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Arc–continent collision and the formation of continental crust: a new geochemical and isotopic record from the Ordovician Tyrone Igneous Complex, Ireland

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Abstract: Collisions between oceanic island-arc terranes and passive continental margins are thought to have been important in the formation of continental crust throughout much of Earth's history. Magmatic evolution during this stage of the plate-tectonic cycle is evident in several areas of the Ordovician Grampian–Taconic orogen, as we demonstrate in the first detailed geochemical study of the Tyrone Igneous Complex, Ireland. New U–Pb zircon dating yields ages of 493 ± 2 Ma from a primitive mafic intrusion, indicating intra-oceanic subduction in Tremadoc time, and 475 ± 10 Ma from a light rare earth element (LREE)-enriched tonalite intrusion that incorporated Laurentian continental material by early Arenig time (Early Ordovician, Stage 2) during arc–continent collision. Notably, LREE enrichment in volcanism and silicic intrusions of the Tyrone Igneous Complex exceeds that of average Dalradian (Laurentian) continental material that would have been thrust under the colliding forearc and potentially recycled into arc magmatism. This implies that crystal fractionation, in addition to magmatic mixing and assimilation, was important to the formation of new crust in the Grampian–Taconic orogeny. Because similar super-enrichment of orogenic melts occurred elsewhere in the Caledonides in the British Isles and Newfoundland, the addition of new, highly enriched melt to this accreted arc terrane was apparently widespread spatially and temporally. Such super-enrichment of magmatism, especially if accompanied by loss of corresponding lower crustal residues, supports the theory that arc–continent collision plays an important role in altering bulk crustal composition toward typical values for ancient continental crust.

The processes responsible for the formation and maintenance of the continental crust are complex and continue to be debated by Earth scientists. Although >40% of extant cratonal crust formed in Archaean time (e.g. Rudnick & Fountain 1995; Hawkesworth & Kemp 2006), additional growth has occurred through accretion of oceanic arcs, plateaux, and microcontinental terranes, and by continental flood volcanism. Mass balancing suggests that arc accretion is essential to compensate for the continuing loss of continental crust in subduction zones (Clift & Vannucchi 2004). Shared trace-element characteristics between intra-oceanic arc volcanism and continental material (depletion in high field strength elements (HFSE), such as Nb, relative to light rare earth element (LREE), K, and Ba) imply that continental material could form at convergent margins (e.g. Davidson 1996). However, the concept of island arcs being the building blocks of continents is not easily reconciled with the mafic, LREE-depleted composition of known intra-oceanic arc crust compared with the andesitic, LREE-enriched continental crust (Taylor 1967; Bryan *et al*. 1972; Taylor & McLennan 1985; Ellam & Hawkesworth 1988; Rudnick & Fountain 1995). Seismic-velocity profiles and field studies of the active Aleutian arc (Holbrook *et al*. 1999) and ancient, accreted arc terranes in Kohistan (Miller & Christensen 1994) and Alaska (DeBari & Coleman 1989; Kelemen *et al*. 2003) reveal dominantly mafic and ultramafic arc crust inconsistent with development of average continental-type material; one notable exception is the observation of low-velocity, siliceous mid-crustal material in the Izu–Bonin Arc by Suyehiro *et al.* (1996). Pearcy *et al.* (1990) and Holbrook *et al.* (1999) proposed a resolution to this paradox: the process of arc–continent collision might alter the composition of arc crust such that the accreted crust is more LREE enriched and andesitic than the arc crust before accretion. Based on the Early Ordovician accretion of an oceanic island arc onto the Laurentian continent as preserved in the Grampian orogen of western Ireland (Connemara and South Mayo terranes; Fig. 1), Draut *et al.* (2002) showed that crystal fractionation producing LREE-enriched, silica-rich melts, coupled with lower crustal loss after orogeny, could drive magmatic compositions toward that of average continental crust. Here, we revisit and expand that finding further to the NE in the Caledonide suture zone. We document more fully the magmatic evolution that occurred during this arc–continent collision, and in doing so, we present the first detailed petrological and geochemical study of the Tyrone Igneous Complex, Ireland.

Geological setting

Early Ordovician collision of an intra-oceanic island arc with the Laurentian passive continental margin was the first substantial orogenic event to occur as the Iapetus Ocean closed (van Staal *et al*. 1998, 2007). This event, which significantly predates final closure of the Iapetus Ocean at *c*. 400 Ma, is known as the Grampian orogeny in the British Isles, where it formed part of the Caledonide suture zone, and as the Taconic orogeny in its

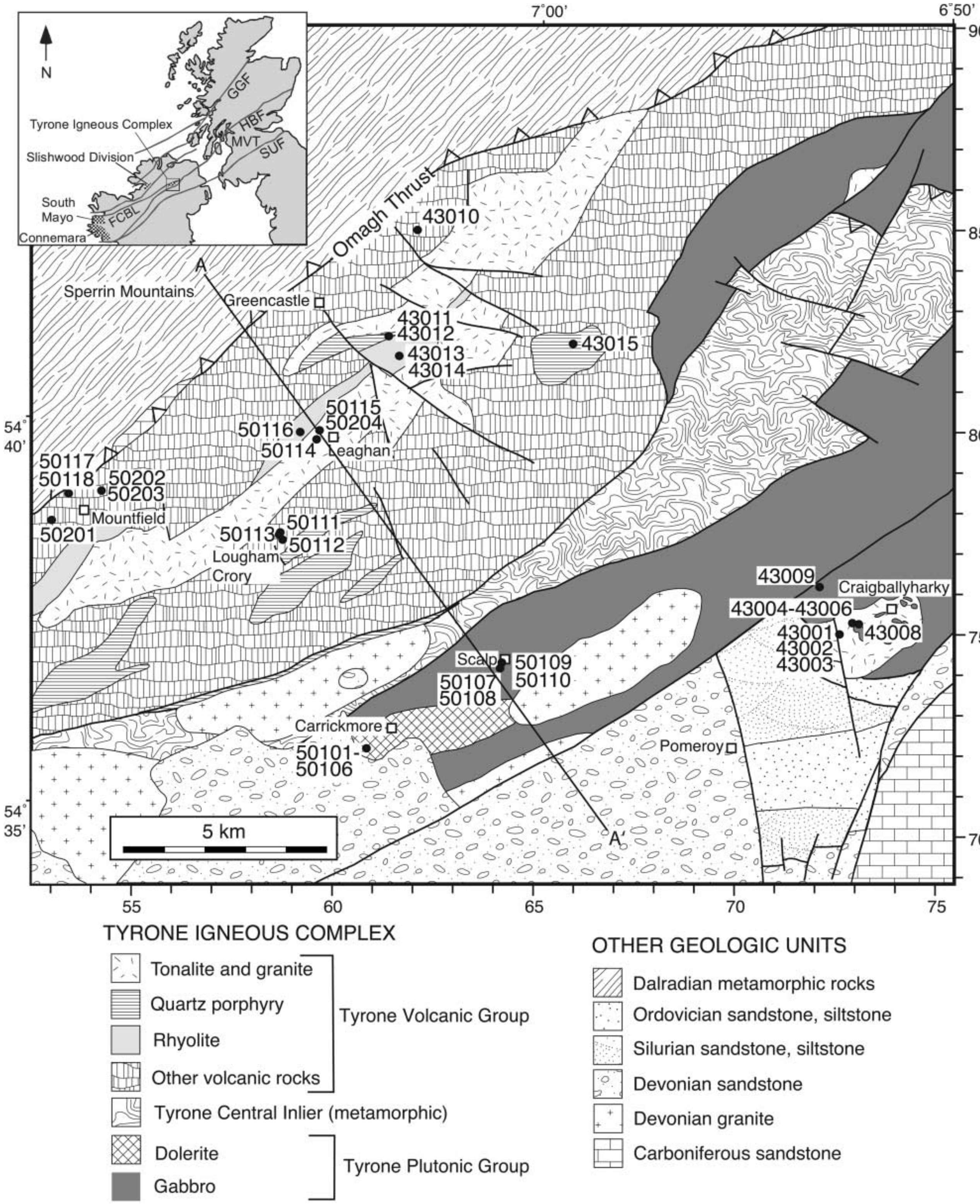

Fig. 1. Geological map of the Tyrone Igneous Complex, based on published maps (Institute of Geological Sciences 1978*a*,*b*; Geological Survey of Northern Ireland 1995). Sampled localities are indicated in the Tyrone Igneous Complex, with the final five digits of sample numbers (see Table 1 for full sample names and descriptions). The intrusion dated by Hutton *et al*. (1985) was sampled in the Craigballyharky area near our samples TY07043001-3. The region shown as 'other volcanic rocks' contains poorly exposed rocks mapped by the Geological Survey of Northern Ireland as basalts and basaltic andesites. Inset map shows the Tyrone Igneous Complex in the context of the Caledonide suture zone in the British Isles: major faults (GGF, Great Glen Fault; HBF, Highland Boundary Fault; FCBL, Fairhead–Clew Bay Line; SUP, Southern Uplands Fault) and the Midland Valley Terrane (MVT) of Scotland, as well as Grampian exposures in Ireland (Connemara, South Mayo, Slishwood Division, and Tyrone Igneous Complex). Line A–A′ shows the orientation of the schematic cross-section in Figure 2.

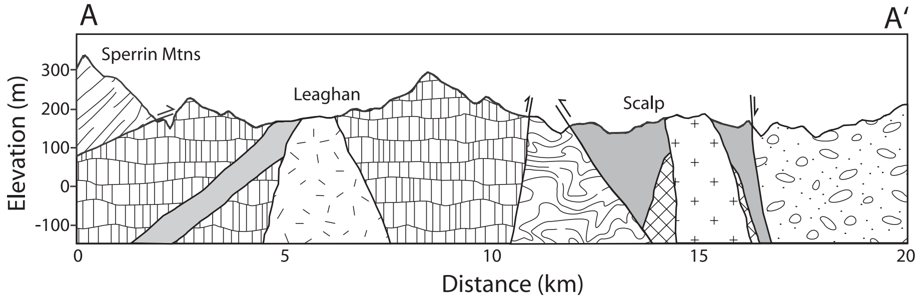

Fig. 2. Schematic cross-section across the Tyrone Igneous Complex from NW to SE, oriented along the line A–A′ in Figure 1 (after Chew *et al.* 2008, and Geological Survey of Northern Ireland maps).

continuation in North America (northern Appalachian suture; e.g. Swinden *et al*. 1997; van Staal *et al*. 1998). Before collision, the intra-oceanic subduction zone involved a north-facing arc that formed above a south-dipping slab (Dewey & Ryan 1990). This oceanic arc is known variously as the Lough Nafooey arc in Ireland (Clift & Ryan 1994; Draut & Clift 2001), the buried Midland Valley arc in Scotland (Armstrong & Owen 2001; Oliver *et al*. 2008), and the Shelburne Falls arc in New England (Karabinos *et al*. 1998), and is thought to correlate with the Baie Verte Oceanic Tract and overlying Snooks Arm Group in Newfoundland (van Staal *et al*. 2007). In Newfoundland exposures, there is evidence that this arc, at least in that part of the margin, was built upon a microcontinent (Dashwoods block) that had rifted away from Laurentia in Cambrian time and was re-accreted onto the continent as the Grampian Orogeny progressed (Waldron & van Staal 2001).

A reversal of subduction polarity followed arc–continent collision, with the new subducting plate dipping to the north beneath the active Laurentian margin (e.g. McKerrow *et al*. 1991). Although the post-collisional (continental) arc is not well exposed in Ireland, elsewhere in the Caledonide suture it is recognized as the Bronson Hill arc of New England (Karabinos *et al.* 1998), as the younger units of the Notre Dame terrane of Newfoundland (van Staal *et al.* 1998, 2007), and as related to the Southern Uplands accretionary prism in Scotland (Armstrong & Owen 2001).

U–Pb analyses of zircon from syncollisional gabbro intrusions in Connemara (Fig. 1; Cliff *et al*. 1996; Friedrich *et al*. 1999), and from tonalite and granitoid bodies in the Slishwood Division (Flowerdew *et al*. 2005), together with trace-element analyses of volcanic rocks from South Mayo in western Ireland (Draut & Clift 2001), indicate that the arc–continent collision event was brief in the British Isles, lasting *c*. 10 Ma (*c*. 475–465 Ma). Nd isotopic ratios of plagiogranite clasts from South Mayo imply that continental material started to enter the trench as early as *c*. 490 Ma, substantially earlier than regional metamorphism and orogeny (Chew *et al*. 2007). Other age constraints on the Grampian orogeny in Ireland include mineral cooling ages from Connemara (Friedrich *et al.* 1999) and the Slishwood Division (Flowerdew *et al*. 2000; Fig. 1), which indicated rapid orogenic exhumation after *c*. 460 Ma, and detailed graptolite biostratigraphy from pre-, syn-, and post-collisional volcaniclastic rocks in South Mayo (Graham *et al*. 1989); a detailed discussion of stratigraphic age correlation in Grampian units of South Mayo and Connemara has been given by Dewey & Mange (1999).

The Tyrone Igneous Complex, covering *c*. 350 km^2 of Counties Tyrone and Londonderry, Northern Ireland, was described by Hartley (1933) as consisting of a dominantly mafic plutonic complex with younger silicic intrusions (Stillman 1981; Tyrone Plutonic Group of Cooper *et al*. 2008) that Hutton *et al.* (1985) identified as an ophiolite related to the Ballantrae ophiolite in SW Scotland (Bluck 1985), and a silicic volcanic sequence (Tyrone Volcanic Group of Cooper *et al*. 2008). Structurally below both groups is the high-grade metasedimentary Tyrone Central Inlier. The lithology of the Tyrone Central Inlier suggested possible correlation with Dalradian (Laurentian passive margin) units from which it could have been offset by post-Grampian strike-slip faulting (see Dewey & Shackleton 1984). Structural, thermochronological, and detrital-zircon analyses led Chew *et al.* (2008) to interpret the Tyrone Central Inlier as a microcontinental block with which the Lough Nafooey arc collided *c*. 475 Ma, before accretion of the amalgamated arc–microcontinent onto Laurentia proper as the Grampian Orogeny progressed (compare the Dashwoods microcontinent of Waldron & van Staal (2001) and van Staal *et al*. (2007)). The entire Tyrone Igneous Complex is bounded to the NW by a 10 km thick ductile shear zone along the NE SW-trending Omagh Thrust, which emplaced Dalradian rocks over the Tyrone Igneous Complex during the Caledonide orogeny and which was reactivated during Late Palaeozoic time (Alsop & Hutton 1993; Figs 1 and 2).

The Tyrone Igneous Complex was assigned an Arenig–Llanvirn age (478–461 Ma; we use the traditional stage names of Tucker & McKerrow (1995) although some of those do not appear on the more recent geological time scale by Gradstein *et al.* (2004), whose stage-boundary ages we use) based on a graptolite specimen from shales interbedded with the volcanic sequence, first analysed by Hartley (1936) and reinterpreted by Hutton & Holland (1992). The mafic assemblage of the Tyrone Igneous Complex is intruded by a siliceous pluton near Craigballyharky (Fig. 1) from which Hutton *et al.* (1985) obtained an Arenig U–Pb zircon age of 471 +2/−4 Ma. Cooper *et al.* (2008) acquired a U–Pb zircon age of 473 $\pm$ 0.8 Ma from a rhyolite exposure within the Tyrone Volcanic Group, and further refined a biostratigraphic age by identifying Arenig (Whitlandian) graptolite specimens in the northeastern exposures of the volcanic assemblage.

Despite several detailed structural and age-determining studies, the geochemistry of the Tyrone Igneous Complex has remained largely unknown. Here, we present major- and trace-element analyses, and Nd isotopic data, from rocks of the Tyrone Plutonic Group, the Tyrone Volcanic Group, and from igneous intrusions within them, as well as two new U–Pb zircon ages. These new data constrain the tectonic setting of the magmatism and trace the magmatic evolution corresponding to significant tectonic events in the early history of Iapetus Ocean closure. We demonstrate that the Tyrone Igneous Complex corresponds to the arc units exposed in Connemara and South Mayo, along the strike of the Grampian suture zone. By comparing the geochemical progression during arc–continent collision as recorded in the Tyrone Igneous Complex with that of other Caledonide exposures in the British Isles and North America, we assess on a regional basis whether magmatism accompanying this terrane accretion could drive the bulk composition of accreted arc crust

Table 1. *Sample numbers, localities and rock types; major-element contents (%) and LOI, trace-element and REE concentrations (ppm) and Nd isotopic ratios of Tyrone Igneous Complex whole-rock samples*

Sample	Locality	Rock type	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	LOI
Tyrone Plutonic Group													
TY07043001	Craigballyharky [72710, 75053]	Gabbro	51.68	15.21	7.61	8.73	11.85	2.190	1.078	0.389	0.162	0.029	1.780
TY07043002	Craigballyharky [72710, 75053]	Gabbro	51.21	15.60	7.85	8.88	10.59	2.000	1.105	0.392	0.182	0.034	1.890
TY07043003	Craigballyharky [72710, 75053]	Gabbro	U–Pb analysis only										
TY07043004	Craigballyharky [73024, 75333]	Granite	73.34	14.12	1.35	0.65	0.61	3.840	3.886	0.163	0.033	0.057	0.970
TY07043005	Craigballyharky [73024, 75333]	Basalt	51.39	14.72	8.99	8.07	12.30	2.970	0.232	0.645	0.139	0.028	0.660
TY07043006	Craigballyharky [73024, 75333]	Granite	75.57	13.77	2.15	0.60	0	2.950	2.394	0.183	0.019	0.011	1.530
TY07043008	Craigballyharky [73191, 75301]	Diorite	57.85	15.10	7.13	4.22	7.91	3.760	1.188	0.535	0.160	0.057	1.320
TY07043009	Craigballyharky [72212, 76224]	Basalt	50.30	15.24	9.46	8.10	11.51	2.170	0.551	0.641	0.174	0.013	1.790
TY07050101	Carrickmore Quarry [60917, 72242]	Diabase	49.48	15.70	9.49	8.77	11.59	1.370	0.644	0.624	0.186	0.019	1.880
TY07050102	Carrickmore Quarry [60917, 72242]	Diabase	49.76	15.54	9.91	8.26	9.94	1.650	1.604	0.673	0.178	0.028	1.900
TY07050103	Carrickmore Quarry [60917, 72242]	Gabbro	48.15	14.61	9.38	10.86	12.40	0.740	0.414	0.347	0.172	0	2.300
TY07050104	Carrickmore Quarry [60917, 72242]	Diabase	49.69	14.22	11.99	8.62	10.36	2.190	0.210	0.914	0.195	0.039	1.340
TY07050105	Carrickmore Quarry [60917, 72242]	Gabbro	48.39	14.04	12.24	7.29	10.43	2.270	0.916	1.688	0.197	0.158	1.570
TY07050106	Carrickmore Quarry [60917, 72242]	Gabbro	48.18	14.32	13.14	9.15	6.36	2.890	0.691	1.779	0.180	0.091	2.610
TY07050107	The Scalp [64255, 74219]	Diabase	49.63	16.51	10.24	8.26	9.99	1.970	0.694	0.585	0.174	0.022	1.920
TY07050108	The Scalp [64255, 74219]	Gabbro	46.02	14.73	18.39	5.67	9.80	1.950	0.220	1.593	0.235	0.079	0.760
TY07050109	The Scalp [64296, 74364]	Tonalite	62.20	15.38	7.21	2.26	3.97	3.400	2.635	0.648	0.129	0.200	1.410
TY07050110	The Scalp [64296, 74364]	Gabbro	49.30	13.34	10.99	10.20	12.79	0.700	0.322	0.485	0.208	0	1.790
Tyrone Volcanic Group													
TY07043010	Sperrin Mtns [64249, 65583]	Andesite	61.94	15.27	6.23	4.50	4.91	2.390	0.392	0.472	0.098	0.050	3.060
TY07043011	SE of Greencastle [61474, 82432]	Andesite	61.99	15.07	4.90	4.37	3.18	3.200	1.260	0.411	0.121	0.034	4.760
TY07043012	SE of Greencastle [61474, 82432]	Diorite	57.79	17.09	6.66	4.80	5.35	3.030	0.671	0.488	0.096	0.054	3.340
TY07043013	SE of Greencastle [61731, 81950]	Rhyolite	75.64	13.82	2.15	0.60	0	2.940	2.399	0.181	0.020	0.009	1.430
TY07043014	SE of Greencastle [61731, 81950]	Dacite	59.06	16.40	6.94	4.32	2.78	1.020	2.665	0.470	0.128	0.063	6.610
TY07043015	SE of Greencastle [65839, 81600]	Quartz porphyry	67.98	13.91	3.97	1.37	2.62	2.670	3.529	0.535	0.088	0.090	1.760
TY07050111	Lougham Crory [58772, 77577]	Pillow basalt	53.75	14.66	9.25	5.09	5.50	6.230	0.458	1.203	0.156	0.096	2.800
TY07050112	Lougham Crory [58825, 77396]	Rhyolitic volcanic breccia	87.85	5.40	1.90	1.16	0	0.430	0.828	0.219	0.008	0.029	1.550
TY07050113	Lougham Crory [58772, 77577]	Rhyolitic volcanic breccia	70.75	13.40	2.75	1.27	1.89	2.310	2.997	0.377	0.034	0.050	3.240
TY07050114	Leaghan [59671, 79884]	Tonalite–diorite	57.77	15.05	5.95	4.14	4.31	2.910	1.853	0.474	0.078	0.066	5.400
TY07050115	Leaghan [59747, 80105]	Tonalite	64.61	15.19	5.75	3.66	2.52	3.220	0.885	0.445	0.086	0.054	2.770
TY07050204	Leaghan [59747, 80105]	Tonalite	U–Pb analysis only										
TY07050116	W of Leaghan [59264, 80070]	Rhyolite	73.73	13.38	2.13	0.52	0	3.390	2.702	0.221	0.010	0.022	1.410
TY07050117	Mountfield, old quarry [53502, 78541]	Basalt	49.79	12.46	13.55	4.03	7.53	2.480	0.340	2.850	0.163	0.439	5.390
TY07050118	Mountfield, old quarry [53502, 78541]	Basalt	47.56	12.51	12.11	3.65	8.03	2.480	0.877	2.758	0.152	0.438	8.330
TY07050201	Mountfield, second old quarry [53070, 77883]	Basalt	46.46	13.34	15.03	6.37	7.40	1.910	0.253	2.791	0.222	0.305	5.360
TY07050202	Mountfield, active quarry [54321, 78609]	Basalt	48.02	12.96	14.66	4.25	7.44	3.360	0.434	3.038	0.181	0.461	4.390
TY07050203	Mountfield, active quarry [54321, 78609]	Pyroxene-phyric basalt	46.56	13.51	13.40	6.28	9.91	2.400	0.373	2.215	0.203	0.217	4.010

(*continued*)

Table 1. (*continued*)

Sample	Locality	Rock type	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ba	Th	Nb	Y	Hf	Ta	U	Pb	Rb	Cs	Sr	Sc	Zr	$^{143}Nd/^{144}Nd$ (measured)	$\varepsilon_{Nd(t)}$
Tyrone Plutonic Group																															
TY07043001	Craigballyharky [72710, 75053]	Gabbro	6.59	13.81	1.76	7.41	1.85	0.59	1.87	0.32	2.04	0.44	1.20	0.17	1.14	0.17	245	2.33	1.60	10.75	1.07	0.21	0.47	3.49	25.6	1.40	223	43.9	35		
TY07043002	Craigballyharky [72710, 75053]	Gabbro	6.91	14.03	1.84	7.70	1.91	0.59	1.96	0.33	2.13	0.45	1.26	0.19	1.16	0.18	310	2.48	1.65	10.95	1.07	0.30	0.51	5.00	28.4	1.48	210	45.7	35	0.512192	−5.89
TY07043003	Craigballyharky [72710, 75053]	Gabbro	U–Pb analysis only																												
TY07043004	Craigballyharky [73024, 75333]	Granite	14.53	29.14	3.73	13.89	3.21	0.76	2.64	0.36	1.80	0.32	0.77	0.11	0.66	0.10	492	6.79	7.79	7.79	2.70	1.39	1.78	23.55	122.6	2.35	121	4.0	82	0.511839	−12.18
TY07043005	Craigballyharky [73024, 75333]	Basalt	1.65	4.80	0.83	4.63	1.74	0.69	2.43	0.47	3.16	0.69	1.93	0.29	1.83	0.29	41	0.24	0.44	17.31	1.08	0.28	0.12	2.21	3.0	0.04	196	33.9	32		
TY07043006	Craigballyharky [73024, 75333]	Granite	16.84	28.73	3.92	14.63	3.30	0.81	2.80	0.39	1.97	0.33	0.85	0.12	0.71	0.11	457	7.14	7.68	9.53	2.74	1.39	1.73	26.86	116.5	1.92	119	4.2	83		
TY07043008	Craigballyharky [73191, 75301]	Diorite	12.93	25.91	3.24	13.11	3.02	0.90	3.01	0.52	3.32	0.71	1.96	0.29	1.87	0.30	290	3.11	3.94	17.84	2.69	0.54	0.58	9.35	32.7	0.71	226	26.8	97		
TY07043009	Craigballyharky [72212, 76224]	Basalt	0.97	3.04	0.57	3.49	1.52	0.65	2.38	0.47	3.15	0.70	1.98	0.29	1.83	0.28	85	0.11	0.39	17.66	0.92	0.22	0.04	3.82	12.6	0.89	200	45.1	25		
TY07050101	Carrickmore Quarry [60917, 72242]	Diabase	1.03	3.18	0.58	3.37	1.44	0.62	2.29	0.44	3.03	0.67	1.88	0.28	1.74	0.28	47	0.14	0.27	16.41	0.89	0.21	0.06	0.61	18.9	0.52	212	41.0	24	0.513131	5.92
TY07050102	Carrickmore Quarry [60917, 72242]	Diabase	1.14	3.57	0.67	3.90	1.69	0.68	2.54	0.50	3.45	0.76	2.18	0.32	2.01	0.33	89	0.17	0.26	19.13	0.99	0.13	0.06	20.29	24.0	0.71	318	37.1	26		
TY07050103	Carrickmore Quarry [60917, 72242]	Gabbro	0.66	1.90	0.33	1.91	0.80	0.36	1.23	0.24	1.62	0.37	1.02	0.15	0.95	0.15	55	0.07	0.25	8.79	0.43	0.13	0.05	0.44	17.1	0.33	128	46.4	11	0.513196	7.49
TY07050104	Carrickmore Quarry [60917, 72242]	Diabase	1.13	3.97	0.78	4.73	2.04	0.74	3.00	0.59	4.08	0.90	2.52	0.37	2.37	0.38	16	0.12	0.34	22.04	1.40	0.24	0.03	0.82	5.1	0.24	90	41.5	39		
TY07050105	Carrickmore Quarry [60917, 72242]	Gabbro	9.21	21.89	3.12	14.59	4.14	1.55	4.65	0.80	4.94	0.98	2.61	0.36	2.19	0.34	98	0.84	8.02	23.95	2.85	0.69	0.24	1.15	25.9	0.60	327	42.4	103		
TY07050106	Carrickmore Quarry [60917, 72242]	Gabbro	2.05	6.72	1.35	8.11	3.51	1.30	4.98	0.98	6.68	1.44	4.01	0.59	3.68	0.58	34	0.09	0.60	34.37	2.83	0.17	0.14	1.49	13.3	0.33	100	49.0	86		
TY07050107	The Scalp [64255, 74219]	Diabase	1.49	4.34	0.79	4.68	2.05	0.79	2.92	0.58	4.03	0.88	2.49	0.37	2.35	0.37	40	0.15	0.32	21.51	0.77	0.22	0.03	1.45	11.7	0.62	180	41.9	18		
TY07050108	The Scalp [64255, 74219]	Gabbro	1.94	5.48	0.94	5.41	2.14	1.00	3.08	0.59	4.10	0.88	2.52	0.37	2.32	0.37	22	0.19	0.45	21.49	0.79	0.35	0.05	1.01	2.9	0.12	122	47.6	19		
TY07050109	The Scalp [64296, 74364]	Tonalite	49.51	95.96	11.42	42.67	7.96	1.79	6.02	0.84	4.79	0.96	2.60	0.39	2.46	0.40	923	12.97	8.93	24.42	4.38	0.80	3.15	6.73	65.5	0.73	388	18.7	151		
TY07050110	The Scalp [64296, 74364]	Gabbro	1.46	4.37	0.76	4.47	1.95	0.65	3.00	0.61	4.25	0.93	2.67	0.40	2.40	0.37	28	0.21	0.30	22.72	0.93	0.20	0.09	1.23	4.9	0.32	126	57.1	23	0.513074	4.48
Tyrone Volcanic Group																															
TY07043010	Sperrin Mtns [64249, 65583]	Andesite	13.61	28.63	3.18	11.66	2.61	0.79	2.50	0.42	2.62	0.55	1.51	0.23	1.47	0.23	126	5.49	6.59	13.86	3.30	0.77	1.82	14.90	11.9	0.74	268	22.0	115		
TY07043011	SE of Greencastle [61474, 82432]	Andesite	13.51	26.76	3.09	11.70	2.46	0.77	2.17	0.35	2.11	0.45	1.25	0.19	1.22	0.20	189	3.68	4.02	10.81	2.94	0.53	1.46	11.74	41.7	0.75	134	21.2	106		
TY07043012	SE of Greencastle [61474, 82432]	Diorite	13.44	24.53	2.76	10.16	2.19	0.85	2.00	0.32	1.98	0.41	1.12	0.17	1.12	0.18	187	3.77	4.27	10.41	3.60	0.47	1.30	17.62	21.0	0.36	351	23.3	144	0.511961	−9.24
TY07043013	SE of Greencastle [61731, 81950]	Rhyolite	21.20	42.12	4.64	15.98	3.01	0.60	2.51	0.43	2.79	0.61	1.81	0.29	1.94	0.31	588	13.02	9.72	16.14	5.02	1.21	4.62	7.64	78.3	2.06	86	4.2	169		
TY07043014	SE of Greencastle [61731, 81950]	Dacite	58.75	51.22	10.73	38.25	6.69	1.61	5.67	0.80	4.46	0.88	2.40	0.34	2.15	0.34	362	7.07	6.70	22.82	3.23	0.68	2.26	12.68	88.7	1.96	69	20.6	110		
TY07043015	SE of Greencastle [65839, 81600]	Quartz porphyry	33.50	66.18	7.87	29.45	5.77	1.40	4.77	0.72	4.18	0.84	2.23	0.32	2.02	0.31	845	10.02	9.83	21.10	4.77	0.93	1.95	11.84	82.6	1.09	267	15.1	167		
TY07050111	Lougham Crory [58772, 77577]	Pillow basalt	17.95	40.37	5.36	22.93	5.91	1.53	6.26	1.09	6.78	1.39	3.80	0.56	3.39	0.52	199	3.54	13.27	34.83	5.30	1.03	1.00	6.77	8.3	0.06	226	32.2	199	0.512633	2.35
TY07050112	Lougham Crory [58825, 77396]	Rhyolitic volcanic breccia	9.93	19.38	2.25	8.12	1.46	0.33	1.08	0.16	0.95	0.20	0.59	0.09	0.61	0.10	275	2.98	3.83	4.90	1.79	0.98	0.69	2.56	25.0	0.35	31	5.8	65		
TY07050113	Lougham Crory [58772, 77577]	Rhyolitic volcanic breccia	40.80	74.28	8.55	30.25	5.68	1.50	4.73	0.75	4.48	0.92	2.68	0.39	2.43	0.39	990	12.14	11.11	23.88	4.05	0.89	2.60	11.83	93.0	0.50	117	9.4	134		
TY07050114	Leaghan [59671, 79884]	Tonalite–diorite	17.06	33.63	3.93	15.02	3.20	0.81	2.95	0.47	2.85	0.57	1.58	0.24	1.49	0.23	555	5.83	6.50	14.55	3.19	0.65	1.75	4.38	51.8	1.64	142	21.9	111	0.511841	−11.49
TY07050115	Leaghan [59747, 80105]	Tonalite	17.96	33.82	3.78	13.82	2.80	0.75	2.51	0.40	2.38	0.48	1.35	0.20	1.27	0.20	498	6.81	6.66	12.23	2.88	0.84	1.68	15.30	23.3	1.72	264	19.3	98	0.511836	−11.20
TY07050204	Leaghan [59747, 80105]	Tonalite	U–Pb analysis only																												
TY07050116	W of Leaghan [59264, 80070]	Rhyolite	30.25	57.12	6.29	21.85	4.21	0.83	3.47	0.53	3.25	0.66	1.85	0.29	1.88	0.29	719	12.24	9.19	17.65	4.77	1.00	3.43	8.41	93.9	3.57	72	5.0	165	0.511934	−8.92
TY07050117	Mountfield, old quarry [53502, 78541]	Basalt	22.04	49.80	6.64	28.45	6.76	2.40	6.70	1.05	6.10	1.18	3.02	0.41	2.42	0.37	107	2.51	19.63	28.69	5.36	1.40	0.77	5.03	10.0	0.38	243	33.6	213		
TY07050118	Mountfield, old quarry [53502, 78541]	Basalt	23.69	52.52	6.95	29.42	6.88	2.70	7.10	1.27	7.93	1.52	3.72	0.49	2.77	0.41	57	2.43	18.94	36.06	5.25	1.38	0.89	14.32	28.4	0.97	178	33.0	207		
TY07050201	Mountfield, second old quarry [53070, 77883]	Basalt	14.85	35.39	5.07	23.40	6.46	2.38	7.21	1.22	7.51	1.50	3.93	0.55	3.29	0.50	339	1.75	13.41	36.47	4.50	0.95	0.49	3.82	5.7	0.49	182	43.8	170		
TY07050202	Mountfield, active quarry [54321, 78609]	Basalt	22.23	50.94	6.82	29.07	7.12	2.48	7.10	1.11	6.41	1.27	3.20	0.44	2.56	0.39	214	2.72	21.25	30.12	5.72	1.51	0.78	3.49	7.1	0.15	318	35.5	227	0.512553	1.26
TY07050203	Mountfield, active quarry [54321, 78609]	Pyroxene-phyric basalt	12.37	29.43	4.18	19.29	5.30	1.93	5.88	0.98	6.05	1.22	3.23	0.45	2.69	0.41	136	1.32	11.45	29.80	3.85	0.87	0.37	3.19	5.6	0.10	300	40.9	146		

Localities are given in Irish Grid coordinates. Nd isotopic results are reported as measured $^{143}Nd/^{144}Nd$ ratios and as $\varepsilon_{Nd(t)}$, age-corrected for decay of ^{147}Sm to ^{143}Nd (using Sm and Nd concentrations obtained by ICP-MS analyses and assuming an age of 470 Ma).

toward that of average continental crust, thereby testing a subduction-zone origin for the formation of continents.

Sampling and analytical methods

Rock samples were collected from the Tyrone Igneous Complex at sites shown in Figure 1 and specified in Table 1. Localities sampled within the Tyrone Plutonic Group include outcrops near Craigballyharky, an active quarry near Carrickmore, and outcrops on a hill known as the Scalp. Sample localities within the Tyrone Volcanic Group include outcrops near Lougham Crory, Leaghan, east and SE of Greencastle, in the Sperrin Mountains east of the Omagh Thrust, and three quarries sampled in and around Mountfield. In this initial survey we sampled a variety of lithologies at different stratigraphic levels in the Tyrone Igneous Complex to evaluate the diversity of compositions erupted at different stages in the generation of the igneous complex. More detailed sampling of limited regions may be appropriate in future focused studies.

Geochemical and Nd isotopic analyses

The major-element content of 34 powdered whole-rock samples was determined by XRF using a Philips PW2404 automatic X-ray spectrometer at the University of Edinburgh. XRF techniques, and analytical accuracy and precision, were essentially those described by Fitton *et al.* (1998) with modifications noted by Fitton & Godard (2004). Trace-element composition was determined for the same 34 whole-rock samples by inductively coupled plasma mass spectrometry (ICP-MS) at Washington State University. US Geological Survey standard BCR-1 was used to determine internal and external precision of the ICP-MS analyses. Uncertainty, determined from duplicate analyses of samples and standards, is $<3\%$ for REE and $<5\%$ for other elements.

A subset of 11 samples were selected for Nd isotopic analysis using a Neptune multi-collector ICP-MS system at the Woods Hole Oceanographic Institution. The precision of Nd data is better than 0.002%. Reproducibility is better than 0.003% based on multiple analyses of a La Jolla standard. An age correction (DePaolo & Wasserburg 1976) was performed to account for radioactive decay of ^{147}Sm to ^{143}Nd since eruption, taken to be 470 Ma; values for that time are reported as $\varepsilon_{Nd(t)}$.

U–Pb geochronology

Two additional rock samples were collected from which zircon grains were separated for U–Pb dating. One was a gabbro sample from the Craigballyharky area (sample TY07043003, from the same outcrop as samples TY07043001 and TY07043002, which were analysed for geochemistry and Nd isotopes; Table 1). The other was a tonalite sample collected near Leaghan (sample TY07050204, from the same outcrop as sample TY07050115, which was analysed for geochemistry and Nd isotopes; Table 1).

U–Pb dating was conducted using sensitive high-resolution ion microprobe, reverse geometry (SHRIMP-RG) at the US Geological Survey–Stanford University Ion Probe Facility. Approximately 10 kg of sample were crushed using a jaw crusher and disc grinder and processed for mineral separations using a Gemeni water table. Zircon grains were concentrated using methylene iodide (MEI) and a Frantz magnetic separator. Zircons were hand-picked from material that sank in MEI and was non-magnetic at 1.8 A. Errors on spot ages of individual zircons grains are reported at 1σ, and weighted mean ages were calculated and reported at the 2σ level. About 30–50 zircons were put on 2.5 cm epoxy mounts for single-grain analysis. A 30 μm diameter, 8–12 nA O_2 primary beam was used to sputter the zircon grains for analysis, following 90 s of rastering to remove potential surface contamination. U, Th, and Pb concentrations were standardized against RG-6 zircons that were analysed after every four unknown analyses. Data were reduced using the SQUID program (Ludwig 2001). Decay constants of Steiger & Jäger (1977) were used for all U–Pb dating. Pb/U ratios were corrected for common Pb using ^{204}Pb and the model Pb evolution curve of Stacey & Kramers (1975). Weighted mean U–Pb ages and concordia plots were derived using Isoplot (Ludwig 2003). Laser ablation, multi-collector, inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) dating of inherited zircons was conducted at the University of Arizona LaserChron laboratory. A 35 μm diameter beam was used. Further details of LA-MC-ICP-MS dating techniques have been given by Gehrels *et al*. (2008).

Results

Geochemical and Nd isotopic analyses

Chemical compositions in the Tyrone Plutonic Group rocks indicate a dominantly mafic host rock intruded by multiple siliceous plutons and associated dykes. Silicic intrusions were observed in outcrop at the Craigballyharky and Scalp localities; granite sampled at Craigballyharky was the same intrusion as the 'tonalite' from which Hutton *et al.* (1985) obtained a U–Pb intrusion age of 471 +2/−4 Ma. At the active quarry in Carrickmore, the same locality where Hutton *et al.* (1985) described an ophiolite sheeted dyke complex, fresh gabbro and basalt, including well-exposed dykes, were abundant in the quarry walls exposed in 2007. However, the unequivocal sheeted-dyke characteristics described by Hutton *et al*. were not observed. Mafic samples from all three localities in the Tyrone Plutonic Group are tholeiitic (with the exception of one alkali gabbro at Carrickmore; Fig. 3) with trace-element compositions characteristic of island-arc tholeiite (Pearce & Cann 1973; Fig. 4). Mafic samples of the Tyrone Plutonic Group are generally LREE-depleted (Fig. 5), relatively depleted in HFSE (e.g. Nb, Zr), and enriched in Pb (Fig. 6), consistent with a supra-subduction-zone origin. LREE enrichment in some mafic samples from Craigballyharky may have been caused by small veins from the adjacent granitic intrusion having been present in the sampled rocks.

$\varepsilon_{Nd(t)}$ values for Carrickmore quarry samples are typical of oceanic petrogenesis, at +5.9 and +7.2 for dolerite and gabbro samples, respectively. Similarly, gabbro sampled at the Scalp gave an $\varepsilon_{Nd(t)}$ value of +4.5. At Craigballyharky, a more continental $\varepsilon_{Nd(t)}$ value of −5.9 from a gabbro may have been influenced (as mentioned above) by inadvertently sampled veins from the granitic intrusion that has a strong continental signature ($\varepsilon_{Nd(t)}$ −12.2; sample TY07043004 in Table 1). Intermediate and felsic samples from the Tyrone Plutonic Group show pronounced geochemical differences from the mafic rocks into which they intruded: granite and tonalite samples from Craigballyharky and the Scalp are enriched in LREE and other incompatible trace elements, although still showing HFSE depletion and Pb enrichment. Plotted on the granite discrimination diagram of Pearce *et al.* (1984), granitic samples from Craigballyharky indicate a syncollisional affinity, whereas other samples generally fall within the volcanic-arc field (Fig. 7).

The Tyrone Volcanic Group, exposed north of the Tyrone

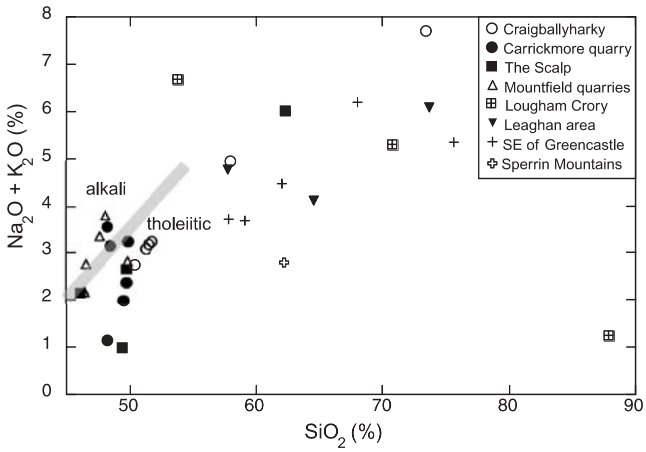

Fig. 3. Plot of silica v. alkali components in all Tyrone Igneous Complex samples, with the division between tholeiitic and alkaline compositions indicated for the mafic end of the spectrum (after Rollinson 1993).

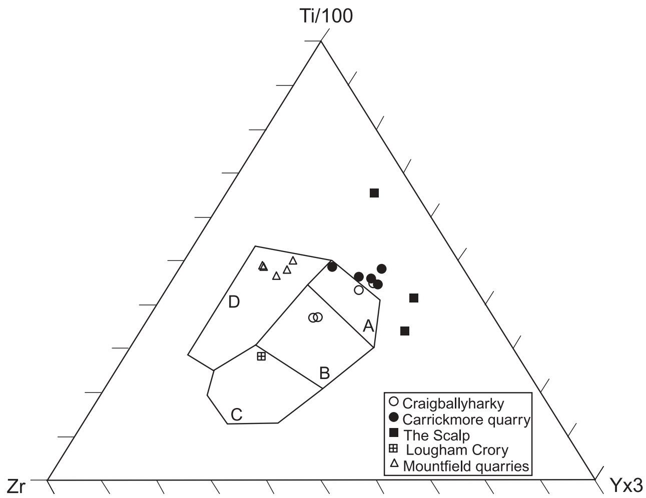

Fig. 4. Ternary Ti/100–Zr–Y × 3 discrimination diagram for Tyrone Igneous Complex (mafic samples only), after Pearce & Cann (1973). Polygonal fields: A, island-arc tholeiites; B, mid-ocean-ridge basalt (MORB); C, calc-alkali basalts; D, within-plate basalts.

Plutonic Group and Tyrone Central Inlier, shows a broader range of major-element composition than do the plutonic rocks. All Tyrone Volcanic Group samples are LREE enriched (Fig. 5), and all samples except those from the Mountfield quarries exhibit subduction-zone HFSE depletion and Pb enrichment (Fig. 6). Several samples gave relatively continental Nd isotopic signatures: $\varepsilon_{Nd(t)}$ of −9.2 in a diorite SE of Greencastle, and −8.9 to −11.5 in tonalite and rhyolite near Leaghan (Table 1). However, calc-alkaline pillow basalts near Lougham Crory had a more oceanic $\varepsilon_{Nd(t)}$ signature of +2.4. Mafic volcanic rocks sampled near Mountfield, stratigraphically close to the top of the section (Cooper *et al*. 2008) and just below the Omagh Thrust, are generally alkaline (Fig. 3), show a lesser degree of LREE enrichment than other Tyrone Volcanic Group rocks, and show no HFSE depletion that would characterize supra-subduction-zone magmatism (Fig. 6). Mountfield rocks have trace-element signatures more similar to within-plate magmatism than to volcanic arcs according to the scheme of Pearce & Cann (1973; Figs 4 and 7). The $\varepsilon_{Nd(t)}$ value of a basalt sample from one Mountfield quarry was +1.3.

U–Pb geochronology

Eight zircon grains were analysed from a gabbro sample (Table 2) collected at Craigballyharky within the Tyrone Plutonic Group, the host rock into which granitic melt intruded at *c*. 471 Ma (Hutton *et al*. 1985). Zircon grains had very high U concentrations (852–8090 ppm). The grain with 8090 ppm U and *c*. 5% Th was reversely discordant and was not used in the age calculation, as extremely high-U zircons typically yield unreliable ages using SHRIMP. The weighted mean $^{238}U/^{206}Pb$ age of the oldest three concordant ages from the gabbro was 493 ± 2 Ma (MSWD = 0.36), interpreted as the magmatic age of the gabbro (Figs 8a and 9). The 2σ analytical uncertainty is low because only three analyses with high precision were used to calculate the mean. Three younger zircons with ages around 470 Ma are possibly attributable to contamination by veins of granitic material of that age (from the adjacent intrusion, as mentioned above) having been accidentally included in the whole-rock sample from which these zircons were separated. The two youngest ages are interpreted as having experienced Pb loss.

The tonalite intrusion sampled near Leaghan, in the Tyrone Volcanic Group, yielded 10 Palaeozoic zircon grains (Fig. 10) with U concentrations 93–368 ppm. The ages are all concordant but vary from 499 to 454 Ma. It is possible that the zircons of *c*. 490 Ma were inherited from earlier arc magmatism (such as that of the Tyrone Plutonic Group, as in our gabbro sample discussed above), but the distinctive high-U composition of the zircons in the gabbro (sample TY07043003) was not observed in the tonalite zircon sample. It is also possible that the two younger zircons experienced Pb loss, but the low U concentrations in the tonalite zircons make this less likely. A weighted mean of all of the Palaeozoic $^{206}Pb/^{238}U$ ages is 475 ± 10 Ma, with a high MSWD (Fig. 8b). We also dated Archaean cores in three zircon grains from the Leaghan tonalite (sample TY07050204) using SHRIMP and LA-MC-ICP-MS; two of those dates are concordant and have $^{207}Pb/^{206}Pb$ ages of 2.25 Ga and 2.32 Ga. The other was discordant and has a $^{207}Pb/^{206}Pb$ age of 2.58 Ga.

Discussion

Tectonic affinity of the Tyrone Igneous Complex

The pervasive supra-subduction-zone and island-arc tholeiite geochemical signatures in rocks of the Tyrone Igneous Complex, together with their Early Ordovician age, confirm that these units formed within an intra-oceanic subduction-zone setting in the Iapetus Ocean and thus are part of the accreted island-arc terrane complex within the Grampian suture. We interpret the Tyrone Plutonic Group and Tyrone Volcanic Group to represent, respectively, the primitive intra-oceanic phase of the Lough Nafooey Arc and the syn- and post-collisional upper crust of the accreted arc. Although consistent with the oceanic crust interpretation of Hutton *et al.* (1985), the geochemical characteristics of the Tyrone Plutonic Group indicate it is not an ophiolite formed at a mid-ocean ridge, but one that formed by magmatism at a subduction zone, as have most large ophiolites (Bloomer *et al.* 1995).

Having correlated the Tyrone Igneous Complex with other accreted-arc units in the Grampian suture zone, we can use geochemistry and Nd isotopic composition to compare Gram-

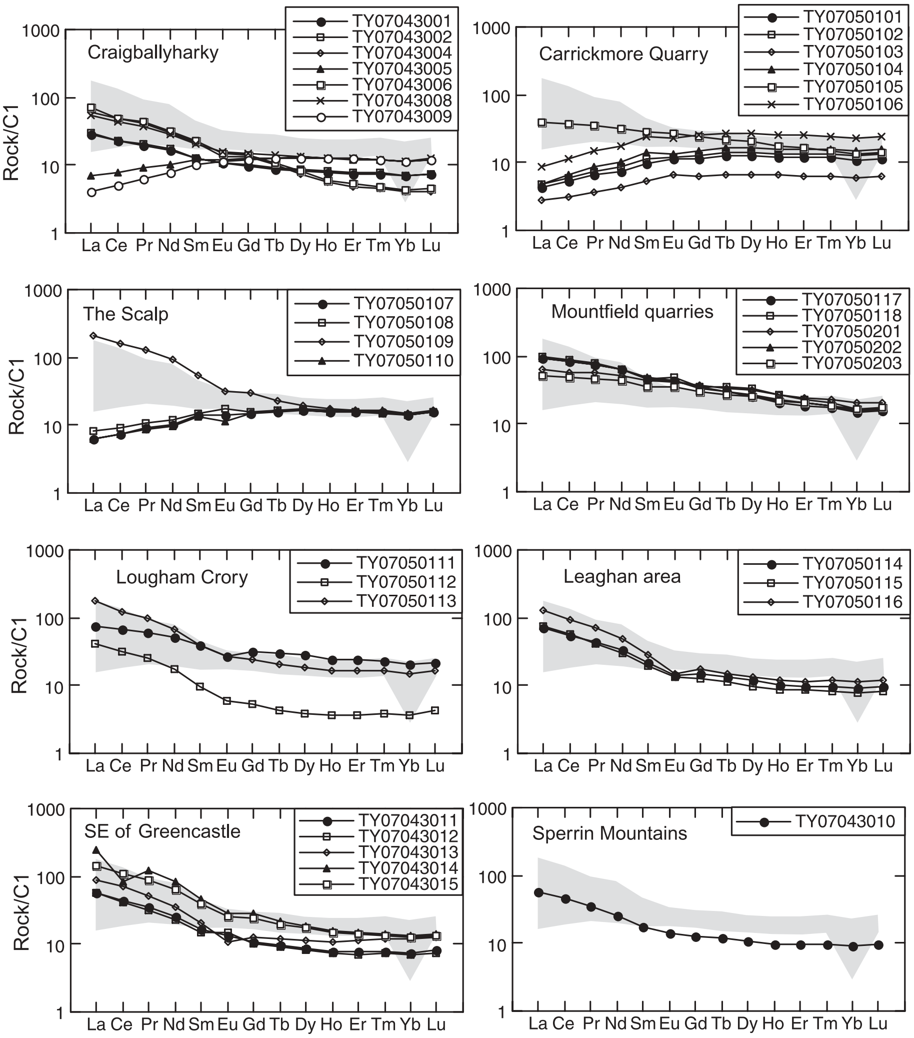

Fig. 5. Chondrite-normalized REE plots for all Tyrone Igneous Complex samples; C1 chondrite values from Anders & Grevesse (1989). For comparison, the shaded regions show the range of average REE compositions of lavas from various parts of the intra-oceanic Mariana Arc (from Pearce *et al.* 2005).

pian tectonics recorded by rocks in the Tyrone Igneous Complex with those in South Mayo and Connemara, situated 170 km to the SW (Fig. 11). As the most primitive portions of the Tyrone Igneous Complex, mafic assemblages of the Tyrone Plutonic Group have trace-element signatures and Nd isotope ratios similar to, or more primitive than, those of modern western Pacific intra-oceanic arcs (Fig. 6; e.g. Ewart & Hawkesworth 1987; Pearce *et al.* 2005). Disregarding gabbro samples from Craigballyharky that were probably contaminated by granitic intrusion around 471 Ma (the gabbro being LREE enriched and with $\varepsilon_{Nd(t)}$ of −5.9), mafic units of the Tyrone Plutonic Group apparently formed in a purely intra-oceanic subduction setting in Tremadoc time (*c*. 493 Ma) with no continent-derived material involved in petrogenesis. As such, these mafic units are inferred to correlate with primitive basalts of the Bohaun Group and the lower Lough Nafooey Group of South Mayo (Fig. 11; Clift & Ryan 1994; Draut & Clift 2001).

Through late Tremadoc time (as early as 490 Ma; Chew *et al*. 2007), the Lough Nafooey arc neared the continental margin of Laurentia, and, along at least part of the subduction zone, amalgamated with a microcontinental terrane outboard of Laurentia before full arc–continent collision began (Waldron & van Staal 2001; Flowerdew *et al*. 2005; Chew *et al*. 2008). Given the proximity of the Tyrone Igneous Complex to the Slishwood Division (Fig. 1) and the fault-bounded Tyrone Central Inlier, early Arenig magmatism recorded in the Tyrone Igneous Complex probably reflects amalgamation of the oceanic arc with a continental fragment, most probably the Tyrone Central Inlier as proposed by Chew *et al.* (2008). Such an event could explain the lowering of $\varepsilon_{Nd(t)}$ values, but not as low as to normal continental values; $\varepsilon_{Nd(t)}$ of +2.4 observed in mafic volcanism at Lougham Crory is still substantially more primitive than Laurentian (Dalradian) crust (Draut *et al*. 2004). Similar lowering of Nd isotopic ratios to weakly oceanic values occurs in the upper Lough Nafooey Group of South Mayo, a stage referred to as ‘soft collision’ (involving continental sediment and outermost continental crust) by Draut *et al.* (2002).

By early to middle Arenig time (*c*. 478–475 Ma), ‘hard’ collision (orogeny and regional deformation) is inferred to be the reason for strongly LREE-enriched volcanism at Lougham Crory, SE of Greencastle, and elsewhere in the Tyrone Volcanic Group. This tectonic stage would have involved collision of an amalgamated arc–microcontinent with the Laurentian margin, which was under way at least by *c*. 474 Ma, based on the ages of the oldest syncollisional intrusions in Connemara (Friedrich *et al*. 1999; Fig. 11), which are consistent with our 475 ± 10 Ma U–Pb zircon age obtained for the Leaghan tonalite (Fig. 8b). Our new data are consistent, therefore, with the tectonic model

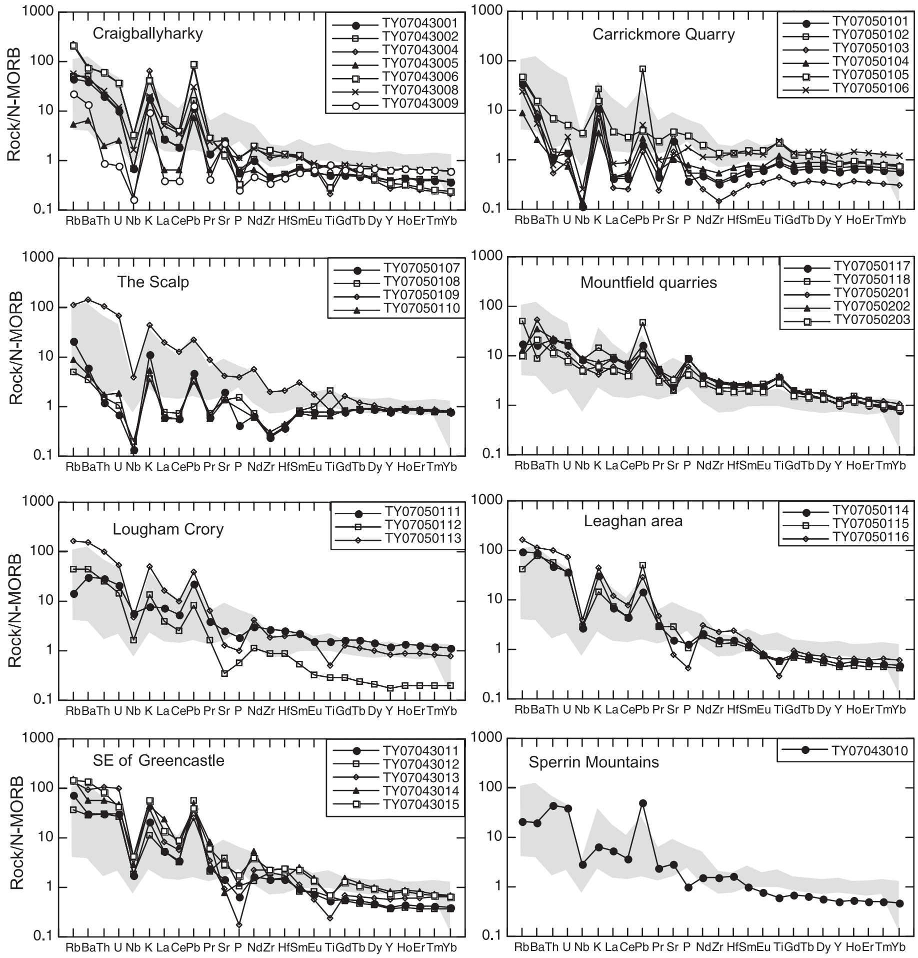

Fig. 6. Multi-element discrimination diagrams (after Pearce 1982) for all Tyrone Igneous Complex samples, with element concentrations normalized against normal mid-ocean-ridge basalt (N-MORB) values of Sun & McDonough (1989). For comparison, the shaded regions show the range of average compositions of lavas from various parts of the intra-oceanic Mariana Arc (from Pearce *et al.* 2005).

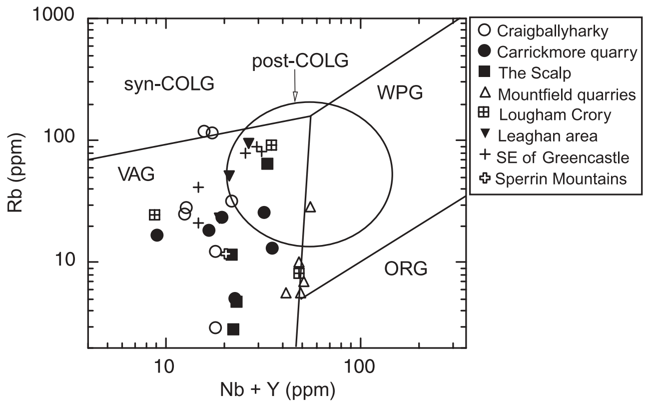

Fig. 7. All Tyrone Igneous Complex samples plotted on a Rb–(Nb + Y) discrimination diagram (after Pearce *et al*. 1984). Fields indicate syncollisional granites (syn-COLG), within-plate granites (WPG), volcanic-arc granites (VAG), and ocean-ridge granites (ORG). The field for post-collisional granites (post-COLG) overlaps those of syn-COLG, VAG, and WPG.

illustrated by Chew *et al.* (2008). Subduction-related trace-element signals persisted in the Tyrone Volcanic Group (e.g. relative Nb depletion; Fig. 6), possibly reflecting development of a continental arc as subduction polarity reversed (Dewey & Ryan 1990). Tonalitic–granitic intrusion accompanied this stage of orogeny and subduction polarity flip, affecting rocks of both the Tyrone Plutonic Group and the Tyrone Volcanic Group. Intrusion and eruption of silicic melts concentrated around 475–471 Ma in the Tyrone Igneous Complex (our tonalite date and those of Hutton *et al.* (1985) and Cooper *et al.* (2008)), but continued until 462 Ma in Connemara as the orogen collapsed and was exhumed (Friedrich *et al*. 1999; Clift *et al*. 2004). As in volcanic rocks of the Tourmakeady Group in South Mayo, Tyrone Igneous Complex petrogenesis accompanying hard collision involved recycling of continental material. Continental wallrock incorporated by intruding melt explains the strongly continental $\varepsilon_{Nd(t)}$ values in Tyrone Volcanic Group samples and the presence of Archaean zircons in the Leaghan tonalite; the most evolved Tyrone Igneous Complex samples show that intrusion must have occurred in a syn- or post-collisional setting (Fig. 7). Similar to the 2.58 Ga zircon core found in our Leaghan tonalite sample, detrital zircons from metasedimentary rocks in the Tyrone Central Inlier (Chew *et al*. 2008) and in the Argyll and Southern Highland Groups of the Dalradian metasedimentary rocks in Scotland (Cawood *et al*. 2003, 2007) contain populations dated to 2.5–2.7 Ga.

The tectonic affinity of rocks sampled in three quarries near Mountfield (Tyrone Volcanic Group) remains unclear. Sampled rock types included fresh pyroxene-phyric basalt and tectonized basalt with minor quartz veins. At one quarry, metasedimentary rocks (not sampled) appeared to be tectonically interleaved with basalt, although the basalt composition sampled there (sample TY07050201) did not differ substantially from that of samples at

Table 2. *U–Pb zircon data collected by SHRIMP and LA-ICP-MS*

Spot	Composition				Isotopic ratios				Dates (Ma)				Comments
	U (ppm)	Th (ppm)	Th/U	^{204}Pb (% of ^{206}Pb)	^{238}U/^{206}Pb*	± (%)	^{207}Pb*/^{206}Pb*	± (%)	^{207}Pb*/^{206}Pb*	±1σ (Ma)	^{206}Pb*/^{238}U	±1σ (Ma)	
Gabbro from Tyrone Plutonic Group (sample TY07043003)													
TG-7.1	2837	5341	1.88	0.76	14.46	0.3	0.0574	1.2	505	26	430	1	Pb loss
TG-6.1	2248	4403	1.96	0.04	13.71	0.3	0.0558	1.2	446	26	454	1	Pb loss
TG-8.1	921	1109	1.20	0.39	13.17	0.4	0.0584	1.5	544	33	471	2	Granite intrusion influence?
TG-5.1	1421	4188	2.95	0.13	13.16	0.4	0.0570	1.0	493	22	472	2	Granite intrusion influence?
TG-1.1	3124	4869	1.56	<0.01	13.11	0.2	0.0561	0.7	456	15	474	1	Granite intrusion influence?
TG-3.1	2366	4291	1.81	<0.01	12.62	0.3	0.0562	0.7	462	16	492	1	
TG-4.1	2104	5334	2.54	<0.01	12.58	0.3	0.0565	0.8	474	19	493	1	
TG-9.1	852	1268	1.49	<0.01	12.57	0.4	0.0565	1.1	471	25	494	2	
TG-2.1	8090	49130	6.07	<0.01	11.06	0.2	0.0530	0.3	328	8	562	1	High U
Tonalite from Tyrone Plutonic Group (sample TY07050204)													
TT-3.1	98	39	0.39	0.04	13.74	1.4	0.0542	4.6	380	104	454	6	
TT-1.1	113	41	0.36	0.33	13.67	1.3	0.0557	4.6	440	102	455	6	
TT-9.1	217	97	0.45	0.07	13.33	0.9	0.0556	3.0	436	68	466	4	
TT-10.1	93	42	0.45	0.01	13.19	1.3	0.0566	3.7	474	81	471	7	
TT-2.1	141	61	0.43	0.54	13.06	1.1	0.0595	3.4	585	74	475	6	
TT-7.1	102	39	0.39	<0.01	13.06	1.3	0.0509	5.9	237	136	478	6	
TT-8.1	157	59	0.38	0.12	12.93	1.0	0.0560	3.2	453	71	479	5	
TT-5.1	146	64	0.44	0.00	12.73	1.1	0.0569	2.8	489	63	486	5	
TT-4.1	93	34	0.36	0.03	12.66	1.4	0.0529	5.7	324	130	492	7	
TT-6.1	122	49	0.40	<0.01	12.44	1.2	0.0562	3.1	461	68	499	6	
TT-11C.1	368	366	0.99	4.92	2.50	0.6	0.1718	0.7	2575	11	2166	13	Inherited core
Inherited zircons from tonalite (sample TY07050204), analysed by LA-MC-ICP-MS													
TT-36	73	33	0.45	<0.01	2.37	2.3	0.1414	2.4	2245	42	2272	43	Inherited core
TT-39	82	71	0.87	<0.01	2.28	1.0	0.1479	2.2	2321	38	2344	20	Inherited core

*Radiogenic Pb, corrected for common Pb. ^{204}Pb(% of ^{206}Pb) is the ^{204}Pb expressed as a percentage of the ^{206}Pb.

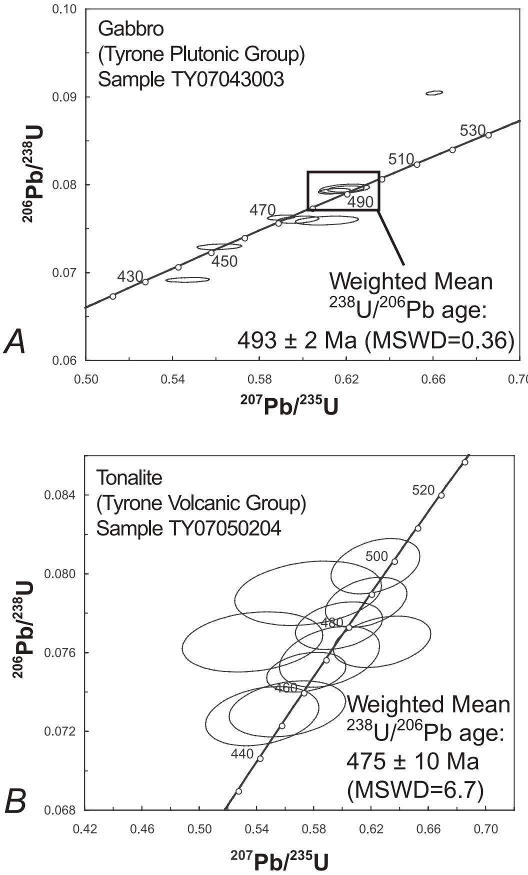

Fig. 8. U–Pb concordia diagrams for (**a**) zircon grains from a gabbro sampled at Craigballyharky (Tyrone Plutonic Group, sample TY07043003), and (**b**) zircon grains in a tonalite sampled near Leaghan (Tyrone Volcanic Group, sample TY07050204). In (**a**), the weighted mean of three concordant ages from the gabbro was 493 ± 2 Ma. Younger ages are probably attributable to the presence of younger, intruded granitic material in the sample, or to Pb loss in high-U grains. In (**b**), the Palaeozoic-aged zircon grains gave concordant ages with a weighted mean of 475 ± 10 Ma. Cores in three other zircons from the Leaghan tonalite yielded Archaean ages (2.25, 2.32, and 2.58 Ga).

other Mountfield quarries where metasedimentary rocks are absent. The lack of a strong relative Nb depletion demonstrates that the Mountfield volcanic rocks were not generated above a rapidly subducting oceanic slab. Mountfield basalts are also more evolved than other mafic rocks of the Tyrone Igneous Complex (Fig. 3), and show within-plate magmatic affinity according to the scheme of Pearce & Cann (1973; Figs 4 and 7), though they display weakly oceanic $\varepsilon_{Nd(t)}$ values. Contamination by Dalradian metasedimentary material during shearing along the Omagh Thrust is considered unlikely because addition of any fluid derived from Dalradian rocks would be expected to cause further relative depletion of fluid-immobile Nb. Based on their stratigraphic position near the top of the Tyrone Igneous Complex volcanic exposures (Cooper *et al*. 2008), we infer that the Mountfield basalts most probably formed late in the Grampian orogeny when no strong plate underthrusting occurred, perhaps contemporaneously with subduction polarity reversal and/or gravitationally induced loss of the lower crust. The lower degree of LREE enrichment in Mountfield samples compared with others from the Tyrone Volcanic Group is consistent with high heat flow having increased the melting percentage late in the orogeny, as would occur after lower crustal loss (Kay & Kay 1993).

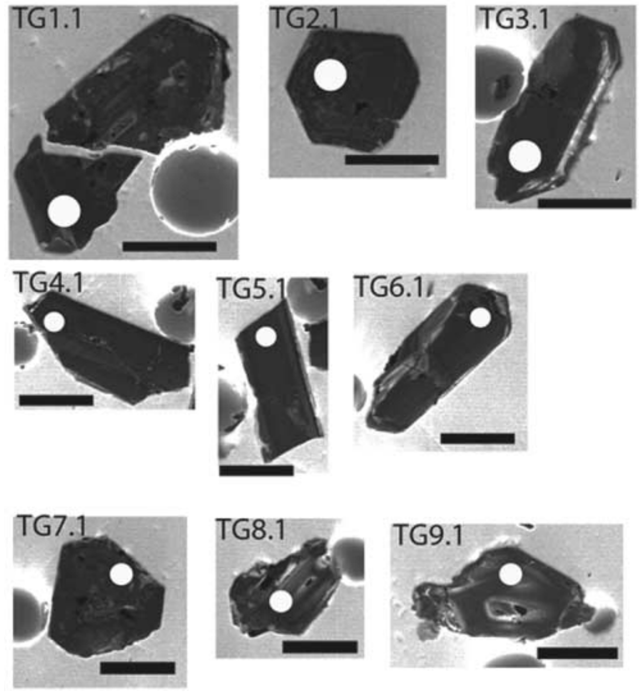

Fig. 9. Cathodoluminescence (CL) images of zircon grains analysed from sample TY07043003, a gabbro within the Tyrone Plutonic Group near Craigballyharky. Scale bar represents 100 µm. Point numbers refer to analyses shown in Table 2. White spots indicate analysis location. The dark CL images for this sample resulted from extremely high (>2000 ppm) U concentrations.

The Grampian–Taconic orogen and formation of continental crust

Silicic lavas of the Tyrone Volcanic Group, as well as the tonalite and granite that intrude the Tyrone Igneous Complex, show pronounced relative enrichment of LREE, as reflected by the La/Sm ratios (Fig. 11). Some of these rocks are more LREE enriched than bulk continental crust (which has chondrite-normalized La/Sm of *c*. 3.0; Taylor & McLennan 1985; Rudnick & Fountain 1995), and some are more LREE enriched than typical Irish Dalradian composition, from which material was incorporated in syncollisional melts (average chondrite-normalized La/Sm ranges from 0.5 to 3.5 for various Irish Dalradian units, based on calculations using data of Senior & Leake (1978)). Pronounced LREE enrichment in syn- and post-collisional volcanic units of the Tyrone Igneous Complex, South Mayo, and some Connemara plutons indicates that crystal fractionation played an important role during and after Grampian collision, enriching magmatism more than could occur simply from mixing of continental and primitive-arc melts (see Draut *et al.* 2002). Using the standard equation for fractional crystallization, assuming a typical basaltic parent melt of 20% olivine, 30% clinopyroxene, and 50% plagioclase, and using bulk partition coefficients of La and Sm in the parent melt of 0.1131 and 0.1709, respectively (Rollinson 1993), a chondrite-normalized La/Sm ratio of four is reached when fractional crystallization has progressed far enough that the melt fraction is reduced to *c*.

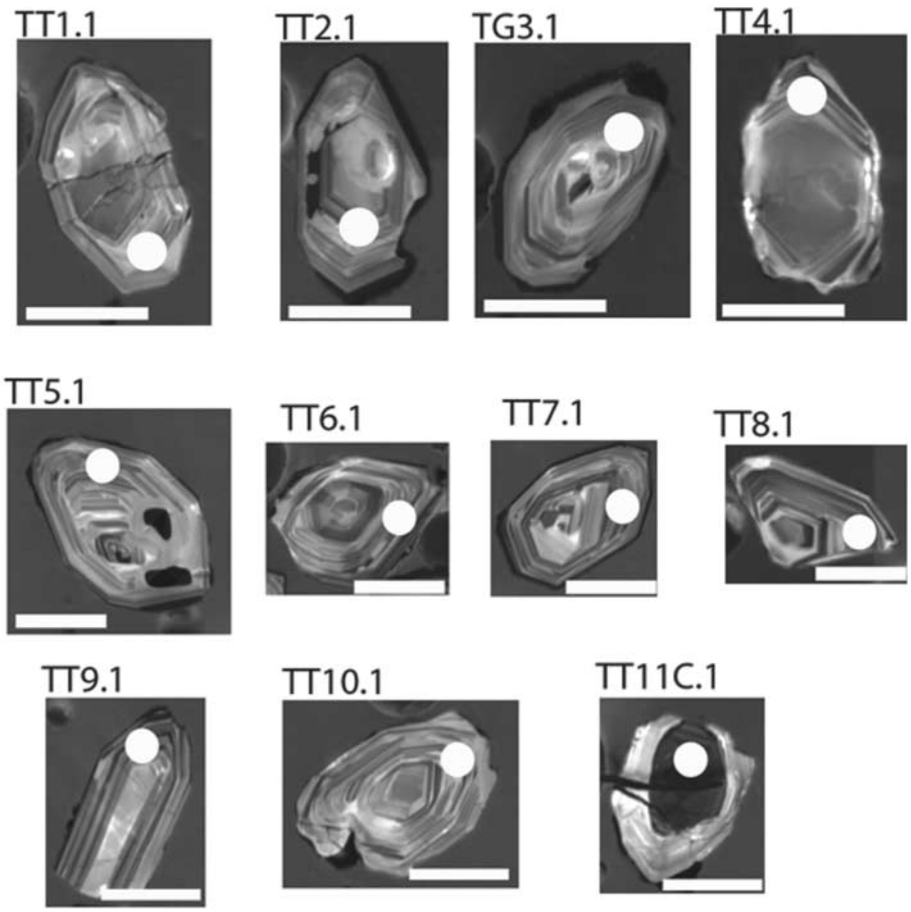

Fig. 10. Cathodoluminescence (CL) images of zircon grains analysed from sample TY07050204, a tonalite within the Tyrone Volcanic Group near Leaghan. Scale bar represents 100 μm. Point numbers refer to analyses shown in Table 2. White spots indicate analysis location.

40%. Chondrite-normalized La/Sm ratios above five, seen in one Tyrone Igneous Complex sample (a dacite collected SE of Greencastle), require melt fractions <2%. Derivation of all the Tyrone Igneous Complex magmatic products by crystal fractionation in only one parent magma is neither required nor likely; such calculations simply demonstrate that this degree of LREE enrichment can be readily attained by crystal fractionation but cannot be explained only by mixing bulk continental melt with mafic arc melt (because the degree of LREE enrichment in some Tyrone Igneous Complex samples is substantially higher than that of continental crust). Because new, mantle-derived magmatism constituted at least 20% of the crustal material accreted in the Grampian collision, rather than merely re-melting of pre-existing crust (calculations of Draut *et al*. 2004), the highly enriched character of the new crust could effectively drive the bulk composition of the accreted arc terrane toward the composition of average (andesitic, LREE-enriched) continental crust, especially if accompanied by loss of corresponding dense lower-crustal residues (discussed below).

Having demonstrated the highly LREE-enriched composition of volcanic and plutonic units emplaced during the Grampian orogeny into the Tyrone Igneous Complex (this study) as well as in South Mayo and Connemara (Draut *et al*. 2002), it is worth while to assess whether such trends represent isolated occurrences of super-enriched magmatism in Ireland or are also present elsewhere along the Caledonide suture. Calculations using ICP-MS trace-element data of Steinhoefel *et al.* (2008) from the Grampian Highlands in Scotland, associated with the same arc–continent collision, show only one granitic syncollisional intrusion more LREE enriched than both average continental crust and typical Dalradian compositions (sample M-4 of Steinhoefel *et al.* (2008), with a chondrite-normalized La/Sm ratio of 4.92). However, LREE enrichment was consistently greater than that of Dalradian and bulk continental crust in Grampian Highland intrusions that represent later continental arc activity and the docking of the Avalonian continental block against Laurentia (several intrusions with La/Sm >5; Steinhoefel *et al*. 2008; Oliver *et al*. 2008).

Farther along the strike of the Grampian–Taconic orogen, super-enriched syncollisional magmatism is also apparent in the 50 km wide Notre Dame subzone, Newfoundland, identified as containing Ordovician accreted arc units approximately equivalent to those studied in Ireland and Scotland (e.g. Whalen *et al*. 1997; van Staal *et al*. 1998, 2007). Within the Notre Dame subzone, 35 of 172 samples that span the age range of the Grampian–Taconic orogeny show chondrite-normalized La/Sm ratios >4, ranging to >10 (our calculations using data from Whalen *et al*. (1997) and Rogers (2004)). These highly enriched compositions occur in the Cape Ray granodiorite complex (488 Ma) and the Cormacks Lake tonalitic orthogneiss (483 Ma), both identified by van Staal *et al.* (2007) as associated with the first phase of Notre Dame arc activity (i.e. amalgamation of the Notre Dame arc and Dashwoods microcontinent; 490–480 Ma). Strong LREE enrichment continued during the second phase of Notre Dame arc activity, as the Dashwoods terrane collided with Laurentia, reflected in igneous complexes dated to 480–459 Ma (Southwest Brook and Hungry Mountain Complexes; van Staal *et al*. 2007). We infer, therefore, that the eruption and intrusion

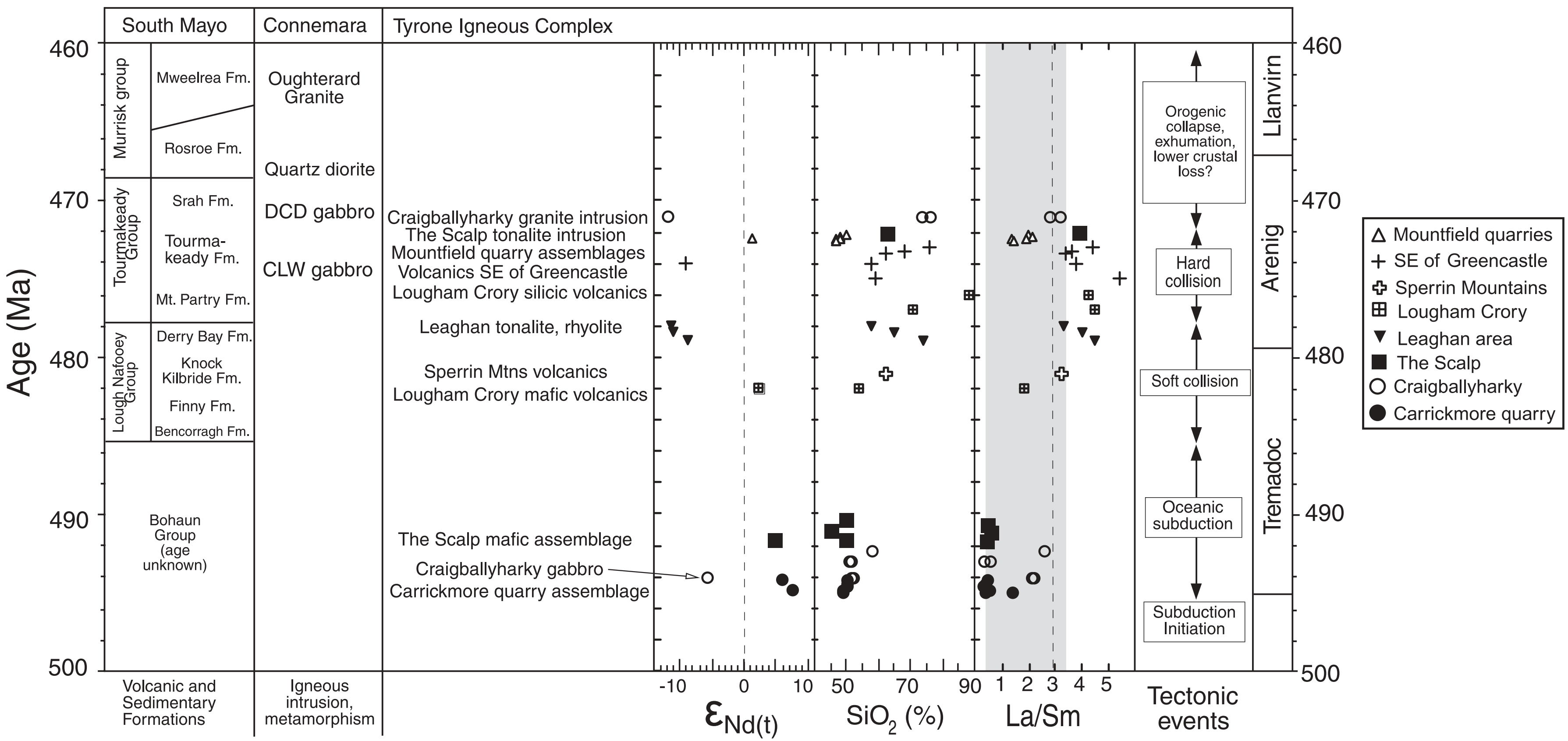

Fig. 11. Proposed correlation of Grampian rock units and tectonic history across three areas of the Irish Caledonides: South Mayo, Connemara, and the Tyrone Igneous Complex. Stratigraphy of volcanic and volcaniclastic sedimentary formations in South Mayo was defined by Graham *et al.* (1989). Ages of igneous intrusions in Connemara are taken from Friedrich *et al.* (1999); DCD, Dawros–Currywongaun–Doughruagh intrusion; CLW, Cashel–Lough Wheelaun gabbro. Tectonic affinity of South Mayo and Connemara units was interpreted by Dewey & Ryan (1990), Clift & Ryan (1994), Dewey & Mange (1999), Friedrich *et al.* (1999), Clift *et al.* (2004), Draut *et al.* (2004), and others. $\varepsilon_{Nd(t)}$, SiO_2, and La/Sm ratios (a measure of LREE enrichment, here normalized against chondrite values of Anders & Grevesse (1989)) are plotted for Tyrone Igneous Complex samples using U–Pb ages from this study, Hutton *et al.* (1985), and Cooper *et al.* (2008) to constrain intrusion and volcanism where possible, and estimating likely ages of other samples based on geochemical characteristics. $\varepsilon_{Nd(t)}$ is age-corrected to 470 Ma. On the La/Sm plot, the shaded area represents chondrite-normalized La/Sm ratio for Irish Dalradian rocks (hundreds of samples analysed by Senior & Leake 1978) and the dashed line shows the chondrite-normalized La/Sm ratio of average continental crust (Taylor & McLennan 1985; Rudnick & Fountain 1995). Notably, LREE enrichment (La/Sm) is greater in some Tyrone Igneous Complex samples than in the Dalradian units with which primitive Ordovician arc magma would have mixed. This implies that crystal fractionation, not mixing alone, is important in generating magmatism associated with the arc–continent collision.

of super-enriched magmatism associated with this Ordovician arc–continent collision was not a rare phenomenon restricted to one part of the Irish Caledonides, but was spatially and temporally pervasive during the Grampian–Taconic orogeny. As such, the generation of melts more enriched than the local continental crust during an arc accretion event is probably a common process widespread enough to drive the bulk composition of accreted crust toward typical continental values on a regional scale.

In addition to the formation of highly enriched melts, loss of corresponding dense, depleted residues (cumulates) in the lower crust is also required for accreted arc crust to attain a composition close to that of continental material. Removal of the lower crust by delamination (Bird 1978) or convective instability (Jull & Kelemen 2001) is believed to have occurred in other arc settings (e.g. Kay *et al.* 1994; Ducea & Saleeby 1998), and may have contributed to rapid orogenic exhumation and collapse after the Grampian Orogeny in western Ireland (Flowerdew *et al.* 2000; Draut *et al.* 2002). Seismic profiles across the Caledonide suture zone show that no Ordovician lower crust is present today beneath Connemara (Klemperer *et al.* 1991), although the timing of its loss cannot be known with certainty. We speculate that the anomalous geochemistry of the Mountfield samples relative to other Tyrone Volcanic Group units (within-plate affinity, less LREE enrichment, and weak or absent subduction-zone signature) may have been related to magmatism following loss of the lower crust in the late stages of the Grampian orogeny. In terms of their mafic composition and trace-element characteristics (e.g. La/Yb ratios and lack of relative HFSE depletion) our Mountfield samples resemble lavas from the Puna Plateau of the Andes, which are associated with melting above a zone of lower-crustal loss (Kay & Kay 1993).

Conclusions

Primitive mafic intrusions of the Tyrone Igneous Complex, Ireland, indicate intra-oceanic arc activity no later than *c.* 493 Ma (Tremadoc), followed by a transition to more enriched magmatism as arc–continent collision began. LREE-enriched sialic magmatism linked to mixing of mantle melts with Laurentian continental material had begun by early Arenig time, as is evident from incorporation of Archaean zircon grains into a tonalite intrusion *c.* 475 Ma. The degree of LREE enrichment in Arenig volcanism and silicic intrusions of the Tyrone Igneous Complex exceeds that of the Dalradian continental material that would have been thrust under the colliding forearc and potentially recycled into arc magmatism. Magmatic compositions therefore cannot be explained simply by mixing primitive melts with assimilated continental material. Rather, substantial crystal fractionation (melt fractions 2–40%) must have accompanied the formation of new crust in the Grampian–Taconic orogeny. As the super-enrichment of orogenic melts is observed elsewhere in the Caledonide orogen in both the British Isles and in Newfoundland, the addition of new, highly enriched melt to this accreted arc terrane was apparently widespread, and, particularly if accompanied by loss of the dense lower crust, could drive the bulk composition of accreted crust toward that of enriched continental crust. This, therefore, supports the theory that arc–continent collision has played an important role in forming extant continental crust.

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