U–Pb zircon geochronology of plagiogranites from the Lough Nafooey (= Midland Valley) arc in western Ireland: constraints on the onset of the Grampian orogeny

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The timing of peak Grampian metamorphism is well constrained from the detrital record of the adjacent fore-arc basin fill and geochronology of synorogenic intrusive rocks, but the onset of collision is less certain. Proximal Silurian conglomerates contain plagiogranite boulders unequivocally derived from the Lough Nafooey arc, two of which yield U–Pb secondary ionization mass spectrometry zircon ages of 489.9 ± 3.1 Ma and 487.8 ± 2.3 Ma. Nd isotopic evidence (ɛNd(490) c. 0) demonstrates that the plagiogranites assimilated significant amounts of old continental crust. This provides an absolute age constraint on a previously poorly constrained and inferred event, demonstrating that the arc had encountered subducting Laurentian margin sediments by 490 Ma.

The Grampian–Taconic orogeny is now widely regarded to be related to the collision of Laurentia with an oceanic arc during the Early Ordovician (Dewey & Shackleton 1984). There is now a wealth of data (e.g. detrital record of the adjacent basin fill, geochronology of synorogenic intrusive rocks and metamorphic cooling ages) that constrains peak metamorphism and deformation in the Grampian sector of the belt to a short time interval from 475 to 465 Ma (Friedrich et al. 1999; Dewey 2005). There is, however, significantly less information (either geochronological or biostratigraphical) for the early orogenic history, particularly concerning (1) the timing of the initiation of subduction and (2) the onset of subduction of continental margin sediments. This paper documents U–Pb zircon geochronological and Nd isotopic evidence from South Mayo in the western Irish Caledonides for the early history of this arc–continent collision event.

South Mayo is one of the most complete sections through the Grampian orogen, with all of the major components of the orogen well exposed (Fig. 1b), including Laurentian cover (the Dalradian Supergroup), accretionary complex (Clew Bay Complex), supra-subduction ophiolite (Deer Park Complex) and arc volcanic rocks and fore-arc basin (Lough Nafooey arc and South Mayo Trough). Both the detrital record of the basin fill and the chemistry of the arc volcanic rocks can be used to reconstruct the evolution of the orogeny.

Whole-rock geochemistry demonstrates that the lower portions of the northern limb of the South Mayo Trough are derived from a source enriched in Mg, Cr and Ni, indicative of an ultramafic (ophiolitic) source region (Wrafter & Graham 1989). This prominent ultramafic signature decreases up sequence, as does the abundance of detrital chrome spinel. The drop in detrital chrome spinel abundance coincides with a sudden influx of metamorphic detritus (garnet, staurolite, stilpnomelane and muscovite) in the Lower Llanvirn Derrylea Formation (Dewey & Mange 1999). These data suggest the progressive unroofing of an ophiolite complex in the Arenig followed by the exhumation of the Grampian metamorphic belt during the Llanvirn (Wrafter & Graham 1989; Dewey & Mange 1999).

The arc volcanic rocks are exposed in a series of small, fault-bounded inliers, which are collectively referred to in this paper as the Lough Nafooey arc, and this arc presumably forms the basement to the South Mayo Trough. The Lough Nafooey arc includes the Late Tremadoc–Early Arenig Lough Nafooey Group (Ryan et al. 1980), the Arenig Tourmakeady Group and the Bohaun Group of unknown age (Graham et al. 1989; Clift & Ryan 1994) (Fig. 1b). As the arc volcanism spans the Grampian arc–continent collision event, the chemistry of the arc volcanic rocks can be used to constrain the onset of collision.

The oldest biostratigraphically dated (pre-collisional) arc volcanic rocks are the Lough Nafooey Group (Fig. 1b). The age of basaltic lavas that make up the Bohaun Group is not known, but their boninitic chemistry (Clift & Ryan 1994) and strongly positive ɛNd(t) values (Draut et al. 2004) could indicate earliest-stage formation above a young subduction zone. The light rare earth element (LREE) depletion (Draut & Clift 2001) and strongly positive ɛNd(t) values (Draut et al. 2004) of the tholeiitic basalts at the base of the Lough Nafooey Group (the Bencorragh and Finny Formations, Fig. 1b) and the lack of continental detritus in the oldest sediments of that group also suggest an origin removed from the Laurentian margin (Ryan et al. 1980).

Younger volcanic units in the Lough Nafooey Group (the Knock Kilbride and Derry Bay Formations, Fig. 1b) exhibit a trend toward higher-silica, higher-K compositions (Ryan et al. 1980) with increasing LREE enrichment and lower ɛNd(t) values (Draut et al. 2004). The Arenig Tourmakeady Volcanic Group (Fig. 1b) contains andesitic and rhyolitic tuffs and volcanioclastic sediments (Graham et al. 1989). These volcanic rocks are LREE enriched (Draut & Clift 2001), and have strongly negative ɛNd(t) values (Draut et al. 2004) indicating substantial assimilation of old continental material. Later volcanism within the South Mayo Trough is recorded by andesitic tuffs and ignimbrites of the Rosroe Formation and ignimbritic tuffs of the Llanvirn Mweelrea Formation. These are interpreted as syn- to post-collisional arc volcanism, and are LREE enriched, with strongly negative ɛNd(t) values (Draut & Clift 2001).

Constraints on the early evolution of the Grampian orogeny. Although there are some temporal constraints on the early history of ophiolitic slivers in Scotland, none of these rocks occur in conjunction with arc volcanic rocks, and therefore the evolution of the arc-ophiolite package with time cannot be assessed. Plagiogranites associated with the Shetland ophiolite have yielded a 492 ± 3 Ma U–Pb zircon age (Spray & Dunning et al. 1980).
1991), whereas plagiogranites associated with the Ballantrae ophiolite have yielded a 483 ± 4 Ma U–Pb zircon age, with amphibolites yielding marginally younger K–Ar hornblende ages (Bluck et al. 1980). Although the South Mayo section is probably most complete, there is no biostratigraphic and geochronological control for the ophiolitic rocks and the lower portions of the arc complex. The Deer Park Complex ophiolite is undated, and the lowermost 1.5 km of the Lough Nafooey Group (the Bencorragh and Finny Formations) is unfossiliferous. The overlying Knock Kilbride Formation has yielded a Late Tremadoc graptolite fauna, equivalent to the Lancefield Zone (La2) in the Australian zonal scheme (Williams & Harper 1994).

Field relationships of the plagiogranite clasts. The Lough Nafooey arc rocks are unconformably overlain on their southern side by a Silurian succession that commences with terrestrial sediments (Lough Mask Formation). Locally there is a lenticular basal conglomerate (Fig. 1c) that rests unconformably on a slightly irregular surface of the Lough Nafooey Group. These conglomerates are coarse grained (clasts up to 55 cm) and poorly sorted. They contain clasts that can be easily matched with the subjacent Lough Nafooey arc, such as angular jaspers, various basic igneous rocks and, at the eastern end, clasts identical to the distinctive Derry Bay Felsite. A local northerly derivation is consistent with the palaeocurrent data for the Lough Mask Formation (Piper 1972). Because of the poor temporal control on the age of the Lough Nafooey Group, two large (>50 cm) plagiogranite boulders (samples DC 10/1/5 and DC 10/1/6) were selected for further analysis, including U–Pb zircon geochronology.

Petrography of the plagiogranite clasts. Samples DC 10/1/5 and DC 10/1/6 are petrographically very similar, and consist of 42% quartz, 50% albite and 3% microcline, with minor chlorite (3%) and oxides (2%). The chlorite has replaced a primary ferromagnesian phase (possibly pyroxene or biotite). The samples are classified as tonalites using a QAPF plot and are fine-grained, with a mean grain size of 2 mm. The albite exhibits oscillatory zoning, and is occasionally rimmed by a thin overgrowth of microcline, suggesting late-stage growth of K-feldspar from a residual magma enriched in K. The quartz usually occurs in aggregates, and exhibits well-developed trilete grain boundaries. The interstitial space between the quartz grain boundaries is commonly filled by thin, vermicular, fine-grained feldspathic material. Occasional perfectly euhedral quartz crystals are also present. Small (up to 4 mm) inclusions of substantially finer-grained (mean grain size 0.15 mm) igneous material are also present, and are interpreted as micro-xenoliths of andesite or dacite. The plagiogranites therefore probably represent shallow-level intrusion(s) that were able to incorporate fragments of their own volcanic edifice.

Geochemistry. A plagiogranite boulder (DC 10/1/6) along with four samples from the Deer Park Complex ophiolitic rocks were selected for major, trace and REE geochemistry and Nd isotopic analysis. Analytical techniques and data are available online at http://www.geolsoc.org.uk/SUP18272. A hard copy can be obtained from the Society Library. REE profiles are illustrated in Figure 2, and εNd(490) values are illustrated in Figure 1b.

The four samples from the Deer Park Complex comprise two metadolerites (samples DC 8/1/26 and DP 11) and two garnet-grade metasedimentary rocks (samples DC 8/1/24 and DC 8/1/25), which are tectonically interleaved within the ophiolitic mélangé. The metadolerites are usually strongly foliated, but sometimes a primary igneous mineralogy of augite and plagioclase is preserved. They are interpreted as ophiolitic sheeted dykes (Ryan et al. 1983). The metasedimentary rocks have the same tectonic fabric as the metadolerites, and are of substantially higher metamorphic grade than the adjacent accretionary complex rocks of the Clew Bay Complex (the Killadangan Formation). These metasediments are interpreted here as slivers of
pelagic Laurentian margin sediment that were caught up in the metamorphic sole during obduction of the Deer Park Complex ophiolite. Chondrite-normalized REE profiles (Fig. 2) of the metadolerites are slightly LREE depleted (La/SmN = 0.5), typical of normal mid-ocean ridge basalt (N-MORB), and εNd(400) values are strongly positive (c. +6; Fig. 1b), indicating minimal assimilation of old continental material. These juvenile initial Nd isotopic ratios are similar to those of the basal portions of the Lough Nafooey Group (+7; Draut et al. 2004). The metasedimentary samples exhibit strong LREE enrichment (La/SmN = 4.9) and strongly negative εNd(400) values (−7 and −15, which correspond to crustal residence ages (TDM) of 1.75 Ga and 2.2 Ga, respectively). The Nd isotopic data are consistent with an upper Dalradian origin for this distal slope sediment (Daly & Menuge 1989).

Sample DC 10/1/6 classifies as a plagiogranite (76.5% SiO₂, 0.45% K₂O, 8 ppm Rb, 43 ppm PREE; see Coleman & Perman 1975) and is moderately LREE enriched (Fig. 2, La/SmN = 1.9), with a slightly negative Eu anomaly and an εNd(400) value of 0.41 (Fig. 1b), which corresponds to a crustal residence age (TDM) of 1.39 Ga. The LREE enrichment of the plagiogranite contrasts with the flat REE profiles of plagiogranites from ‘classic’ ophiolite sequences such as the Semail (Pallister & Knight 1981; Fig. 2) or Troodos ophiolites. LREE enrichment is characteristic of plagiogranites from the Tasriwine (Samson et al. 2004; Fig. 2) and Apennine ophiolites, where it is attributed to LREE enrichment of the source region prior to plagiogranite petrogenesis. A similar origin is inferred here, but in contrast to the Tasriwine plagiogranites (which exhibit juvenile [strongly positive] εNd values), the LREE enrichment in the Lough Nafooey plagiogranites is attributed to assimilation of old continental crust (Laurentian slope sediment with strongly negative εNd values) such as the pelagic Deer Park metasedimentary rocks (Fig. 2). This would have the effect of modifying the flat REE profiles seen in basal parts of the arc-ophiolite package, such as the lower portions of the Lough Nafooey Group (Drait & Clift 2001) or the Deer Park metadolerites (Fig. 2).

**U–Pb ion-probe zircon geochronology of the plagiogranite clasts.** U–Pb isotopic data, calculated U–Pb ages and detailed analytical technique are listed in the Supplementary Publication (see p. 000). SEM–CL images of representative dated zircons and U–Pb Tera–Wasserburg concordia diagrams are shown in Figure 3a and b. As no significant common Pb was detected, no correction was applied to the data.

Both samples DC 10/1/5 and DC 10/1/6 have a single (petrographically identical) zircon population, consisting of short prismatic grains (l:w of 2:1). The grains are typically about 50–100 µm long and are euhedral (Fig. 3a and b). The grains are generally bright under CL (with dark zones concentrated near the rims) and exhibit prominent oscillatory zoning. No inherited cores were observed, and Th/U ratios of the dated crystals typically cluster between 0.2 and 0.4. Eleven spots from 11 crystals from sample DC 10/1/5 were analysed. Eight spots yield a concordia age of 489.9 ± 3.1 Ma. Two spots (9 and 16; Fig. 2b) were interpreted as having undergone Pb loss, and one discordant spot (2; Fig. 3a) exhibits significant amounts of common Pb. The eight spots that yield the concordia age plus the discordant spot yield an intercept age of 488.7 ± 2.9 Ma, assuming the anchor for the intercept has a modern-day average terrestrial common Pb composition of 207Pb/206Pb = 0.88 (Stacey & Kramers 1975). Thirteen spots from 12 crystals from sample DC 10/1/6 were analysed. All the spots were used in the age calculation, which yields a concordia age of 487.8 ± 2.3 Ma.

**Conclusions.** Proximal Silurian conglomerates in western Ireland contain coarse detritus that can be unequivocally linked to the underlying Lough Nafooey arc. This detritus includes
plagiogranite boulders (76.5% SiO₂, 0.45% K₂O, 8 ppm Rb, \( \sum \text{REE} \) 43 ppm), two of which have yielded U–Pb secondary ionization mass spectrometry (SIMS) zircon ages of 489.9 ± 3.1 Ma and 487.8 ± 2.3 Ma, respectively. An \( \varepsilon_{Nd}(400) \) value of +0.41 (TDM = 1.39Ga) for one of the boulders suggests that the plagiogranites are crystallization products of a basaltic melt in the Lough Nafooey arc that had previously assimilated old continental crust. This is inferred to be due to subducted, distal Laurentian slope sediment, probably similar to the slivers of metasedimentary rock incorporated into the metamorphic sole of the Deer Park Complex ophiolite, the suprasubduction ophiolite upon which the Lough Nafooey arc was sited. The metasedimentary rocks have strongly negative \( \varepsilon_{Nd}(400) \) values (−7 and −15, equal to TDM ages of 1.75 Ga and 2.2 Ga, respectively), whereas metadolerites of the Deer Park Complex ophiolite have strongly positive \( \varepsilon_{Nd}(400) \) values (c. +6), similar to the lower portions of the Lough Nafooey Group and indicating minimal assimilation of old continental material. The temporal variations in arc chemistry used to infer the onset of the subduction of continental margin sediments suffer from a lack of biostratigraphical control, and the uncertainty involved in correlating biostratigraphical zones with an extremely sparse geochronological database for the base of the Ordovician period (Cooper & Sadler 2004). This study provides direct evidence that the Lough Nafooey arc had encountered subducting Laurentian margin sediments by 490 Ma, 15 Ma prior to the major phase of crustal thickening and peak metamorphism at 475–465 Ma (Friedrich et al. 1999; Dewey 2005).

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