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Age and geochemistry of the Charlestown Group, Ireland: implications for the Grampian orogeny, its mineral potential and the Ordovician timescale

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ABSTRACT

Accurately reconstructing the growth of continental margins during episodes of ocean closure has important implications for understanding the formation, preservation and location of mineral deposits in ancient orogens. The Charlestown Group of county Mayo, Ireland, forms an important yet understudied link in the Caledonian-Appalachian orogenic belt located between the well documented sectors of western Ireland and Northern Ireland. We have reassessed its role in the Ordovician Grampian orogeny, based on new fieldwork, high-resolution airborne geophysics, graptolite biostratigraphy, U-Pb zircon dating, whole rock geochemistry, and an examination of historic drillcore from across the volcanic inlier. The Charlestown Group can be divided into three formations: Horan, Carracastle, Tawnyinah. The Horan Formation comprises a mixed sequence of tholeiitic to calc-alkaline basalt, crystal tuff and sedimentary rocks (e.g. black shale, chert), forming within an evolving peri-Laurentian affinity island arc. The presence of graptolites *Pseudisograptus* of the *manubriatus* group and the discovery of *Exigraptus uniformis* and *Skiagraptus gnomonicus* favour a latest Dapingian (i.e. Yapeenian Ya 2 / late Arenig) age for the Horan Formation (equivalent to c. 471.2-470.5 Ma according to the timescale of Sadler et al., 2009). Together with three new U-Pb zircon ages of 471.95-470.82 Ma from enclosing felsic tuffs and volcanic breccias, this fauna provides an important new constraint for calibrating the Middle Ordovician timescale. Overlying deposits of the Carracastle and Tawnyinah formations are dominated by LILE- and LREE-enriched calc-alkaline andesitic tuffs and flows, coarse volcanic breccias and quartz-feldspar porphyritic intrusive rocks, overlain by more silicic tuffs and volcanic breccias with rare occurrences of sedimentary rocks. The relatively young age for the Charlestown Group in the Grampian orogeny, coupled with high Th/Yb and zircon inheritance (c. 2.7 Ga) in intrusive rocks indicate the arc was founded upon continental crust (either composite Laurentian margin or microcontinental block). Regional correlation is best fitted to an association with the post-subduction flip volcanic/intrusive rocks of the Irish Caledonides, specifically the late-stage development of the Tyrone Igneous Complex, intrusive rocks of Connemara (western Ireland) and the Slishwood Division (Co. Sligo). Examination of breccia textures and mineralization across the volcanic inlier questions the previous porphyry hypothesis for the genesis of the Charlestown Cu deposit, which are more consistent with a volcanogenic massive sulfide (VMS) deposit.

1. Introduction

Accurately reconstructing the growth of continental margins during episodes of ocean closure has important implications for understanding the formation, preservation and location of mineral deposits in ancient orogens (van Staal, 2007; Rogers et al., 2007; Herrington and Brown, 2011; Herrington et al., 2017). Orthomagmatic and volcanogenic massive sulfide (VMS) deposits may be preserved in accreted oceanic tracts or rifted island arcs (Herrington et al., 2005; Piercey, 2011), whereas mesothermal gold mineralization typically forms during the later stages of orogenesis associated with orogenic collapse and deep-seated crustal structures (Kerrich et al. 2005, Herrington and Brown, 2011). An integrated approach using detailed field mapping, whole rock geochemistry, U-Pb zircon geochronology and biostratigraphy forms a powerful tool for unraveling complex orogens, and may highlight the prospectivity of accreted terranes for different styles of mineralization.

The Caledonian-Appalachian orogenic belt records the opening of the Iapetus ocean during the late Proterozoic (c. 565 Ma: van Staal et al., 2014; **Fig. 1a**) and the events associated with its closure during the early Paleozoic (Dewey, 2005; Draut et al., 2004; Chew et al., 2010; Cooper et al., 2013). The Grampian event preserves the first major phase of this closure in the British and Irish Caledonides, and was associated with the accretion of ophiolites, island arcs and microcontinental blocks to the Laurentian margin between the Late Cambrian and Middle Ordovician (Dewey and Shackleton, 1984; Draut et al., 2004; Dewey and Mange, 1999; Cooper et al., 2011; Chew et al., 2008, 2010; Hollis et al., 2012). The Grampian is broadly equivalent to the Taconic event of the Canadian Appalachians (van Staal et al., 2007; **Fig. 1b-c**), with VMS deposits that developed in oceanic and arc/backarc settings (Piercey, 2007) emplaced during three phases of arc/ophiolite accretion (van Staal et al. 2007; 2014).

Figure 2 shows the broad evolution of the Grampian orogeny as it applies to the current region of study, based on the three equivalent and well-documented arc/ophiolite accretion events in the Newfoundland Appalachians (modified after van Staal et al. 2007; 2014; Chew et al. 2010; Hollis et al. 2012). In the British and Irish Caledonides, the accretion of early c. 510-495 Ma suprasubduction affinity oceanic crust (e.g. Deer Park Complex, Highland Boundary ophiolite, Chew et al., 2010) occurred shortly after its formation, most likely onto outboard blocks of Laurentian-affinity microcontinetal crust (**Fig. 2a**; see Chew et al., 2010). As ocean closure continued, subduction was associated with the development of the juvenile c. 490-477 Ma Lough Nafooey arc system (i.e. Lough Nafooey Group: Ryan et al., 1980; Draut et al., 2004; Chew et al. 2007; Ryan and Dewey, 2011; McConnell et al., 2009; **Fig. 1a, Fig. 2b**), with its accretion to the Laurentian margin constrained to c. 484-477 Ma (Draut et al., 2004; Hollis et al., 2013a). Syncollisional volcanism during the deposition of the c. 477-468 Tourmakeady Group (**Fig. 2c**) was contemporaneous with Grampian deformation and metamorphism (c. 475-465 Ma; Friedrich et al., 1999a,b; Chew et al., 2008). Following a reversal in subduction polarity (from south to northward directed), magmatic activity in western Ireland is recorded by the eruption of c. 464 Ma ignimbrites of the Murrisk Group (Dewey and Mange, 1999) and the continued emplacement of granitic rocks across the Connemara terrane (Friedrich et al. 1999a; **Fig. 1a, Fig. 2d**).

The c. 484-470 Ma Tyrone and Ballantrae arc-ophiolite complexes most likely record the development of an arc system distinct to that of western Ireland (Hollis et al., 2012, 2013ab; Stone, 2014; **Fig. 1a, Fig. 2b, d**). In the west of Ireland, the Lough Nafooey arc developed from c. 490 Ma above a south-dipping subduction zone away from the Laurentian margin (**Fig. 2b**), whilst the Tyrone and Ballantrae arcs are much younger, were accreted later (**Fig. 2d**; Hollis et al., 2013a), and show evidence for widespread arc-rifting and VMS-style mineralization (Hollis et al., 2014). The accretion of these younger arcs to outboard fragments of microcontinental crust (such as the Tyrone Central Inlier and Midland Valley block; prior to c. 470 Ma in Tyrone) was followed by the emplacement of continental arc intrusive rocks across the composite Laurentian margin until at least c. 464 Ma in Ireland (Cooper and Mitchell, 2004; Flowerdew et al., 2005; Cooper et al., 2011) and c. 457 in Scotland (Oliver et al., 2000, 2008; Carty et al., 2013). Remnants of peri-Laurentian affinity island arcs also occur along the Iapetus Suture zone south of the Southern Uplands – Down-Longford accretionary prism, such as at Grangegeeth (McConnell et al., 2010) (**Fig. 1a**).

The Charlestown Group, exposed across approximately 45 km^2 of Co. Mayo, Ireland (**Fig. 3**), forms an important link between the well documented Grampian rocks of western Ireland (Clift and Ryan, 1994; Dewey and Mange, 1999; Draut et al., 2002, 2004) and Northern Ireland (Hutton et al., 1985; Cooper et al., 2008; Chew et al., 2008; Draut et al., 2009; Cooper et al., 2011; Hollis et al., 2012). Previous work has largely been restricted to field mapping and graptolite biostratigraphy (e.g. Cummins, 1954; O'Connor, 1987; Dewey et al., 1970), and consequently it was not clear whether the Charlestown Group formed during the syncollisional stage of the Lough Nafooey arc system (broadly correlating with the Tourmakeady Group; see review by Chew, 2009), or as part of the younger Tyrone arc system (Hollis et al., 2013a). The latter is considered prospective for VMS mineralization (Clifford et al., 1992; Peatfield, 2003; Hollis et al., 2014, 2016) and its accretion to the Laurentian margin has been implicated in subsequent mesothermal Au mineralization in the overlying Dalradian Supergroup at

Curraghinalt (Earls et al., 1996; Parnell et al., 2000; Herrington and Brown, 2011; Rice et al., 2016).

Here we present the results of new fieldwork, whole rock geochemistry, airborne geophysics from the Tellus Border project, and the first U-Pb zircon ages for the Charlestown Group. In addition, we have refined biostratigraphic age constraints based on a new graptolite locality and a reexamination of a fauna collected by Cummins (1954). This work has important implications for understanding the evolution of the Grampian orogeny and the calibration of the Middle Ordovician timescale. Implications for base metal mineralization in County Mayo are discussed based on examination of drillcore from across the volcanic inlier.

2. Previous work

Although the Charlestown Group forms an integral part of the Irish Caledonides, published and unpublished research is limited to a handful of studies (Cummins, 1954; Charlesworth, 1960; Dewey et al., 1970; O'Connor and Poustie, 1986; O'Connor, 1987; Long et al., 2005). The Charlestown Group is unconformably overlain to the east by Silurian cover sequences, which together form the Charlestown Inlier, and bounded to the south, north and west by Carboniferous rocks (**Fig. 3a**). Cummins (1954) originally divided the sequence into an older tuffaceous group with agglomerates, lavas, fine tuffs interbedded with cherty graptolitic shales; and the structurally lower felsic group to the south, with subsidiary tuffs and lavas. An Arenig age was obtained for the lower part of the Charlestown Group (Cummins, 1954), later refined by Dewey et al. (1970) to the Yapeenian stage of the Australian sequence. Charlesworth (1960) provided the first detailed structure and stratigraphy of the succession, and based around new exposure O'Connor (1987 unpublished PhD thesis) reassessed the stratigraphy and divided the succession into three formations (see **Fig. 3a**), renamed by Long et al. (2005):

(i) Horan Formation (lowest unit – formerly known as the Airport Mixed Formation), ~630 m thick, characterized by minor sedimentary rocks (i.e. red cherts, siltstones and silicified black shales), extrusive basalts, spillites and mixed tuffs which crop out along the hinge of the Lurga Anticline. The upper boundary of this formation is defined as the southern southeast dipping contact of the pyroxene diorite, as shown in **Figure 3a**.

(ii) Carracastle Formation (formerly known as the Carracastle Andesitic Formation), ~290 m thick, dominated by andesitic tuffs and flows, with coarse volcanic breccias. The formation is characterized by a general lack of sedimentary rocks, a dominance of pyroxene-feldspar porphyry over quartz-feldspar porphyry (QFP) derived lithologies, and the presence of thick ungraded volcanic breccias which are almost exclusively andesitic.

(iii) Tawnyinah Formation (formerly known as the Cloonnamna Formation), ~300 m thick, dominated by more silicic (crystal, ash and lapilli) tuffs and volcanic breccias. Some sedimentary rocks (black silty tuffs) have been observed in drillcore and rare occurrences of chert in outcrop. On the southern limb of the Lurga Anticline, the formation is silicified, chloritized and/or sericitised due to the formation of the Charlestown Cu deposit.

Nowhere are the contacts between the formations currently exposed, the boundary between the Carracastle and Tawnyinah is defined by O'Connor (1987) as the first occurrence of quartz-feldspar crystal tuffs and light coloured silicic ashes, an observation presumably based on drillcore evidence in addition to surface mapping.

A detailed account of key exposures and field relationships across the Charlestown Group are given in O'Connor (1987). O'Connor and Poustie (1986) recorded the presence of abundant breccia units at Charlestown associated with quartz-feldspar porphyritic rocks, with mineralization hosted within intrusive units showing sheet-like morphologies. Four breccia types were described (**Fig. 4**) with their 'type 1' consistent with shallow intrusions of felsic magmas and unconsolidated mudrocks or tuffs, forming brecciated intrusive rocks injected with unconsolidated sediment (by definition forming peperites). These breccias are found along the margins of the quartz-feldspar porphyry units. In one case, chalcopyrite mineralization directly associated with the development of this peperitic brecciation. In other cases, silicic alteration appears to be always associated with these high-level porphyry units, whilst the three other types of breccia relate to autobrecciation or hydraulic fracturing during magma emplacement (**Fig. 4**).

Sub-economic mineralization at Charlestown is developed within and confined to the hydrothermally altered brecciated sill-like bodies of felsic porphyry. The defined resource is 3 Mt grading 0.6% Cu with subsidiary resources of Zn-Pb-Ba-Ag mineralization (O'Connor and Poustie, 1986; **Fig. 3a**). The alteration is described as largely comprising concentric zones of silicic, sericitic, sericitic-chloritic and chloritic, with clay-rich zones associated with sericitic alteration (**Fig. 4**). Also recorded are poorly constrained zones of hematization. Mineralization is largely spatially linked to the zones of silicic alteration, but is also described in the sericitic alteration zone. Chalcopyrite, sphalerite and galena are the dominant minerals of economic interest, mainly developed in fractures in brecciated silicic-altered rocks. This fracturing type constitutes O'Connor and Poustie's (op cit.) 'type 4 breccia' which the authors link to processes of hydraulic fracturing. Widespread pyrite represents the earliest phase of sulfide mineralisation, followed by successively chalcopyrite,sphalerite and barite. Galena with barite represents the last phase of mineralization.

Previous geochemical data from the Charleston Group are limited to major element data plus Zr, Rb, Sr, Cu and Zn, with trace elements Ni, Y, Nb, Th, U and Pb frequently near or below detection levels (O'Connor, 1987). No rare earth element (REE) geochemistry data prior to our work have been published.

3. Sampling and methods

Major exposures described by O'Connor (1987) were visited during 2012 and 2013, with additional traverses made across the well exposed Knock Airport section of the pyroxene diorite and uppermost Horan Formation (**Fig. 3a**, locality C). The stratigraphy through this sequence (from 146991E 296428N to 146949E 296469N Irish Grid) is described below and shown in **Figure 5**. Samples were collected from this section and elsewhere for petrography, whole rock geochemistry (**Fig. 2b**), U-Pb zircon CA-ID-TIMS geochronology, and biostratigraphy.

Of 46 samples collected from the Charlestown Group, 18 were characterized by optical microscopy and SEM analysis. These included samples from three diamond drillholes through the Charlestown Group, which were logged to better understand the nature of the hydrothermal alteration and mineralization across the inlier. Core from these holes (2137-14, 2137-16 and 2137-17: **Fig. 3b**) is stored at the GSI core shed, Dublin, summarized in Section 4, and described in detail in Stobbs (2013 unpublished MSci thesis).

3.1. Tellus Border Geophysics

The Tellus Border project (Hodgson and Ture, 2014) was an as an EU INTERREG IVA-funded regional mapping project collecting geo-environmental data on soils, water and rocks across the six border counties of Ireland, continuing the analysis of existing data in Northern Ireland (Young and Donald, 2013) to produce seamless data coverage over the island of Ireland. The geophysical survey was completed in 2012 and was flown at 200m line spacing orientated towards 345°. Magnetic field (**Fig. 3b**), electromagnetic conductivity, and radiometric (Th, U, K) data were acquired (Hodgson and Ture, 2014). An extension of the Tellus Border EU project area to cover the adjacent area of the Charlestown Group was co-funded by Oriel Selection Trust Ltd as part of a mineral exploration programme.

3.2 Biostratigraphy

Two principal collections of Ordovician fossils have been studied from the Charlestown Inlier. The first of these was made and reported on by Cummins (1954). Part of this initial collection, preserved in the Sedgwick Museum, Cambridge, was reexamined. The second collection was made in 2012 and 2013 by the authors, from a new temporary exposure immediately north of Knock International Airport (graptolite locality C in **Fig. 3a**) within the upper Horan Formation. The base of the Horan Formation is not seen at Charlestown. This locality is thought to lie close to the original site of Cummins (Irish Grid approx. 147900E 295900N, locality A in **Fig. 3a**), which was not located during recent fieldwork. Locality B of Cummins (1954) has yielded only fragmentary and indeterminable graptolites.

3.3 U-Pb Geochronology

Four samples (KGC1-3,5) were selected for LA-ICPMS U-Pb zircon geochronology at the Natural History Museum, London, to constrain the age of the Horan Formation. Samples were processed using standard techniques at Trinity College Dublin by Quentin Crowley who produced heavy mineral separates. Zircon grains were hand-picked and mounted in epoxy resin. The grains were sectioned and polished. Reflected and transmitted light photomicrographs and cathodoluminescence (CL) SEM images were prepared for all zircon grains. The CL images were used to decipher the internal structures of the sectioned grains and to target specific areas within the zircon crystals.

The grains were initially analyzed in the Department of Mineralogy, Natural History Museum, London, using an ESI New Wave UP193FX laser ablation system coupled to an Agilent 7500cs quadrupole-based ICP-MS. Samples and standards, mounted together, were ablated in an air-tight sample chamber flushed with either Ar or He for sample transport. The samples were rastered up and down lines, using a constant raster speed for each analysis. Data were collected in discrete runs of 20 analyses, comprising 12 unknowns bracketed before and after by 4 analyses of the standard zircon 91500 (Wiedenbeck et al., 1995). Data were collected for up to 180 s per analysis with a gas background taken during the initial ca. 60 s. Background and mass bias corrected signal intensities and counting statistics were calculated for each isotope. Concordia age calculations, weighted averages, intercept ages and plotting of concordia diagrams were performed using Isoplot/Ex rev. 2.49 (Ludwig, 2001). For each analysis, time resolved signals were collected and then carefully studied to ensure that only flat stable signal intervals were included in the age calculations. The detailed analytical procedure is outlined in Jeffries et al. (2003). Data are presented as **Supplementary Material.**

Following LA-ICPMS screening, zircons were selected and removed from epoxy mounts for high-precision chemical abrasion isotope dilution thermal ionization mass spectrometry (CA-ID-TIMS) analysis at the NERC Isotope Geosciences laboratory, British Geological Survey, Keyworth. The methodology for analytical procedure, instrument conditions, corrections and data reduction follows that outlined in detail in Tapster et al., (2016). The key features for this study are that: (1) zircons removed from the epoxy mounts were annealed at 900ºC for 60 hrs and leached in high-pressure vessels in 29N HF for 10-12 hrs at 180ºC as part of the chemical abrasion technique to reduce open system behavior within the crystals (Mattinson, 2005); (2) Zircons were spiked with the mixed ($\pm^{202}$Pb)–^{205}Pb–^{233}U–^{235}U EARTHTIME tracer solutions (ET535; ET2535; Condon et al., 2015; Mclean et al., 2015); (3) ^{206}Pb/^{238}U dates were corrected for initial Th disequilibrium with a $Th/U_{(melt)} = 3.5$ (±1; 1σ). Uncertainties on the best age interpretations are presented in the form ± x/y/z (2σ), where x = analytical uncertainty only, permitting comparison with data sets using the EARTHTIME tracers; y = analytical and tracer calibration uncertainty for comparison with U-Pb data sets that do not use EARTHTIME tracers; z = total uncertainty including U decay constants for comparison with dates yielded by other radio-isotopic systems. Data are presented in **Table 1**.

3.4 Geochemistry

Fifteen samples from representative units across the Charlestown Group were analyzed for whole rock geochemistry at the Natural History Museum, London. Samples were collected from field localities and diamond drillcore. Element concentrations were obtained by fusing whole rock powders with lithium metaborate flux and subsequent digestion by concentrated HF, HNO_3 and $HClO_4$. This method ensured all zircon and other resistive minerals were destroyed. Solutions were analyzed by ICP-AES (Thermo iCap 6500 Duo) for major and minor elements and ICP-MS (Agilent 7700x) for trace element analysis. All samples selected for geochemical analysis were also characterized by X-Ray Diffraction (XRD) at the Natural History Museum, London. Additional information is presented in Stobbs (2013), with geochemical data included as **Supplementary Material**.

4. Results

4.1. Geology of the Charlestown Group

The geology of the Charlestown Group has been comprehensively described by O'Connor (1987), as summarized in section 2 above. Here we supplement that account with new observations from Tellus Border geophysics (**Fig. 3b**), the well exposed Knock Airport section of the Horan Formation (**Fig. 5**), diamond drillcore, and key outcrops in the Carracastle and Tawnyinah formations. These results have significant implications for understanding the genesis of the Charlestown Cu deposit.

4.1.1 Tellus Border Geophysics

Due to the generally poor exposure of the Charlestown Group the new Tellus Border geophysical data provides new insight into the structure of the inlier and its extension beneath Carboniferous cover sequences (**Fig. 3b**). The Charlestown Group shows a distinctive pattern in the total magnetic intensity (TMI) data and it can be clearly extrapolated to extend under Carboniferous cover for at least 4 km to the NE and 10 km to the SW. Only the SE limb of the mapped Horan Formation appears to be highly magnetic, coincident to where mafic rocks are well exposed along road cuttings. Significant magnetite was confirmed in samples CT-114 and 12-0339 by XRD. The NE limb of the Horan Formation dominated by crystal tuff and sedimentary rocks (**Fig. 5**) has a low magnetic signature, as do the Carracastle and Tawnyinah formations. Drillhole data suggest that several small TMI highs throughout these formations correspond either to localized occurrences of mafic rocks (e.g. drillhole 2137-14, see following) or intrusive quartz-feldspar porphyry (QFP) units (such as those SW of drillholes 2137-14 and 2137-17, and near the Charlestown Cu deposit: **Fig. 3b**). Two circular magnetic features approximately 2 km by 4 km located to the east of the Charlestown Group most likely represent Late Caledonian intrusions concealed under Carboniferous rocks. These are sited on the southerly extension of the deep-seated Donegal Lineament. Deep seated crustal lineaments are well documented across the north of Ireland, influencing Neoproterozoic sedimentation patterns, and the location of Proterozoic to Late Caledonian magmatism and mineral deposits (Cooper et al., 2013).

4.1.2 Breccia types, hydrothermal alteration and mineralization

The Knock Airport section of the Horan Formation is dominated by banded and stratified tuff interbedded with finely laminated, silicified black mudstones (**Fig. 5**). Local sills of pyroxene diorite locally intrude the stratigraphy and it is evident these intrusions are both synvolcanic and high-level. Intermediate crystal tuffs of the Horan Formation occur where these magmas were locally erupted.

The QFP units throughout the Charlestown stratigraphy most likely represent the high-level intrusive equivalent of the more silicic tuffs. The development of peperitic textures in the Charlestown QFP units was observed in a number of places exposed along the Knock Airport road, confirming the subvolcanic high-level nature of these units and the cause of the type 1 brecciation described by O'Connor and Poustie (1986; **Fig. 4**). The unit observed in the airport road cutting is largely unmineralized, although fragments of mudrocks rarely contain disseminated pyrite. The QFP unit shows epidote alteration in a number of places.

A felsic crystal tuff unit is exposed in the road cross-section adjacent to an isolated exposure of a pillowed basaltic unit (**Fig. 3b**). Chloritic alteration and the development of minor hematite is evident in hand specimen (sample CT113). In thin section, the presence of hematite and barite was confirmed within chlorite-rutile aggregates forming infilling to sericite-altered feldspar crystal tuff. SEM analysis indicated highly anomalous copper (>200 ppm) in the Fe-oxide masses (**Fig. 6a**).

The autobrecciated QFP intrusives of the Carracastle formation (Fig. 4) show distinct evidence for hydrothermal alteration. In thin section (CT206), abundant irregular voids are developed between highly altered pyroxene and feldspar phyric fragments with the voids infilled by cryptocrystalline quartz and barite, suggesting that hydrothermal silica, calcite and barite infilled the autobreccia (likely type 3 breccia; **Fig. 6b**).

Only three drillholes from the sub-surface drilling have been preserved. These three cores all show evidence for extensive hydrothermal alteration. Drillhole 2137-14 (**Fig. 3b**) comprises predominantly chert and clastic rocks interbedded with felsic tuffs within the Carracastle Formation, and is located near to the Knock Airport runway. The unit here is variably silicified, hematized and chloritized. Samples of volcanic breccia (possibly type 2 or type 3; 12-0326) and a vesicular mafic volcanic rock (12-0327) are characterized by quartz, chlorite, sericite and rutile with additionally epidote and calcite present in sample 12-0327. No ore minerals were recorded in this material.

Core from drillhole 2137-16 forms part of the lowermost Carracastle Formation (**Fig. 3b**) and is dominated by a chloritized and epidote-altered thick mafic intrusion occurring structurally below an overlying chloritized crystal tuff. Bleaching and carbonate alteration is present throughout the hole, but no sulfides were observed.

Rocks close to the contact between the Carracastle and Tawnyinagh formations were tested by drillhole 2137-17 (**Fig. 3a**), and largely comprise an assemblage of altered clastic rocks and tuffs cut by minor intrusions carrying disseminated pyrite mineralization. Two samples taken from the core that contained significant base-metal mineralization (12-0336 and

12-0341) were examined in thin section. Sample 12-0336 was shown to contain abundant vugs infilled by quartz and barite. Disseminations of pyrite-sphalerite-galena are seen at the margins of the vugs with overgrowths of anglesite within in the vug (associated with barite and quartz). Farther down the hole, sample 12-0341 was taken from a thin quartz veinlet (5mm) containing intergrown pyrite, chalcopyrite, sphalerite and minor galena. In reflected light, the sphalerite is characterized by chalcopyrite disease.

4.2 Biostratigraphy

The Cummins collection was originally taken from a roadside quarry in the Horan Formation, ~1 mile SSW of Lurga crossroads (locality A, **Fig. 3a**). This quarry was not located and is believed to have been destroyed by road development in the area. Cummins (1954) reported the species in **Table 2**, with the names of the graptolites as revised by Bulman. Dewey et al. (1970) updated the identifications (**Table 2**). In addition, the brachiopods Lingulella and Acrotreta cf. sagittalis (Salter) were identified by Cummins (1954), who gave the age as Arenig. Dewey et al. (1970, p. 30) refined this by restricting age to the Yapeenian Stage of the Australasian succession, and to the British Didymograptus hirundo Zone and the North American Isograptus caduceus Zone.

The Knock Airport collection obtained here is similar to, but not identical to that of Cummins (1954). All the taxa listed below were described by Rushton (2014), who reported that although the graptolites show no observable tectonic deformation, they are mostly fragmentary and strongly flattened by compaction, and accordingly presented difficulties for identification and interpretation.

Pseudisograptus sp. of the *manubriatus* (T.S. Hall) species group (**Fig. 7a**)
Yutagraptus? *v-deflexus* (Harris) (**Fig. 7b**)
Arienigraptus? sp. (**Fig. 7e**)
Isograptus caduceus? cf. *nanus* Ruedemann. (**Fig. 7d**)
Clonograptus aff. *timidus* Harris & Thomas?
Dichograptid and dendroid? fragments
Didymograptus (*Expansograptus*) spp. (fragments), including *D.* (*E.*) aff. *nitidus* (Hall)
Exigraptus uniformis Mu (**Fig. 7g-i**)
Pseudophyllograptus sp.
Skiagraptus gnomonicus (Harris & Keble) (**Fig. 7j-k**)

Tetragraptus spp.

Brachiopods: two species of lingulellids

According to Rushton (2014), the presence of Pseudisograptus of the manubriatus group, with Exigraptus uniformis and Skiagraptus gnomonicus, support Dewey et al.'s interpretation of a Yapeenian age (= latest Dapingian of the international scale and late Arenig in the British regional standard; Cocks et al. 2010). Some of the graptolites identified in the fauna from Knock Airport, e.g. Y.? v-deflexus and Skiagraptus, resemble species that extend up from the Yapeenian into the lowest part of the overlying Darriwilian Stage (= latest Arenig), but key indicators of the Darriwilian, such as Paraglossograptus tentaculatus and species of Undulograptus, are not present. The Knock Airport fauna is therefore considered to be referable to the upper Yapeenian (Ya2) substage of the Australasian succession (Rushton, 2014).

4.3 U-Pb Geochronology

Four samples (KGC1-3,5) were chosen for age determination from the fossiliferous section of the Horan Formation, NW of the airport runway (Locality C in **Fig. 3**). Three samples were collected from the host stratigraphy (KGC2: banded olive to dark green tuff with mudstone rip up clasts; KGC3: chloritized quartz feldspar porphyry; KGC5: very coarse volcanic breccia) while one sample was taken from the pyroxene diorite intrusive body exposed at the base of the section (KGC1; **Fig. 5**). Samples KGC3 and KGC5 were not collected from the section illustrated in **Figure 5**, but were collected from higher in the stratigraphy (Irish Grid 47467-96761 & 47524-96748).

LA-ICPMS results

Initial LA-ICPMS U-Pb analysis yielded Concordia ages ranging from 466 ± 5 Ma to 460 ± 12 Ma (**Supplementary Figure 1**), yet with high MSWDs and ages significantly younger than the biostratigraphic age according to Sadler & Cooper (2009; see discussion) that are likely to be induced by a component of Pb loss within the zircon populations However, analysis using laser-ablation did allow the cores of a number of the zircons to be analysed. Only two inherited grains were identified - both from sample KGC1 (coarse grained epidote-altered diorite). These yielded $^{206}Pb/^{238}U$ ages of c. 2765 and 2620 Ma. Given the broad spread of errors in the derived dates, and the potential to solve discussion concerning the fossil-derived biostratigraphic age, it was decided to analyse the same zircons using CA-ID-TIMS methods.

CA-ID-TIMS results

Weighted mean dates inclusive of all single analyses for each sample, demonstrate MSWDs in excess of that statistically acceptable at the 95% CI (confidence interval) for the given number of analyses. This indicates scatter within dates in excess of analytical precision that is likely to be derived from xenocrystic- antecrystic zircon and residual open system behavior (as identified within the LA-ICPMS data) following the chemical abrasion procedure despite all data points overlapping with Concordia within their given uncertainty. These factors yield dates older and younger than the emplacement age of interest respectively. Our preferred age interpretations for the specific units are derived from weighted mean dates of the youngest populations with statistically acceptable MSWDs. These correspond to the following dates - KGC1 pyroxene diorite: 469.11 ± 0.61/0.63/0.80 (n=4; MSWD=0.12); KGC2 banded tuff: 471.95 ± 0.22/0.25/0.56 (n=4; MSWD=1.27); KGC3 quartz-feldspar porphyry: 471.26 ± 0.20/0.29/0.58 (n=5; MSWD=1.13); KGC5 volcanic breccia: 470.82 ± 0.18/0.27/0.57 (n=4; MSWD=1.35) (**Fig. 8**).

4.4 Geochemistry of the Charlestown Group

The geochemistry of the Charlestown Group is presented in **Figures 9 and 10**. Due to the extensive hydrothermal alteration present across the Charlestown Group and subsequent greenschist facies metamorphism, only elements demonstrated to be immobile under such conditions should be used to elucidate petrogenesis. It has been recognized for some time that most of the major elements, such as SiO_2, K_2O, Na_2O, CaO, MgO, Fe_2O_3, and a number of trace elements (e.g. Sr, Rb, Ba, Cu, Pb, Zn) are easily mobilized by hydrothermal activity (MacLean, 1990). Only Al_2O_3, TiO_2, Th, Cr, Co, V, Sc, Ga, the high field strength elements (HFSE: Zr, Nb, Y, Hf, Ta), and the rare earth elements (± Eu) will remain immobile under such conditions (Pearce and Cann, 1973; Wood, 1980; MacLean, 1990). Mobile elements are used here to determine the intensity and style of hydrothermal alteration (see O'Connor, 1987 for a more detailed account), whereas immobile elements were used to determine tectonic setting and the magmatic evolution of the Charlestown Group.

Immobile element geochemistry: Samples analyzed from the Horan Formation and lower part of the Carracastle Formation include basalts which range from tholeiitic (CT114, 12-0327) to calc-alkaline in affinity (CT112) according to the classification scheme of Barrett and MacLean (1999; also Ross and Bédard, 2009; **Fig. 9a**). Chondrite normalized rare earth element (REE) profiles are variable for mafic volcanic rocks (La/Yb 1.05 to 10.0), but steep for all samples of crystal tuff regardless of composition (La/Yb 10.8-14.7; **Fig. 10a-b**). Samples are typically light rare earth element (LREE)-enriched and have flattish heavy rare earth element (HREE) profiles. A tholeiitic Zr/Y ratio of 3:1 is exhibited by the basaltic intrusion in drillhole 2137-16 (Sample 12-0339), similar to the extrusive basalts (2.7 to 5.6; CT112 and CT114). These three samples also have similar chondrite-normalized extended REE-profiles (**Fig. 10b**). A mafic volcanic breccia from drillhole 2137-14 (sample 12-0326) is the only rock which shows LREE-depletion relative to the HREE (**Fig. 9d**). Although all mafic rocks analyzed from the Charlestown Group plot within the calc-alkaline basalt field of Wood (1980; **Fig. 9g**), this reflects the high Th/HFSE ratios present in the samples analyzed (**Fig. 9e**) – possibly a consequence of crustal contamination (see discussion). Mafic rocks from Charlestown straddle the backarc, transitional arc and calc-alkaline arc fields of Cabanis and Lecolle (1989; **Fig. 9f**).

The mafic lava and felsic tuffs from drillhole 21-3717 (Carracastle/Tawnyinagh Formation) are characterized by similar extended-REE profiles to crystal tuffs of the Horan Formation (**Fig. 10c**). All rocks analyzed from the Charlestown Group display pronounced negative Nb anomalies and weak negative Y anomalies consistent with their formation above a subduction zone (**Fig. 10**). One of the samples in drillhole 21-3717 (sample 12-0337) shows very high Nb/Y (0.9), Zr/Y (24.2; **Fig. 9c**), Th/Yb (6.5) ratios, a moderate La/Yb (8.6) ratio and displays a broadly U-shaped REE profile (**Fig. 10c**). This U-shaped REE profile together with high Nb/Y and Zr/Y may indicate mobility of REE and/or Y during alteration.

Quartz-feldspar porphyritic rocks consistently plot within the volcanic arc granite field of Pearce et al. (1984) according to Nb-Y (**Fig. 9b**), Ta-Yb, Rb-Y+Nb and Rb-Ta+Yb discrimination diagrams, and are of FII to FIIIa affinity (i.e. high field strength element enriched) according to the VMS fertility plot of Lesher et al. (1986; **Fig. 9c**). All samples of quartz-feldspar porphyry, and the single sample of pyroxene diorite analyzed, show similar, strongly fractionated (La/Yb 9.6-14.0), calc-alkaline extended REE profiles with prominent negative Nb and Ti anomalies, positive Zr anomalies and weakly negative Y anomalies (**Fig. 10e-f**).

Hydrothermal alteration:

As evident from the petrographic work discussed above, most samples examined from the Charlestown Group have been hydrothermally altered to some degree. Extrusive rocks have variable SiO_2, Fe_2O_{3T}, CaO (to 11.08%), K_2O (to 4.49%), Na_2O (down to 0.07%), MgO (to 7.52%) and Ba (to 849ppm) concentrations due: to the infilling of voids by silica, carbonate and barite; epidote veining in mafic volcanic rocks; and varying degrees of silicification, chloritization, sericitization (associated with Na-loss), hematization and carbonate-alteration. Only three samples, all from drillhole 2137-17, contain significant amounts of sulfides (>0.1% S). Base metal concentrations are low in all samples anaysed (<0.1% Pb, Cu and Zn) except for a mafic volcanic rock (12-0341) from drillhole 2137-17, which contains high concentrations of Zn (3.96%), Pb (1.76%), Cu (635ppm), As (371ppm), Cd (100ppm) and Mo (133ppm). Tin and W concentrations are low in all samples analyzed (to 1.7ppm and 4ppm respectively).

To assess the degree of hydrothermal alteration in volcanic rocks associated with VMS systems, Large et al. (2001) combined two alteration indices - the Alteration Index (AI) and Carbonate-Chlorite-Pyrite Index (CCPI) and developed the Box Plot as shown in **Figure 9h**. Together these indices can be used to document the progressive replacement of sodic feldspar and volcanic glass by sericite, chlorite, carbonate and pyrite. Most samples from the Charlestown Group plot within the least altered fields (**Fig. 9h**; also the data of O'Connor, 1987), with only two samples falling on common trends associated with VMS proximal hydrothermal alteration. Sample 12-0341, a sulfide bearing mafic rock from drillhole 2137-17 (described above) plots along a chlorite-pyrite-(sericite) trend typical of relatively proximal footwall alteration. Sample 12-0337, a bleached felsic volcanic rock of 'trachytic' composition (also from drillhole 2137-17) plots near the sericite mineral node indicative of slightly more distal alteration, and is by comparison more intensely silicified (85.83% SiO_2). The intensity of alteration in the upper part of this drillhole indicates it is near a hydrothermal up-flow zone and represents a prime target area for mineral exploration. This is consistent with the presence of elevated base and trace metal concentrations these samples (described above). Although the data of O'Connor (1987) is limited, there is a broad correlation between Zn concentration and Alteration Index values in both quartz-feldspar and feldspar porphyritic rocks.

5. Discussion

5.1 Evolution of the Charlestown Group and implications for regional correlations

In **Figure 2** our current understanding of the Grampian event as it applies to the northern British and Irish Caledonides was presented. Early formation of the Deer Park and Highland Border ophiolites (between the outriding blocks and the Laurentian margin; **Fig. 2a**) was followed by obduction of these ophiolites (Chew et al., 2010), subduction reversal and the formation of the Lough Nafooey arc system from c. 490 Ma (Draut et al., 2004; **Fig. 2b**). Using the timescale of Sadler et al. (2009), 'hard' collision of the Lough Nafooey arc with the Laurentian margin in western Ireland (**Fig. 2c**) is constrained to between c. 484 Ma and 476 Ma (based on graptolite biostratigraphy from the Knock Kilbride and Mt. Partry formations). This occurred around the same time as the exumation of the Deer Park ophiolitic melange at 482 ± 1 Ma (Chew et al., 2010), with ophiolitic detritus recorded in the younger Letterbrock Formation (Wrafter and Graham, 1989, Dewey and Mange, 1999; **Fig. 11**).

In Northern Ireland, the obduction of the Tyrone arc (=Tyrone Volcanic Group) and its associated ophiolite (=Tyrone Plutonic Group) to an outboard microcontinental block (=Tyrone Central Inlier) occurred prior to c. 470 Ma (Hutton et al., 1985; Cooper et al., 2011; Hollis et al., 2013b, **Fig. 2d**), though most likely not before c. 473 Ma (due to the absence of xenocrystic zircons in the Formil rhyolite: Cooper et al., 2008). In western Scotland, a Ca4 to Ya1 (Ca=Castlemanian, Ya=Yapeenian) age was obtained for a graptolite fauna from the North Ballaird borehore (references in Stone, 2014). This clastic sequence contains granules of altered serpentine with algal rims in one of these late Arenig beds, implying ophiolitic material at Ballantrae was available for erosion and incorporation by c. 472 Ma (**Fig. 11**). This is in agreement with K-Ar dating of the metamorphic sole of the Ballantrae ophiolite (478 ± 8 Ma: Bluck et al., 1980). The Charlestown Group (ca. 470 Ma, *this study*) clearly fits within the later stages of the Grampian event (**Fig. 11**), and developed after the first two stages of arc-ophiolite accretion (i.e. Deer Park/Highland Border, and Lough Nafooey). Its relationship to the Tyrone/Ballantrae arc system, and syn-collisional stage of the Lough Nafooey arc (i.e. Tourmakeady Group) will be discussed below.

Whole rock geochemical data from the c. 472-469 Ma Charlestown Group are consistent with its formation as part of a peri-Laurentian affinity volcanic arc, in a similar tectonic setting to the Tyrone and Ballantrae arcs (**Fig. 2d**). Early magmatism generated the tholeiitic and calc-alkaline mafic rocks of the Horan Formation and lower part of the Carracastle Formation (e.g. drillhole 2737-14). These are interbedded with mafic volcanic breccias, crystal tuff and sedimentary rocks (chert, siltstone and mudstone). Overlying deposits of the upper Carracastle and Tawnyinah formations are dominated by LILE- and LREE-enriched, calc-alkaline andesitic and felsic volcaniclastic rocks respectively. Together these three formations record the evolution of the Charlestown Group, from a relatively juvenile arc system in a deep marine setting to a progressively more mature, fractionated, volcaniclastic dominated successions. High Th/Yb ratios for calc-alkaline volcanic/volcaniclastic rocks suggest the Charlestown arc was founded upon continental crust (either composite Laurentian margin or microcontinental block), supported by the presence of inherited zircons (>2 Ga) in sample KGC1 (intrusive pyroxene diorite). The Horan Formation yields U-Pb zircon dates of between 472 and 469 Ma (Fig. 7). The Carracastle and Tawnyinah formations remain undated, but are stratigraphically younger than the volcaniclastic rocks of the Horan Formation (470.82

± 0.57 Ma).A geochemical comparison of extended REE profiles from the Charlestown Group to the arc sequences of western Ireland (i.e. Lough Nafooey, Tourmakeady and Murrisk groups) and Northern Ireland (the Tyrone Igneous Complex) is presented in **Figure 10**. Rare LREE-depleted volcanic breccias at Charlestown (sample 12-0326) are similar to those of the Beaghmore Formation of the lower Tyrone Volcanic Group and less so to the >490 Ma Bencorragh Formation of the lower Lough Nafooey Group (**Fig. 10d**). A correlation can be ruled out with both formations on the basis of age constraints presented here (**Fig. 11**). Similar rocks (island arc, LREE-depleted tholeiitic basalts) also occur in the juvenile Ballantrae arc sequences, which are poorly constrained by Sm-Nd ages with large errors (Thirlwall and Bluck, 1984; **Fig. 11**). Large ion lithophile element (LILE) enriched volcanic/volcaniclastic rocks which comprise most the Charlestown Group stratigraphy are geochemically similar to those of the Tourmakedy, Murrisk and Tyrone Volcanic groups (**Fig. 10a-c**). No Fe-Ti enriched mafic rocks of eMORB affinity have been recognized in the Charlestown Group or other western Ireland sequences. These lavas are common in the c.475-474 Ma lower Tyrone Volcanic Group, less so in the c. 469 Ma uppermost Tyrone Volcanic Group (Hollis et al., 2012), and abundant at Ballantrae (the 'within plate' lavas of Stone, 2014 and earlier workers). Data for the Tourmakeady Group is shown on Fig. 10b where it is comparable to Charlestown. The Delaney Dome Formation (not shown in **Fig. 11**) represents a tectonic window through the continental arc intrusive rocks of Connemara, western Ireland. A U-Pb zircon age of 474.6 ± 5.5 Ma presented by Draut and Clift (2002) is within error of the Charlestown Group. Its LREE-enrichment and trace element characteristics are most similar to the c 475 Ma Tourmakeady Group (see Draut and Clift, 2002) and these authors consider the Delaney Dome Formation and Tourmakeady Group to be along-strike equivalents.

Syn- to post-continental arc intrusive rocks which are of similar age to the Charlestown Group (c. 470 Ma) occur in Co. Tyrone (the late arc intrusive suite of the Tyrone Igneous Complex: Cooper et al., 2011), Co. Sligo (Slishwood Division: Flowerdew et al., 2005) and Connemara (Friedrich et al., 1999a,b; Draut et al., 2002) (**Figs. 1,11**). Chondrite normalized REE profiles for QFP intrusive rocks from the Charlestown Group are geochemically similar to samples of c. 465 Ma quartz-feldspar porphyritic dacite and c. 467-464 Ma granite which intrudes the upper levels of the Tyrone Igneous Complex (Draut et al. 2009; Cooper et al. 2011; **Fig. 10e**). The single sample of pyroxene diorite analyzed from Charlestown (CT105) also displays a similar chondrite normalized extended REE-profile, falling within the range of compositions present for c. 470-465 Ma diorites which intrude the Tyrone Igneous Complex (**Fig. 10f**). The slightly younger age of the pyroxene diorite (KGC1: c. 469 Ma) than all other dated rocks of the Charlestown Group (**Fig. 8**) is consistent with its intrusive nature. Zircon inheritance is also a common feature in late (post 470 Ma) intrusive rocks of the Tyrone Igneous Complex (Hutton et al., 1985; Cooper et al., 2011; Hollis et al., 2012, 2013a), with zircons most likely inherited from the underlying Tyrone Central Inlier - a possible outboard Laurentian-affinity microcontinental block (Chew et al., 2008). The geochemistry of the syn- to post-collisional continental arc intrusives of Connemara has been presented by Draut et al. (2002). All samples show LREE enrichment, with comparable La/Sm ratios to the Tourmakeady Group. No geochemical data is available for the Slishwood intrusive rocks (Flowerdew et al., 2005). The presence of syn- post- collisional intrusive rocks in Dalradian sequences of Laurentian margin confirms the sequence of arc-continent collision and continued northward dipping subduction post 470 Ma.

Based on the above, we favour a correlation between the Charlestown Group and the late (i.e. post-subduction flip) arc sequences of the Irish Caledonides – particularly the late development of the upper Tyrone Volcanic Group (i.e. post accretion Broughderg Formation), and the late c. 470-457 Ma continental arc intrusive rocks of these accreted terranes: Co. Tyrone (470.3 ± 1.9 to 464.9 ± 1.5 Ma: Draut et al., 2009; Cooper et al., 2011), Connemara (474.5 ± 1.0 Ma to 462.5 ± 1.2 Ma: Friedrich et al., 1999a,b), Co. Sligo (474 ± 5 Ma to 467 ± 6 Ma: Flowerdew et al., 2005). Continental arc intrusive rocks also intruded the Dalradian sequences of eastern Scotland until to 457 ± 1 Ma (Oliver et al., 2000, 2008; Carty et al., 2013). Although a correlation to the youngest stage of the Tourmakeady Group (i.e. uppermost Tourmakeady and Srah formations) cannot be ruled out based on our geochronology and the geochemistry of tuffs and felsic volcanic rocks, the presence of abundant subaqueous and geochemically juvenile mafic rocks at Charlestown is difficult to reconcile a syncollisional tectonic setting (as is the presence of VMS mineralization, typically associated with rifted arc or backarc settings – see section 5.3.).

5.2 Implications for the Middle Ordovician timescale

Despite its importance, there are relatively few U-Pb constraints for the Early to Middle Ordovician timescale (Cooper and Sadler, 2012; Lindskog et al. 2016). Based on the fauna recovered from the Knock Airport sequence, the upper part of the Horan Formation is correlated with the Upper Yapeenian or Ya2 stage of the Australian succession (i.e. late Dapingian global stage / Late Arenig) (Ruston, 2014; **Fig. 12**). Together with the new CA-ID-TIMS ages presented here, this site represents an important new constraint for calibrating the Middle Ordovician timescale.

Sadler et al. (2009) assessed the duration of the Yapeenian Stage as less than 2 Ma, with Ya2 lasting from 471.21 to 470.54 Ma (**Fig. 12**). This was based on calibration points bracketing the interval at 486.78 ± 2.57 Ma, 481.13 ± 2.76 Ma, 469 ± 6.00 Ma and 465.46 ± 3.53 Ma (total 2σ uncertainty; Schmitz, 2012). The Ordovician timescale was later revised by Cooper and Sadler (2012) who modified the duration of Ya2 to a period from 467.7 to 467.3 Ma, significantly younger than that of Sadler et al. (2009) and inconsistent with the combined graptolite and U-Pb constraints presented here. It is important to note that this revised Ordovician timescale included a calibration point based on the correlation of a U-Pb zircon age of 473 ± 1 Ma from the Formil rhyolite (Tyrone Igneous Complex) with a Ca1 graptolite fauna from Slieve Gallion (as described in Cooper et al., 2008). This proposed correlation between the Formil rhyolite and volcanic succession on Slieve Gallion (Cooper et al. 2008) has now been shown to be incorrect based on recent mapping and geochemistry (Hollis et al., 2013a). The erroneously correlated c. 473 Ma age clearly pushes the Floian part of the Cooper and Sadler (2012) chart to younger ages with the point lying above their calibration line (point O3 on their Fig. 20.11). This is confirmed by the recent study of Lindskog et al. (2016) who report a U-Pb zircon date of 467.50 ± 0.28 Ma from the distinct 'Likhall' meteorite bed of Sweden. Lindskog et al. (2016) provide a revised Middle Ordovician timescale for the Darriwilian global stage and suggest that the base of the Darriwilian, presently cited as 467.3 ± 1.1 Ma must be moved back in time. However, this refined timescale of Lindskog et al. (2016; **Fig. 12**) still includes the erroneous correlation of the Formil age to the graptolite bearing sequence at Slieve Gallion (Cooper et al., 2008). Limitations with the late Cambrian to Early Ordovician section of the International Chronostratigraphic Charts have been discussed by Landing et al. (2015).

Our four U-Pb ages of 471.95 ± 0.56 Ma, 471.26 ± 0.58 Ma, 470.82 ± 0.57 and 469.11 ± 0.80 Ma (2σ total uncertainty) for the Knock Airport sequence of the Horan Formation are in agreement with the original Sadler et al. (2009) duration of the Ya2 stage of the earlier Dapingian (471.21 to 470.54 Ma). The Knock Airport sequence of latest Dapingian (Ya2) age is well constrained by sample KGC2 (banded tuff; 471.95 ± 0.56 Ma; **Fig. 5**) which underlies the graptolite bearing horizon and samples KGC3 and KGC5 (**Fig. 5, 7**) which overlie it. The younger age of 469.11 ± 0.80 Ma is from a pyroxene diorite that intrudes the sequence. We suggest that the Formil rhyolite age be removed from all future Ordovician calibrations, with the Lindskog et al. (2016) age providing an important constraint for the lower Darriwilian, and the Knock Airport fauna for the latest Dapingian (**Fig. 12**). The newly presented geochronology for the Knock Airport sequence, provides a significant refinement of the existing 469 ± 6.00

Ma Dapingian constraint, determined from a rhyolite of the Cutwell Group, central Newfoundland (Dunning and Krogh, 1991).

5.3 Regional mineral potential

From the work presented here it is evident that the Charlestown Cu deposit is not consistent with 'porphyry copper' style mineralization (e.g. Berger et al., 2008), as stated by O'Connor and Poustie (1986). Breccia textures, the nature of hydrothermal alteration and the style of mineralization (**Fig. 4**) are more consistent with a VMS system. Volcanogenic massive sulfide deposits develop in volcanic sequences undergoing extension, as metal bearing hydrothermal fluids are focused from depth and mix with ambient seawater to precipitate sulfides at or below the seafloor (Franklin et al., 2005). In Phanerozoic rocks, VMS deposits are typically restricted to arc, ophiolite and backarc sequences (reviewed in Piercey, 2011). Despite their abundance in accreted arc and ophiolite terranes of the Newfoundland Appalachians (van Staal, 2007; Piercey, 2007), few VMS deposits have been recognized in the British and Irish Caledonides (Hollis et al., 2014). Economic deposits identified to date are restricted to peri-Gondwanan affinity arc and backarc terranes south of the Iapetus Suture, such as at Avoca and Parys Mountain (Hollis et al., 2014).

Evidence presented here and in O'Connor (1987) suggests that the entire volcanic stratigraphy of the Charlestown Group was deposited in a submarine arc environment. This includes the repeated occurrence of deep sea sedimentary rocks (i.e. mudstone, jasper, chert) throughout all three formations, and the presence of interbedded, well stratified tuffs with arc like geochemical characteristics (**Figs. 9,10**). Furthermore, where the quartz-feldspar porphyritic rocks are observed in outcrop, breccia textures are consistent with peperite, autobrecciation and hydraulic fracturing (section 4.4.2). This suggests these thin units were emplaced as high-level synvolcanic sills into unconsolidated wet sediments and tuffs just below the seafloor. Localized occurrences of crystal tuff occur where these magmas were erupted.

Hydrothermal activity is well developed throughout the Charlestown Cu deposit (**Fig. 4**), and also throughout the entire sequence. The concentric zoning of alteration assemblages associated with the Charlestown mineralization only superficially resembles that of porphyry Cu deposits worldwide; which typically encompass a potassic core surrounded by concentric phyllic and propylitic shells (Lowell and Guilbert, 1970). The characteristic potassic alteration from porphyry Cu style mineralization is absent at Charlestown, and furthermore the patchy hematitic alteration is not usually recorded in porphyry copper systems (O'Connor and Poustie 1986). O'Connor and Poustie (op. cit.) unconvincingly suggest the silicic and sericitic alteration seen at Charlestown represents the phyllic core associated with porphyry systems, whilst localized clay rich alteration to argillic zones, and chloritic alteration to propylitic zones. This type of alteration is much more typical for VMS systems (Franklin et al. 2005)

Within the Charlestown Cu deposit, the intense zone of chloritic alteration appears to be restricted underneath the deposit, and increases in thickness below the zone of pyrite-chalcopyrite mineralization (**Fig. 4**). This, together with the presence of a central core of silicification already discussed, is consistent with VMS systems, particularly feeder zones (e.g. Franklin et al., 2005) which will be characterized by stockwork like ‘type 4’ brecciation and base metal mineralization caused by hydraulic fracturing. A broader halo of sericitic-chloritic alteration is consistent with the more distal portions of felsic-hosted VMS systems (Yeats et al., 2017). The development of similar alteration assemblages in the hanging-wall of the deposit (**Fig. 4**), together with localized ‘type 1’ peperite development with ash tuffs, suggests that mineralization occurred sub-seafloor and was predominantly replacive. Minor exhalation is indicated by the presence of unmineralized jaspers (see following). The concentration of sphalerite-barite and sphalerite-galena-barite mineralization towards the periphery of the deposit (**Fig. 4**) is also consistent with VMS systems (Franklin et al., 2005). Further evidence for VMS activity includes the observation of ‘chalcopyrite disease’ (Barton and Bethke, 1987) in many samples from across the volcanic inlier, and the presence of significant sphalerite mineralization in drillhole 2137-17 (3.96 wt% Zn, 635 ppm Cu) in the upper Carracastle Formation (sample 12-0341; **Fig. 3b**).

Cathelineau (1988) proposed an empirical chlorite mineral geothermometer where formation temperature $T(°C) = -61.92 + 321.98(Al_{(IV)})$. $Al_{(IV)}$ can be calculated from SEM analysis and substituted to derive formation temperature (Stobbs 2013). Results from sample CT206, a felsic breccia from the Carracastle Formation, indicates temperatures ranging between 340°C - 395°C, within the range for formation conditions for a VMS deposit, equivalent to higher greenschist metasomatic conditions, and importantly well below temperatures associated with porphyry copper deposits (reviewed in Berger et al., 2008). Most rocks from the Charlestown Group display at least some evidence for seawater interaction, such as calcite amygdales in mafic lavas (e.g. 12-0327) or voids associated with autobrecciation infilled with barite, calcite and quartz (CT206; **Fig. 6b**). In sample CT113, a crystal tuff from the Horan Formation, SEM results show some form of iron oxide with 200 ppm copper associated with chlorite (**Fig. 6a**). The texture of the chlorite is most likely explained by the precipitation in voids from a silica-rich hydrothermal fluid.

Sample 12-0336 from drillhole 2137-17 (upper Carracastle Formation), contains vuggy quartz in association with barite implying hydrothermal activity similar in nature to the above samples. Anglesite [$PbSO_4$], an oxidation product of galena, was also observed. The oxidation of this phase could be associated with the apron zone of a VMS deposit, which is normally characterized by oxidized ore minerals along with barite and hematite and iron-rich cherts and jaspers (Herrington et al., 2005; Hollis et al., 2015; Ayupova et al. 2016), similar to the successions found at the top hole 2137-14 but also comparable to sample CT113, with copper rich hematite and barite. Large blocks of jasper float were noted by the authors north of Knock Airport, similar in appearance to that associated with hydrothermal alteration and base metal occurrences in the Tyrone Igneous Complex (Hollis et al., 2015, 2016). Such jaspers may form as silica-iron gels, precipitated from the non-buoyant parts of hydrothermal plumes or through the replacement of the volcanic stratigraphy (Hollis et al., 2015).

Together these results indicate that the mineralization at Charlestown is more consistent with a VMS system than a porphyry copper deposit (**Fig. 13**). The link established herein to the Tyrone Igneous Complex further highlights the VMS prospectivity of the Charlestown area. In the Tyrone Igneous Complex numerous sub-economic Cu-Pb-Zn-Ag-Au occurrences have been identified, associated with locally intense hydrothermal activity (Hollis et al., 2014). Most base metal mineralization is restricted to the uppermost Tyrone Volcanic Group of similar age (c. 473-469 Ma; Hollis et al., 2012) to the Charlestown Group. Sub-economic VMS-style mineralization in Co. Tyrone is predominantly associated with silificied and variably sericitized and chloritized felsic tuffs, flows and rhyolite domes (Hollis et al., 2016).

CONCLUSIONS

We have reassessed the role of the Charlestown Group in the context of the c. 474-465 Ma Grampian orogeny, based on new fieldwork, high-resolution airborne geophysics, graptolite biostratigraphy, U-Pb zircon dating, whole rock geochemistry, and an examination of historic drillcore from across the volcanic inlier. The Charlestown Group has been divided into three formations: Horan, Carracastle, Tawnyinah. The Horan Formation comprises a mixed sequence of tholeiitic to calc-alkaline basalt, crystal tuff and sedimentary rocks (e.g. black shale, chert), forming within an evolving peri-Laurentian affinity island arc. The presence of graptolites *Pseudisograptus* of the *manubriatus* group and the discovery of *Exigraptus uniformis* and *Skiagraptus gnomonicus* favour a Yapeenian (= late Arenig; Ya2 stage) age for the Horan Formation (equivalent to c. 471.2-470.5 Ma according to the timescale of Sadler et al., 2009). Together with three new U-Pb zircon ages of ca. 471.95-470.82 Ma from enclosing felsic tuffs and volcanic breccias, this fauna provides an important new constraint for calibrating the Middle Ordovician timescale. Overlying deposits of the Carracastle and Tawnyinah formations are dominated by LILE- and LREE-enriched calc-alkaline andesitic tuffs and flows, coarse volcanic breccias and quartz-feldspar porphyritic intrusive rocks, overlain by more silicic tuffs and volcanic breccias with rare occurrences of sedimentary rocks. The relatively young age for the Charlestown Group in the Grampian orogeny, coupled with high Th/Yb and zircon inheritance (c. 2.7 Ga) in intrusive rocks indicate the arc was founded upon continental crust (either composite Laurentian margin or microcontinental block). Regionally, this best correlates with the post-subduction flip volcanic/intrusive rocks of the Irish Caledonides, specifically the late-stage development of the Tyrone Igneous Complex, Murrisk Group ignimbrites, the late intrusive rocks of Connemara (western Ireland) and the Slishwood Division in Co. Sligo. Breccia textures and mineralization is incompatible with the porphyry hypothesis for the genesis of the Charlestown copper deposit and this study suggests that features are more consistent with a volcanogenic massive sulfide (VMS) deposit.

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References

Ayupova, N.R., Maslennikov, V.V., Tessalina, S.G., Shilovsky, O.P., Sadykov, S.A., Hollis, S.P., Danyushevsky, L.V., Safina, N.P. & Statsenko, E.O., 2016, Tube fossils from gossanites of the Urals VHMS deposits, Russia: authigenic mineral assemblages and trace element distributions. Ore Geology Reviews. DOI: 10.1016/j.oregeorev.2016.08.003

Barton, P.B. Jr & Bethke, P.M, 1987, Chalcopyrite disease in sphalerite: pathology and epidemiology. *American Mineralogist*, **72**, 451-467.

Berger, B.R., Ayuso, R.A., Wynn, J.C. & Seal, R.R., 2008, Preliminary model of porphyry copper deposits. U.S. Geological Survey Open-File Report 2008-1321, 55p.

Bluck, B.J., Halliday, A.N., Aftalion, M. & Macintyre, R.M., 1980, Age and origin of Ballantrae ophiolite and its significance to the Caledonian orogeny and Ordovician time scale. *Geology*, **8**, 492–495.

Cabanis, B. & Lecolle, M., 1989, Le diagramme La/10-Y/15-Nb/8; un outil pour la discrimination des series volcaniques et al mise en evidence des processus de mélange et/ou de contamination crustale. The La/10-Y/15-Nb/8 diagram; a tool for distinguishing volcanic series and discovering crustal mixing and/or contamination. *Comptes Rendus de l'Academie des Sciences, Serie 2, Mecanique, Physique, Chimie, Sciences de l'Univers, Sciences, de la Terre*, **309**, 2023-2029.

Carty, J.P., Connelly, J.N., Hudson, N.F.C. & Gale, J.F.W., 2013, Constraints on the timing of deformation, magmatism and metamorphism in the Dalradian of NE Scotland. *Scottish Journal of Geology*, **48**, 103-117.

Cathelineau, M., 1988, Cation site occupancy in chlorites and illites as a function of temperature. Clay Minerals, 23, 471-485

Charlesworth, H.A.K., 1960, The Lower Palaeozoic inlier of the Curlew Mountain anticline. *Proceedings of the Royal Irish Academy*, **61B**, 37-50.

Chew, D.M., 2009. Grampian orogeny, in Holland, C.H. & Saunders, A.D. (eds) *The Geology of Ireland. 2nd edition*, 69-93.

Chew, D. & Stillman, C.J., 2009, Late Caledonian orogeny and magmatism. *In:* Holland, C. H. & Saunders, I. S. (eds) *The Geology of Ireland*. Second edition, 143-173.

Chew, D.M., Graham, J.R. & Whitehouse, M.J., 2007. U-Pb zircon geochronology of plagiogranites from the Lough Nafooey (= Midland Valley) arc in western Ireland: constraints on the onset of the Grampian orogeny. *Journal of the Geological Society, London,* **164**, 747-750.

Chew, D.M., Flowerdew, M.J., Page, L.M., Crowley, Q.G., Daly, J.S., Cooper, M. R. & Whitehouse, M.J., 2008. The tectonothermal evolution and provenance of the Tyrone Central Inlier, Ireland: Grampian imbrication of an outboard Laurentian microcontinent? *Journal of the Geological Society, London*, **165**, 675-685.

Chew, D.M., Daly, J.S., Magna, T., Page, L.M., Kirkland, C.L., Whitehouse, M.J. & Lam, R., 2010, Timing of ophiolite obduction in the Grampian orogen. *Geological Society of America Bulletin*, **122**, 1787-1799.

Clift, P.D. & Ryan, P.D., 1994. Geochemical evolution of an Ordovician island arc, South Mayo, Ireland. *Journal of the Geological Society, London*, **151**, 329-342.

Clifford, J.A., Earls, G., Meldrum, A.H. & Moore, N., 1992, Gold in the Sperrin Mountains, Northern Ireland: an exploration case history. *In:* Bowden, A.A., Earls, G., O'Connor, P.G. & Pyne, J.F. (eds) *The Irish Minerals Industry 1980-1990*. Irish Association for Economic Geology, Dublin, pp 77-87

Cocks, L. R. M., Fortey, R. A. & Rushton, A. W. A. 2010. Correlation for the Lower Palaeozoic. *Geological Magazine*, **147**, 171-180.

Condon, D.J., Schoene, B., McLean, N.M., Bowring, S.A., & Parrish, R.R., 2015. Metrology and traceability of U–Pb isotope dilution geochronology (EARTHTIME Tracer Calibration Part I). Geochimica et Cosmochimica Acta 164, 464–480. doi:10.1016/j.gca.2015.05.026

Cooper, M.R., Crowley, Q.G. & Rushton, A.W.A., 2008. New age constraints for the Ordovician Tyrone Volcanic Group, Northern Ireland. *Journal of the Geological Society, London*, **165**, 333-339.

Cooper, M.R., Crowley, Q.G., Hollis, S.P., Noble, S.R., Roberts, S., Chew, D., Earls, G., Herrington, R. & Merriman, R.J., 2011. Age constraints and geochemistry of the Ordovician Tyrone Igneous Complex, Northern Ireland: implications for the Grampian orogeny. *Journal of the Geological Society, London*, **168**, 837-850.

Cooper, M.R., Crowley, Q.G., Hollis, S.P., Noble, S.R. & Henney, P.J., 2013, A U-Pb age for the Late Caledonian Sperrin Mountains minor intrusions suite in the north of Ireland: timing of slab break-off in the Grampian terrane and the significance of deep-seated, crustal lineaments. *Journal of the Geological Society*, **170**, 603-614.

Cooper, M.R. & Mitchell, W.I., 2004. Midland Valley Terrane, in Mitchell, W.I. (ed)., *The Geology of Northern Ireland. Our Natural Foundation, second edition*. Geological Survey of Northern Ireland.

Cooper, R.A. & Sadler, P.M., 2012, The Ordovician Period. In: Gradstein, F.M., Ogg, J.G., Schmitz, M. & Ogg, G. (eds.) The Geologic Time Scale 2012. Elsevier B.V.

Crowley, Q.G. & Strachan, R.A., 2014, U-Pb zircon constraints on obduction initiation of the Unst Ophiolite: an oceanic core compelx in the Scottish Caledonides? *Journal of the Geological Society, London,* **172**, 279-282.

Cummins, W. A., 1954. An Arenig volcanic series near Charlestown, Co. Mayo. *Geological Magazine*, 91, 102-104.

DePaolo, D.J., 1981, Trace element and isotopic effects of combined wallrock assimilation and fractional crystallization. *Earth and Planetary Science Letters*, **53**, 189-202.

DePaolo, D.J. & Wasserburg, G.J., 1976, Nd isotopic variations and petrogenetic models. *Geophysical Research Letters*, **3**, 249-252.

Dewey, J.F., 2005, Orogeny can be very short. *PNAS*, **102**, 15286-15293.

Dewey, J.F. & Mange, M.A., 1999, Petrography of Ordovician and Silurian sediments in the western Irish Caledonides: tracers of a short-lived Ordovician continent-arc collision orogeny and the evolution of the Laurentian Appalachian-Caledonian margin. *In:* MacNiocaill, C. & Ryan, P.D., (eds)., *Continental Tectonics*. Geological Society of London, Special Publication, **164**, 55-107.

Dewey, J.F. & Shackleton, R.M., 1984, A model for the evolution of the Grampian tract in the early Caledonides and Appalachians. *Nature*, **312**, 115-121.

Dewey, J. F., Rickards, R. B. & Skevington, D., 1970. New light on the age of Dalradian deformation and metamorphism in western Ireland. *Norsk geologisk Tidsskrift*, **50**, 19-44.

Draut, A.E. & Clift, P.D., 2002, The origin and significance of the Delaney Dome Formation, Connemara, Ireland. *Journal of the Geological Society, London*, **159**, 95-103.

Draut, A.E., Clift, P.D., Hannigan, R.E., Layne, G. & Shimizu, N., 2002, A model for continental crust genesis by arc accretion: rare earth element evidence from the Irish Caledonides. *Earth and Planetary Science Letters*, **203**, 861-877.

Draut, A.E., Clift, P.D., Chew, D.M., Cooper, M.J., Taylor, R.N. & Hannigan, R.E., 2004, Laurentian crustal recycling in the Ordovician Grampian Orogeny: Nd isotopic evidence from western Ireland. *Geological Magazine*, **141**, 195-207.

Draut, A.E., Clift, P.D., Amato, J.M., Blusztajn, J. & Schouten, H., 2009, Arc-continent collision and the formation of continental crust: a new geochemical and isotopic record from the Ordovician Tyrone Igneous Complex, Ireland. *Journal of the Geological Society, London*, **166**, 485-500.

Dunning, G.R. & Krogh, T.E., 1991. Stratigraphic correlation of the Appalchian orogeny using advances U-Pb zircon geochronology techniques. In: Barnes, C.R. & Williams, S.H. (Eds.)

Fifth International Symposium on the Ordovician system. Geological Survey of Canada Paper 90-09, Ottawa, 85-92.

Earls, G., Hutton, D.W.H., Wilkinson, J., Mole, N., Parnell, J., Fallick, A. & Boyce, A., 1996, The gold metallogeny of northwest Northern Ireland. Geological Survey of Northern Ireland Techinical Report 96/6, 107pp.

Flowerdew, M.J., Daly, J.S. & Whitehouse, M.J., 2005, 470 Ma granitoid magmatism associated with the Grampian Orogeny in the Slishwood Division, NW Ireland. *Journal of the Geological Society, London*, **162**, 563-575.

Franklin, J.M., Gibson, H.L., Galley, A.G. & Jonasson, I.R., 2005. Volcanogenic massive sulfide deposits. In: Hedenquist, J.W., Thompson, J.F.H., Goldfarb, R.J. & Richards, J.P. (Eds). Economic Geology 100th Anniversary Volume. Society of Economic Geologists, p523-560.

Friedrich, A.M., Bowring, S., Martin, M.W. & Hodges, K.V., 1999a, Short-lived continental magmatic arc at Connemara, western Irish Caledonides: Implications for the age of the Grampian orogeny. *Geology*, **27**, 27-30.

Friedrich, A.M., Hodges, K.V., Bowring, S. & Martin, M.W., 1999b, Geochronological constraints on the magmatic, metamorphic and thermal evolution of the Connemara Caledonides, western Ireland. *Journal of the Geological Society, London*, **156**, 1217-1230.

Fujisaki, W., Asanuma, H., Suzuki, K., Sawaki, Y., Sakata, S., Hirata, T., Maruyama, S. & Windley, B.F., 2015, Ordovician ocean plate stratigraphy and thrust duplexes of the Ballantrae Complex, SW Scotland: implications for pelagic deposition rate and forearc accretion in the closing Iapetus Ocean. Tectonophysics. Online First – DOI: 10.1016/j.tecto.2015.04.2014

Hamilton, P.J., O'Nions, R.K., Bridgwater, D. & Nutman, A., 1983, Sm-Nd studies of Archaean metasediments and metavolcanics from West Greenland and their implications for the Earth's early history. *Earth and Planetary Science Letters*, **62**, 263-272.

Herrington, R.J. & Brown, D., 2011, The generation and preservation of mineral deposits in arc-continent collision environments. *In:* Brown, D. & Ryan, P.D. (eds)., *Arc-Continent Collision*. Frontiers in Earth Sciences. Springer-Verlag, Berlin Heidelberg. 145-159.

Herrington, R., Maslennikov, V., Zaykov, V., Seravkin, I., Kosarev, A., Buschmann, B., Orgeval, J-J., Holland, N., Tesalina, S., Nimis, P. & Armstrong, R., 2005, 6: Classification of VMS deposits: Lessons from the South Uralides. *Ore Geology Reviews*, **27**, 203-237.

Herrington, R., Plotinskaya, O.Y., Maslennikov, V.V. & Tessalina, S.G., 2017. An overview of mineral deposits in the Urals: a special issue of Ore Geology Reviews. Ore Geology Reviews. DOI: 10.1016/j.oregeorev.2016.12.016

Hodgson, J.A. & Ture, M.D. 2014. Tellus Border Project; Airborne geophysical interpretation report. Geological Survey of Ireland and Geological Survey of Northern Ireland, 118 pages. http://www.tellusborder.eu/NR/rdonlyres/1D774DD2-E14D-421A-95AB-0ADC60CD6C1C/0/TBGPH07_Interpretation_Report_27June_2014.pdf

Hollis, S.P., Roberts, S., Cooper, M.R., Earls, G., Herrington, R.J., Condon, D.J., Cooper, M.J., Archibald, S.M. & Piercey, S.J., 2012. Episodic-arc ophiolite emplacement and the growth of continental margins: Late accretion in the Northern Irish sector of the Grampian-Taconic orogeny. *GSA Bulletin,* **124**, 1702-1723.

Hollis SP, Cooper MR, Roberts S, Herrington RJ, Earls G, & Condon, D.J., 2013a. Stratigraphic, geochemical and U-Pb zircon age constraints from Slieve Gallion, Northern Ireland: A correlation of the Irish Caledonian arcs. *Journal of the Geological Society, London*, **170**, 737-752.

Hollis S.P., Cooper M.R., Roberts S., Earls G., Herrington R.J., Condon D.J. & Daly, J.S., 2013b. Late obduction of the Tyrone ophiolite, Northern Ireland, during the Grampian-Taconic orogeny: a correlative of the Annieopsquotch ophiolite of Newfoundland? *Journal of the Geological Society, London*, **170**, 861-876.

Hollis, S.P., Roberts, S., Earls, G., Herrington, R., Cooper, M.R., Piercey S.J., Archibald, S.M., & Moloney, M., 2014. Petrochemistry and hydrothermal alteration within the Tyrone Igneous Complex, Northern Ireland: implications for VMS mineralization in the peri-Laurentian British and Irish Caledonides. *Mineralium Deposita*, 49, 575-593.

Hollis, S.P., Cooper, M.R., Herrington, R.J., Roberts, S., Earls, G., Verbeeten, A., Piercey, S.J., & Archibald, S.M., 2015, Distribution, mineralogy and geochemistry of silica-iron exhalites and related rocks from the Tyrone Igneous Complex: implications for VMS mineralization in Northern Ireland. *Journal of Geochemical Exploration*, 159, 148-168.

Hollis, S.P., Cooper, M.R.., Earls, G., Roberts, S., Herrington, R.J. & Piercey, S.J. (2016). Using Tellus data to enhance targeting of volcanogenic massive sulphide mineralization in the Tyrone Igneous Complex. In: Young, M.E. (ed.) Unearthed: impacts of the Tellus surveys of the north of Ireland. Dublin. Royal Irish Academy, p157-168.

Hutton, D.H.W., Aftalion, M. & Halliday, A.N., 1985, An Ordovician ophiolite in County Tyrone, Ireland. *Nature*, **315**, 310-312.

Jeffries, T.E., Fernández-Suárez, J., Corfu, F. & Alonso, G.G., 2003, Advances in U-Pb geochronology using frequency quintupled Nd:YAG based laser ablation system (lambda = 213nm) and quadrupole based ICP-MS. *Journal of Analytical Atomic Spectrometry*, **18**, 847-855.

Kerrich, R., Goldfarb, R.J. & Richards, J.P., 2005, Metallogenic provinces in an evolving geodynamic framework. Society of Economic Geologists, Inc., Econ. Geol. 100th Anniversary Vol., 1097–1136.

Landing, E., Rushton, A.W.A., Fortey, R.A. & Bowring, S.A., 2005, Improved geochonologic accuracy and precision for the ICS chronostratigraphic charts: examples from the late Cambrian – Early Ordovician. *Episodes*, **38**, 154-161.

Large, R.R., Gemmell, J.B. & Paulick, H., 2001, The alteration box plot: a simple approach to understanding the relationship between alteration mineralogy and lithogeochemistry associated with volcanic-hosted massive sulfide deposits. *Economic Geology*, **96**, 957-971.

Lesher, C.M., Goodwin, A.M., Campbell, I.H. & Gorton, M.P., 1986, Trace-element geochemistry of ore-associated and barren, felsic metavolcanic rocks in the Superior province, Canada. *Canadian Journal of Earth Sciences*, **23**, 222-237.

Lindskog, A., Costa, M.M., Rasmussen, C.M.Ø., Conneally, J.N. & Eriksson, M.E., 2016. Refined Ordovician timescale reveals no link between asteroid breakup and biodiversification. Nature Communications. DOI: 10.1038/ncomms14066

Long, C. B., McConnell, B.J., & Philcox, M.E., 2005. Geology of South Mayo: a Geological Description, with accompanying Bedrock Geology 1:100,000 Scale Map, Sheet 11, South Mayo. Geological Survey of Ireland, Dublin.

Lowell, J.D. & Guilbert, J.M., 1970, Lateral and vertical alteration-mineralization zoning in porphyry ore deposits. Economic Geology, 65, 373-408.

Ludwig, K.R., 2001, Isoplot/Ex, rev. 2.49. A Geochronological Toolkit for Microsoft Excel: Berkeley Geochronology Center , Special Publication No. 1a.

MacLean, W.H, 1990, Mass change calculation in altered rock series. *Mineralium Deposita*, **23**, 231-238.

McLean, N.M., Condon, D.J., Schoene, B. & Bowring, S.A., 2015, Evaluating uncertainties in the calibration of isotopic reference materials and multi-element isotopic tracers (EARTHTIME Tracer Calibration Part II). *Geochimica et Cosmochimica Acta,* **164**, 481–501

Mattinson, J.M., 2005. Zircon U–Pb chemical abrasion (‘CA-TIMS’) method: Combined annealing and multi-step partial dissolution analysis for improved precision and accuracy of zircon ages. Chemical Geology 220, 47–66. doi:10.1016/j.chemgeo.2005.03.011

McConnell, B., Crowley, Q.G. & Riggs, N., 2010, Laurentian origin of the Ordovician Grangegeeth volcanic arc terrane, Ireland. *Journal of the Geological Society, London*, **167**, 469-474.

McConnell, B., Riggs, N. & Crowley, Q.G., 2009, Detrital zircon provenance and Ordovician terrane amalgamation, western Ireland. *Journal of the Geological Society, London*, **166, 473-484.**

McDonough, W.F. & Sun S-S., 1995, The composition of the Earth. *Chemical Geology*, **120**, 223-254

O’Connor, P.G., 1987, Volcanology, geochemistry and mineralization in the Charlestown Ordovician inlier, Co. Mayo. PhD thesis, University College Dublin, Ireland.

O’Connor, P.G. & Poustie, A., 1986, Geological setting of, and alteration associated with, the Charlestown mineral deposit. *In:* Andrew, C.J., Crowe, R.W.A., Finley, F., Pennell, W.M., & Pyne, J.F.L. (eds). *The Geology and Genesis of Mineral Deposits in Ireland*. Irish Association of Economic Geology, 89-102.

Oliver, G.J.H., Chen, F., Buchwaldt, R. & Hegner, E., 2000, Fast tectonometamorphism and exhumation in the type area of the Barrovician and Buchan zones. *Geology*, **28**, 459-462.

Oliver, G.J.H., Wilde, S. & Wan, Y., 2008, Geochronology and geodynamics of Scottish granitoids from the late Neoproterozoic break-up of Rodinia to Palaeozoic collision. *Journal of the Geological Society, London*, **165**, 661-674.

Parnell, J., Earls, G., Wilkinson, J.J., Hutton, D.H.W., Boyce, A.J., Fallick, A.E., Ellam, R.M., 2000, Regional fluid flow and gold mineralization in the Dalradian of the Sperrin Mountains, Northern Ireland. Economic Geology, **95**, 1389-1416.

Pearce, J.A., 1996, A user’s guide to basalt discrimination diagrams. *In:* Wyman, D.A. (ed.), *Trace element geochemistry of volcanic rocks: applications for massive-sulphide exploration*. Geological Association of Canada, Short Course Notes 12, 79-113.

Pearce, J.A., 2008, Geochemical fingerprinting of oceanic basalts with applications to ophiolite classification and the search for Archean oceanic crust. *Lithos*, **100**, 14-48.

Pearce, J.A. & Cann, J.R., 1973, Tectonic setting of basic volcanic rocks determined using trace element analyses. *Earth and Planetary Science Letters*, **19**, 290-300.

Pearce, J.A., Harris, N.B.W. & Tindle, A.G., 1984, Trace element discrimination diagrams for the tectonic interpretation of granitic rocks. *Journal of Petrology*, **25**, 956-983.

Peatfield, G.R., 2003, Updated technical review report on the Tyrone mineral exploration property, (prospecting licences UM 11/96 and UM 12/96, County Tyrone, Northern Ireland – 20 January, 2003. Published report for Tournigan Gold Corporation

Poustie, A., 1982, The discovery of a new mineral deposit within an Ordovician volcanic series near Charlestown, Co. Mayo. *In:* Brown, A.G. (ed)., *Mineral Exploration in Ireland: Progress and Developments 1971-1981.* Irish Association for Economic Geology.

Piercey, S.J., 2007, Volcanogenic massive sulphide (VMS) deposits of the Newfoundland Appalachians: An overview of their setting, classification, grade-tonnage data, and unresolved questions. *In* Pereira, C.G.P. & Walsh, D.G. (eds) *Current Research*. Newfoundland Department of Natural Resources, Geological Survey, Report 07-01: pp 169-178

Piercey, S.J., 2011, The setting, style, and role of magmatism in the formation of volcanogenic massive sulfide deposits. *Mineralium Deposita*, **46**, 449-471

Reynolds, G., 2014, Charlestown – the copper mine that got away. *Earth Science Ireland*, **15**, 37-38.

Rice, C. M., Mark, D. F., Selby, D. & Neilson, J.E., & Davidheiser-Kroll, B. 2016, Age and geologic setting of quartz vein-hosted gold mineralization at Curraghinalt, Northern Ireland: implications for genesis and classification. *Economic Geology*, **111**, 127-150.

Rogers, N., van Staal, C.R., Zagorevshki, I., Skulski, T., Piercey, S. & McNicoll, V.J., 2007, Timing and tectonic setting of volcanogenic massive sulphide bearing terranes within the Central Mobile Belt of the Canadian Appalachians. *In*: Milkereit, B. (ed.) *Exploration in the New Millennium, Proceedings of the Fifth Decennial International Conference on Mineral Exploration*. Decennial Mineral Exploration Conferences, Toronto, Canada, 1199–1205.

Ross, P.-S. & Bédard, J.H., 2009, Magmatic affinity of modern and ancient subalkaline volcanic rocks determined from trace-element discrimination diagrams. *Canadian Journal of Earth Science*, **46**, 823-839.

Rushton, A.W.A., 2014, A Yapeenian (Late Arenig) graptolite fauna from the Ordovician rocks of the Charlestown Inlier, Co. Mayo, Ireland. *Irish Journal of Earth Sciences*, **32**, 79-87.

Ryan, P.D. & Dewey, J.F., 2011, Arc-continent collision in the Ordovician of western Ireland: stratigraphic, structural and metamorphic evolution. *In:* Brown, D. & Ryan, P.D., (eds.). *Arc-Continent Collision*. Frontiers in Earth Sciences. Springer-Verlag Belin Heidelberg, 373-401.

Ryan, P.D., Floyd, P.A. & Archer, J.B., 1980, The stratigraphy and petrochemistry of the Lough Nafooey Group (Tremadocian), western Ireland. *Journal of the Geological Society, London*, **137**, 443-458.

Sadler, P.M., Cooper, R.A. & Melchin, M., 2009, High-resolution, early Paleozoic (Ordovician-Silurian) time scales. *GSA Bulletin*, **121**, 887-906.

Schandl, E.S. & Gorton, M.P., 2002, Application of high field strength elements to discriminate tectonic settings in VMS environments. *Economic Geology*, **97**, 629-642.

Schmitz, M.D, 2012, Appendix 2 – Radiometric ages used in GTS2012. In: Gradstein, F.M., Ogg, J.G., Schmitz, M. & Ogg, G. (eds.) The Geologic Time Scale 2012. Elsevier B.V. Pages 1045-1082.

Spray, J.G. & Dunning, G.R., 1991, A U/Pb age for the Shetland Island oceanic fragment, Scottish Caledonides: evidence from anatectic plagiogranites in 'layer 3' shear zones. *Geological Magazine*, **128**, 667-671.

Stobbs, I., 2013, The Charlestown Inlier, Co. Mayo: mineralisation, geochemistry and regional correlation with allochtonous Caledonian island arcs across Ireland. MSci thesis, Imperial College London, 61pp.

Stone, P., 2014, A review of geological origins and relationships in the Ballantrae Complex, SW Scotland. *Scottish Journal of Geology*, **50**, 1-25.

Tapster, S., Condon, D.J., Naden, J., Noble, S.R., Petterson, M.G., Roberts, N.M.W., Saunders, A.D. & Smith, D.J., 2016. Rapid thermal rejuvenation of high-crystallinity magma linked to porphyry copper deposit formation; evidence from the Koloula Porphyry Prospect, Solomon Islands. *Earth and Planetary Science Letters*, **442**, 206-217.

Thirlwall, M.F. & Bluck, B.J., 1984, Sr–Nd isotope and geological evidence that the Ballantrae "ophiolite", SW Scotland, is polygenetic. *In*: Gass, I.G., Lippard, S.J., Shelton, A.W. (eds.), *Ophiolites and Oceanic Lithosphere*. Journal of the Geological Society, London, Special Publication 13, 215–230.

van Staal, C.R., 2007, Pre-Carboniferous tectonic evolution and metallogeny of the Canadian Appalachians. *In* Goodfellow, W.D. (ed) *Mineral Deposits of Canada: A synthesis of major deposit-types, district metallogeny, the evolution of geological provinces, and exploration methods*. Geological Association of Canada, Mineral Deposits Division, Special Publication 5, 793-818

van staal, C.R., Chew, D.M., Zagorevski, A., McNicoll, V., Hibbard, J., Skulski, T., Castonguay, S., Escayola, M.P., Sylvester, P.J., 2014, Evidence of Late Ediacaran hyperextension of the Laurentian Iapetan margin in the Birchy Complex, Baie Verte

Peninsula, northwest Newfoundland: implications for the Opening of Iapetus, Formation of peri-Laurentian microcontinents and Taconic-Grampian orogenesis. *Geoscience Canada*, **40**, http://dx.doi.org/10.12789/geocanj.2013.40.006.

Wiedenbeck, M., Allé, P., Corfu, F., Griffin, W. L., Meier, M., Oberli, F., von Quadt, A., Roddick, J. C. & Spiegel, W., 1995, Three natural zircon standards for U-Th-Pb, Lu-Hf, trace element and REE analysis: Geostandards Newsletter, v. 19, p. 1- 23.

Wood, D.A., 1980, The application of a Th-Hf-Ta diagram to problems of tectonomagmatic classification and to establishing the nature of crustal contamination of basaltic lavas of the British Tertiary Volcanic Province. *Earth and Planetary Science Letters*, **50**, 11-30.

Wrafter, J.P. & Graham, J.R., 1989, Ophiolitic detritus in the Ordovician sediments of South Mayo, Ireland. *Journal of the Geological Society, London*, **146**, 213–215.

Yeats, C.J., Hollis, S.P., Halfpenny, A., Corona, J-C., LaFlamme, C., Southam, G., Fiorentini, M., Herrington, R.J. & Spratt, J., 2017, Actively forming Kuroko-type volcanic-hosted massive sulfide (VHMS) mineralization at Iheya North, Okinawa Trough, Japan. *Ore Geology Reviews*, **84**, 20-41.

Young, M.E. & Donald, A.W., 2013, A guide to the Tellus data. Geological Survey of Northern Ireland, Belfast, p233.

Figure Captions:

Fig. 1. (a) Setting of the Charlestown Group 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. (2011).

Fig. 2. Cartoon detailing the tectonic evolution of the northern British and Irish Caledonides during the Grampian event, based on the three equivalent and well-documented arc/ophiolite accretion events recognized in the Newfoundland Appalachians (modified after van Staal et al. 2007; 2014; Chew et al. 2010; Hollis et al. 2012). **(a)** Early formation of the suprasubduction affinity Deer Park (DP; >514 ± 3 Ma) and Highland Border (HB; 499 ± 8 Ma) ophiolites (Chew et al., 2010) between the Laurentian margin and outriding microcontinental blocks (such as the Slishwood Division, Tyrone Central Inlier and Midland Valley block). **(b)** Continued closure of the Iapetus Ocean and clogging of the subduction channel led to ophiolite obduction at c. 490 Ma, and subduction polarity reversal. Metamorphism and obduction of the HB ophiolite is constrained by ^{40}Ar-^{39}Ar ages of 490 ± 4 Ma (hornblende) and 488 ± 1 Ma (muscovite) (Chew

et al., 2010). The juvenile Lough Nafooey arc system developed above a south-dipping subduction zone from c. 490 Ma (Draut et al., 2004), with its fore-arc preserved as the South Mayo Trough (SMT), and accretionary prism preserved as the Clew Bay Complex (CBC). The Shetland/Unst ophiolite formed at this time (c. 492 ± 3 Ma: Spray and Dunning, 1991), most likely as an oceanic core complex (see Crowley and Strachan, 2014; not shown) along strike from the Lough Nafooey arc system. **(c)** Hard arc-continent collision between the Lough Nafooey arc and the Laurentian margin occurred between c. 484 and 478 Ma (Draut et al., 2004; **Fig. 11**), resulting in the exhumation of the DP ophiolite at 482 ± 1 Ma (Chew et al., 2010), with ophiolitic detritus recorded in the younger Letterbrock Formation of the SMT (Wrafter and Graham, 1989, Dewey and Mange, 1999; **Fig. 11**). The obduction of the Shetland ophiolite also occurred around this time (484 ± 4 Ma; Crowley and Strachan, 2014; not shown). Hard arc-continent collision at was associated with syncollisional volcanism in the Tourmakeady Group, and led to the initiation of north-dipping subduction outboard of the composite Laurentian margin and the formation of the late c. 484-479 Ma suprasubduction affinity ophiolites (i.e. Tyrone and Ballantrae; Hollis et al., 2013a; Stone, 2014). Both the Ballantrae and Tyrone ophiolites may have been obducted shortly after their formation as collisional thickening progressed SE. Rapid obduction is indicated by K-Ar ages from the metamorphic sole of the Ballantrae ophiolite (c. 478 ± 9 Ma; Bluck et al., 1980) and the recognition of S-type granites in Co. Tyrone constrained to c. 479 Ma (Hollis et al., unpublished). **(d)** Peak deformation and metamorphism was reached in the Grampian event between c. 475 and 465 Ma (reviewed in Chew, 2009). The Tyrone and Ballantrae arc volcanics most likely developed outboard of the composite margin (from c. 475 Ma; **Fig. 11**), as they show evidence for extensive arc-rifting, with arc-obduction in Tyrone occurring prior to c. 470 Ma (Hollis et al., 2013a). Continued northward subduction led to the development of the Southern Uplands (SU) – Down Longford (DL) Terrane, a Late Ordovician to Silurian accretionary prism.

Fig. 3. **(a)** Geological map of Charlestown Inlier (after Long et al., 2005). White crosses A to C denote graptolite localities (A and B from Cummins, 1954; C new Knock Airport fauna). C also denotes the position of samples for CA-ID-TIMS U-Pb zircon geochronology. **(b)** Geological line work of the Charlestown Group (from **Fig. 3a**) superimposed over the Tellus Border (Hodgson and Ture, 2014) Total Magnetic Intensity map highlighting the extension of the Charlestown Group under Carboniferous cover for at least 4km to the NE and 10km to the

SW. Two 2km x 4km circular magnetic features to the east of the Charlestown Inlier most likely represent concealed Late Caledonian intrusions.

Fig. 4. Cross section through the Charlestown Cu deposit (modified after O'Connor and Poustie, 1986). Type 1 and 2 breccias developed around the upper margins of the QFP units as magma was intruded into unconsolidated wet sediment (forming peperitic contacts) just below the seafloor. Chalcopyrite mineralization occurred directly below, and within, the zone of pyrite mineralization, above the chloritic feeder zone. Sphalerite mineralization occurs down-dip of the pyrite zone, precipitating from cooler hydrothermal fluids during seawater entrainment into the brecciated QPF margin. The barite zone of O'Connor and Poustie (1986) is not shown, but overlaps the area of pyrite and chalcopyrite mineralization. Chloritic-sericitic alteration occurs in the hanging-wall and flanks of the deposit. A silicified central zone is also consistent with a VMS system.

Fig. 5. (a) Knock Airport logged section showing the position of samples collected for biostratigraphy and U-Pb zircon dating. **(b)** Banded crystal tuff (KGC2). **(c)** Graptolite bearing mudstone which yielded the Ya2 fauna described in Rushton (2014). **(d)** Contact between pyroxene diorite and laminated mudstones.

Fig. 6. Scanning Electron Microscope (SEM) images of alteration assemblages throughout the Charlestown Group. (a) CT113: Crystal tuff from the Horan Formation. (b) CT206: Altered felsic volcanic breccia from the Carracastle Formation.

Fig. 7. Selected graptolite fauna identified from the Charlestown Group. **(a)** *Pseudisograptus manubriatus* (Hall) group, Natural History Museum QQ.265. Knock Airport section. **(b)** *Yutagraptus? v-deflexus* (Harris), Natural History Museum QQ.262. Knock Airport section. **(c)** *Didymograpsus (Expansograptus)* aff. *nitidus* (J. Hall), Sedgwick Museum A.61368. Cummins' locality A. **(d)** *Isograptus caduceus?* cf. *nanus* Ruedemann, Natural History Museum QQ.263b, partly restored from the counterpart, QQ.263a. Knock Airport section. **(e)** *Arienigraptus?* sp., Natural History Museum QQ.264. Knock Airport section. **(f)** *Oncograptus* sp., Sedgwick Museum A.24401. Cummins' locality A. **(g-i)** *Exigraptus uniformis* Mu, Natural History Museum, QQ.277, QQ.275 and QQ.274a. Graptolite shown in g is a juvenile specimen.

Knock Airport section. **(j-k)** *Skiagraptus gnomonicus* (Harris and Keble), Natural History Museum QQ.269 and QQ.270. Knock Airport section. All scale bars are 2mm in length.

Fig. 8. U-Pb zircon ages for the four dated samples from the Horan Formation of the Charlestown Group.

Fig. 9. Geochemical variation of the Charlestown Group. **(a)** Zr/Ti vs. Nb/Y discrimination diagram for the classification of hydrothermally altered volcanic rocks after Pearce (1996). Ellipses represent 10% probability contours (that is 10% of the samples from that group will plot outside the respective contour) to highlight potential misidentifications using the diagram. **(b)** Nb vs. Y discrimination diagram for the classification of felsic rocks after Pearce et al. (1984; ORG, orogenic granite; synCOLG, syncollisional granite; VAG, volcanic arc granite; WPG, within-plate granitic). **(c)** Zr/Y vs. Y diagram for the classification of VMS fertile felsic rocks after Lesher et al. (1986). Samples which plot in the FIII fields are considered the most prospective for Phanerozoic arcs. **(d)** Nb/Y vs Zr/Y diagram highlighting the geochemical affinity of samples from Charlestown (tholeiitic to calc-alkaline) and similarities to the Tyrone Volcanic Group of Northern Ireland (data compiled from Draut et al., 2009; Cooper et al., 2011; Hollis, 2013; Hollis et al. 2012, 2013b; 2014). **(e)** Th/Yb vs. Nb/Yb diagram of Pearce (2008). Samples from the Charlestown Group plot on a trend parallel to the mantle array indicating a subduction affinity for the lavas. **(f)** La-Nb-Y ternary discrimination diagram for the classification of mafic volcanic rocks after Cabanis and Lecolle (1989). **(g)** Th-Zr-Nb ternary discrimination diagram for the classification of mafic volcanic rocks after Wood (1980; alk, alkaline basalt; CAB, calc-alkaline basalt; eMORB, enriched mid ocean ridge basalt; nMORB, normal mid ocean ridge basalt; IAT, island arc tholeiitic basalt). **(h)** Alteration Box Plot of major element mobility (after Large et al. 2001). Red arrows show 5 common trends during hydrothermal alteration. *Alteration mineralogy:* carb, carbonate; chl, chlorite; kfeld, K-feldspar; py, pyrite; ser, sericite. $AI=100*[K_2O+MgO]/[K_2O+MgO+CaO+Na_2O]$. $CCPI=100*[Fe_2O_{3T}+MgO]/[Fe_2O_{3T}+MgO+K_2O+Na_2O]$.

Fig. 10. Chondrite normalized extended REE diagrams for samples analyzed herein from the Charlestown Group. Grey fields denote datasets from western Ireland (Draut et al., 2002, 2004) and the Tyrone Igneous Complex (Draut et al., 2009; Cooper et al., 2011; Hollis, 2013; Hollis et al. 2012, 2013b; 2014). Chondrite normalization values from McDonough and Sun (1995).

Fig. 11. Stratigraphy, geochemistry and absolute ages for the Ordovician successions of the Irish Caledonides and western Scotland. Diagram modified after Ryan and Dewey (2011) and Hollis et al. (2013a). 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. Stratigraphy of the Tyrone Volcanic Group after Hollis et al. (2012, 2013a, 2014). North and south limbs refer to the Mweelrea syncline (South Mayo Trough). References to biostratigraphic and U-Pb zircon constraints are from Hollis et al. (2013a). Biostratigraphic and U-Pb zircon constraints from the Ballantrae Ophiolite Complex are from the recent review of Stone (2014) and Fujisaki et al. (2015). Correlations for sedimentary dominated successions are shown in greyscale. Red horizontal bars mark the position of ignimbrites and tuffs.

Fig. 12. Timescale of the Middle Ordovician modified after Lindskog et al. (2016). Note that both the GTS 2012 and Lindskog et al. (2016) timescales include the erroneous calibration point from Formil (Cooper et al., 2008). Only on the Sadler et al. (2009) timescale, which does not include the Formil age, do our new CA-ID-TIMS ages match the Ya2 graptolite constraints.

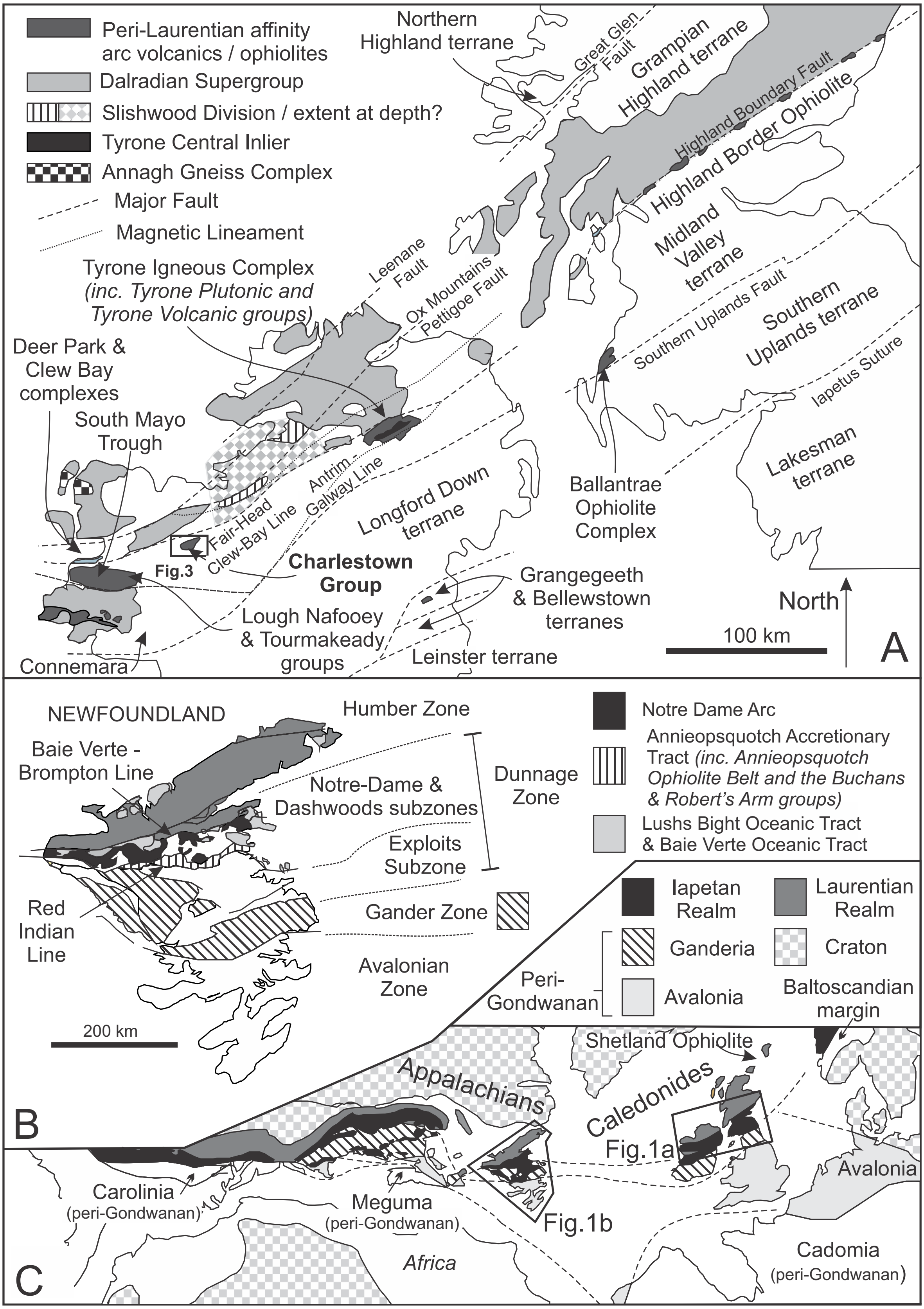
Fig. 13. Schematic cartoon showing the evolution of the Charlestown Cu deposit. A) Emplacement of a subvolcanic intrusion into unconsolidated sediments and volcaniclastics. B) Extrusion of quartz-feldspar phyric dacitic lava and the deposition of crystal tuffs, with localized peperite development. Synvolcanic sills are also emplaced at shallow levels. Hydrothermal circulation is developed through cold down-welling seawater, with heat provided by the underlying magmatism. C) Iron-silica-oxyhydroxides are precipitated as a jasper apron from seafloor exhalation. Mineralization develops where hydrothermal fluids are focused towards the seafloor, with the separation of sphalerite, pyrite and chalcopyrite. Underlying volcanic rocks are hydrothermally altered, with intense chloritization in the feeder zone and more distal zones of quartz-sericite±chlorite alteration. D) Continued burial of the system, with the development of sericitic-chloritic alteration in the hanging-wall of the Charlestown Cu deposit.

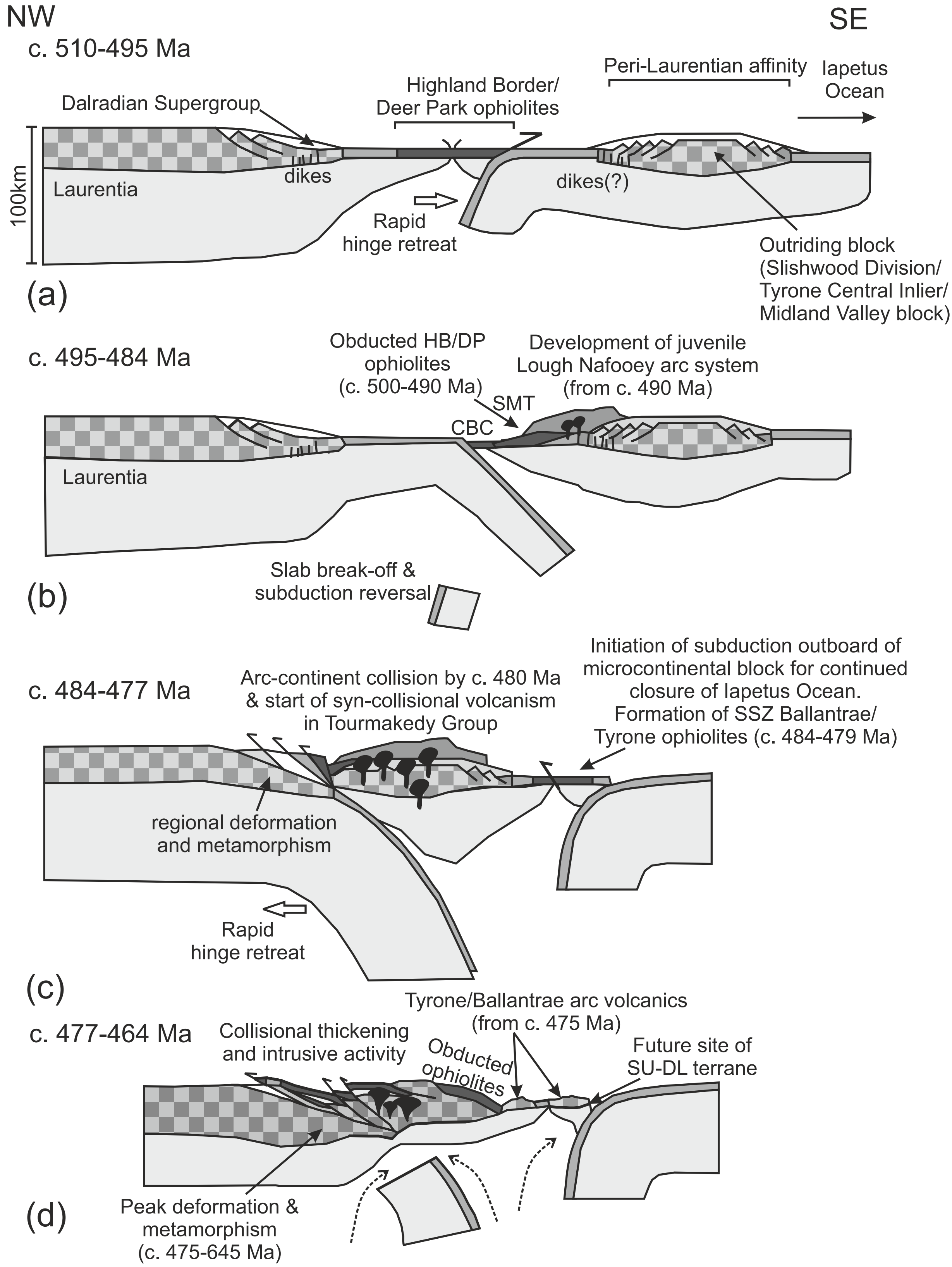
Table 1. U-Pb zircon geochronology data for samples analyzed by CA-ID-TIMS from the Charlestown Group.

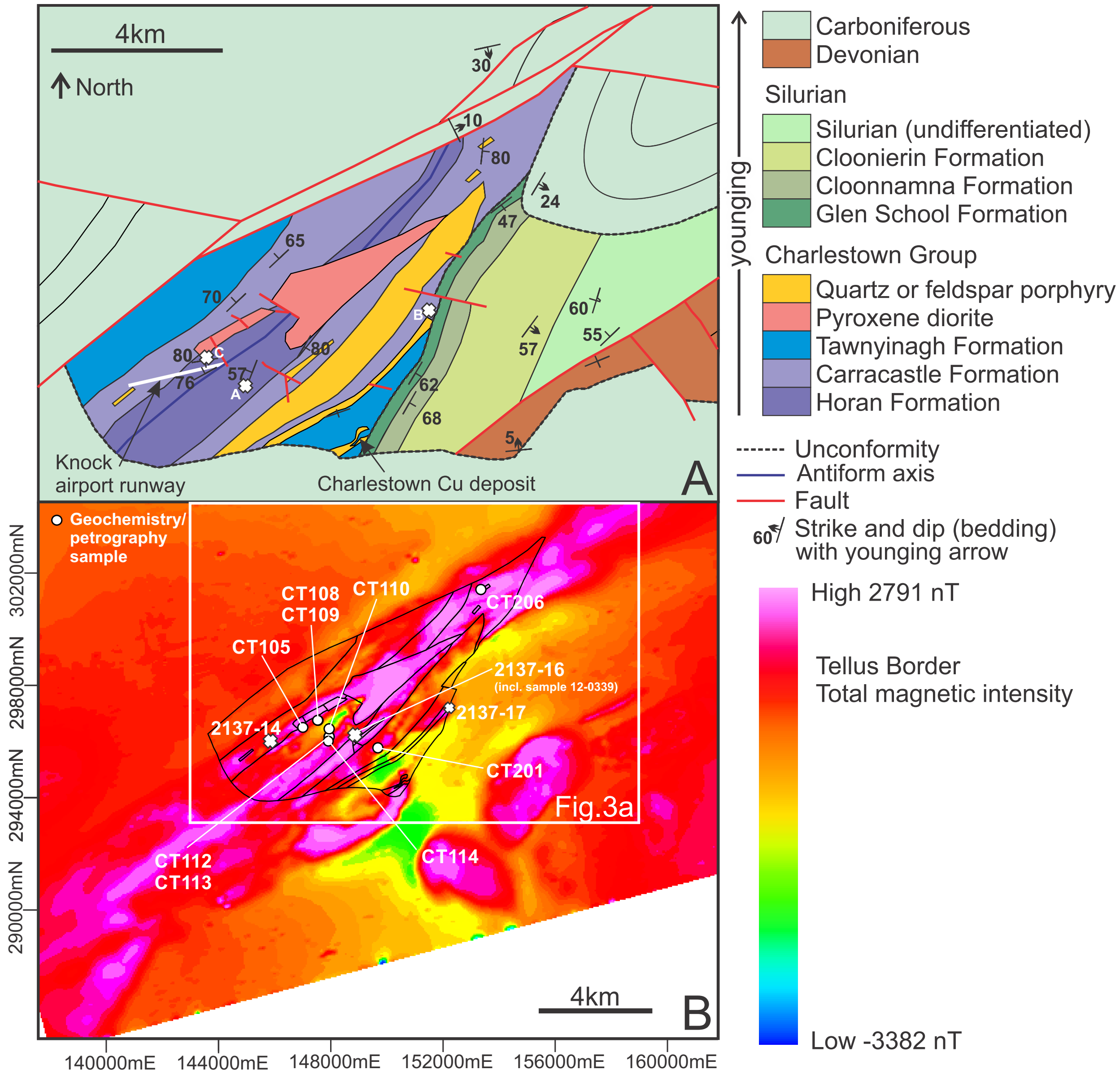
Table 2. Graptolite fauna originally identified by Cummins (1954) and revised by Dewey et al. (1970) from the Charlestown Group.

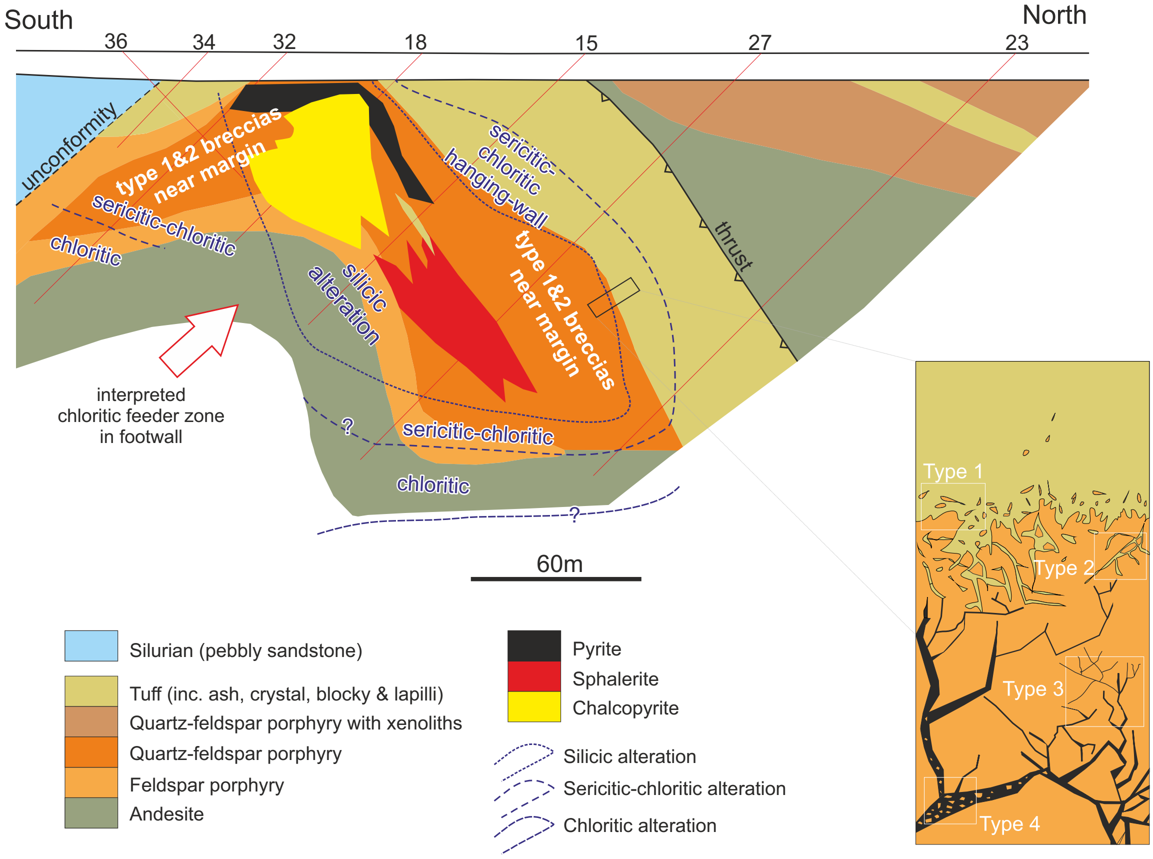
Cummins (1954)	**Dewey et al. (1970)**	
Didymograptus spp. (extensiform)	*D*. cf. *extensus* and *D*. aff. n*itidus*	**Fig. 7c**
D. cf. *deflexus* Elles & Wood	*D*. cf. *v-deflexus* Harris	
Isograptus gibberulus cf. *nanus* Ruedeman	*Oncograptus*? [juv.]	**Fig. 7f.**
Glossograptus sp.	?*G. crudus gisbornensis* Harris & Thomas	
Oncograptus sp.	?*O. upsilon biangulatus* Hall	
Phyllograptus? sp.	?*Trigonograptus ensiformis*	
Tetragraptus sp.		

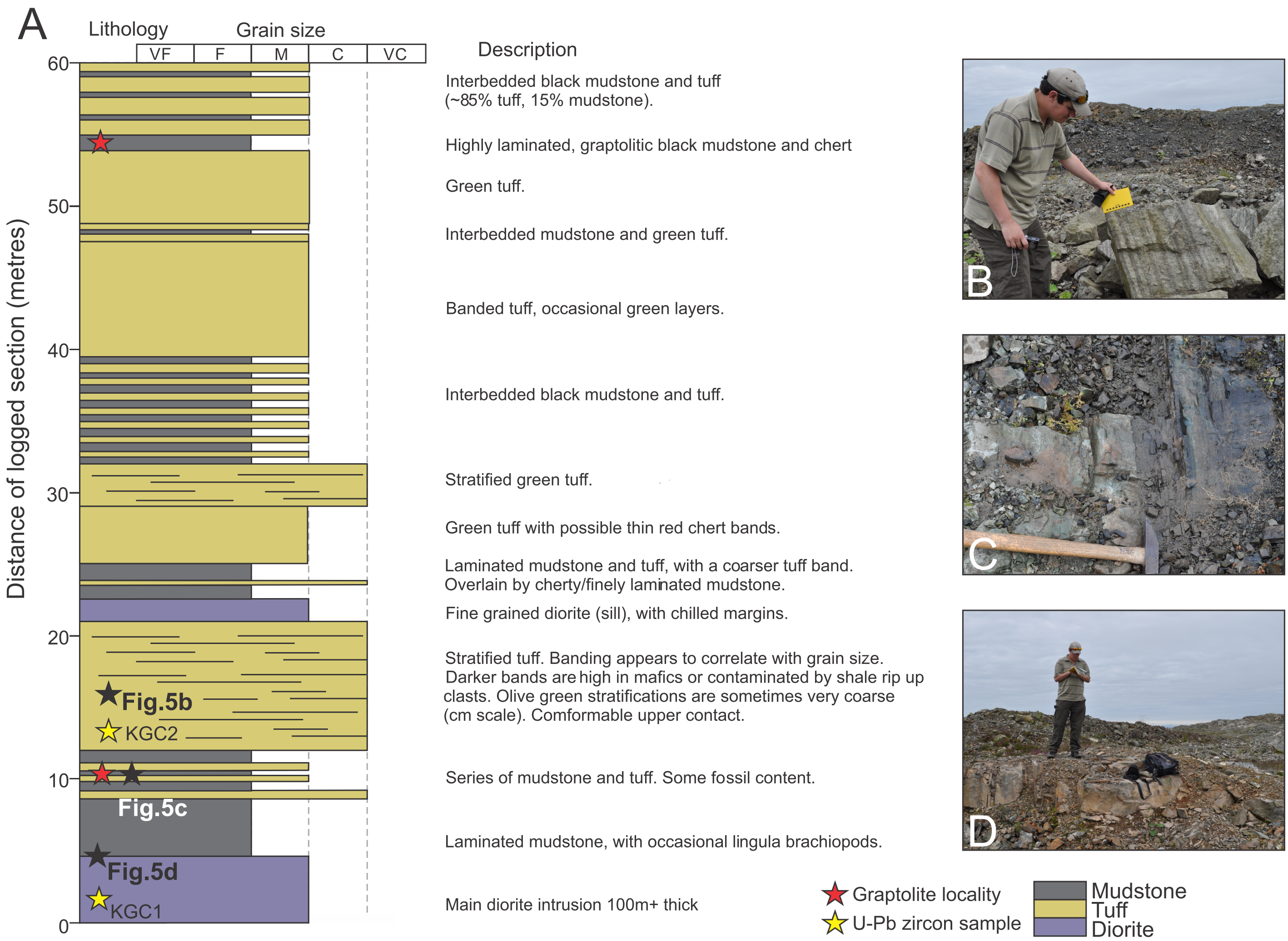
Supplementary Information. Whole rock geochemistry data from the Charlestown Group.


Peri-Laurentian affinity arc volcanics / ophiolites
Dalradian Supergroup
Slishwood Division / extent at depth?
Tyrone Central Inlier
Annagh Gneiss Complex
Major Fault
Magnetic Lineament
Northern Highland terrane
Great Glen Fault
Grampian Highland terrane
Highland Boundary Fault
Highland Border Ophiolite
Midland Valley terrane
Tyrone Igneous Complex (inc. Tyrone Plutonic and Tyrone Volcanic groups)
Leenane Fault
Ox Mountains Pettigoe Fault
Southern Uplands Fault
Southern Uplands terrane
Iapetus Suture
Deer Park & Clew Bay complexes
South Mayo Trough
Lakesman terrane
Antrim Galway Line
Fair-Head Clew-Bay Line
Longford Down terrane
Ballantrae Ophiolite Complex
Fig.3
Charlestown Group
Grangegeeth & Bellewstown terranes
Lough Nafooey & Tourmakeady groups
North
100 km
Connemara
Leinster terrane
A
NEWFOUNDLAND
Humber Zone
Notre Dame Arc
Annieopsquotch Accretionary Tract (inc. Annieopsquotch Ophiolite Belt and the Buchans & Robert's Arm groups)
Lushs Bight Oceanic Tract & Baie Verte Oceanic Tract
Baie Verte - Brompton Line
Notre-Dame & Dashwoods subzones
Dunnage Zone
Exploits Subzone
Red Indian Line
Gander Zone
Avalonian Zone
200 km
B
Iapetan Realm
Laurentian Realm
Ganderia
Craton
Peri-Gondwanan
Avalonia
Baltoscandian margin
Shetland Ophiolite
Appalachians
Caledonides
Fig.1a
Avalonia
Carolinia (peri-Gondwanan)
Meguma (peri-Gondwanan)
Fig.1b
Africa
Cadomia (peri-Gondwanan)
C

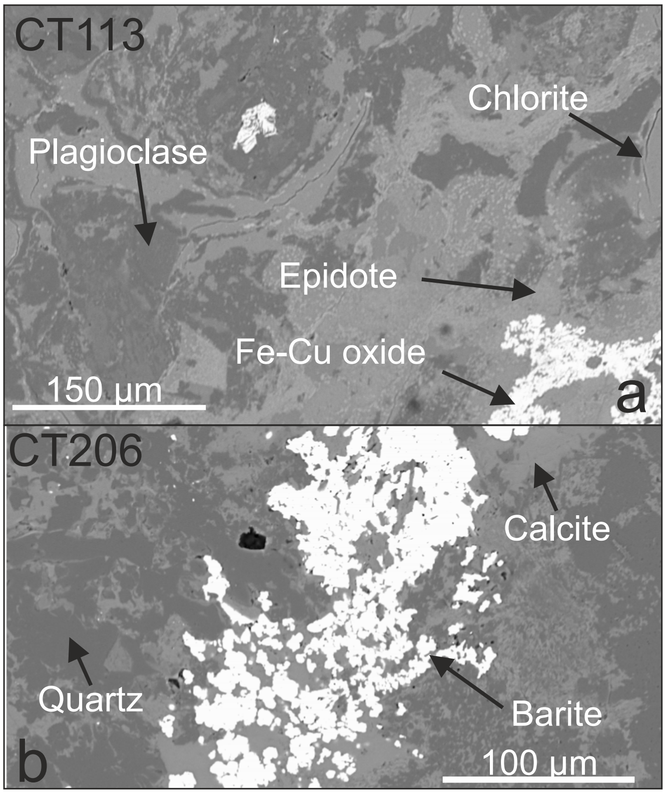

NW
SE
c. 510-495 Ma
Peri-Laurentian affinity
Iapetus Ocean
Highland Border/ Deer Park ophiolites
Dalradian Supergroup
100km
Laurentia
dikes
dikes(?)
Rapid hinge retreat
Outriding block (Slishwood Division/ Tyrone Central Inlier/ Midland Valley block)
(a)
c. 495-484 Ma
Obducted HB/DP ophiolites (c. 500-490 Ma)
Development of juvenile Lough Nafooey arc system (from c. 490 Ma)
SMT
CBC
Laurentia
Slab break-off & subduction reversal
(b)
c. 484-477 Ma
Arc-continent collision by c. 480 Ma & start of syn-collisional volcanism in Tourmakedy Group
Initiation of subduction outboard of microcontinental block for continued closure of Iapetus Ocean. Formation of SSZ Ballantrae/ Tyrone ophiolites (c. 484-479 Ma)
regional deformation and metamorphism
Rapid hinge retreat
(c)
c. 477-464 Ma
Tyrone/Ballantrae arc volcanics (from c. 475 Ma)
Collisional thickening and intrusive activity
Obducted ophiolites
Future site of SU-DL terrane
Peak deformation & metamorphism (c. 475-645 Ma)
(d)

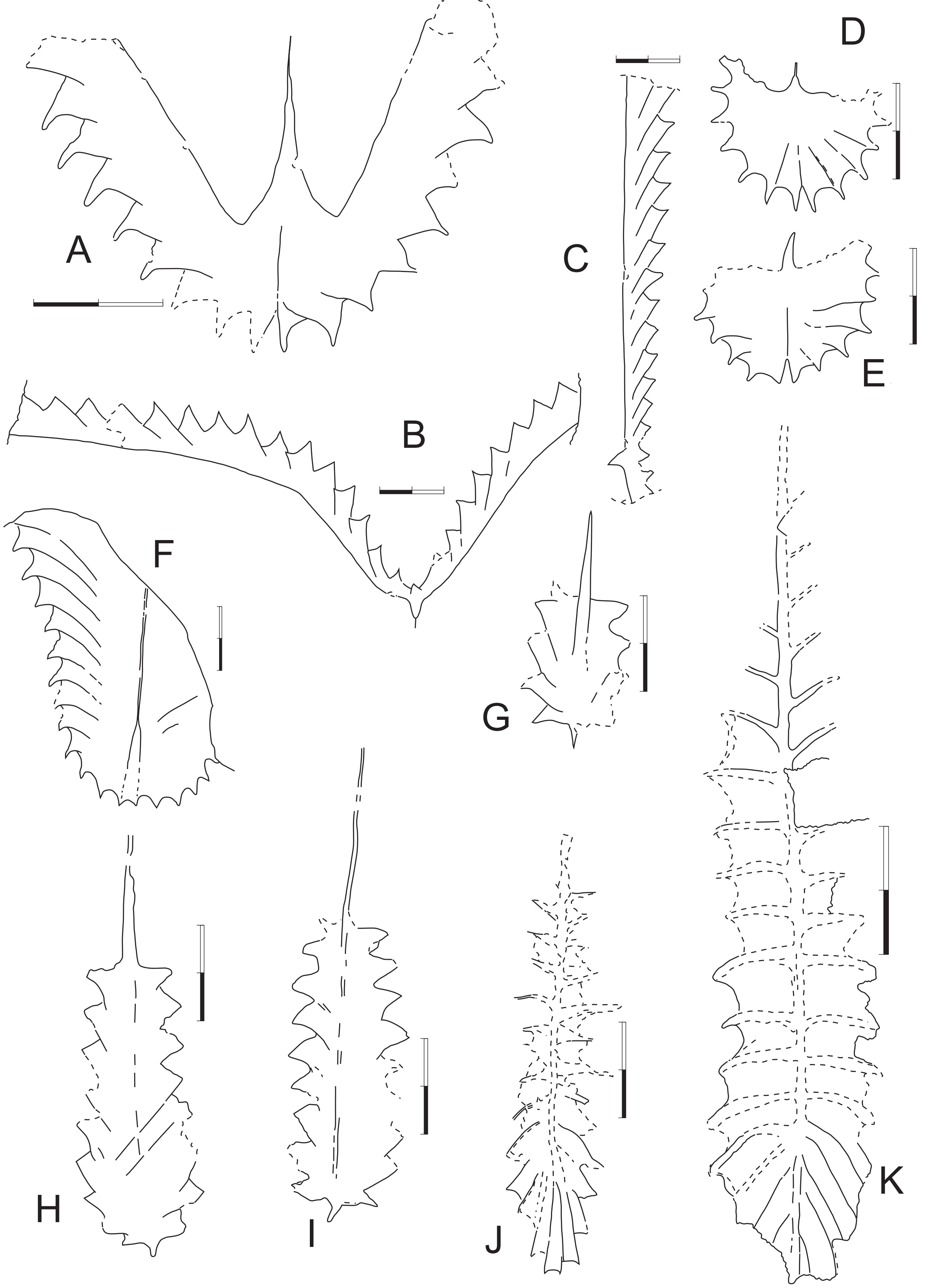

4km
North
30
10
80
24
47
65
70
80
C
76
57
A
80
B
60
55
57
62
68
5
Knock
airport runway
Charlestown Cu deposit
A
Carboniferous
Devonian
Silurian
Silurian (undifferentiated)
Cloonierin Formation
Cloonnamna Formation
Glen School Formation
Charlestown Group
Quartz or feldspar porphyry
Pyroxene diorite
Tawnyinagh Formation
Carracastle Formation
Horan Formation
younging
Unconformity
Antiform axis
Fault
60
Strike and dip (bedding)
with younging arrow
Geochemistry/
petrography
sample
CT108
CT109
CT110
CT206
CT105
2137-16
(incl. sample 12-0339)
2137-17
2137-14
CT201
Fig.3a
CT112
CT113
CT114
4km
B
302000mN
298000mN
294000mN
290000mN
140000mE
144000mE
148000mE
152000mE
156000mE
160000mE
High 2791 nT
Tellus Border
Total magnetic intensity
Low -3382 nT


South
North
36
34
32
18
15
27
23
unconformity
type 1&2 breccias near margin
sericitic-chloritic
chloritic
silicic alteration
sericitic-chloritic hanging-wall
type 1&2 breccias near margin
thrust
interpreted chloritic feeder zone in footwall
?
sericitic-chloritic
chloritic
?
60m
Silurian (pebbly sandstone)
Tuff (inc. ash, crystal, blocky & lapilli)
Quartz-feldspar porphyry with xenoliths
Quartz-feldspar porphyry
Feldspar porphyry
Andesite
Pyrite
Sphalerite
Chalcopyrite
Silicic alteration
Sericitic-chloritic alteration
Chloritic alteration
Type 1
Type 2
Type 3
Type 4



A
Lithology
Grain size
VF
F
M
C
VC
Description
Distance of logged section (metres)
60
50
40
30
20
10
0
Interbedded black mudstone and tuff (~85% tuff, 15% mudstone).
Highly laminated, graptolitic black mudstone and chert
Green tuff.
Interbedded mudstone and green tuff.
Banded tuff, occasional green layers.
Interbedded black mudstone and tuff.
Stratified green tuff.
Green tuff with possible thin red chert bands.
Laminated mudstone and tuff, with a coarser tuff band. Overlain by cherty/finely laminated mudstone.
Fine grained diorite (sill), with chilled margins.
Stratified tuff. Banding appears to correlate with grain size. Darker bands are high in mafics or contaminated by shale rip up clasts. Olive green stratifications are sometimes very coarse (cm scale). Comformable upper contact.
Series of mudstone and tuff. Some fossil content.
Laminated mudstone, with occasional lingula brachiopods.
Main diorite intrusion 100m+ thick
Fig.5b
KGC2
Fig.5c
Fig.5d
KGC1
Graptolite locality
U-Pb zircon sample
Mudstone
Tuff
Diorite
B
C
D


CT113
Chlorite
Plagioclase
Epidote
Fe-Cu oxide
150 µm
a
CT206
Calcite
Quartz
Barite
b
100 µm


A
B
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D
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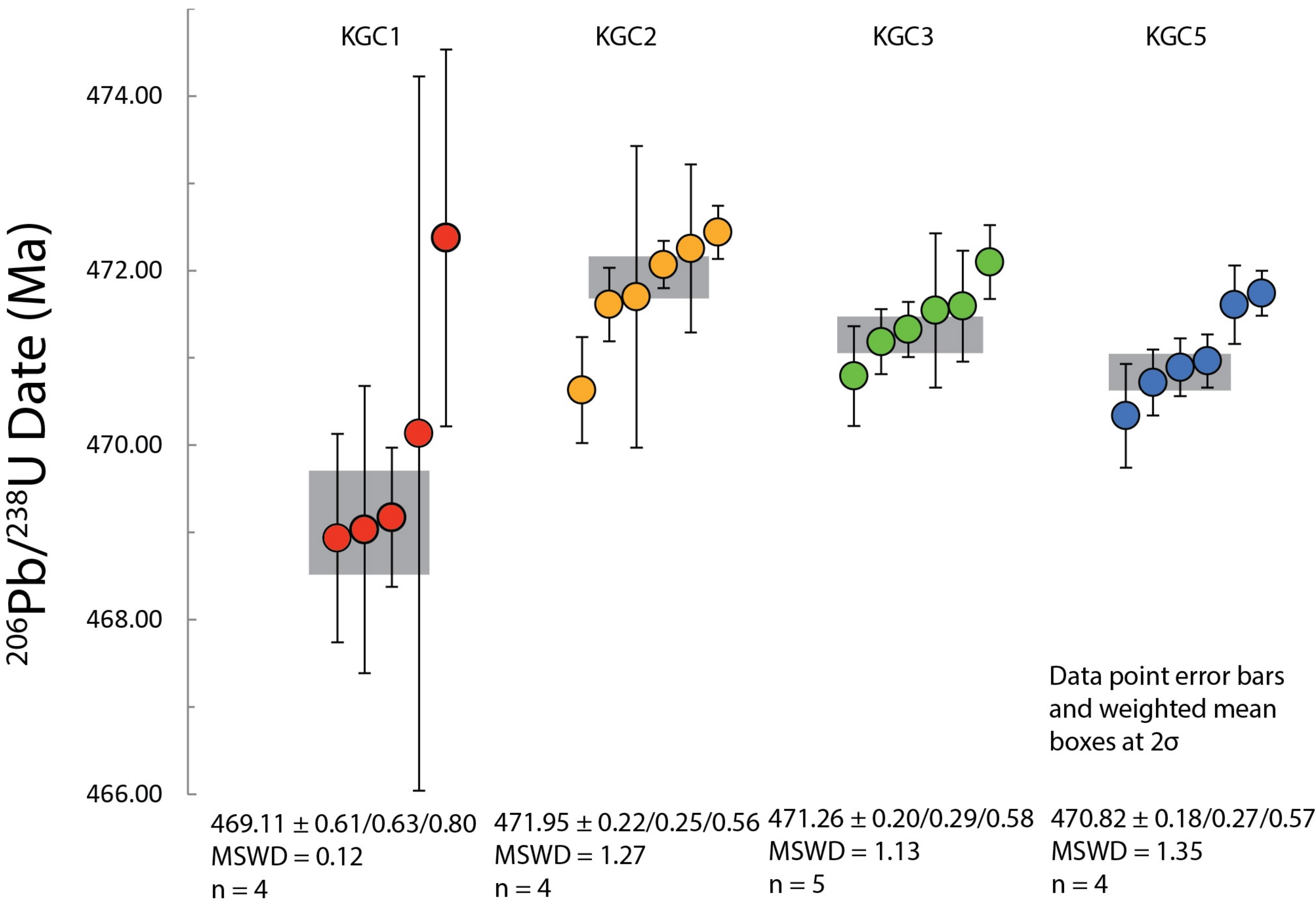
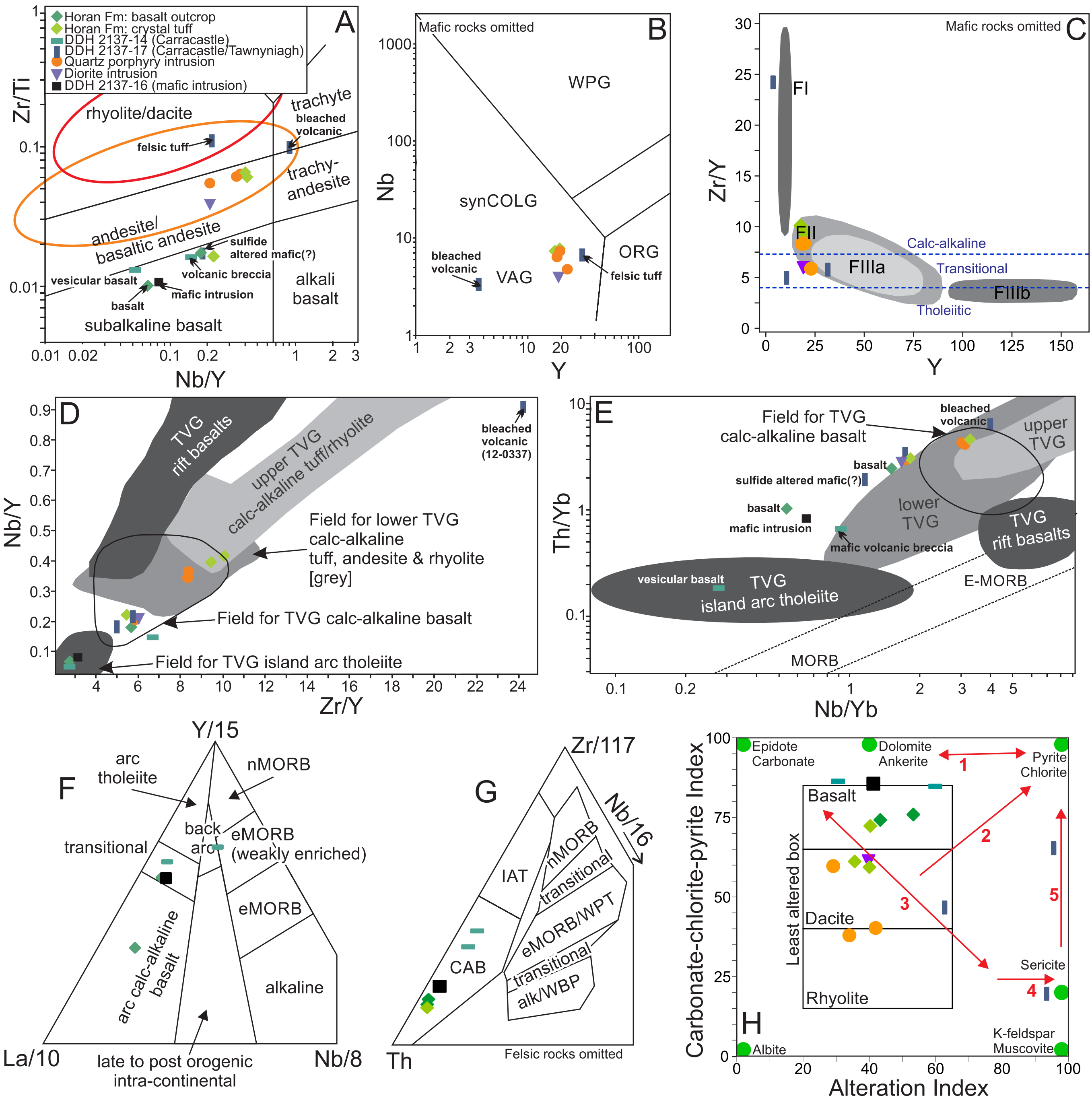
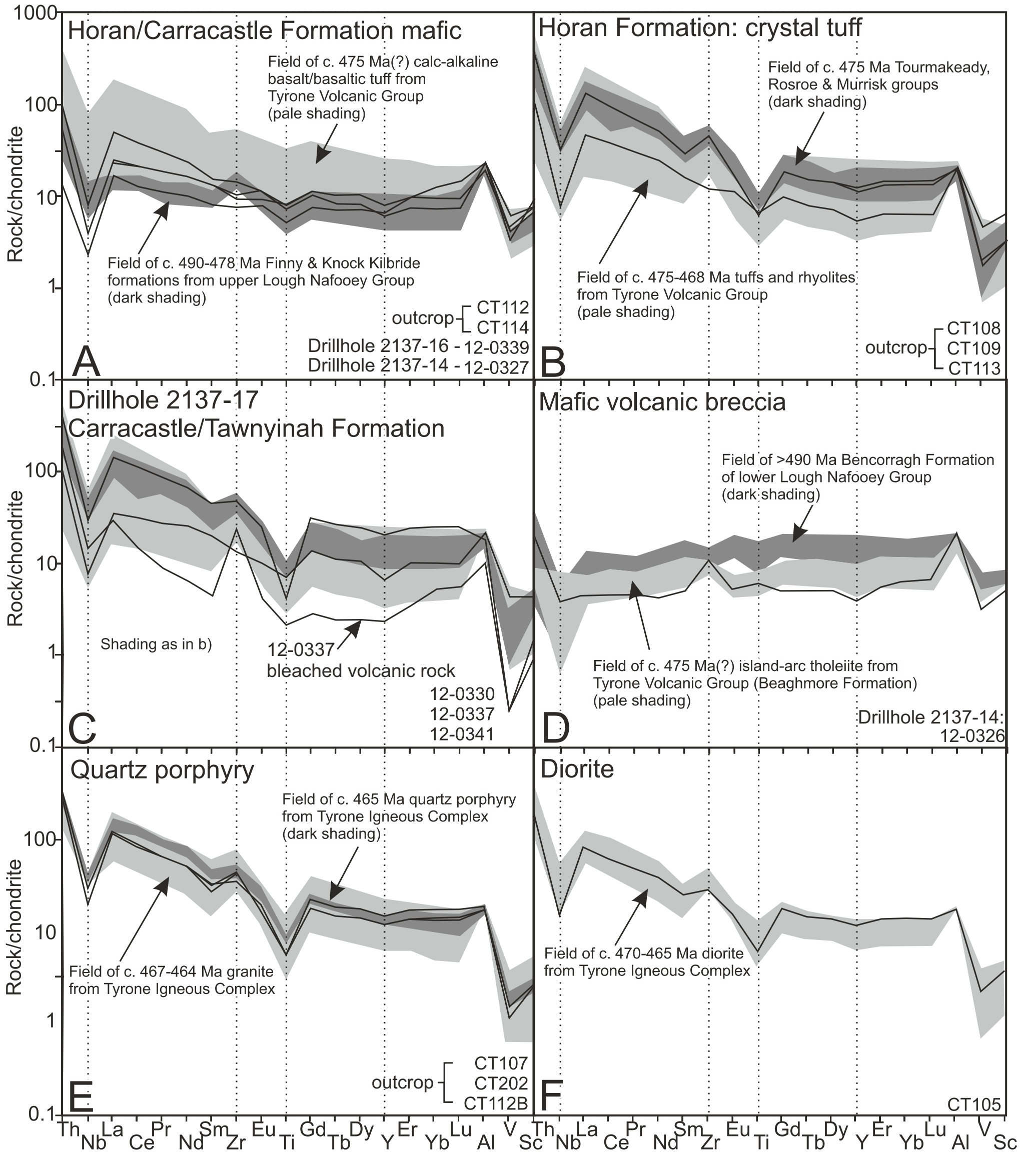
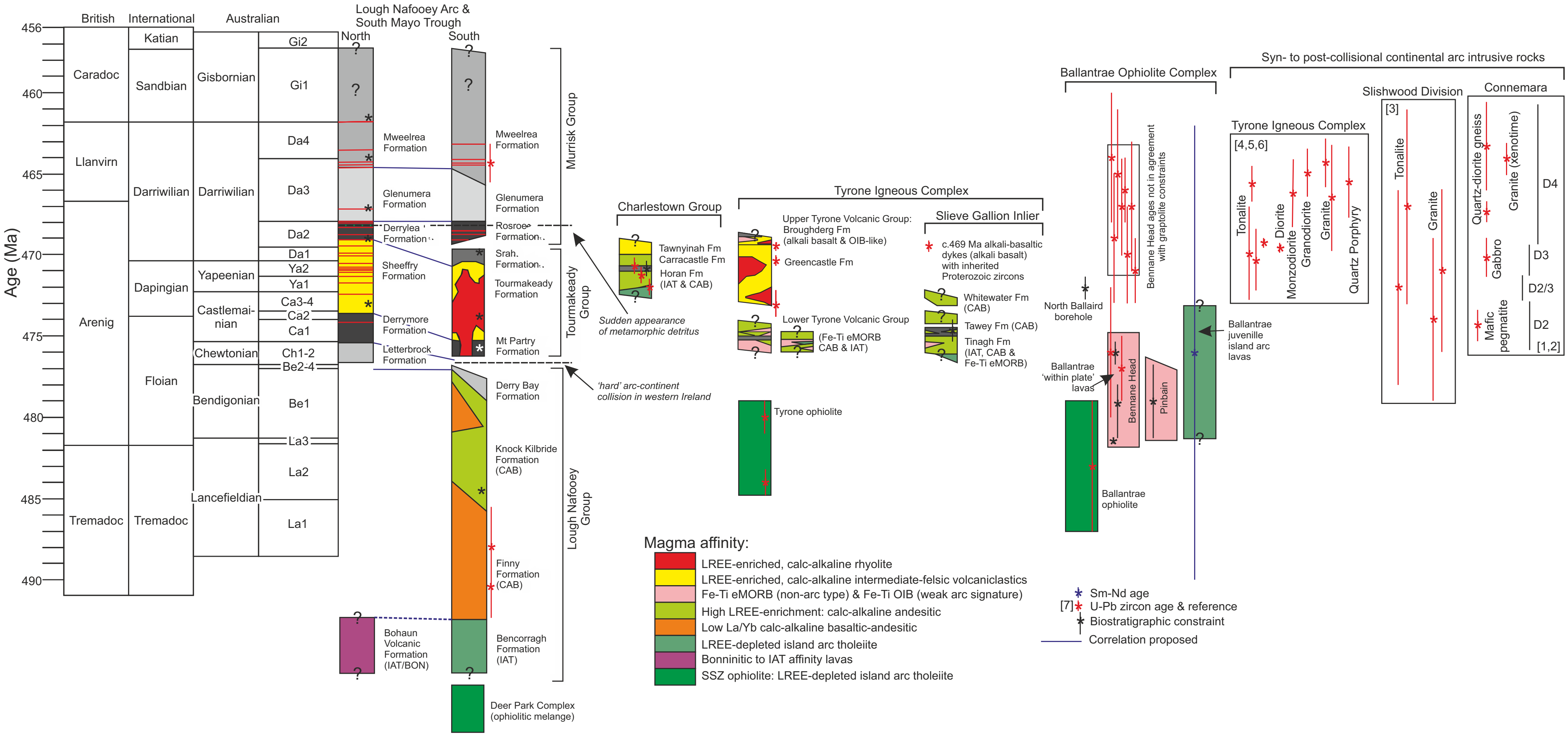
I
J
K


KGC1
KGC2
KGC3
KGC5
474.00
472.00
470.00
468.00
466.00
206Pb/238U Date (Ma)
Data point error bars and weighted mean boxes at 2σ
469.11 ± 0.61/0.63/0.80
MSWD = 0.12
n = 4
471.95 ± 0.22/0.25/0.56
MSWD = 1.27
n = 4
471.26 ± 0.20/0.29/0.58
MSWD = 1.13
n = 5
470.82 ± 0.18/0.27/0.57
MSWD = 1.35
n = 4

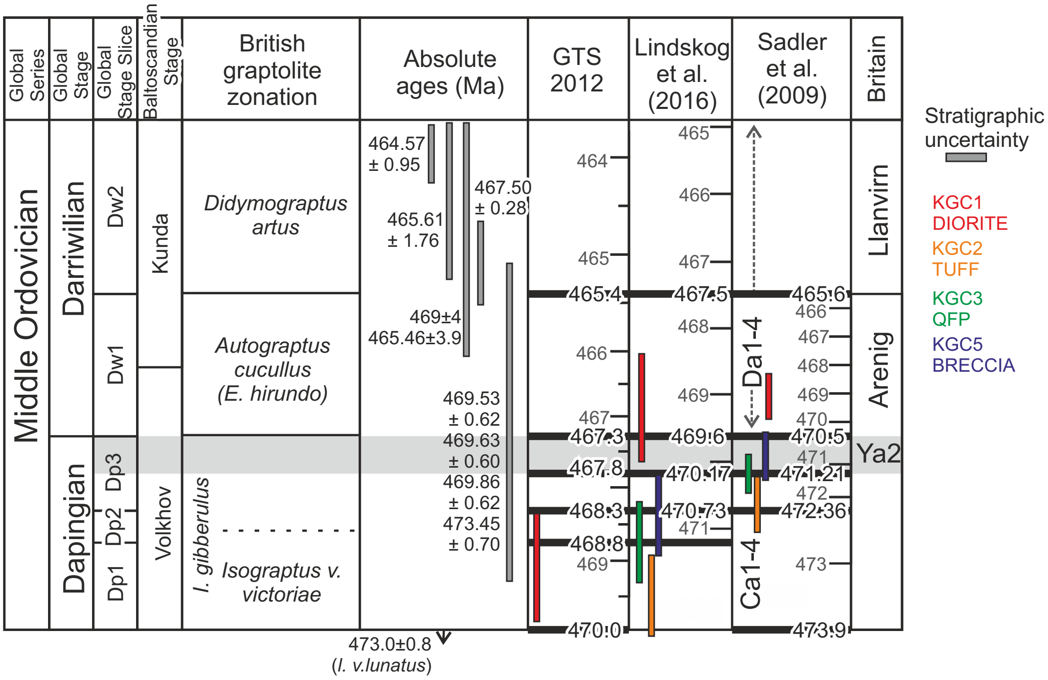


A
Horan Fm: basalt outcrop
Horan Fm: crystal tuff
DDH 2137-14 (Carracastle)
DDH 2137-17 (Carracastle/Tawnyniagh)
Quartz porphyry intrusion
Diorite intrusion
DDH 2137-16 (mafic intrusion)
Zr/Ti
rhyolite/dacite
trachyte
bleached volcanic
felsic tuff
trachy-andesite
andesite/basaltic andesite
sulfide altered mafic(?)
volcanic breccia
vesicular basalt
basalt
mafic intrusion
alkali basalt
subalkaline basalt
Nb/Y
B
Mafic rocks omitted
WPG
synCOLG
VAG
ORG
bleached volcanic
felsic tuff
Nb
Y
C
Mafic rocks omitted
FI
FII
FIIIa
FIIIb
Calc-alkaline
Transitional
Tholeiitic
Zr/Y
Y
D
TVG rift basalts
upper TVG calc-alkaline tuff/rhyolite
bleached volcanic (12-0337)
Field for lower TVG calc-alkaline tuff, andesite & rhyolite [grey]
Field for TVG calc-alkaline basalt
Field for TVG island arc tholeiite
Nb/Y
Zr/Y
E
Field for TVG calc-alkaline basalt
bleached volcanic
upper TVG
basalt
sulfide altered mafic(?)
lower TVG
basalt
mafic intrusion
mafic volcanic breccia
TVG rift basalts
vesicular basalt
TVG island arc tholeiite
E-MORB
MORB
Th/Yb
Nb/Yb
F
Y/15
arc tholeiite
nMORB
transitional
back arc
eMORB (weakly enriched)
eMORB
arc calc-alkaline basalt
alkaline
La/10
late to post orogenic intra-continental
Nb/8
G
Zr/117
Nb/16
IAT
nMORB
transitional
eMORB/WPT
transitional
alk/WBP
CAB
Th
Felsic rocks omitted
H
Epidote Carbonate
Dolomite Ankerite
Pyrite Chlorite
Basalt
Dacite
Rhyolite
Least altered box
Sericite
Albite
K-feldspar Muscovite
Carbonate-chlorite-pyrite Index
Alteration Index

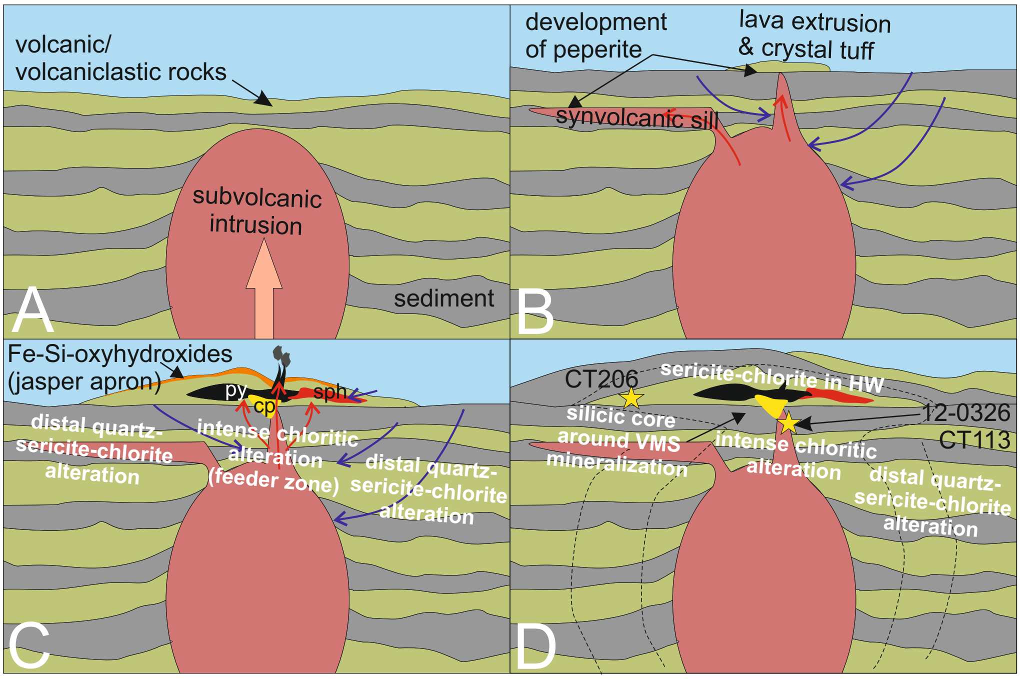

Horan/Carracastle Formation mafic
Field of c. 475 Ma(?) calc-alkaline basalt/basaltic tuff from Tyrone Volcanic Group (pale shading)
Field of c. 490-478 Ma Finny & Knock Kilbride formations from upper Lough Nafooey Group (dark shading)
outcrop CT112 CT114
Drillhole 2137-16 - 12-0339
Drillhole 2137-14 - 12-0327
A
Horan Formation: crystal tuff
Field of c. 475 Ma Tourmakeady, Rosroe & Murrisk groups (dark shading)
Field of c. 475-468 Ma tuffs and rhyolites from Tyrone Volcanic Group (pale shading)
outcrop CT108 CT109 CT113
B
Drillhole 2137-17
Carracastle/Tawnyinah Formation
Shading as in b)
12-0337 bleached volcanic rock
12-0330
12-0337
12-0341
C
Mafic volcanic breccia
Field of >490 Ma Bencorragh Formation of lower Lough Nafooey Group (dark shading)
Field of c. 475 Ma(?) island-arc tholeiite from Tyrone Volcanic Group (Beaghmore Formation) (pale shading)
Drillhole 2137-14: 12-0326
D
Quartz porphyry
Field of c. 465 Ma quartz porphyry from Tyrone Igneous Complex (dark shading)
Field of c. 467-464 Ma granite from Tyrone Igneous Complex
outcrop CT107 CT202 CT112B
E
Diorite
Field of c. 470-465 Ma diorite from Tyrone Igneous Complex
CT105
F
Rock/chondrite
1000
100
10
1
0.1
Th Nb La Ce Pr Nd Sm Zr Eu Ti Gd Tb Dy Y Er Yb Lu Al V Sc



Age (Ma)
British
International
Australian
Lough Nafooey Arc & South Mayo Trough
North
South
Caradoc
Llanvirn
Arenig
Tremadoc
Katian
Sandbian
Darriwilian
Dapingian
Floian
Tremadoc
Gisbornian
Darriwilian
Yapeenian
Castlemai-nian
Chewtonian
Bendigonian
Lancefieldian
Gi2
Gi1
Da4
Da3
Da2
Da1
Ya2
Ya1
Ca3-4
Ca2
Ca1
Ch1-2
Be2-4
Be1
La3
La2
La1
Mweelrea Formation
Glenumera Formation
Derrylea Formation
Sheeffry Formation
Derrymore Formation
Letterbrock Formation
Rosroe Formation
Srah. Formation
Tourmakeady Formation
Mt Partry Formation
Derry Bay Formation
Knock Kilbride Formation (CAB)
Finny Formation (CAB)
Bencorragh Formation (IAT)
Bohaun Volcanic Formation (IAT/BON)
Deer Park Complex (ophiolitic melange)
Murrisk Group
Tourmakeady Group
Lough Nafooey Group
Charlestown Group
Tawnyinah Fm
Carracastle Fm
Horan Fm (IAT & CAB)
Sudden appearance of metamorphic detritus
'hard' arc-continent collision in western Ireland
Tyrone Igneous Complex
Upper Tyrone Volcanic Group: Broughderg Fm (alkali basalt & OIB-like)
Greencastle Fm
Lower Tyrone Volcanic Group
(Fe-Ti eMORB CAB & IAT)
Tyrone ophiolite
Slieve Gallion Inlier
c.469 Ma alkali-basaltic dykes (alkali basalt) with inherited Proterozoic zircons
Whitewater Fm (CAB)
Tawey Fm (CAB)
Tinagh Fm (IAT, CAB & Fe-Ti eMORB)
Ballantrae Ophiolite Complex
Bennane Head ages not in agreement with graptolite constraints
North Ballaird borehole
Ballantrae 'within plate' lavas
Bennane Head
Pinbain
Ballantrae juvenile island arc lavas
Ballantrae ophiolite
Syn- to post-collisional continental arc intrusive rocks
Tyrone Igneous Complex
[4,5,6]
Tonalite
Diorite
Monzodiorite
Granodiorite
Granite
Quartz Porphyry
Slishwood Division
[3]
Tonalite
Granite
Connemara
Quartz-diorite gneiss
Granite (xenotime)
Gabbro
Mafic pegmatite
D4
D3
D2/3
D2
[1,2]
Magma affinity:
LREE-enriched, calc-alkaline rhyolite
LREE-enriched, calc-alkaline intermediate-felsic volcaniclastics
Fe-Ti eMORB (non-arc type) & Fe-Ti OIB (weak arc signature)
High LREE-enrichment: calc-alkaline andesitic
Low La/Yb calc-alkaline basaltic-andesitic
LREE-depleted island arc tholeiite
Bonninitic to IAT affinity lavas
SSZ ophiolite: LREE-depleted island arc tholeiite
Sm-Nd age
[7] U-Pb zircon age & reference
Biostratigraphic constraint
Correlation proposed



Global Series
Global Stage
Global Stage Slice
Baltoscandian Stage
British graptolite zonation
Absolute ages (Ma)
GTS 2012
Lindskog et al. (2016)
Sadler et al. (2009)
Britain
Middle Ordovician
Darriwilian
Dapingian
Dw2
Dw1
Dp3
Dp2
Dp1
Kunda
Volkhov
Didymograptus artus
Autograptus cucullus (E. hirundo)
I. gibberulus
Isograptus v. victoriae
464.57 ± 0.95
467.50 ± 0.28
465.61 ± 1.76
469±4
465.46±3.9
469.53 ± 0.62
469.63 ± 0.60
469.86 ± 0.62
473.45 ± 0.70
473.0±0.8 (I. v.lunatus)
465.4
467.3
467.8
468.3
468.8
470.0
467.5
469.6
470.17
470.73
465.6
470.5
471.21
472.36
473.9
Da1-4
Ca1-4
Llanvirn
Arenig
Ya2
Stratigraphic uncertainty
KGC1 DIORITE
KGC2 TUFF
KGC3 QFP
KGC5 BRECCIA


volcanic/
volcaniclastic rocks
subvolcanic
intrusion
sediment
A
development
of peperite
lava extrusion
& crystal tuff
synvolcanic sill
B
Fe-Si-oxyhydroxides
(jasper apron)
py
cp
sph
distal quartz-
sericite-chlorite
alteration
intense chloritic
alteration
(feeder zone)
distal quartz-
sericite-chlorite
alteration
C
CT206
sericite-chlorite in HW
silicic core
around VMS
mineralization
intense chloritic
alteration
12-0326
CT113
distal quartz-
sericite-chlorite
alteration
D