured on the presence of specimens identified as *Dicranograptus* and *Climacograptus* (Hartley 1936). Re-collection by Hutton and Holland (1992) further identified the presence of *Tetragraptus serra* (Brongniart) and *Simagraptus sensu lato*, demonstrating an earlier Arenig to Llanvirn age. Most recently Cooper *et al.* (2008) collected more than 20 graptolites and a lingulate brachiopod, and reexamined the specimens of Hutton and Holland (1992). They concluded through the presence of *Isograptus victoriae lunatus*, the index fossil of the *Isograptus victoriae lunatus* Zone of the Australasian graptolite succession, the fauna can be assigned to the lowest Cal subdivision of the Castlemainian Stage. This is approximately equivalent to the top of the Whitlandian Stage of the Arenig (c. 475-474 Ma after Sadler *et al.* 2009).

In addition to their evaluation of the Sruhanleanantawey Burn fauna, Cooper *et al.* (2008) determined a U-Pb zircon date for a flow-banded rhyolite from Formil Hill from the main outcrop of the Tyrone Volcanic Group to the SW (473 ± 0.8 Ma). Rhyolites are common across the upper Tyrone Volcanic Group, exposed from Racolpa through Cashel Rock to Formil (Fig. 2) within the Greencastle Formation (c.473-469 Ma), and structurally and stratigraphically below the graphitic pelite and chert bearing localities around Mountfield and Broughderg (e.g. Crosh; c. 469 Ma Broughderg Formation; Hollis *et al.* 2012). Cooper *et al.* (2008) suggested that the chert, thinly-bedded tuffaceous siltstone and pyritic mudstones, with greenish-grey tuffs and lavas at Slieve Gallion formed synchronously with the succession at Broughderg. At this time, U-Pb geochronology from the Tyrone Volcanic Group *sensu stricto* was restricted to their one high-resolution age from Formil Hill and no detailed stratigraphic or petrochemical account of the Tyrone Volcanic Group existed. Two similar, albeit slightly younger, U-Pb zircon TIMS dates have subsequently been obtained from the Greencastle Formation (469.42 ± 0.79 Ma from rhyolite, 470.37 ± 0.76 Ma from tuff; Hollis *et al.* 2012).

STRATIGRAPHY

The Slieve Gallion Inlier has been re-mapped through the integration of previous geological survey data and new fieldwork, geochemistry (see following) and the Tellus airborne geophysical survey of Northern Ireland. A new map is presented in Figure 3. Magnetic, radiometric and electromagnetic (EM) data were acquired as part of the Tellus Project in 2005-2006 (see GSNI 2007). Details on survey specification and geophysical data processing are summarised within Beamish *et al.* (2007). The volcanic succession at Slieve Gallion is hereby divided into three formations: Tinagh, Tawey, and Whitewater (Figs. 3-4). Each is described below. Major ESE-WNW orientated faults divide the volcanic succession into three stratigraphic packages. South of the Tirgan Fault, the Tinagh and Tawey formations are exposed; the latter is restricted to the W of Slieve Gallion. North of the Tirgan Fault the structurally overlying Whitewater Formation is exposed. An older set of NW-SE striking faults cut the formations and are offset by the Tirgan Fault. Several of these NW-SE striking faults, which are clear from regional magnetics (Fig. 3) are directly mapable (e.g. NE of Tinagh; GSNI 1983, 1995). Ordovician intrusive rocks of quartz-porphyry, hornblende- and biotite-granodiorite, aplite and diorite cut the volcanic succession. Units have been metamorphosed to subgreenschist facies assemblages and consequently the prefix meta- is omitted from all lithologies.

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180 **Tinagh Formation:** The Tinagh Formation crops out extensively across the southern side of
181 the Slieve Gallion Inlier and includes the following informal stratigraphic units: Derryganard
182 Lavas, Windy Castle Lavas, Letteran Volcanics, Torys Hole Ironstone, and the Mobuy Wood
183 Basalts, each named after their type localities. The Tinagh Formation is dominated by calc-
184 alkaline hornblende porphyritic tuffs and lavas, and non-arc type Fe-Ti enriched basalt of e-
185 MORB affinity (see following sections). Lesser amounts of calc-alkaline, feldspar
186 porphyritic andesite, mafic crystal tuff, ferruginous jasperoid (ironstone), mafic agglomerate
187 (interpreted as interpillow breccias), tholeiitic pillow lavas, and rhyodacite are also present.
188 The formation has a maximum exposed thickness of 1.2 km, although the rift-related Mobuy
189 Wood Basalts appear have been erupted locally at different times (Fig. 4) and packages of the
190 Windy Castle Lavas vary considerably in thickness along strike.

191

192 Pillow lavas exposed at Derryganard (=Derryganard Lavas) are believed to represent the
193 oldest stage of volcanism within the Slieve Gallion Inlier and are restricted to this area. The
194 succession is at least 130 m thick with pillow structures younging north towards the Windy
195 Castle Lavas. The succession is bounded to the south and east by younger intrusions of c.
196 465-464 Ma quartz-porphyry and a large body of biotite granite, and is succeeded in the
197 northwest by the Windy Castle Lavas which dip NW to NE (Fig. 3). Pillows are generally
198 aphanitic, highly vesicular and range between 8 and 35 cm in diameter (Fig. 5a,f). Flows
199 become more massive up section, and rare augite phenocrysts occur in some near the base of
200 the sequence. No interpillow chert or sediment was observed. The Derryganard Lavas are
201 non-magnetic and are geochemically distinct from all other units present in the Slieve Gallion
202 Inlier, displaying tholeiitic and LREE-depleted geochemical characteristics (see
203 petrochemistry).

204

205 Immediately overlying the Derryganard Lavas, the Tinagh Formation is dominated by calc-
206 alkaline tuffs and andesites (Fig. 5b, 5i), with flows becoming increasingly pillowed and
207 associated with agglomerate up section. This sequence, has been divided into the Windy
208 Castle Lavas and Letteran Volcanics on the basis of the dominant phenocryst type in flows,
209 intensity of magnetic response, and type of associated tuff (i.e. mafic or hornblende-phyric).
210 The contact with the underlying Derryganard Lavas was placed at the first occurrence of
211 hornblende-phyric basaltic andesite/andesite or tuff. The Windy Castle Lavas are
212 characterized by vesicular hornblende-phyric andesites with lesser mafic crystal tuff; type

localities occur at Windy Castle and W of Letteran. Locally the Windy Castle Lavas reaches a thickness of 275 m. The Letteran Volcanics are characterized by non-magnetic, calc-alkaline, and feldspar-phyric, massive and pillowed andesites (which lack abundant hornblende phenocrysts; Fig. 5i) and sheared hornblende-bearing crystal tuffs (Fig. 4). The Letteran Volcanics locally vary in thickness between ~275 to 340 m. Packages of the Windy Castle Lavas alternate with the Letteran Volcanics both up sequence and along strike (Fig. 3). This suggests different areas experienced pyroclastic and effusive activity at different times, most likely associated with rifting (see following). This is further supported by the geochemistry of the closely associated Mobuy Wood Basalts (see petrochemistry) and the occurrence of ironstone at Tors Hole, where a 1 m thick bed is exposed towards the base of the Tinagh Formation. This unit is characterized by a mosaic of quartz and haematite (Cameron & Old 1997).

Non-arc type basalts of eMORB affinity are restricted to the SW of the Slieve Gallion Inlier, exposed between Sruhanleanantawey Burn and Letteran (Fig. 3), and around Mobuy Wood. These lavas are geochemically distinct to all others analysed from the Slieve Gallion Inlier, having rift-related characteristics (see petrochemistry). They are herein termed the Mobuy Wood Basalts. Flows are often highly vesicular (Fig. 5c), and either massive or display well developed pillow structures with radial fractures. Basaltic agglomerates, interpreted as interpillow breccias (Fig. 5d), are commonly associated with the latter. Although the Mobuy Wood Basalts are largely aphanitic, some flows contain rare augite phenocrysts which can display evidence for rounding (Fig. 5g). This suggests these may be xenocrysts derived from the underlying Derryganard Lavas. The Mobuy Wood Basalts can be distinguished based on their geochemistry and high total magnetic intensity, and from underlying flows of the Windy Castle Lavas and Letteran Volcanics by a lack of hornblende phenocrysts. It is not known if the Mobuy Wood Basalts are present on the E side of Slieve Gallion as these lavas were not sampled for geochemistry, although augite bearing andesites have been reported on GSNI fieldsheets north of Tirgan. A single unit of rhyodacite also occurs at Mobuy Wood near the base of the overlying Tawey Formation. This rhyodacite is extensively sheared and is associated with rare hornblende-phyric lava, tuff and small intrusions of quartz diorite.

Tawey Formation: The overlying Tawey Formation is defined in the section exposed in Sruhanleanantawey Burn (Fig. 3). The formation is at least 1.45 km thick (discounting intrusive units) and is dominated by crystal and lithic tuffs, hornblende-phyric lavas with

247 lesser fine-grained sedimentary rocks (banded chert, pyritic mudstone, banded siltstone and
248 phyllite) (Fig. 4). Poorly exposed, the Tawey Formation is restricted to the western side of
249 Slieve Gallion. It has been broadly divided into sequences dominated by lava (associated
250 with high total magnetic intensity due to the presence of Fe-oxides; Fig. 3) and those
251 dominated by tuff and sedimentary rocks. The base of the Tinagh Formation was placed at
252 the first occurrence of sedimentary rocks or layered chert, as crystal tuffs and hornblende-
253 phytic lavas occur in both formations. No evidence for faulting between these formations is
254 apparent from field relationships or geophysics. No pillowed or vesicular flows have been
255 recognized in the Tawey Formation, unlike the underlying Tinagh Formation. Way up criteria
256 in the formation is scarce due to patchy outcrop. Bedding towards the base of the
257 Sruhanleanantawey Burn dips steeply NW, whereas towards the top bedding dips moderately
258 SE (Fig. 3). It is believed this variation in the SE is due to localized doming associated with
259 intrusive activity. Intrusions are abundant in the stream section and include quartz-porphyry,
260 a >35 m thick unit of hornblende-rich diorite, and alkali-basalt (see MRC335 discussion). A
261 large NW-SE orientated fault also cuts the upper part of the stream, perpendicular to bedding
262 below the SE dipping graptolite-bearing succession. Due to poor exposure combined with
263 structural complications the succession is described as a transverse up Sruhanleanantawey
264 Burn (as in Cameron and Old 1997).

265
266 Near the base of the Sruhanleanantawey Burn section the formation is characterized by
267 greenish-grey hornblende and feldspar phytic tuff and lava, which have been intruded by sills
268 of reddish and pink weathered quartz porphyritic dacite common throughout the Tyrone
269 Igneous Complex (Figs. 2-3). Euhedral quartz, plagioclase feldspar and occasional greenish
270 mica phenocrysts occur in a fine-grained pink dacitic matrix (Cameron & Old 1997). Quartz-
271 porphyritic dacite that intrudes the lower Tyrone Volcanic Group has been dated at 465 ± 1.7
272 Ma (Cooper *et al.* 2011). Contacts of alternating exposures between quartz-porphyritic dacite
273 and greenish-grey tuff and lava, which contain hornblende and feldspar phenocrysts, are not
274 well exposed, although at Torys Hole and Tinagh quartz-porphyry is chilled against tuffs and
275 dark greenish-grey dacite respectively. Bedding is clear in coarse tuffs and banded phyllites,
276 although extensive shearing often makes it difficult to distinguish between hornblende-
277 bearing crystal tuffs and lavas.

278
279 The upper reaches of Sruhanleanantawey Burn have been mapped and logged in detail by the
280 GSNI (Cameron & Old 1997), which is summarized here. Pale grey, chert-like phyllites

display faintly visible bedding and are composed of very fine-grained quartz, schistose sericite with weathered-out pyrite porphyroblasts surrounded by limonite haloes (Cameron & Old 1997). Further upstream, phyllites are interbedded with coarse tuffs and dark grey coarse-grained crystal tuff. A horizon of pale grey tuffaceous chert also occurs with bands of crystal-rich material and light grey thinly-bedded tuffaceous siltstone. Towards the top of the Sruhanleanantawey Burn section, dark blue-grey pyritiferous mudstones and thin coarse tuff bands are overlain by strongly banded blue-grey siltstones (Fig. 5e). Cooper et al. (2008) obtained a Ca1 Whitlandian age from a sparse graptolite fauna from this part of the sequence. Coarse crystal tuff further up Sruhanleanantawey Burn is associated with blocks of chert. A thick (>30 m) feldspar-phyric silicified basaltic rock (Fig. 5h) is also present in Sruhanleanantawey Burn downstream from the graptolite bearing horizon. This unit is non vesicular, massive and appears to contain small angular xenoliths of aphanitic basalt or fine-grained silicified sediment. Its contacts with adjacent units are not exposed, although due to U-Pb zircon geochronology and its unique geochemical characteristics (see following) it is interpreted as intrusive.

Whitewater Formation: Whitewater River and its tributaries provide the most complete section through the Whitewater Formation. The lower part of this formation (>650 m thick) is characterized by thick accumulations of interbedded hornblende-phyric andesite and tuff, and is in faulted contact with the Tinagh and Tawey formations (Fig. 3). Tuffs are often schistose on the northern side of Slieve Gallion and are often chloritic and/or silicified. Lithic and crystal varieties occur with broken crystals of hornblende, augite, epidote, orthoclase and plagioclase set in a feldspathic groundmass with quartz, chlorite and epidote (Hartley 1933). Augite and plagioclase would suggest a mafic source and glass fragments can display a devitrified perlitic structure (Hartley 1933). Rare agglomerate containing chert fragments crop out SE of Windy Castle, whilst at Tirgan a 30 cm thick bed of layered chert occurs which contains intercalated tuff bands (Cameron & Old 1997; Fig. 3). Some of the andesites NE of Slieve Gallion and N of Tirgan display pillow structures with a consistent orientation suggesting younging towards the north. A rare horizon of ironstone (quartz-hematite) is exposed at Drummuck (=Drummuck Ironstone: Fig. 3), with float occurring along strike to the north of Slieve Gallion. The upper part of the Whitewater Formation is best exposed around Straw Mountain and is composed of a >750 m thick sequence of chloritic and silicified lithic and crystal tuff with rare andesite. Locally tuffs in Whitewater River (S of Straw Mountain) can be intensely sericitised and pyritic. Ironstone (quartz-

hematite) float is also common around Straw Mountain, suggesting a second stratigraphically higher unit may be present in the Whitewater Formation above the Drummuck Ironstone (Fig. 3).

PETROCHEMISTRY:

Volcanic rocks from all major stratigraphic horizons within the Slieve Gallion Inlier were sampled for whole-rock geochemical analysis. All signs of weathering, alteration and veining were removed prior to powdering in a Cr-steel TEMA. Major-elements and trace-elements were determined for whole-rock samples on fused glass beads and powder-pellets, respectively, by X-ray fluorescence (Philips® MagiX-Pro 4kW Rh x-ray tube) at the University of Southampton. Rare earth-elements (REE; plus Nb, Hf, Ta, Th, U) were determined by inductively coupled plasma mass spectrometry (Thermo Scientific Xseries 2) on the same powders following an HF/HNO₃ digest. Accuracy (%RD) and Precision (%RSD) was typically <3 % for ICP-MS analyses and <5 % for XRF analyses based on replicate analyses of a range of international standards (XRF: JR-1, JR-2, JG-3, JB-1a, JA-a; ICP-MS: BHVO-2, JB-1a, JB-3, JGB-1, JR-1) (detailed in Hollis 2013). Elements with accuracy and precision >10% (ICP-MS: Ta, Hf; XRF: Cu, Co) are considered poor (Jenner, 1996) and were not used. Neodymium was isolated for Nd isotope analysis from ICP-MS mother solutions using 6.5ml Dowex AG50W-X8 (200-400 mesh) cation columns and Ln-spec reverse phase columns. Nd isotope ratios were measured using a VGMicromass Sector 54 thermal ionization mass spectrometer at the University of Southampton. ¹⁴³Nd/¹⁴⁴Nd was measured in multidynamic mode, exponentially corrected for instrumental fractionation relative to ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. The JNdi standard gave a value of 0.512091 ± 14 (2sd, n=20). Further detail on methods is reported in Hollis *et al.* (2012). All results are presented as Supplementary Information. Geochemical analyses of Cooper *et al.* (2011; MRC prefixes) are also included where appropriate. Due to the extensive hydrothermal alteration and metamorphism across the Tyrone Volcanic Group, only elements demonstrated to be immobile are used to elucidate petrogenesis, tectonic affinities and chemostratigraphy (after Cooper *et al.* 2011; Hollis *et al.* 2012). These include: TiO₂, Th, V, Sc, high field strength elements (HFSE: e.g. Nb, Zr, Y), and the rare-earth elements (REE).

Tinagh Formation: A single sample was analysed from the Derryganard Lavas. This sample (SPH525) is unusual within the Slieve Gallion Inlier displaying low Th (Th_{CN} 8.21) and LREE depletion relative to the HREE (La/Yb_{CN} 0.7). Low Zr/Y (2.24), Zr/TiO₂ and

Nb/Y (0.03) ratios suggest these lavas are primitive subalkaline basalts of tholeiitic affinity (Figs. 6, 7a). Pronounced negative Nb and Ti anomalies are consistent with formation in an island-arc setting. Sample SPH525 is characterized by high MgO (9.71 wt.%), Cr (650 ppm), Ni (247 ppm) and low SiO₂ (47.1 wt.%).

Non-pillowed hornblende-phyric lavas of the Windy Castle Lavas were sampled between Derryganard and Slieve Gallion (=SPH506, SPH511, SPH528 and SPH534). These units are strongly calc-alkaline (Zr/Y 6.45-12.1), LILE enriched (Th_{CN} 201.8-458.6) and display high LREE enrichment relative to the HREE (La/Yb_{CN} 9.52-14.00) (Figs. 6,7b). TiO₂ (0.48-0.61 wt.%) and Cr (59-173) contents are low, and Nb/Y values range between 0.35 and 0.65. Sample SPH532, collected from pillow lavas NE of Letteran, is calc-alkaline (Zr/Y 7.93) and displays extreme LILE enrichment (Th_{CN} 600) and low MgO (1.06 wt.%), TiO₂ (0.24 wt.%), Cr (99 ppm) and V (34 ppm). All units from the Windy Castle Lavas display island-arc geochemical characteristics including pronounced negative Nb anomalies (Figs. 6,7b). A single sample of feldspathic andesite (SPH530) from the Letteran Volcanics is also strongly calc-alkaline (Zr/Y 10.37) and LILE and LREE enriched (Th_{CN} 237.4, La/Yb_{CN} 12.69) (Figs. 6,7b). This sample yielded a strongly negative εNd_t value of -9.02 (Fig. 6c) and displayed strong island-arc geochemical characteristics (e.g. negative Nb anomalies).

The Mobury Wood Basalts are geochemically distinct to all other mafic rocks in the Slieve Gallion Inlier and resemble rift-related lavas of the Tyrone Volcanic Group (Hollis *et al.* 2012). Low Zr/TiO₂ and high Nb/Y (0.36-0.64) classify these lavas as sub-alkaline basalts, whilst Zr/Y ratios (3.82-6.46) locate them within the calc-alkaline field of Ross and Bédard (2009) (Figs. 6a,d,f). All of the samples analysed are characterized by high Fe₂O_{3T} (11.56-13.07 wt.%) and TiO₂ (1.83-2.33 wt.%). εNd_t values are the most primitive of all samples analysed from the Slieve Gallion Inlier (+0.6 to +2.5; Fig. 6c). Th/Yb-Nb/Yb systematics and various discrimination diagrams (e.g. Pearce & Cann 1973; Pearce & Norry 1979; Wood 1980; Meschede 1986) suggest these lavas are of eMORB affinity and slightly enriched in subduction zone components (Fig. 7c-d). On multi-element variation diagrams all three samples analysed from the Mobury Wood Basalts show high LILE (Th_{CN} 38.8-155.3) and REE enrichment, and LREE enrichment relative to the HREE (La/Yb_{CN} 3.44-4.82) (Fig. 7c-d). Sample SPH533 (vesicular pillowed basalt) displays a small positive Nb anomaly and minor negative Ti anomaly (Fig. 7c), whereas samples SPH508 and SPH517 (unpillowed basalt) show negative Nb and Ti anomalies (Fig. 7d). Sample SPH533 is characterized by

slightly lower TiO₂, Th, REE, HFSE, higher Zr/Y, Cr and MgO, and a more primitive εNd_t value than SPH508 and SPH517 (Fig. 7c).

Tawey Formation: Four samples have been analysed from the Tawey Formation: lithic tuff (SPH493), tuff associated with chert (SPH494), chert (SPH52) and siltstone (SPH496). The volcanic samples are subalkaline, transitional to calc-alkaline (Zr/Y 3.94-8.57) and display high Th_{CN} (172.4-275.8) (Fig. 6). Chert is characterized by high Th_{CN} (343.5), K₂O+Na₂O and Al₂O₃ (11.16 wt.%) consistent with both continentally- and arc-derived components.

Whitewater Formation: All samples analysed from the Whitewater Formation (SPH467 to SPH488, and SPH502) are basaltic andesitic or andesitic in composition. These rocks are subalkaline (0.45-0.7), strongly calc-alkaline (Zr/Y 5.69-10.57), LILE (Th_{CN} 227.72-310.41) and LREE enriched relative to the HREE (La/Yb_{CN} 7.88-10.91), and are characterized by strongly negative εNd_t values (-12.68 to -13.86) (Fig. 6,7f). Cr contents are high (282-405 ppm). All samples show pronounced negative Nb and HFSE anomalies, and positive Zr anomalies, on multi-element variation diagrams (Fig. 7f).

Sruhanleanantawey Burn alkali basaltic rock: An extensively altered feldspar-phyric basaltic rock from the upper portions of Sruhanleanantawey Burn (MRC335 and SPH25) was sampled for geochemistry and U-Pb geochronology downstream of the c. 475-474 Ma graptolite bearing rocks analysed by Cooper et al. (2008) and previous workers. This unit is characterized by high TiO₂ (3.53-3.84 wt.%), Fe₂O_{3T} (17.82-18.28 wt.%), P₂O₅ (0.56-0.62 wt.%), LOI (4.51-4.85 %), V (403-463 ppm), Zr (249-283 ppm), and low Cr (4-19 ppm), and Th (2-4 ppm). Sample MRC335 is alkalic (Nb/Y 0.89), of eMORB to OIB affinity (Nb/Yb 8.96) and displays positive Ti and Zr anomalies and weakly negative Nb and Y anomalies (Fig. 7e).

U-Pb GEOCHRONOLOGY

Two samples were dated by U-Pb thermal ionization mass spectrometry (TIMS) geochronology at the NERC Isotope Geoscience Laboratory (NIGL): (i) MRC335, a silicified Fe-Ti enriched alkali basaltic rock collected from Sruhanleanantawey Burn [IGR 27895-38795], and (ii) MRC351, diorite from Crooked Bridge [IGR 27755-38630]. Zircons were isolated using conventional mineral separation techniques. Prior to isotope dilution thermal ionization mass spectrometry (ID-TIMS) analysis, zircons were subject to a modified version

of the chemical abrasion technique (Mattinson 2005). Methods are identical to those reported in Hollis *et al.* (2012; also companion publication). Errors for U-Pb dates are reported in the following format: $\pm X(Y)[Z]$, where X is the internal or analytical uncertainty in the absence of systematic errors (tracer calibration and decay constants), Y includes the quadratic addition of tracer calibration error (using a conservative 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 ^{238}U decay constant errors of Jaffey *et al.* (1971). All analytical uncertainties are calculated at the 95% confidence interval. Data is presented in Table 1.

Sample MRC351 was collected from the Crooked Bridge diorite, a 1km long by 400 m wide body exposed within the Slieve Gallion granite (Fig. 2). At its northern margin, approximately 400 m N of Crooked Bridge [2750 3859], the transition from granite to diorite is observed over less than 5 m. In places, the granite includes irregular patches of hornblende-rich diorite that are sometimes diffuse, suggestive of magma mingling and mixing. In thin section, diorite from this marginal location contains mainly early euhedral hornblende and plagioclase crystals with late interstitial quartz that encloses smaller subanhedral plagioclase. The texture is that of a granite-diorite hybrid and indicates synmagmatic crystallisation. Seven zircon fractions (single grains and fragments) were analyzed from MRC351. All seven analyses are concordant when the systematic $\lambda^{238}\text{U}$ and $\lambda^{235}\text{U}$ decay constant errors are considered. Six form a coherent single population yielding a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date of 469.58 ± 0.32 (0.57)[0.77] Ma (MSWD = 1.4) which we interpret as being the age of sample (Fig. 8a). One older analysis (z7: Fig. 8a) is considered to reflect incorporation of older material (c. 473 Ma) derived from the Tyrone Volcanic Group into the magmatic system.

Sample MRC335 represents a silicified and feldspar porphyritic, Fe-Ti enriched alkali basaltic rock which crops out towards the top of Sruhanleanantawey Burn. As detailed above, this unit is non vesicular, massive and appears to contain angular xenoliths of aphanitic basalt or silicified sediment. Its contacts with adjacent units are not exposed. Five zircon fractions (single grains) were analyzed from MRC335. One grain yielded a Proterozoic age (c.1033 Ma) indicating incorporation of older basement material. Within the remaining population each of the analyses are concordant however there is dispersion with $^{206}\text{Pb}/^{238}\text{U}$ dates ranging from 467.43 ± 0.48 to 470.38 ± 0.40 Ma (Fig. 8). The youngest $^{206}\text{Pb}/^{238}\text{U}$ date (z1: Fig. 8a)

we interpret to reflect minor Pb-loss. The age of the sample is approximated by the population of three equivalent $^{206}\text{Pb}/^{238}\text{U}$ dates (z6, z11 and z14) to 469.36 ± 0.34 (0.58)[0.78] Ma (MSWD 0.42). Visual inspection, and limited CL imaging, of the zircons (including ones dated) indicates they are typical of magmatic zircons (including other samples dated in this study) based upon their external morphology and internal concentric zonation (Fig. 8b).

DISCUSSION

Petrochemical evolution

Earliest magmatism within the Slieve Gallion Inlier (Tinagh Formation) is characterized by the eruption of tholeiitic pillow basalt of island-arc affinity (=Derryganard Basalts). These lavas are the most primitive of all samples analysed (low SiO_2 and Zr/Y, high MgO). Low La/Yb_{CN} and Th_{CN} suggest magmatism at this stage was not contaminated by continental material. Overlying deposits within the Tinagh Formation (= Letteran Volcanics & Windy Castle Lavas) are dominated by LILE and LREE-enriched hornblende-phyric and feldspathic calc-alkaline basaltic andesites and andesitic tuffs. Strongly-negative ϵNd_t values, high Th_{CN} and La/Yb_{CN} suggest a sudden and significant input of continental crust and/or detritus occurred at this time into the arc system; or the Derryganard Basalts represent an episode of volcanism associated with extensive back-arc rifting, such as the Beaghmore Formation of the lower Tyrone Volcanic Group (see Hollis *et al.* 2012). Mafic tuffs and lavas become increasingly replaced by those of andesitic composition up sequence. The proportion of agglomerates (inter-pillow breccias) and pyroclastic deposits also increases towards the top of the Tinagh Formation.

Primitive, non-arc type Fe-Ti-P enriched basalt of e-MORB affinity recognized around Mobuy Wood (=Mobuy Wood Basalts) are typical of rift-related lavas present within the Tyrone Volcanic Group (references within Hollis *et al.* 2012). Although ϵNd_t values of Fe-Ti eMORB are the most primitive of all samples analysed within the Slieve Gallion Inlier (+0.6 to +2.5), they are less so than those described in Hollis *et al.* (2012) from main exposures of the lower Tyrone Volcanic Group to the SW (+2.4 to +5.9). Hollis (2013) noted a systematic geochemical variation in Fe-Ti enriched basalts of the Tyrone Volcanic Group, with increasing Fe and Ti associated with: increasing Zr, Th, V, La and Nb; decreasing MgO , CaO , Al_2O_3 , Ni and Cr; and more negative ϵNd_t values. These lavas may have formed through the interaction between an island arc and a propagating rift (Hollis *et al.* 2012).

The occurrence of 1-5 m thick beds of ironstone (or ironstone float) within all formations of the Slieve Gallion Inlier also suggests rifting was episodic. Ironstones are common within Tyrone Volcanic Group, where they occur as laterally continuous beds in the Loughmacrory, Beaghmore and Broughderg formations (Fig. 2a; Hollis *et al.* 2012; Hollis 2013). Clasts of ironstone are also found in some basaltic agglomerates of the Creggan Formation and in tuffs of the aforementioned formations (Hollis *et al.* 2012). Ironstones in the Tyrone Volcanic Group are temporally and spatially associated with rift-related lavas (e.g. Fe-Ti enriched eMORB, OIB, island-arc tholeiite), synvolcanogenic faults, hydrothermal alteration and in some instances base-metal mineralization (Hollis 2013). Whole rock geochemical ratios and positive Eu anomalies at Torys Hole (and Tanderagee of the Loughmacrory Formation) are comparable to volcanic-hosted massive sulphide proximal ironstones which form during rift-related hydrothermal activity (Hollis 2013).

The overlying Tawey and Whitewater formations are dominated by calc-alkaline lavas and volcanoclastics with minor sedimentary rocks. This reflects a switch of the arc system from effusive dominated activity (in the Tinagh Formation), through intermittent extrusive and pyroclastic activity (Tawey Formation and lower Whitewater Formation), to pyroclastic dominated activity (upper Whitewater Formation). ϵNd_t values become progressively more negative up sequence, discounting the Mobuy Wood rift-related lavas (-9.0 Letteran Volcanics; -12.9 lower Whitewater Formation; -12.7 to -13.9 top of Whitewater Formation). This may either represent an increased contribution of continentally derived material during petrogenesis associated with arc-accretion, or may be an artifact of limited sampling. The presence of thick packages of sedimentary rocks in the Tawey Formation and the repeated occurrence of ironstone suggests volcanic activity was interrupted by periods of quiescence at several times.

Correlations with the Tyrone Volcanic Group

Using recently published U-Pb zircon geochronology and geochemistry (Cooper *et al.* 2008, 2011; Draut *et al.* 2010; Hollis *et al.* 2012) and the work presented herein, we can refine possible correlations across the Tyrone Volcanic Group. Stratigraphic divisions established within the main occurrence of the Tyrone Volcanic Group, exposed to the SW of the Slieve Gallion Inlier, are presented in Hollis *et al.* (2012) and summarized in Figure 9. Although the volcanic succession at Slieve Gallion was initially suggested to correlate with the Broughderg

Formation of the upper Tyrone Volcanic Group (Cooper *et al.* 2008), recent geological mapping (Hollis *et al.* 2012) has identified the presence of similar lithologies (e.g. hornblende-phyric lavas, thinly-bedded argillaceous sedimentary rocks, sheared-rhyolitic tuff, layered chert and greenish-grey tuffs) within the Loughmacrory Formation (Fig. 2) of the lower Tyrone Volcanic Group (Fig. 9). In addition, the occurrence of ferruginous jasper (ironstone) at Slieve Gallion would argue against a correlation with the Broughderg Formation (c. 469 Ma), where ironstones are characterized by magnetite-silica-pyrite and graphitic pelite is abundant (Hollis *et al.* 2012). Only at Crosh in the Broughderg Formation has quartz-hematite ironstone been recognized (Fig. 2), where it replaces a tuffaceous horizon in a thick sequence of graphitic-pelite (Hollis 2013). Pillow lavas of calc-alkaline affinity are also absent within the upper Tyrone Volcanic Group, but are present in the Creggan, Loughmacrory and Beaghmore formations of the lower Tyrone Volcanic Group (Hollis *et al.* 2012).

The Loughmacrory Formation is amongst the most diverse succession in the Tyrone Volcanic Group and was divided by Hollis *et al.* (2012) into three members (Figs. 4 & 9). The oldest, the Tanderagee Member, is characterized by a thick succession of crystal and lithic tuff, pillowed calc-alkaline basalt/ basaltic-andesite, hornblende and feldspar phyric andesites, and agglomerate, associated with lesser ironstone, Fe-Ti eMORB, layered chert and sedimentary rocks (including siltstone and rare mudstone). The overlying Merchantstown Glebe Member is characterized by pillowed, massive and sheet-flow Fe-Ti enriched basalt/basaltic andesite of eMORB affinity associated with lesser crystal tuff and agglomerate. The youngest, the Streefe Glebe Member, is characterized by a thick sequence of calc-alkaline LILE and LREE enriched crystal tuff with rare occurrences of lava (of unknown affinity). The Loughmacrory Formation bears a striking resemblance to the volcanic succession exposed in the Slieve Gallion Inlier, with the Tinagh and Tawey formations equivalent to the Tanderagee Member, and the Whitewater Formation broadly equivalent to the Streefe Glebe Member (Fig. 9). Fe-Ti eMORB lavas of the Mobuy Wood Basalts are present both in the Tanderagee and Merchantstown Glebe members, and the underlying Creggan Formation (Figs. 4& 9). Although a number of these lithologies can also be found in the Beaghmore Formation of the lower Tyrone Volcanic Group, which is restricted to the E of the Dungate Fault (Fig. 2), this backarc assemblage is dominated by bimodal tholeiitic volcanism and Fe-Ti eMORB, with few lavas of calc-alkaline affinity (Hollis *et al.* 2012).

Geochemical data from both the Slieve Gallion Inlier and all formations of the Tyrone Volcanic Group are plotted together in Figures 6-7. Multi-element variation profiles allow little distinction between calc-alkaline tuffs of the Tyrone Volcanic Group (Fig. 7b,f). Although samples analysed herein overlap with lavas and tuffs from both the lower and upper Tyrone Volcanic Group, the most evolved samples from the latter are characterized by much higher Zr/Y contents, and Nb/Y ratios toward strongly alkalic compositions (Fig. 6f). For example, c. 469 Ma rhyolites of the Broughderg Formation display A-type affinities and are characterized by high Nb and Zr (Hollis 2013) which have not been recognized at Slieve Gallion.

Mafic lavas of the Tyrone Volcanic Group perhaps provide better discrimination between formations, as many units are geochemically distinct. In the lower Tyrone Volcanic Group mafic flows are characterized by calc-alkaline basalt, Fe-Ti enriched eMORB and island-arc tholeiite. In the upper Tyrone Volcanic Group mafic units are restricted to the Broughderg Formation where they are borderline to strongly alkalic and display OIB-like characteristics (Hollis et al. 2012). Pillowed lava sampled from the Mobuy Wood Basalts (SPH533) has an identical multi-element variation profile to Fe-Ti pillowed lavas from the lower Creggan, Loughmacrory (Tanderagee Member) and Beaghmore formations of the lower Tyrone Volcanic Group, with positive Nb anomalies, and similar LILE and REE concentrations (Fig. 7c). Similarly, massive and vesicular, non-pillowed flows of the Mobuy Wood Basalts (SPH508, SPH517) display slight negative Nb anomalies, and Ti anomalies. These flows are geochemically identical to Fe-Ti lavas from the upper Creggan Formation and Merchantstown Glebe members of the lower Tyrone Volcanic Group (Fig. 7d; see Hollis et al. 2012).

Island arc tholeiite, exposed at Derryganard, is only present in the lower Tyrone Volcanic Group in the Beaghmore Formation (Hollis *et al.* 2012). Although these lavas display similar multi-element profiles to sample SPH525 (Derryganard Lavas: Fig. 7a), they contain higher Nb/Yb, Zr/Y and Nb/Y (Fig. 4a-b, d-e) consistent with backarc volcanism in the Beaghmore Formation following intra-arc rifting (Hollis et al. 2012). Tholeiitic tuffs and rhyolitic agglomerates of the Beaghmore Formation which display flat REE profiles and low Zr/Y and Nb/Yb also appear to be unrepresented in the Slieve Gallion Inlier, although rhyodacite from Mobuy Wood was not analysed.

Nd-isotope constraints of samples from Slieve Gallion are shown together with samples from the Tyrone Volcanic Group in Figure 6c. Tuffs and lavas of the Loughmacrory Formation are slightly more primitive (ϵNd_t -4.1 to -7.0) than the Tinagh Formation (Letteran Volcanics: ϵNd_t -9.0), although chert from the underlying Creggan Formation has produced a similar value (ϵNd_t -8.0) (Hollis *et al.* 2012). No Nd-isotope constraints have been carried out on tuffs of the Streefe Glebe Member, which would equate to the Whitewater Formation (ϵNd_t -12.7 to -13.9). It is possible the upper part of the Whitewater Formation records the onset of arc-accretion (= lower Greencastle Formation), as similar ϵNd_t values have also been produced from the syncollisional upper Tyrone Volcanic Group (e.g. rhyolite from Greencastle -8.9, tuff associated with graphitic pelite at Broughderg -11.6). An alternate explanation is the Slieve Gallion volcanics may have been founded upon a thicker portion of continental crust and experienced a greater degree of crustal contamination. This latter scenario is consistent with the geochemistry of the Mobuy Wood Basalts, which display less primitive ϵNd_t and higher Th/Yb values (Fig 6d-e) than similar units of the Loughmacrory Formation.

In summary, new stratigraphic and petrochemical data from Slieve Gallion suggests the succession at Slieve Gallion is more analogous to the lowermost parts of the Tyrone Volcanic Group, specifically the Loughmacrory Formation (Figs. 6-7). This is also consistent with U-Pb zircon dating of the upper Tyrone Volcanic Group at c.473-469 Ma (Cooper *et al.* 2008; Hollis *et al.* 2012), and an age of c. 475-474 Ma from the graptolite bearing succession of Sruhanleanantawey Burn (Cooper *et al.* 2008).

Intrusive rocks

The Fe-Ti enriched alkali basaltic rock of eMORB to OIB-like affinity from Sruhanleanantawey Burn dated herein to c. 469 Ma is geochemically similar to the Fe-Ti enriched basalts exposed at Mountfield Quarry (Fig. 5c) and Broughderg, both of which sit stratigraphically above c. 473-469 Ma rhyolites of the Greencastle Formation. The Sruhanleanantawey Burn and Broughderg Formation basalts plot in similar positions along the mantle array, at higher Nb/Yb than eMORB (Fig. 6d-e). Zr/Y ratios are slightly lower in the Mountfield Basalts, although the Sruhanleanantawey Burn samples follow the same trend of increasing alkalinity with Zr/Y (Fig 4f). Sample MRC335 also shows a similar slight negative Nb anomaly, and positive Zr and Ti anomalies (Fig. 7e). We interpret the Sruhanleanantawey Burn alkali basaltic rock as a late intrusive and representative of a suite

which fed the rift related lavas of the uppermost Tyrone arc. The inherited zircon fraction dated at c. 1033 Ma is consistent with the assimilation of continental material into the magmatic arc at this time. Accretion of the Tyrone arc onto the peri-Laurentian, Dalradian-affinity, Tyrone Central Inlier (Chew *et al.* 2008) is placed at c. 470 Ma coeval with widespread tonalite emplacement (Cooper *et al.* 2011; also Hollis *et al.* 2012). Undated Fe-Ti enriched dykes similar to MRC335 also intrude S-type muscovite granite at Tremoge Glen (SPH129 in Hollis *et al.* companion publication).

The Crooked Bridge diorite, dated herein to 469.58 ± 0.32 (0.57)[0.77] Ma, displays a clear magma mixing-mingling relationship with hornblende-granite. Biotite-granite dated by Cooper *et al.* (2011) from the eastern side of Slieve Gallion yielded a U-Pb zircon age of 466.5 ± 3.3 Ma, within error of that presented herein for the Crooked Bridge diorite. Although the biotite- and hornblende-bearing granites of Slieve Gallion may represent distinct magmas, the latter may have been simply contaminated from the underlying Tyrone Plutonic Group as, highly magnetic material of the Tyrone Plutonic Group to be restricted to the southwestern side of Slieve Gallion where hornblende-bearing granite crops out. Both the Slieve Gallion granite and Crooked Bridge diorite belong to the c. 470-464 Ma arc-related intrusive suite of Cooper *et al.* (2011), which stitches the Tyrone Volcanic Group in its present structural position following arc-accretion.

A correlation for the Irish Caledonide arcs

Through the study of fossil and modern orogens, and the use of geodynamic models (e.g. Afonso & Zlotnik 2011; Boutelier & Chemenda 2011; Gerya 2011), it is evident that there is no paradigm that uniquely defines arc-continent collision (reviewed in Brown *et al.* 2011). Natural complexities in key first order parameters such as the nature of the continental margin (e.g. shape, thickness, presence of re-entrants, hydration, composition) and arc-trench complex (e.g. shape of trench, arc thickness, nature of the basement), result in considerable variation between and within orogens (see Brown *et al.* 2011), along with their interactions with spreading centres, oceanic plateaus and microcontinental blocks. Arc and ophiolite complexes may be obducted (e.g. Lushs Bight, Bay of Islands: van Staal *et al.* 2007) or underplated to continental margins (e.g. Annieopsquotch Accretionary Tract: Zagorevski *et al.* 2009) depending on their relative age at the time of accretion and tectonic position. Fore-arcs may be preserved or completely lost due to the location of failures in the overriding plate, which are determined by sites of lithospheric weakness (Boutelier & Chemenda 2011).

655 Accretion may also be diachronous across the margin, with implications for the timing of
656 subduction reversal (Brown *et al.* 2011).

657
658 Using recently presented stratigraphic, geochemical and U-Pb zircon constraints from the
659 Tyrone Volcanic Group (Cooper *et al.* 2011; Hollis *et al.* 2012; and those herein) we can
660 refine possible correlations between the Irish Caledonian arcs which were accreted to the
661 Laurentian margin during the Grampian orogeny. Petrochemical correlations are presented in
662 Figure 9 (modified after Ryan & Dewey 2011) according to the timescale of Sadler *et al.*
663 (2009). Whilst previous work has suggested arc-continent collision during the Grampian
664 orogeny was short-lived and not markedly diachronous (Soper *et al.* 1999; Dewey 2005), the
665 data presented herein along with recently published geochronology from the Tyrone Igneous
666 Complex (Cooper *et al.* 2011; Hollis *et al.* 2012) clearly demonstrate that either: (i) the
667 evolution of arc volcanism and to some extent arc-accretion was diachronous in the peri-
668 Laurentian Irish Caledonides (Cooper *et al.* 2011); or (ii) multiple arc-systems of different
669 age are preserved (e.g. Hollis *et al.* 2012).

670
671 In western Ireland, the generation of suprasubduction zone affinity oceanic crust began prior
672 to c. 514 Ma, the age of high-grade metamorphism and deformation of the Deer Park
673 ophiolitic mélange (514 ± 3 Ma ^{40}Ar - ^{39}Ar hornblende; Chew *et al.* 2010). Early obduction may
674 have occurred to an outboard block of peri-Laurentian affinity microcontinental crust (Chew
675 *et al.* 2010), as in the Newfoundland Appalachians (=Taconic phase 1 of van Staal *et al.*
676 2007). Blocks of muscovite-bearing schist within the Deer Park mélange contain detrital
677 zircon spectra similar to the Dalradian Supergroup and have produced a ^{40}Ar - ^{39}Ar age of $482 \pm$
678 1 Ma (Chew *et al.* 2010). An age of c. 482 Ma for ophiolite exhumation is consistent with
679 heavy mineral studies from western Ireland which record significant quantities of ophiolite-
680 derived sediment entering the fore-arc (South Mayo Trough) of the Lough Nafooe arc from
681 c. 478-476 Ma (Dewey & Mange 1999; Letterbrock Formation: Fig. 9). Together, the South
682 Mayo Trough, Lough Nafooe Group and Tourmakeady Group record the development of
683 the colliding Lough Nafooe arc prior to and during its collision with Laurentia (Ryan *et al.*
684 1980; Clift & Ryan, 1994; Dewey & Mange, 1999; Draut *et al.* 2004; Fig. 9). LREE-
685 depletion and the strongly positive ϵNd_t values of tholeiitic basalts in the lower Lough
686 Nafooe Group suggest an origin far from Laurentia. A switch from the eruption of island-
687 arc tholeiites (and boninitic lavas of the Bohaun Volcanic Formation) to calc-alkaline lavas
688 occurs prior to c. 490 Ma (Fig. 9). Increasing SiO_2 , LILE and LREE enrichment and more

negative ϵNd_t values with stratigraphic height in the Lough Nafooeey arc, reflect an increasing contribution of subducted material into the arc system as it approached the Laurentian margin (Draut *et al.* 2004; Chew *et al.* 2007). The overlying syn-collisional Tourmakeady Group (c. 476-470 Ma) formed synchronously with peak metamorphism and regional deformation within the Dalradian Supergroup. The timing of ‘hard’ collision in western Ireland (= base of the Tourmakeady Group: Draut *et al.* 2004) occurred between c. 484 Ma (=graptolite constraint on Lough Nafooeey Group) and c. 476 Ma (=age of the Mt. Partry Formation) (Fig. 9). This phase of arc-accretion is equivalent to Taconic phase 2 of the Newfoundland Appalachians (van Staal *et al.* 2007; see discussion in Hollis *et al.* companion publication).

While the Lough Nafooeey arc clearly shows an increasing contribution of subducted material into the arc system as it approached the Laurentian margin (Draut *et al.* 2004), no such systematic trend is evident in the Tyrone Volcanic Group (Hollis *et al.* 2012). Both the syn-collisional upper Tyrone Volcanic Group and the pre-collisional basal formations of the lower Tyrone Volcanic Group display strongly negative ϵNd_t values and evidence for strong LILE- and LREE-enrichment (Fig. 6c,f, Fig. 7b,f; Draut *et al.* 2009; Cooper *et al.* 2011; Hollis *et al.* 2012). Two possible scenarios may explain these geochemical characteristics. In the first scenario, the Tyrone Igneous Complex may have developed above a SE-dipping subduction zone and is part of the Lough Nafooeey arc system (after Draut *et al.* 2009). In this instance, extensive crustal contamination would result from subducted sediment derived from the Laurentian margin. Increased contamination may have occurred if the Tyrone arc was founded upon a segment of peri-Laurentian outriding continental crust. Arc-continent collision would have been diachronous from c. 480 Ma in western Ireland to c. 470 Ma in County Tyrone. Similarly, the geochemical evolution of the arc must have also been strongly diachronous (Fig. 9), with a switch from tholeiitic volcanism from <490 Ma in western Ireland (Draut *et al.* 2004) to c. 475 Ma in County Tyrone (Cooper *et al.* 2011). In the second scenario, the Tyrone Igneous Complex may have developed above a north-dipping subduction zone in a manner similar to the Annieopsquotch Accretionary Tract of Newfoundland (Zagorevski *et al.* 2009), and records the evolution of a younger, separate arc system which collided with the composite Laurentian margin at c. 470 Ma (Hollis *et al.* 2012, companion publication). In this model, the Tyrone Igneous Complex formed immediately outboard of the Tyrone Central Inlier, a peri-Laurentian microcontinental block (Chew *et al.* 2008). At c. 484-479 Ma, spreading outboard of this microcontinental block led to the formation of the ophiolitic Tyrone Plutonic Group (Hollis *et al.* companion publication).

This c. 480 Ma rifting may be related to the onset of ‘hard’ collision in Ireland (i.e. Taconic phase 2). If this model is correct, continental contamination of the Tyrone arc would be a direct result of the arc being constructed upon the rifted-off fragment of microcontinental crust.

The Charlestown Group, exposed across approximately 45 km² of Co. Mayo, is an important link between western Ireland and the Tyrone Volcanic Group of Northern Ireland. Although it is typically attributed to the syn-collisional stage of the Lough Nafooe arc system and is believed to broadly correlate with the Tourmakedy Group (e.g. Chew 2009), it remains one of the most understudied components of the orogen. Charlesworth (1960) provided the first detailed structure and stratigraphy of the Charlestown Group. New exposure allowed O’Connor (1987) to reassess the stratigraphy and re-divide the succession into three formations, renamed by Long *et al.* (2005) as; (i) Horan Formation, around 630 m thick, characterized by minor sediments, extrusive basalts, spillites and mixed tuffs; (ii) Carracastle Formation, around 290 m thick, dominated by andesitic tuffs and flows, with coarse volcanic breccias; and (iii) Tawnyinah Formation, around 300 m thick, dominated by more silicic lithologies. A gradual change was noted from tholeiitic island-arc spillites at the base with associated tuffs, into calc-alkaline tuffs and resedimented tuffs of the Carracastle Formation, passing into more felsic tuffs with accompanying intrusions of rhyolite and dacite near the top (O’Connor & Poutsie 1986; also O’Connor 1987).

This lithological and petrochemical change is similar to that observed from both the Tyrone Volcanic Group (e.g. IAT into CAB of the Tinagh Formation to syndepositional rhyolites of the upper Tyrone arc) and the Lough Nafooe arc (e.g. Draut *et al.* 2004), although the timing differs significantly from the latter (Fig. 9). In the Charlestown Group, Cummins (1954) obtained an Arenig age from a graptolite bearing sequence near the top of the Horan Formation. This was later verified by Dewey *et al.* (1970) specifically to British *Didymograptus hirundo* biozone and *Isograptus caduceus* biozone of North America. Cooper and Lindholm (1990) equated the *Didymograptus hirundo* biozone with the Da1 zone of the Darriwilian Australasian stage; which was subsequently renamed to the *Aulograptus cucullus* biozone and suggested to correlate with both the *Undulograptus austrodepressus* biozone (=Da1) and lower part of the *Undulograptus intersitus* biozone (=lower Da2) (see Zalasiewicz *et al.* 2009). The Da1 stage has been calculated by Sadler *et al.* (2009) to 470.54–469.57 Ma, and the upper boundary of Da2 to 467.94 Ma. Although further work is needed

on the Charlestown Group, particularly high-resolution U-Pb zircon geochronology, trace geochemistry and Nd-isotope constraints, preliminary work suggests the Charlestown Group displays many temporal, lithological and geochemical similarities with the Tyrone Volcanic Group (Fig. 9) despite being separated by some distance. We suggest both may belong to the same arc-system (possibly different eruptive centres) which was subsequently juxtaposed with the Lough Nafooeey arc during dextral (Harris 1993) or later sinistral strike-slip activity (Dewey & Strachan 2003). Pb isotope work on galenas from Charlestown and mineral deposits directly NW of (and structurally overlying) the Tyrone Volcanic Group has also suggested a correlation between the two arc terranes (Parnell *et al.* 2000).

In summary, if the Lough Nafooeey, Tourmakeady, Charlestown and Tyrone Volcanic groups formed within the same arc system, the geochemical evolution of this arc must have been strongly diachronous within the Irish Caledonides (Fig. 9) from c. <490 to 475 Ma, with diachronous arc-accretion to Laurentia from c. 480-478 Ma to c. 470 Ma. If correct, this model suggests a continuation of arc-diachroneity into the Scottish Caledonides can be expected. However, as Tremadocian to Early Arenig (c. 490-480 Ma) arc rocks have also been recognized from the Scottish Caledonides this seems unlikely. Chew *et al.* (2010) obtained a U-Pb zircon age of 490 ± 4 Ma from a mica-schist (interpreted as a volcanoclastic rock) intercalated within the c. 499 ± 8 Ma (U-Pb zircon) Highland Border Ophiolite, an along-strike equivalent of the Deer Park Complex. Similar ages have also been obtained from arc sequences at Ballantrae (Sm-Nd 501 ± 12 Ma, 476 ± 14 Ma; Thirlwall & Bluck 1984; K-Ar 487 ± 8 Ma; Harris *et al.* 1965) suggesting a volcanic arc may have been associated with the Ballantrae Ophiolite Complex (483 ± 4 Ma U-Pb zircon; Bluck *et al.* 1980) at this time. We suggest, the absence of a primitive volcanic arc in Tyrone prior to c. 475 Ma, combined with strong temporal, petrochemical, and stratigraphic correlations to ophiolites and arc-successions in the Newfoundland Appalachians along strike (Cooper *et al.* 2011; Hollis *et al.* 2012; companion publication); and the development of the Tyrone Igneous Complex outboard of the Tyrone Central Inlier; together suggest the complex formed within a separate arc-system to the Lough Nafooeey Group.

CONCLUSIONS

The Slieve Gallion Inlier of Northern Ireland, an isolated fragment of the Tyrone Volcanic Group, records the development of a peri-Laurentian island-arc/backarc and its obduction to an outboard microcontinental block (=Tyrone Central Inlier) at c. 470 Ma. Earliest

magmatism is characterized by LREE-depleted island-arc tholeiite. Overlying deposits are dominated by LILE and LREE-enriched, hornblende-phyric and feldspathic calc-alkaline basaltic andesites and andesitic tuffs with strongly-negative ϵNd_t values implying substantial contamination by continental crust and/or detritus. Fe-Ti enriched rift related basalts of eMORB affinity may be associated with propagation of a rift into the island-arc. Biostratigraphic age constraints and petrochemical correlations suggest the Slieve Gallion Inlier formed c. 475-474 Ma and is equivalent to the lower Tyrone Volcanic Group. Late c. 469 Ma intrusive rocks of Fe-Ti enriched alkali basalt appear to have fed the post-collisional rift-related lavas of the uppermost Tyrone arc (=Broughderg Formation). Preliminary temporal, geochemical and stratigraphic correlations between the Slieve Gallion Inlier (Tyrone Volcanic Group) and Charlestown Group of Ireland suggest they may be part of the same island arc. A switch from tholeiitic volcanism to calc-alkaline dominated activity within the Lough Nafoeey arc occurred prior to c. 490 Ma approximately ~15 to 20 Myr earlier than at Charlestown (c. 470 Ma) and Tyrone (c. 475 Ma).

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Figures

Fig. 1. (a) Geological map of NW Ireland showing the setting of the Tyrone Igneous Complex and other comparable ophiolite and volcanic arc associations, major structural features and Precambrian and Lower Paleozoic inliers in the Irish Caledonides. (b) Rocks affected by the Grampian, Acadian and Scandian orogenies. Figure after Chew (2009).

Fig. 2. Geological map of the Tyrone Igneous Complex (after Hollis *et al.* 2012).

Fig. 3. Geological map of the Slieve Gallion Inlier.

Fig. 4. Simplified stratigraphy of the Slieve Gallion Inlier and Tyrone Volcanic Group including the petrochemical affinities of mafic to felsic units within each formation (after

Hollis *et al.* 2012 and unpublished data). DL, Derryganard Lavas; LV, Letteran Volcanics; MWB, Mobuy Wood Basalts; WCL, Windy Castle Lavas.

Fig. 5. Field and petrographic photographs from across the Slieve Gallion Inlier. (a) Tholeiitic basaltic pillow basalt from Derryganard (Tinagh Formation). (b) Sheared, pillowed and brecciated lava near Tinagh. (c) Vesicular eMORB dipping under pillowed calc-alkaline basalt at the top of Slieve Gallion. (d) Pillow breccias at top of Slieve Gallion. (e) Graptolite bearing succession at Sruhanleanantawey Burn. (f) Extensively altered tholeiitic basalt from Derryganard (SPH525). (g) Pyroxene and feldspar phyric, vesicular pillowed Fe-Ti eMORB from Slieve Gallion (SPH533). (h) Feldspathic alkali basaltic intrusive from Sruhanleanantawey Burn (MRC335). (i) Calc-alkaline hornblende- and feldspar-phyric andesite (SPH534) from Letteran. Field of view is approximately 3mm across for f-i.

Fig. 6. Geochemistry of the Slieve Gallion Inlier and Tyrone Volcanic Group (stratigraphy after Hollis *et al.* 2012 and herein). (a-b) Zr-Ti against Nb-Y (after Winchester & Floyd 1977; modified after Pearce 1996); (c) ϵNd_t against TiO_2 ; (d-e) Th-Yb against Nb/Yb diagram (after Pearce 1983); (f) Nb/Y against Zr/Y diagram (Zr/Y ratio cut off values from Ross & Bédard 2009). Grey shading in a-e represents the field of Fe-Ti enriched lavas from the Tyrone Igneous Complex (eMORB, alkali and OIB-like). Grey shading in f represents samples of calc-alkaline affinity from the lower and upper Tyrone Volcanic Group (labeled). Data for the Tyrone Volcanic Group (TVG) from Draut *et al.* (2009), Cooper *et al.* (2011) and Hollis *et al.* (2012). EMORB, enriched mid-ocean-ridge basalt; MORB, mid-ocean-ridge basalt; OIB, ocean-island basalt. Formation abbreviations of Tyrone Volcanic Group (TVG): C, Creggan; L, Loughmacrory; Bm, Beaghmore; G, Greencastle; Bd, Broughderg.

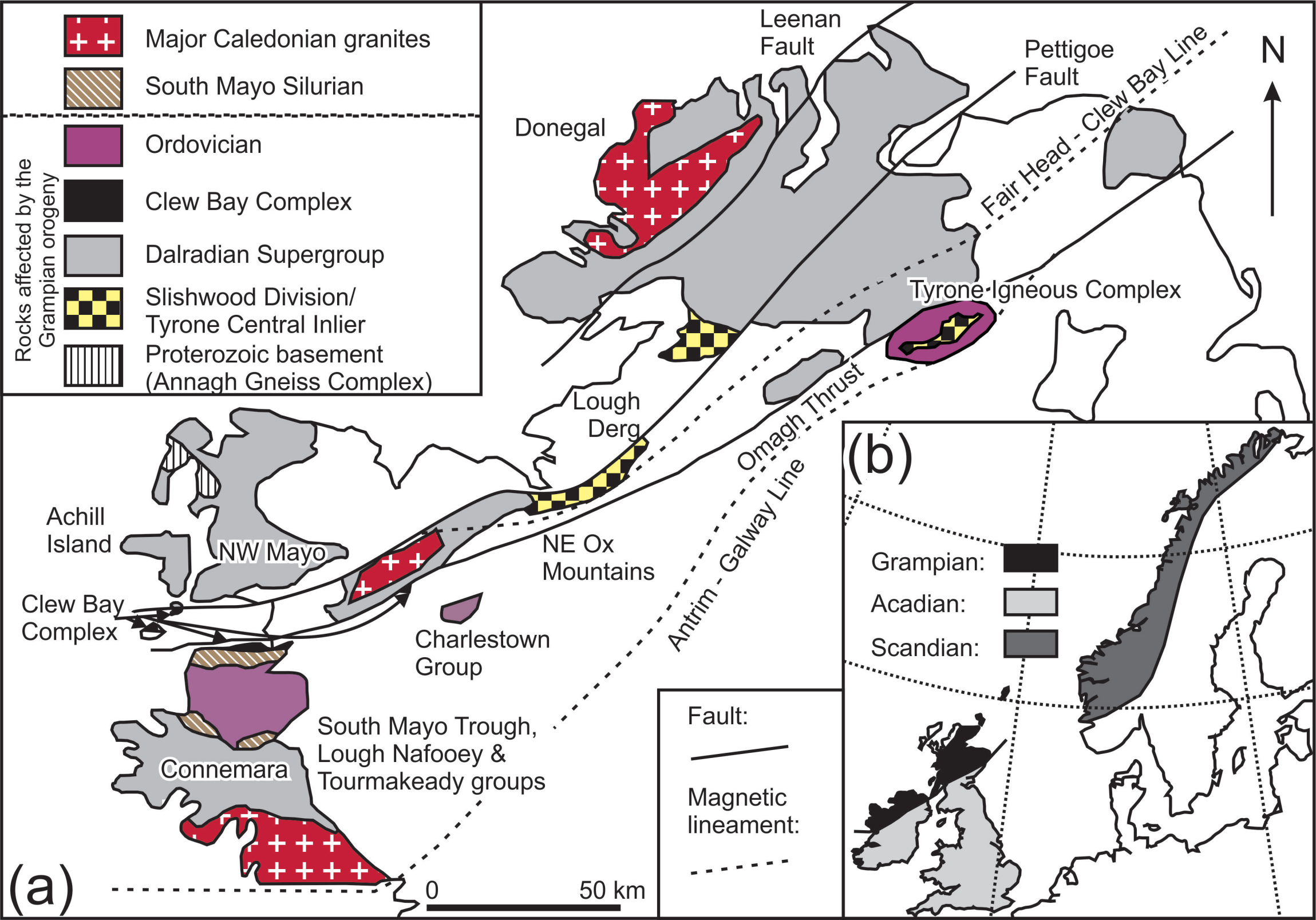
Fig. 7. Multi-element variation diagrams for samples analysed from Slieve Gallion. Multi-element profiles of samples from Slieve Gallion are shown by *bold lines*. Samples from equivalent units in the Tyrone Volcanic Group (after Draut *et al.* 2009; Cooper *et al.* 2011; Hollis *et al.* 2012) are shown by *faint dashed lines*. Chondrite normalization values after McDonough & Sun (1995). Grey shading in 7b and 7f represents field of calc-alkaline lavas from the upper Tyrone Volcanic Group.

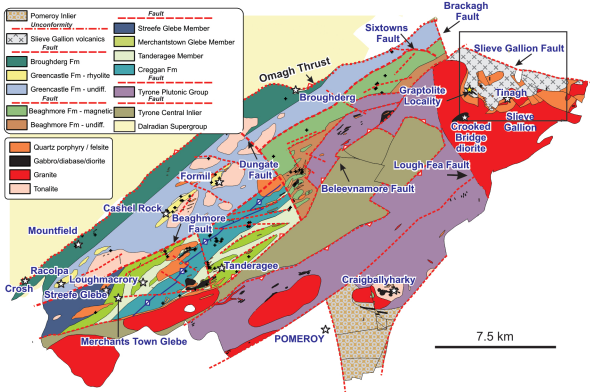
Fig. 8. (a) U-Pb zircon concordia for samples analysed from the Slieve Gallion Inlier and arc-related intrusive suite. The $^{206}\text{Pb}/^{238}\text{U}$ axis has been duplicated. (b) Representative CL images of zircons from MRC335.

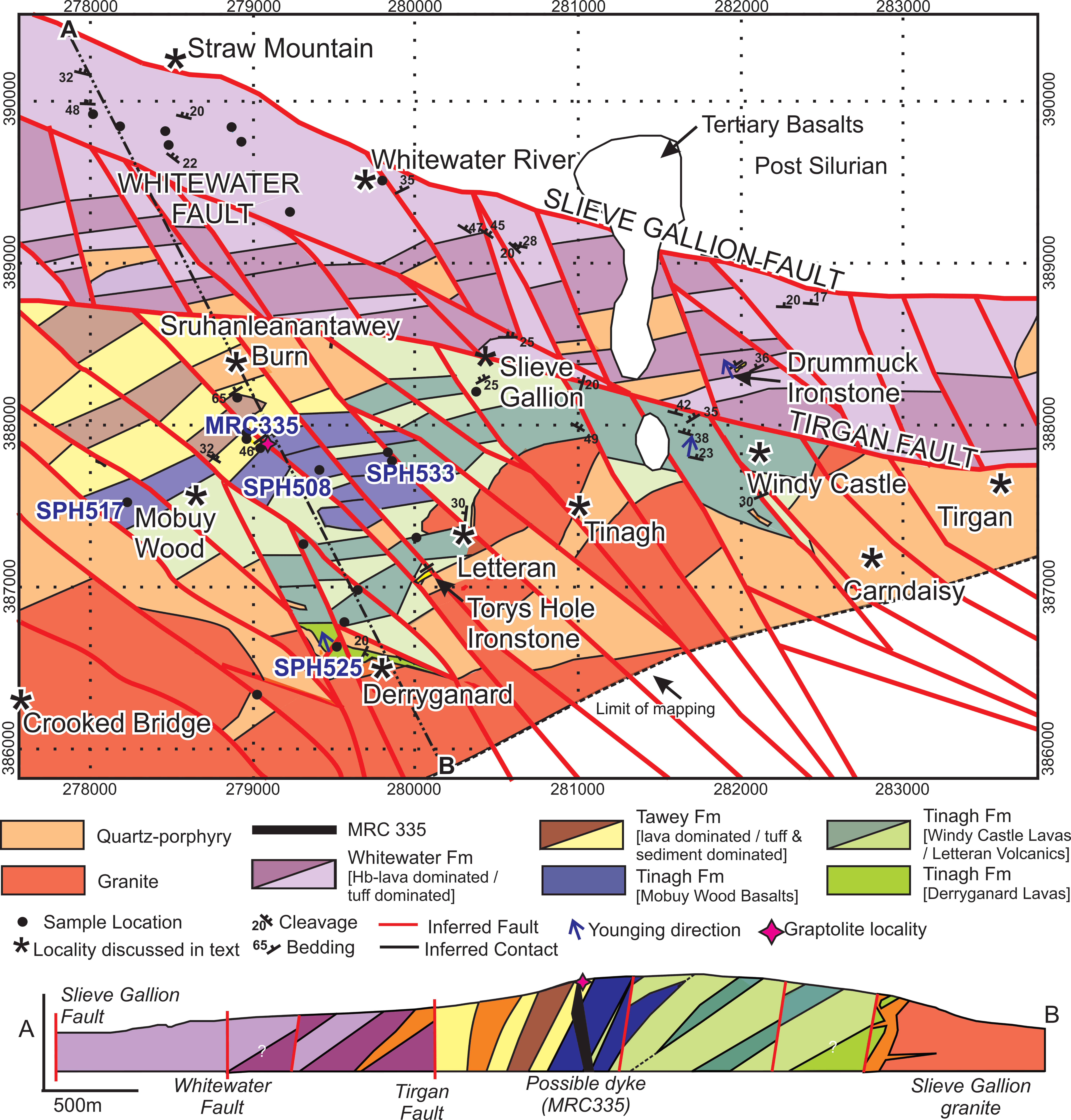
Fig. 9. Stratigraphy, petrochemistry and absolute ages for the Ordovician succession of South Mayo, Charlestown and the Tyrone Igneous Complex. Diagram after Ryan and Dewey (2011). The standard British Ordovician stages, those of the IUGS and the Australian Ordovician graptolite zones are assigned to absolute ages after Sadler *et al.* (2009). Absolute ages for events are represented by red stars with error bars. References: 1=Formil rhyolite (Cooper *et al.* 2008); 2=Tullybrick tuff and Cashel Rock rhyolite of Greencastle Formation, and Cashel Rock tonalite (Hollis *et al.* 2012); 3= clasts in Silurian conglomerate derived from Finny Formation (Chew *et al.* 2007); 4=Ignimbrite of Mweelrea Formation (Dewey & Mange 1999); 5=Arc related intrusive rocks of Cooper *et al.* (2011). Stratigraphy of the Tyrone Volcanic Group from (Hollis *et al.* 2012; Hollis 2013). North and south limbs refer to the Mweelrea syncline (South Mayo Trough).

Table 1. U-Pb zircon geochronology from Slieve Gallion.

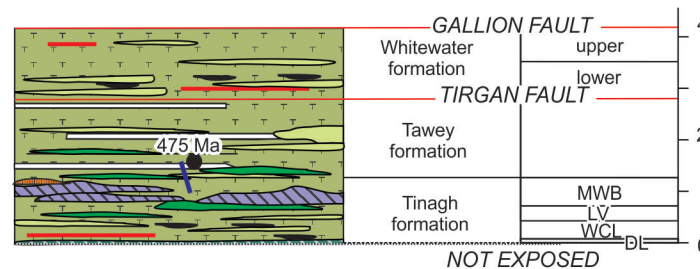
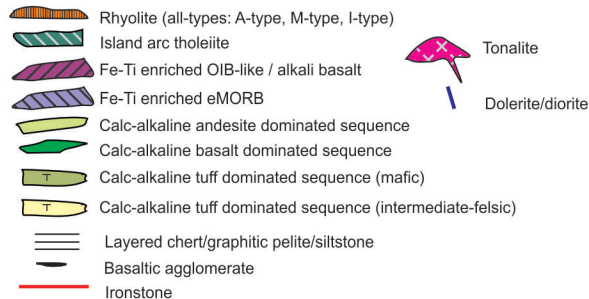
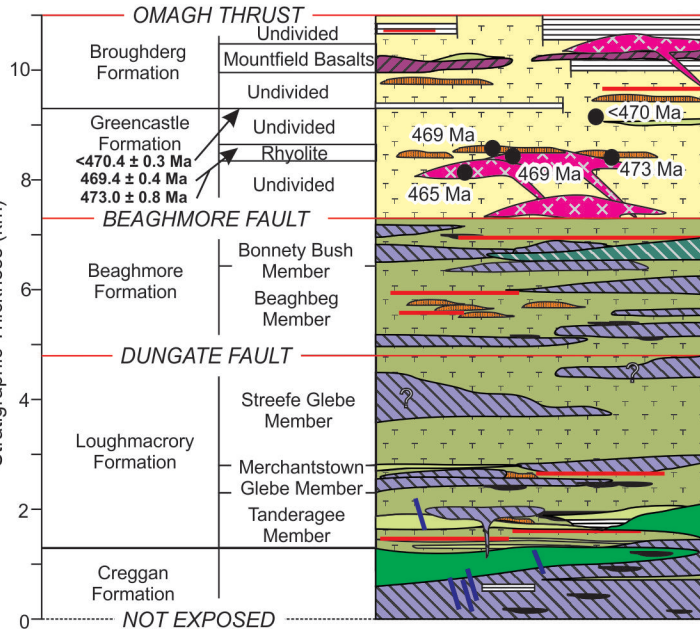
Supplementary Information. Table A. Sampling and geochemical results (major-elements, LOI, trace-elements, REE, Nd-isotopes).

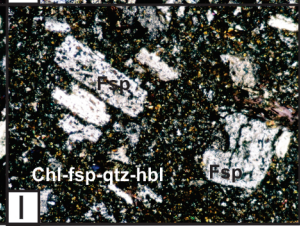
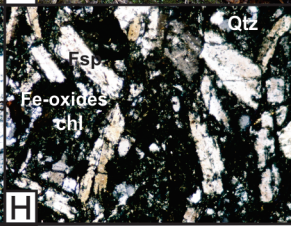
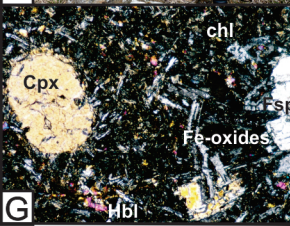
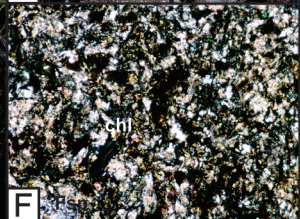


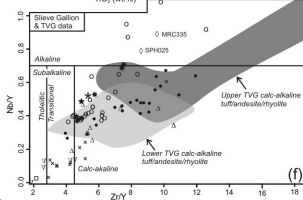
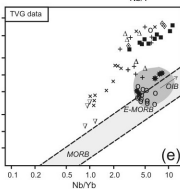
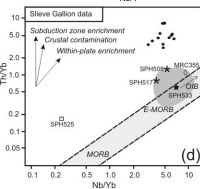
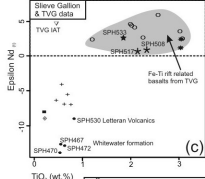
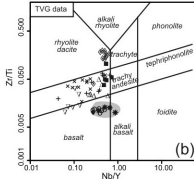
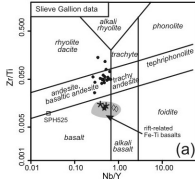




Stratigraphic Thickness (km)







Sieve Gallion samples

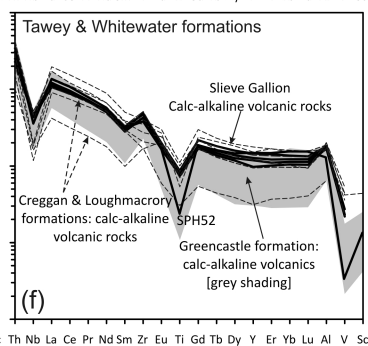
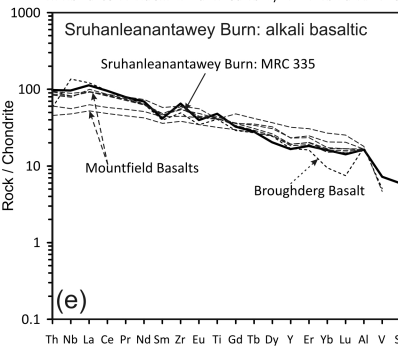
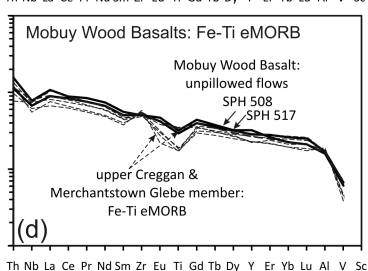
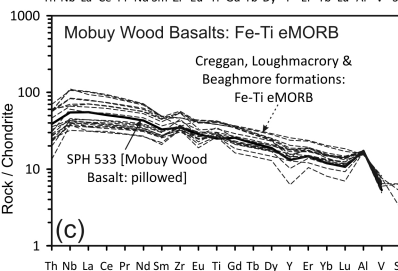
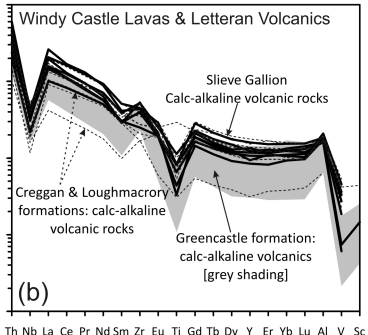
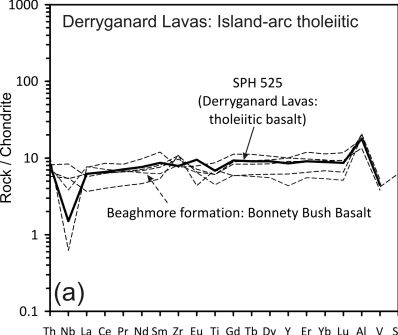
- Derryganard Lavas: IAT (SPH525)
- ★ Mobuy Wood Basalt: unpillowed (SPH508, SPH517)
- ★ Mobuy Wood Basalt: pillowed (SPH533)
- ◇ Sruhanleanantawey Burn alkali basaltic rock (MRC355, SPH25)
- ◇ Calc-alkaline volcanics/sedimentary rocks: all other samples

TVG samples: Lower arc

- C, L, Bm formations: Fe-Ti eMORB
- △ C & L formations: calc-alkaline basalt
- + L formation: tuff/andesite
- × Bm formation: tuff/rhyolite
- ▽ Bm formation: island arc tholeiite

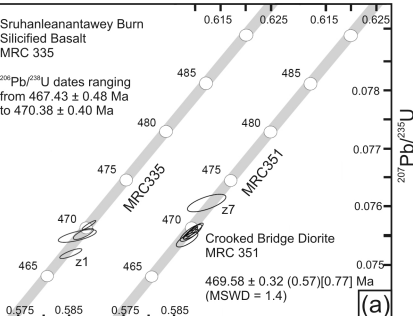
TVG samples: Upper arc

- ◇ G formation: rhyolite
- G & Bd formations: tuff/sandstone
- ★ Bd formation: alkali & OIB-like basalt



Sruhanleanantawey Burn
Silicified Basalt
MRC 335

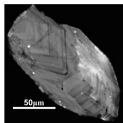
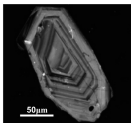
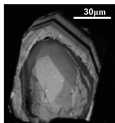
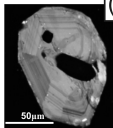
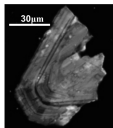
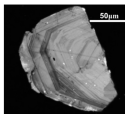
$^{206}\text{Pb}/^{238}\text{U}$ dates ranging
from 467.43 ± 0.48 Ma
to 470.38 ± 0.40 Ma



(a)

$^{206}\text{Pb}/^{238}\text{U}$

(b)



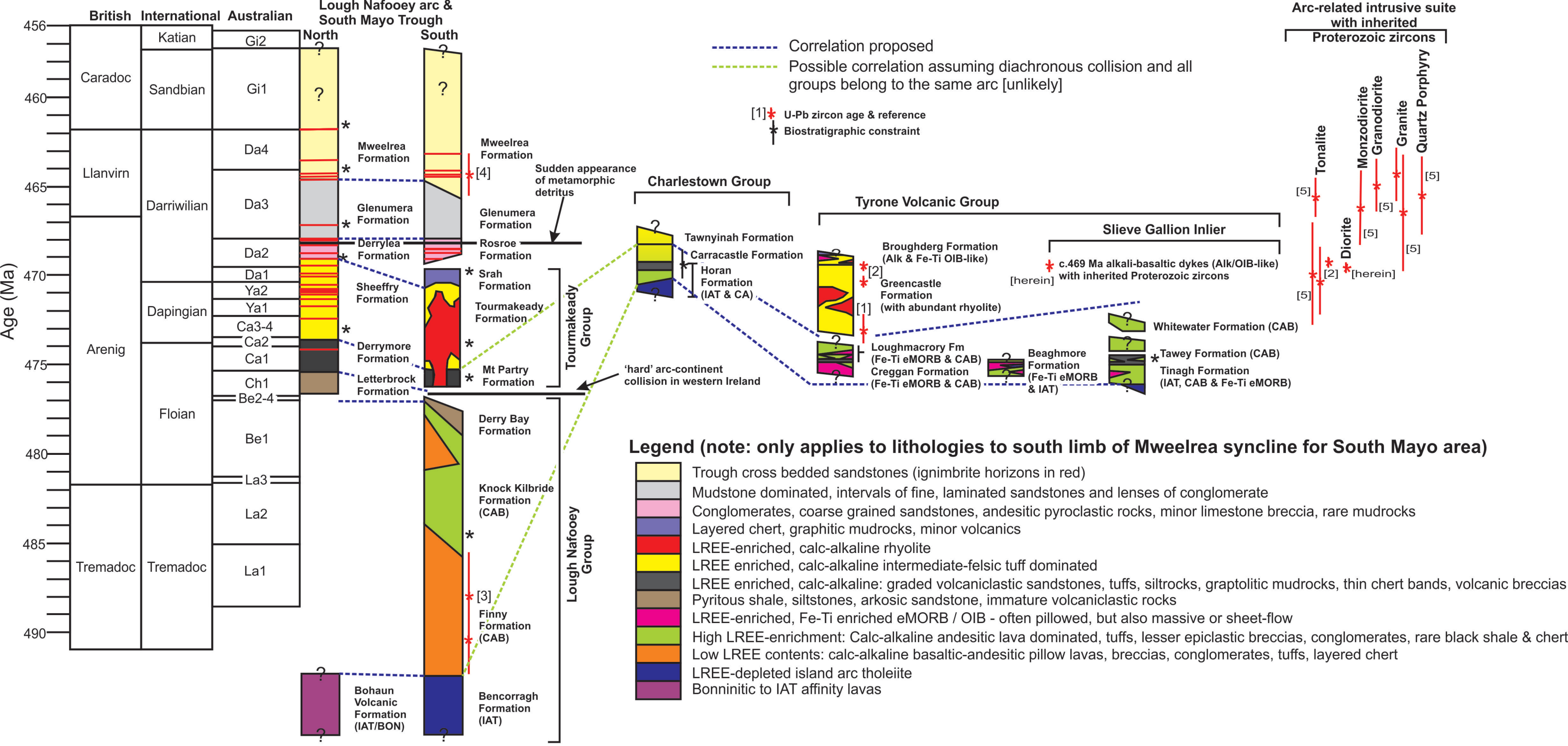


Table 1. *U-Th-Pb isotopic data.*

Sample *	Compositional Parameters						Radiogenic Isotope Ratios								Isotopic Ages					
	Th U	²⁰⁶ Pb* x10 ⁻¹³ mol	mol % ²⁰⁶ Pb*	Pb* 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	±
	†	§	§	§	§	#	**	**	††	**	††	**	††		§§	††	§§	††	§§	††
MRC 335																				
z1	0.745	2.4430	98.43%	20	3.21	1171	0.234	0.05647	0.24	0.5855	0.30	0.075192	0.092	0.813	470.70	5.22	467.99	1.14	467.43	0.42
z4	0.510	3.9679	99.65%	88	1.14	5293	0.157	0.07477	0.11	1.7917	0.23	0.173809	0.160	0.905	1062.04	2.19	1042.46	1.50	1033.14	1.53
z6	1.006	4.4897	99.62%	91	1.39	4917	0.315	0.05645	0.12	0.5891	0.19	0.075685	0.087	0.928	469.67	2.55	470.26	0.72	470.38	0.40
z11	0.738	0.3981	99.19%	39	0.27	2272	0.231	0.05646	0.21	0.5880	0.28	0.075530	0.102	0.761	470.14	4.74	469.58	1.06	469.46	0.46
z14	1.011	0.4433	97.90%	16	0.78	881	0.317	0.05638	0.45	0.5868	0.52	0.075494	0.114	0.689	466.92	10.00	468.84	1.96	469.24	0.52
MRC 351																				
z1	1.365	5.9864	99.83%	219	0.84	10805	0.428	0.05651	0.15	0.5886	0.21	0.075536	0.093	0.771	472.29	3.30	469.96	0.78	469.48	0.42
z2	1.216	4.0148	98.97%	33	3.60	1622	0.381	0.05653	0.14	0.5893	0.23	0.075612	0.127	0.880	472.94	3.03	470.45	0.88	469.94	0.57
z3	1.139	8.6618	99.86%	243	1.04	12538	0.357	0.05648	0.08	0.5886	0.18	0.075588	0.102	0.962	470.95	1.86	469.99	0.67	469.80	0.46
z6	1.108	1.8259	99.79%	162	0.33	8480	0.347	0.05649	0.10	0.5885	0.19	0.075553	0.112	0.927	471.42	2.15	469.90	0.72	469.59	0.51
z7	0.992	0.6754	97.96%	16	1.17	878	0.310	0.05641	0.43	0.5917	0.53	0.076073	0.161	0.681	468.27	9.57	471.95	1.99	472.71	0.74
z8	0.936	1.0390	99.11%	37	0.78	2041	0.294	0.05650	0.19	0.5886	0.30	0.075552	0.158	0.817	471.91	4.28	469.98	1.13	469.59	0.72
z9	0.910	1.5808	99.19%	41	1.07	2243	0.286	0.05652	0.22	0.5879	0.30	0.075440	0.144	0.738	472.39	4.83	469.51	1.13	468.92	0.65

* 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 ²⁰⁸Pb/²⁰⁶Pb ratio and ²⁰⁷Pb/²³⁵U 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: ²⁰⁶Pb/²⁰⁴Pb = 18.60 ± 0.80%;

²⁰⁷Pb/²⁰⁴Pb = 15.69 ± 0.32%; ²⁰⁸Pb/²⁰⁴Pb = 38.51 ± 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).

§§ 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.

Table A. Lithological units, sample numbers, major- (wt. %), trace- (ppm) and rare earth-element (ppm) geochemistry. Nd isotopic data also included. Grid References according to Irish Grid. εNd_t values calculated for age of 475 Ma. Trace and rare-earth element data to 2 decimals places from ICP-MS, otherwise from XRF (indicated by*). Sample MRC 335 is from Cooper et al. (2011).

Sample	Lithology [& Stratigraphic unit]	Grid Reference	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	Mn ₂ O ₄	P ₂ O ₅	¹⁴³ Nd/ ¹⁴⁴ Nd	2SE ±	εNd_t
SPH 525	Pillow lava [Derryganard Lavas]	2795066-386631	47.10	15.47	10.88	9.71	13.45	2.10	0.49	0.50	0.25	0.05	0.512519	7	+0.62
SPH 506	Hornblende-andesite [Windy Castle Lavas]	280365-388203	63.44	15.78	6.73	2.68	3.90	3.99	2.57	0.60	0.13	0.18			
SPH 511	Hornblende-andesite [Windy Castle Lavas]	279299-387267	59.95	14.63	10.26	5.00	4.91	2.50	1.88	0.60	0.13	0.14			
SPH 532	Pillow lava [Windy Castle Lavas]	10m N of SPH533	74.79	13.83	2.08	1.06	1.35	3.57	2.96	0.24	0.05	0.07			
SPH 534	Hornblende andesite [Windy Castle Lavas]	279992-387305	54.85	17.92	10.80	5.48	5.28	4.43	0.25	0.62	0.23	0.15			
SPH 528	Hornblende andesite [Windy Castle Lavas]	279556-386779	67.22	15.42	4.49	2.05	3.99	2.90	3.22	0.48	0.12	0.11			
SPH 530	Feldspathic andesite [Letteran Volcanics]	279636-386982	60.77	13.88	8.57	4.98	7.75	1.93	1.02	0.83	0.14	0.14	0.511896	8	-9.02
SPH 508	Aphanitic basalt [Mobuy Wood Basalts]	279400-387725	53.91	13.61	13.07	5.58	6.03	4.28	0.70	2.33	0.19	0.29	0.512528	5	+0.85
SPH 517	Basalt [Mobuy Wood Basalts]	278214-387525	52.48	14.47	12.91	4.91	8.08	4.17	0.45	2.14	0.08	0.30			
SPH 533	Vesicular lava [Mobuy Wood Basalts]	279822-387828	51.43	14.84	11.56	6.21	9.15	4.30	0.29	1.84	0.17	0.21	0.512623	6	+2.52
SPH 052	Chert [Tawey Fm]	278900-388100	80.99	11.16	1.38	0.98	0.05	2.93	2.29	0.18	0.02	0.03			
SPH 493	Lithic tuff [Tawey Fm]	278893-388169	66.56	15.51	5.06	2.76	2.00	4.72	2.60	0.59	0.07	0.13			
SPH 494	Tuff [Tawey Fm]	278949-387914	69.46	15.88	4.72	2.29	1.07	2.56	3.30	0.52	0.08	0.12			
SPH 496	Siltstone [Tawey Fm]	279033-387857	84.99	7.88	2.40	1.69	0.05	0.08	2.62	0.24	0.03	0.04			
SPH 502	Microdiorite [Lower Whitewater Fm]	279787-389513	63.89	15.17	5.73	4.26	3.55	4.08	2.58	0.57	0.07	0.11			
SPH 467	Andesitic lava [Whitewater Fm]	278004-389914	65.53	14.73	5.63	4.49	4.05	1.96	2.81	0.56	0.12	0.11	0.511716	6	-12.68
SPH 469	Crystal tuff [Whitewater Fm]	278169-389841	64.38	14.73	5.96	4.63	4.61	1.34	3.53	0.59	0.12	0.11			
SPH 470	Tuff [Whitewater Fm]	278445-389813	66.42	14.33	5.31	4.69	3.45	2.74	2.32	0.54	0.10	0.10	0.51166	18	-13.86
SPH 471	Mineralized tuff [Whitewater Fm]	278445-389813	74.37	14.59	4.91	1.10	0.27	0.09	4.01	0.54	0.02	0.10			
SPH 472	Basaltic andesite/andesite [Lower Whitewater Fm]	278861-389838	62.53	15.38	6.31	4.96	4.55	2.44	2.98	0.63	0.11	0.11	0.511737	6	-12.86
SPH 485	Tuff [Whitewater Fm]	278861-389838	65.12	14.99	5.95	4.47	3.61	3.58	1.49	0.57	0.11	0.11			
SPH 486	Tuff [Whitewater Fm]	278917-389748	67.61	13.92	4.77	4.39	5.42	1.84	1.38	0.50	0.07	0.10			
SPH 488	Andesitic lava [Whitewater Fm]	278466-389725	65.83	14.87	5.84	5.06	2.34	2.25	3.01	0.56	0.14	0.11			
SPH 025	Feldspathic Basaltic rock [Intrusive?]	278950-387950	51.88	14.50	18.28	5.81	1.05	3.66	0.20	3.84	0.15	0.62			
MRC 335	Feldspathic Basaltic rock [Intrusive?]	278950-387950	51.95	14.05	17.82	5.66	1.99	3.90	0.16	3.53	0.38	0.56			
SPH 513	Slieve Gallion granite [Intrusive]	279010-386335	73.88	13.51	3.12	1.20	1.76	4.22	1.78	0.39	0.07	0.08			

Table 1. continued

[illegible]