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Laurentian crustal recycling in the Ordovician Grampian Orogeny: Nd isotopic evidence from western Ireland

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Abstract – Because magmatism associated with subduction is thought to be the principal source for continental crust generation, assessing the relative contribution of pre-existing (subducted and assimilated) continental material to arc magmatism in accreted arcs is important to understanding the origin of continental crust. We present a detailed Nd isotopic stratigraphy for volcanic and volcaniclastic formations from the South Mayo Trough, an accreted oceanic arc exposed in the western Irish Caledonides. These units span an arc–continent collision event, the Grampian (Taconic) Orogeny, in which an intra-oceanic island arc was accreted onto the passive continental margin of Laurentia starting at ∼475 Ma (Arenig). The stratigraphy corresponding to pre-, syn- and post-collisional volcanism reveals a progression of $\varepsilon_{Nd(t)}$ from strongly positive values, consistent with melt derivation almost exclusively from oceanic mantle beneath the arc, to strongly negative values, indicating incorporation of continental material into the melt. Using $\varepsilon_{Nd(t)}$ values of meta-sediments that represent the Laurentian passive margin and accretionary prism, we are able to quantify the relative proportions of continent-derived melt at various stages of arc formation and accretion. Mass balance calculations show that mantle-derived magmatism contributes substantially to melt production during all stages of arc–continent collision, never accounting for less than 21 % of the total. This implies that a significant addition of new, rather than recycled, continental crust can accompany arc–continent collision and continental arc magmatism.

Keywords: Grampian Orogeny, western Ireland, continental crust, Nd isotopes, Laurentia, Iapetus Ocean.

1. Introduction

1.a. The problem of continental crust generation

The origin and accretionary history of the continental crust has long been debated by earth scientists. Many have suggested, based upon trace element characteristics, that continental material may form at convergent margins (see Davidson, 1996). However, this model is not easily reconciled with the bulk mafic and light rare earth element (LREE) depleted composition of intra-oceanic arc crust compared to the andesitic, LREE-enriched composition of continental crust (Taylor, 1967; Bryan, Stice & Ewart, 1972; Taylor & McLennan, 1985; Ewart & Hawkesworth, 1987; Rudnick & Fountain, 1995). It was first suggested by Pearcy, Debari & Sleep (1990) that the process of arc–continent collision might alter the composition of arc magmatism to become more LREE-enriched and andesitic. Using the Ordovician accretion of an oceanic island arc onto the Laurentian continent as an example, Draut *et al.* (2002) showed that the combined processes of crystal fractionation producing LREE-enriched, silica-rich melts coupled with lower crustal loss during arc–continent collision may indeed drive magmatic compositions toward that of average continental crust.

In this study, we revisit that Ordovician arc–continent collision to determine the relative proportions of continent- and mantle-derived magmatism before, during and after arc–continent collision. We determine end-member Nd isotopic compositions for the intra-oceanic island arc and for the continental melt with which it mixed, and use mass balance calculations to determine the degree of continental crustal recycling during arc melt production. In this way we assess the proportion of new material added to the continent as a result of such collision, an important step in understanding the generation of the continental crust and the dynamics of arc–continent collision.

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1.b. The Grampian Orogeny in the Irish Caledonides

Volcanic and volcaniclastic sedimentary rocks of the South Mayo Trough, western Ireland, provide a comprehensive record of magmatic evolution during the collision of an intra-oceanic arc, the Lough Nafooey Arc formed within the Iapetus Ocean, with the passive margin of the Laurentian continent during the Early Ordovician (e.g. Graham, Leake & Ryan, 1989; Dewey & Ryan, 1990; Ryan & Dewey, 1991; Dewey & Mange, 1999). This event is known as the Grampian Orogeny in Scotland and Ireland and as the Taconic Orogeny in its continuation in North America (e.g. Swinden, Jenner & Szybinski, 1997; Karabinos *et al*. 1998) and significantly pre-dates final closure of the Iapetus Ocean at ~400 Ma. Prior to arc–continent collision, the intra-oceanic subduction zone involved a N-facing arc situated above a subducting plate that dipped to the south (Dewey & Ryan, 1990; Clift & Ryan, 1994). 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, Dewey & Scotese, 1991; Van Staal *et al*. 1998). Strata within the South Mayo Trough represent volcanic activity of the accreted oceanic arc and its forearc basin, including lavas and volcaniclastic sediments that span the time of collision (Fig. 1). These units have undergone only minimal subsequent metamorphism and deformation, and are now preserved in a broad syncline.

The Connemara block, immediately south of the South Mayo units across a suspected faulted terrane boundary (Fig. 1), comprises highly deformed and metamorphosed sediments of the Dalradian Supergroup (Yardley, 1976; Leake *et al*. 1983; Leake, 1986). Dalradian rocks are considered to represent pre-collisional sedimentary rocks derived from the Laurentian continent, in the form of continental margin and intracratonic basin deposits. Connemara Dalradian units are thus correlated with the Dalradian units of the Scottish Highlands (e.g. Harris *et al*. 1994). The Connemara Dalradian units were intruded by mafic and dioritic plutons during the Grampian Orogeny (e.g. Yardley, 1976; Senior & Leake, 1978; Leake *et al*. 1983; Leake, 1986, 1989; Friedrich *et al*. 1999).

Connemara is one of the best-dated segments of the Caledonide–Appalachian orogenic belt. U–Pb analyses of zircon grains from syn-collisional gabbro intrusions (Cliff, Yardley & Bussy, 1996; Friedrich *et al*. 1999) in Connemara, together with trace element analyses of the volcanic rocks on the South Mayo Trough (Draut & Clift, 2001) indicate that the arc–continent collision event was brief, lasting approximately 10 My (~475 to 465 Ma). Volcanic rocks in South Mayo have been dated using a detailed graptolite biostratigraphy (Graham, Leake & Ryan, 1989), as well as radiometric dating of a tuff from the post-collisional (Llanvirn) Mweelrea Formation (Dewey & Mange, 1999). We use the time scale of Tucker & McKerrow (1995) to correlate biostratigraphic and absolute ages, and so can directly compare the evolution of South Mayo and Connemara during the Grampian Orogeny.

To the north, volcanic and volcaniclastic units of South Mayo are tectonically juxtaposed against the Ordovician Clew Bay Complex (Fig. 1). Rocks of the Clew Bay Complex are exposed along the southern edge of Clew Bay on the mainland (the Killadangan Formation) and on Clare Island (the Ballytoohy Formation), as well as in the southern part of the island of Achillbeg, south of the Achillbeg Fault (D. M. Chew, unpub. Ph.D. thesis, University Coll. Dublin, 2001). This low-grade metasedimentary mélange is composed of fine-grained marine sediments including deep-water turbidites, with fragments of amphibolites and mafic igneous rocks (Williams *et al*. 1994; Harkin *et al*. 1996). The Clew Bay Complex was once believed to contain Silurian microfossils (Williams, Harkin & Higgs, 1996), but this finding was refuted when these rocks were shown to have shared a Grampian deformation history with Dalradian units to the north (D. M. Chew, unpub. Ph.D. thesis, University Coll. Dublin, 2001; Chew, 2003). Lithologically, the Clew Bay Complex indicates sedimentary derivation from a passive continental margin (Harkin *et al*. 1996) and is most reasonably interpreted as the Ordovician accretionary prism to the N-facing Lough Nafooey Arc, composed largely of detritus from the Laurentian continent (Dewey & Ryan, 1990; Dewey & Mange, 1999).

North of the Clew Bay Complex lie additional meta-sedimentary rocks of the Dalradian Supergroup, the North Mayo Dalradian (e.g. Winchester, Max & Long, 1987; Winchester & Max, 1996). The North Mayo Dalradian sequence includes the late Proterozoic Grampian, Appin and Argyll groups, which consist of, respectively, schists and psammites, quartzites derived from mature sands overlain by interbedded shales and carbonates, and quartzites interspersed with metabasic volcanic rocks (Winchester & Max, 1996). SE-verging nappes within these Dalradian units in North Mayo, the Sperrin Mountains and the Ox Mountains inlier, have been shown to have originated during Grampian deformation, as the Dalradian sequence was overthrust over volcanic units and/or basement probably associated with the colliding Lough Nafooey Arc (Alsop & Hutton, 1993; Flowerdew *et al*. 2000; Chew, 2003).

The South Mayo Trough represents a uniquely well-preserved stratigraphic succession encompassing the time of arc–continent collision. This area of the Irish Caledonides has accordingly been used to examine tectonic and magmatic processes of arc–continent collision to a degree not possible in analogous modern collision zones, where middle and lower crustal sequences are inaccessible. South Mayo is thus an ideal location to constrain the involvement of continental material in magmatism at the various stages of collision

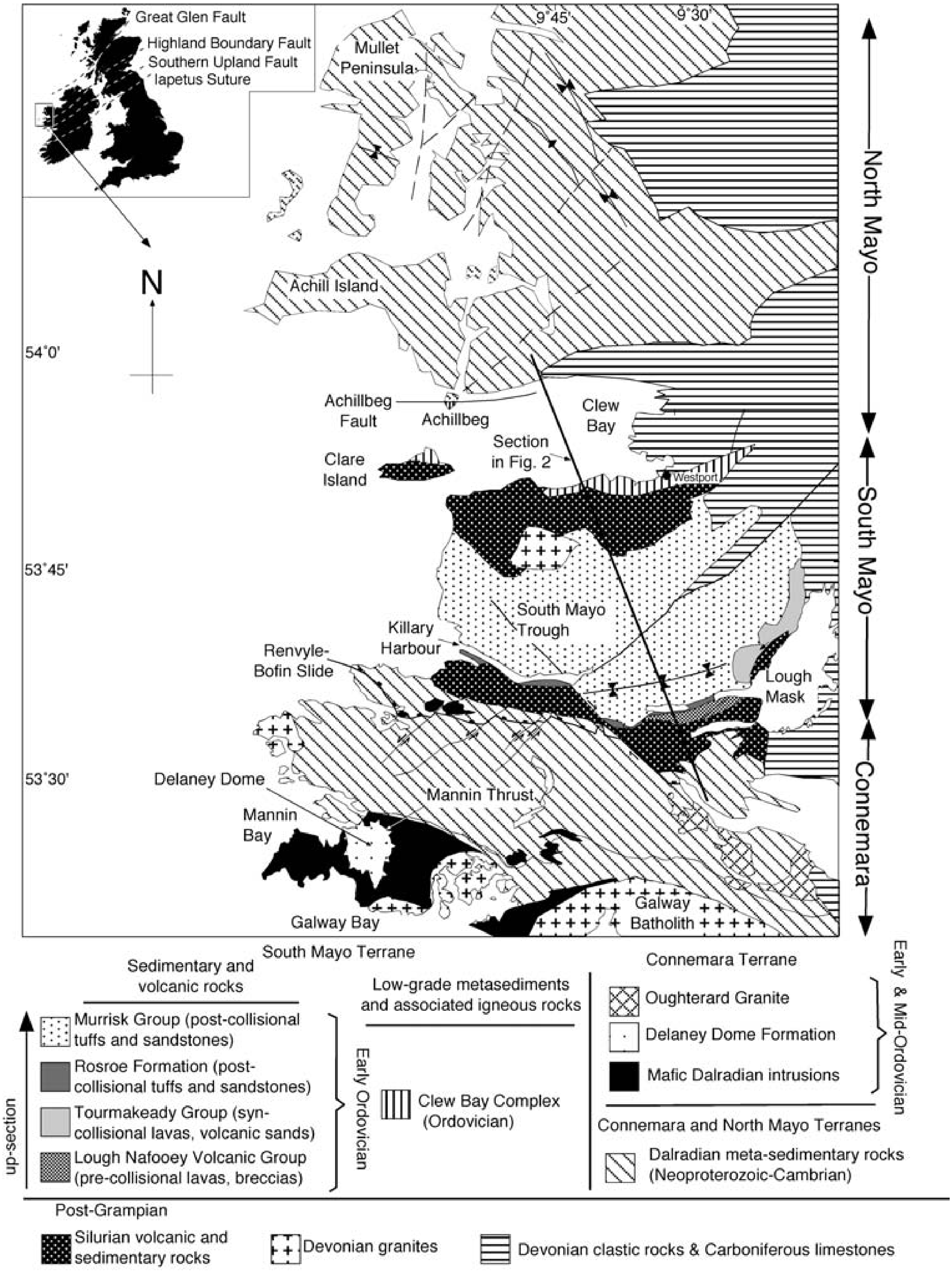

Figure 1. Study area in the western Irish Caledonides, showing the metamorphosed Laurentian (Dalradian) terranes of North Mayo and Connemara, separated by the Ordovician South Mayo volcanic and sedimentary terrane.

during the Grampian Orogeny. We present such an analysis, using the composition of metasedimentary rocks from the Dalradian Supergroup and Clew Bay Complex to represent a Laurentian end-member, and primitive basaltic lavas from the South Mayo Trough to represent mantle melts within the intra-oceanic

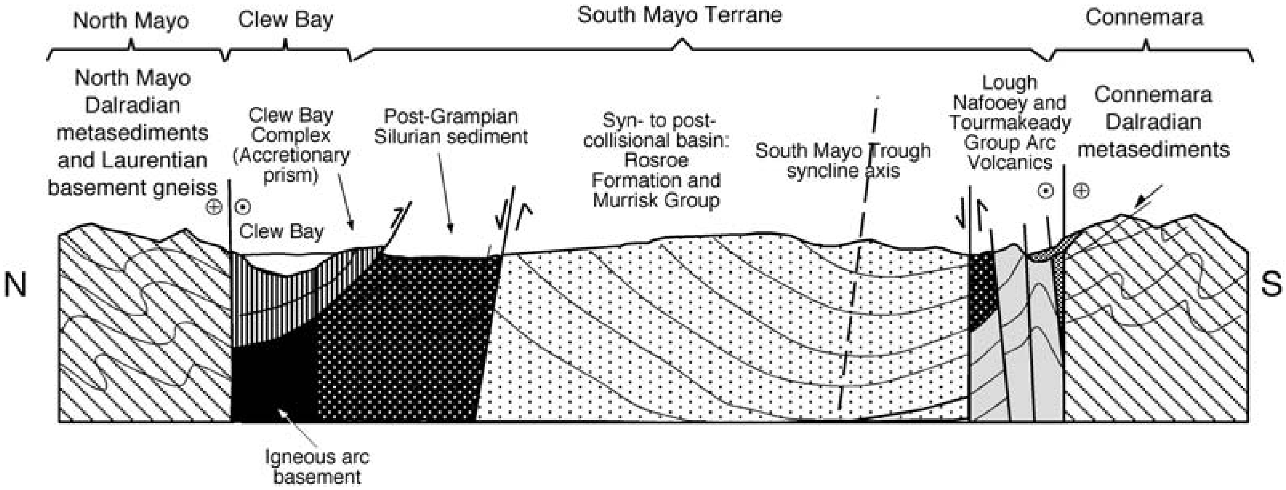

Figure 2. Cross-section from north to south through North Mayo, South Mayo and Connemara. Location of cross-section is shown in Figure 1; for legend, see Figure 1. Figure 2 is not to scale.

island arc. This work builds on prior studies that have traced the geochemical evolution in South Mayo during collision, and on previous analyses made of Nd isotopic composition within South Mayo, the Clew Bay Complex and the Dalradian Supergroup (e.g. Ryan, Floyd & Archer, 1980; O'Nions, Hamilton & Hooker, 1983; Frost & O'Nions, 1985; M. D. Jagger, unpub. Ph.D. thesis, Univ. Glasgow, 1985; Menuge & Daly, 1990; Clift & Ryan, 1994; Harkin *et al*. 1996; R. P. Scanlon, unpub. M.Sc. thesis, University Coll. Dublin, 1998; D. M. Chew, unpub. Ph.D. thesis, University Coll. Dublin, 2001; Draut & Clift, 2001; Chew, 2003).

1.c. Geological setting

The South Mayo Trough consists of a thick accumulation of Ordovician lavas and volcaniclastic sediments, deformed into a broad E–W-trending syncline (Figs 1, 2). The south limb of the syncline contains proximal arc lavas and volcaniclastic debris, with more distal sediments comprising the north limb. To the south, Dalradian high-grade metamorphic lithologies of Connemara are in a presumed high-angle faulted contact with the South Mayo units (Fig. 2), but this contact between the Connemara and South Mayo terranes is covered uncomformably by Silurian strata. The present study focuses on the isotopic chemistry of proximal lavas and volcaniclastic sequences in the south limb of the South Mayo Trough. The Lough Nafooey Group, Tourmakeady Volcanic Group, Rosroe Formation and Murrisk Group of the south limb of the Trough are all separated from each other by faulted contacts of unknown magnitude (e.g. Graham, Leake & Ryan, 1989), although biostratigraphy allows them to be arranged as a coherent, continuous record of arc volcanic activity.

At the base of the sequence, the Bohaun Volcanic Group and Lough Nafooey Group are the oldest and most primitive formations, representing intra-oceanic arc volcanism of the Lough Nafooey Arc prior to its collision with Laurentia. The age of basaltic lavas that comprise the Bohaun Volcanic Group is not precisely known, but their boninitic chemistry (Clift & Ryan, 1994) indicates earliest-stage formation above a young subduction zone undergoing shallow melting (Crawford, Falloon & Green, 1989).

The trace element chemistry of the tholeiitic basalts at the base of the Upper Tremadoc–Lower Arenig (∼495–481 Ma) Lough Nafooey Group and the lack of continental detritus in the oldest sediments of that group suggest an origin far from the Laurentian margin (Ryan, Floyd & Archer, 1980). The basal unit of the Lough Nafooey Group, the Bencorragh Formation, consists of vesicular basalts that are LREE-depleted, as is typical of intra-oceanic arc volcanism (Clift & Ryan, 1994; Draut & Clift, 2001). The initially basaltic composition of the Lough Nafooey Group gives way to a more andesitic, calc-alkaline affinity in volcanic breccias of the overlying Finny and Knock Kilbride formations, and finally to andesitic volcaniclastic rocks of the Derry Bay Formation, as SiO_2 content increases up-section (Clift & Ryan, 1994). Draut & Clift (2001) have shown through REE chemistry and pilot Nd isotopic work that the younger formations of the Lough Nafooey Group spanned initial 'soft' collision between the Lough Nafooey Arc and the Laurentian margin, during which continental sediment and the outermost continental crust entered the subduction zone.

Overlying volcanic units continue the trend toward higher-silica, higher-K composition with increasing LREE enrichment (Ryan, Floyd & Archer, 1980; Clift & Ryan, 1994; Draut & Clift, 2001). The Arenig Tourmakeady Volcanic Group (∼481–470 Ma) contains andesitic and rhyolitic tuffs and volcaniclastic sediments (Graham, Leake & Ryan, 1989). Trace element evidence has demonstrated that the Tourmakeady Volcanic Group spans 'hard' arc–continent collision (orogeny and regional deformation: Draut & Clift, 2001), synchronous with the peak regional metamorphism of the Laurentian margin dated in Connemara (Friedrich *et al*. 1999).

The Murrisk Group (Upper Arenig–Lower Llanvirn, ~477–464 Ma), whose lower members may be approximate temporal equivalents of the Tourmakeady Volcanic Group, comprises the greatest thickness of sediments (~6 km) within the South Mayo Trough. The Murrisk Group is in faulted contact with the Tourmakeady Volcanic Group, and contains shales and turbiditic sandstones with interspersed tuffs. The Llanvirn Mweelrea Formation, at the top of the Murrisk Group, is dominated by quartz sandstones but contains ignimbrites. The Llanvirn Rosroe Formation (~469–467 Ma) lies stratigraphically above the Tourmakeady Volcanic Group, and has been interpreted as an approximate temporal equivalent to the middle Murrisk Group (Graham, Ryan & Leake, 1989). A series of conglomerates and sandstones with andesitic tuffs and ignimbrites, the Rosroe Formation contains increasingly abundant metamorphic clasts up-section (Dewey & Mange, 1999). The Rosroe Formation and upper Murrisk Group (in particular the Mweelrea Formation) most likely represent late syn- to post-collisional arc volcanism associated with a S-facing active Laurentian margin (Dewey & Ryan, 1990; Ryan & Dewey, 1991; Draut & Clift, 2001).

Our sampling strategy was designed to define a Nd isotopic stratigraphy that spanned all phases of arc–continent collision. To constrain the degree of continental involvement in magmatism, we first established the composition of the end-members whose magmas would mix during arc–continent collision: melt from the mantle under the intra-oceanic island arc and melt recycled from the Laurentian continental crust. The composition of the pre-collisional intra-oceanic arc is assumed to be that of the most primitive basalts at the base of the South Mayo volcanic stratigraphy. This is an approximation, since even the most 'oceanic' arc lavas in the modern oceans show some isotopic evidence for sediment involvement in petrogenesis, but nonetheless represents the most primitive lithologies of the Lough Nafooey Arc. We employ previous Nd isotopic studies from various exposures of the Dalradian Supergroup and Clew Bay Complex to represent Laurentian passive margin sediment composition. Using Nd isotopic composition of these end-members, we have calculated the proportions of each that would have contributed to melting during the 10 My collision process.

2. Methods

Samples of lava and volcaniclastic sedimentary rocks were collected from the Bohaun Volcanic Group, Lough Nafooey Group, Tourmakeady Volcanic Group, Rosroe Formation and Mweelrea Formation for isotopic analysis. This study combines nine new analyses with six presented by Draut & Clift (2001) to represent all parts of the volcanic stratigraphy and thus spans all stages of both 'soft' and 'hard' arc–continent collision.

Nine whole-rock samples were dissolved and their Nd and Sr isotopic ratios were measured using a VG-Micromass Sector 54 thermal ionization mass spectrometer (TIMS) at the Southampton Oceanography Centre, UK. $^{143}Nd/^{144}Nd$ was determined in multi-dynamic mode, exponentially corrected for instrumental fractionation relative to $^{146}Nd/^{144}Nd = 0.7219$. The JNdi standard gave a value of 0.512105 ± 9 (2sd, $n = 26$), and data have been corrected to 0.512115 (Tanaka *et al*. 2000). Strontium data were also measured in multi-dynamic mode, and fractionation corrected relative to $^{86}Sr/^{88}Sr = 0.1194$. NBS987 $^{87}Sr/^{86}Sr$ was measured as 0.710252 ± 17 (2sd, $n = 35$) during the course of the analyses, and data are presented relative to NBS987 0.710250. An age correction (DePaolo & Wasserburg, 1976) was performed on the resulting $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ isotopic ratios to account for radioactive decay and ingrowth of ^{143}Nd since eruption. Values are reported accordingly with the subscript t. We use 0.512638 and 0.1967 to represent modern CHUR $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$, respectively, according to Hamilton *et al*. (1983). The decay constant of ^{147}Sm is taken to be 6.54×10^{-12} yr^{-1}. Sm, Nd, Rb and Sr concentrations are from Draut & Clift (2001).

3. Results

Table 1 summarizes the isotopic data for the nine samples analysed and six Nd isotopic analyses from Draut & Clift (2001). Nd isotopic ratios have been used to calculate $\varepsilon_{Nd(t)}$. Positive $\varepsilon_{Nd(t)}$ values indicate derivation from a mantle source depleted relative to bulk earth; continental crust and its sedimentary derivatives are enriched relative to bulk earth, and so are characterized by negative $\varepsilon_{Nd(t)}$.

The primitive Bohaun Volcanic Group shows a strong positive $\varepsilon_{Nd(t)}$ signal; the two samples of basaltic lava analysed from this group yield values of +10.00 and +7.79. The Bencorragh Formation, the oldest and most primitive basalts of the Lough Nafooey Group, also give a strong positive value of +7.25, consistent with the interpreted oceanic origin of the Lough Nafooey Arc. $\varepsilon_{Nd(t)}$ decreases steadily up-section, with a basaltic breccia of the Finny Formation at +3.47, and basaltic andesites of the Knock Kilbride Formation yielding values of +3.30 and +0.44. At the top of the Lough Nafooey Group, volcanic sandstones of the Derry Bay Formation show slightly negative $\varepsilon_{Nd(t)}$ at −2.58.

$\varepsilon_{Nd(t)}$ undergoes a sharp increase across the faulted contact between the Lough Nafooey and Tourmakeady volcanic groups. At the base of the Tourmakeady Volcanic Group, volcanic sandstones of the Mt Partry Formation yielded an $\varepsilon_{Nd(t)}$ value of −11.05, followed

Table 1. Results of Nd and Sr isotopic analyses

Sample	Age (Ma)	Nd (ppm)	Sm (ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	Nd error (σ)	$^{143}Nd/^{144}Nd_{(t)}$	$\varepsilon_{Nd(t)}$	Sr (ppm)	Rb (ppm)	$^{87}Sr/^{86}Sr$	$^{87}Sr/^{86}Sr_{(t)}$	Sr error σ	Formation	Lithology
Omm-8*	466.2	36.8	6.9	0.11	0.511955	0.00005	0.51161	−8.35						Mweelrea Fm., Murrisk Group	Tuff
RR-92-21*	468.6	31.2	6.3	0.12	0.511867	0.00007	0.51149	−10.59						Rosroe Fm.	Tuff
TV-92-3*	471.2	19.3	3.5	0.11	0.511737	0.00005	0.51140	−12.23						Tourmakeady Fm., Tourmakeady Grp.	Calcareous tuff
TV-92-7*	472.0	22.4	4.1	0.11	0.51165	0.00005	0.51130	−14.11						Tourmakeady Fm., Tourmakeady Grp.	Rhyolite breccia
TV-92-18	474.9	24.0	1.9	0.05	0.511864	0.00008	0.51163	−7.77	133.1	34.5	0.72016	0.71951	0.00001	Tourmakeady Fm., Tourmakeady Grp.	Rhyolite breccia
TV-92-44	478.3	29.0	4.5	0.09	0.511746	0.00010	0.51145	−11.14	766.6	276.5	0.72049	0.71958	0.00002	Tourmakeady Fm., Tourmakeady Grp.	Rhyolite lava
TV-92-35	479.6	13.3	2.5	0.11	0.511853	0.00009	0.51149	−10.25	258.4	100.2	0.71883	0.71785	0.00014	Mt Partry Fm., Tourmakeady Grp.	Volcanic sandstone
TV-92-42	479.8	10.8	1.9	0.11	0.5117912	0.00005	0.51145	−11.05	415.2	126.5	0.71724	0.71647	0.00001	Mt Partry Fm., Tourmakeady Grp.	Volcanic sandstone
Ond-3	480.0	5.6	1.6	0.17	0.512433	0.00008	0.51189	−2.58	195.0	101.1	0.71804	0.71673	0.00001	Derry Bay Fm., Lough Nafooey Grp.	Volcanic sandstone
LN-92-52*	481.5	4.6	1.4	0.19	0.512625	0.00013	0.51204	0.44						Knock Kilbride Fm., Lough Nafooey Grp.	Basalt-andesite lava
LN-92-48	482.5	6.3	1.8	0.17	0.5127316	0.00005	0.51219	3.30	103.7	2.9	0.70685	0.70677	0.00001	Knock Kilbride Fm., Lough Nafooey Grp.	Basalt-andesite lava
LN-92-32	485.1	5.8	1.6	0.17	0.512734	0.00005	0.51219	3.47	147.2	0.5	0.70751	0.70750	0.00001	Finny Fm., Lough Nafooey Grp.	Basalt breccia
LN-92-7*	487.8	6.6	2.6	0.24	0.5131339	0.00005	0.51238	7.25						Bencorragh Fm., Lough Nafooey Grp.	Basaltic lava
BV-00-1	495.0	1.5	0.4	0.16	0.512923	0.00009	0.51246	7.79	67.9	4.6	0.70861	0.70843	0.00001	Bohaun Volcanic Group	Basaltic lava
BV-00-2	495.0	1.9	0.4	0.13	0.512926	0.00012	0.51247	10.00	67.9	4.6	0.70794	0.70776	0.00001	Bohaun Volcanic Group	Basaltic lava

* Samples analysed by Draut & Clift (2001)

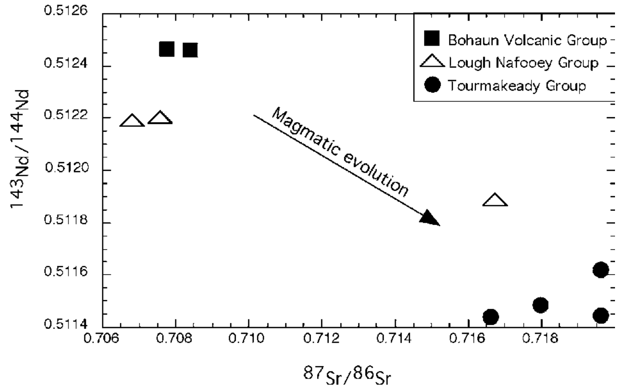

Figure 3. Initial isotope ratios for Nd and Sr obtained for South Mayo samples. Sr isotopic ratios are apparently altered, presumably by hydrothermal activity, but still indicate a progression of magmatic evolution that is consistent with that of the Nd isotopic trend. Ratios of rare earth isotopes are unaffected by hydrothermal alteration and so the Nd data reflect original magmatic composition. These isotopes show a trend from primitive composition in the lower South Mayo stratigraphy (Bohaun Volcanic Group and lower and middle Lough Nafooey Group) to more evolved, radiogenic composition in the uppermost Lough Nafooey Group and Tourmakeady Volcanic Group.

by another sample of the same unit at − 10.25. Higher in the Tourmakeady Volcanic Group, other samples showed similar strongly negative results, ranging from − 7.77 to − 14.11 within the Tourmakeady Formation, although no coherent trend up-section can be seen within that formation. The youngest volcanic units sampled, tuffs of the Rosroe and Mweelrea formations, yield $\varepsilon_{Nd(t)}$ of − 10.59 and − 8.35, respectively.

Sr isotopic ratios increase to more radiogenic values across the boundary between the Lough Nafooey Group and Tourmakeady Volcanic Group. They remain radiogenic with little discernible trend throughout the Tourmakeady Volcanic Group (Table 1).

4. Discussion

4.a. Isotopic evolution of South Mayo Trough volcanism during arc–continent collision

Figure 3 shows age-corrected Nd isotopic ratios plotted against Sr isotopic ratios for South Mayo volcanic samples. A general progression from intra-oceanic type volcanism toward more evolved magmatism can be seen in this diagram. The evolution of magmatism from more primitive basalts of the Bohaun Volcanic Group and basal Lough Nafooey Group toward more evolved tuffs and volcaniclastic rocks of the Tourmakeady Volcanic Group, and then the Rosroe and Mweelrea formations (Section 1.c), is consistent with the evolution of LREE and silica content described by Clift & Ryan (1994) and by Draut & Clift (2001). However, although the negative-sloping trend indicated in Figure 3 is to be expected for such magmatic evolution, the high absolute values of the Sr ratios obtained (well above 0.706, even in the most primitive basaltic units) indicate that substantial alteration has occurred in these rocks, most likely due to remobilization of Sr and its parent Rb by hydrothermal fluids. These rocks yielded a significant loss on ignition during X-ray fluorescence analysis by Clift & Ryan (1994), further suggesting an altered character. Nd, as a rare earth element, is not water-mobile and so would not be affected by hydrothermal alteration. Although the Sr isotopic ratios in Figure 3 and Table 1 likely do not reflect those that accompanied original magmatic derivation, these data illustrate the general trend of magmatic evolution during the Grampian collision.

In general, the strongest trend within our data set is the transition from strongly positive $\varepsilon_{Nd(t)}$ at the base of the section to weakly negative within the upper Lough Nafooey Group, followed by a transition to strong negative values at the base of the Tourmakeady Volcanic Group. The Nd isotopic compositions of the Bohaun Volcanic Group and basal Lough Nafooey Group (Bencorragh Formation) imply that the Lough Nafooey Arc was located far enough from the Laurentian margin that there was little contribution from continental sediments to these early tholeiitic arc basalts. The Nd isotopic character of the Bohaun Volcanic Group and lower Lough Nafooey Group strongly resembles that of modern oceanic island arcs that are similarly unaffected by continental material; the western Pacific Tonga, Mariana and Izu arcs display $\varepsilon_{Nd(t)}$ values that range from +6.7 to +9.2 (Ewart & Hawkesworth, 1987; Woodhead, 1989; Taylor & Nesbitt, 1998). The volcanic succession that comprises the Lough Nafooey Group is believed, on the basis of LREE and major element composition, to span a time when distal sediments derived from the Laurentian continent, and possibly thin portions of the outermost crystalline continental crust, were subducted beneath the arc and contributed to the composition of arc magmatism. The progression toward lower (more continental) $\varepsilon_{Nd(t)}$ through the Lough Nafooey Group implies a progressively greater contribution of continental material to the volcanism during this 'soft' collision.

The transition from 'soft' to 'hard' collision (regional deformation, orogeny and metamorphism) is inferred to occur across the faulted contact between the Lough Nafooey Group and Tourmakeady Volcanic Group volcanic rocks (Draut & Clift, 2001), where a jump to strongly negative $\varepsilon_{Nd(t)}$ is accompanied by a sharp increase in silica content and in LREE enrichment (Clift & Ryan, 1994; Draut & Clift, 2001). This abrupt transition to lower $\varepsilon_{Nd(t)}$ immediately precedes the peak of metamorphism dated in Connemara at 470 Ma (Friedrich *et al*. 1999). Within the Tourmakeady Volcanic Group, fractional crystallization also became an important process affecting magmatic chemistry (Draut *et al*. 2002). This group is inferred to span the time of active orogeny, peak metamorphism and subduction polarity reversal. Within the Tourmakeady Volcanic Group, $\varepsilon_{Nd(t)}$ values remain strongly negative but with no clear trend. This is interpreted to reflect a substantial and relatively constant proportion of continental material involved in collisional arc volcanism.

The Rosroe and Mweelrea formations post-date peak metamorphism, and it is likely that they are contemporaneous with gravitational collapse of the orogen (Clift *et al*. 2003) and possibly the loss of the dense lower crust and upper mantle (Draut *et al*. 2002). Since the influx of new mantle asthenosphere has been inferred under the arc at the time the Rosroe tuffs were erupted (Clift *et al*. 2003), a slightly higher $\varepsilon_{Nd(t)}$ (indicating a relative decrease in the continental signal) might be expected to accompany these late-stage units. This is indeed the case, as the Mweelrea Formation yields an $\varepsilon_{Nd(t)}$ value of −8.35. Nonetheless, this signal still shows a strong continental influence, as these tuffs were erupted at an arc source built on an active continental margin that succeeded subduction polarity reversal.

4.b. Constraints on Laurentian ε_{Nd}

Identifying a crustal signature within the volcanic stratigraphy requires the constraint of two end-member components: melt from the intra-oceanic phase of Lough Nafooey Arc activity, and Laurentian continental material that had been subducted and/or assimilated during the ascent of arc melt. We use as the intra-oceanic arc end-member an $\varepsilon_{Nd(t)}$ value of +8.90, the mean of two samples of the primitive Bohaun Volcanic Group basalts. Since this value lies close to modern Pacific and Atlantic mid-ocean ridge basalt (MORB) values, we infer that these lavas were almost entirely the product of mantle melting within the Iapetus Ocean.

To characterize the Nd isotopic composition of the Laurentian continental margin involved in the Grampian Orogeny, we have used previously published isotopic data from the Dalradian Supergroup, which are metamorphosed Laurentian sedimentary rocks from the continental margin and earlier intracratonic basins, and from the Clew Bay Complex, which contains metamorphosed continental sediments from the accretionary complex to the Lough Nafooey Arc. The results of previous analyses, adjusted to show $\varepsilon_{Nd(t)}$ values at 470 Ma, are summarized in Table 2. Table 2 also includes, for comparison, data from mid- to late Ordovician Southern Uplands sediments of Scotland, believed to represent an accretionary complex to the S-facing continental arc that succeeded Grampian collision, which contain a mixture of primitive ophiolitic debris and quartzo-feldspathic material (Stone & Evans, 1995; see also Stone & Evans, 1999). Not included in this table are data from basaltic

Table 2. Published Nd data for Laurentian-derived rocks in Scotland and Ireland

Location	No. samples	$\varepsilon_{Nd(470)}$ range	Mean	Median	Source
Clew Bay Complex, South Mayo, Ireland (South Achillbeg Formation)*	6	−12.91 to −20.53	−16.20	−15.85	Chew (2003)
Clew Bay Complex, South Mayo (Killadangan and Ballytoohy Formation)	8	−15.62 to −23.77	−19.41	−19.07	Harkin *et al.* (1996)
Annagh Gneiss Complex (Laurentian basement), North Mayo, Ireland†					
Mullet Gneisses	8	−4.37 to −15.82	−10.31	−10.66	Menuge & Daly (1990)
Doolough Gneisses	4	0.05 to −3.85	−1.88	−1.86	Menuge & Daly (1990)
Grampian Group, North Mayo (Formerly Inishkea Division), semipelitic schist	3	−10.11 to −11.55	−10.99	−11.32	Menuge & Daly (1990)
North Mayo Dalradian metasediments	9	−9.48 to −19.23	−14.70	−14.91	Scanlon (unpub. M.Sc. thesis, University Coll. Dublin, 1998)
Connemara Dalradian, Ireland, metasediments‡	7	−12.41 to −18.19	−15.90	−17.30	Jagger (unpub. Ph.D. thesis, Univ. Glasgow, 1985)
Dalradian metasediments, Scotland (Argyll, Appin, S. Highland groups)	7	−12.34 to −22.46	−17.48	−18.00	O'Nions, Hamilton & Hooker (1983)
Dalradian metasediments, Scotland (Appin Group)	5	−6.64 to −22.59	−10.87	−8.66	Frost & O'Nions (1985)
Dalradian tillite clasts, Scotland	7	−0.72 to −9.10	−6.81	−7.07	Fitches *et al.* (1996)
Southern Uplands (Mid–Late Ordovician Leadhills Group sediments)§	24	−0.10 to −11.7	−5.1	−3.2	Stone & Evans (1995)

Data are age-corrected to the time of the Grampian Orogeny (~ 470 Ma), either by the original author or for this study.
* Calculated from data presented in table 1 of Chew (2003).
† Excludes volumetrically minor late metabasic intrusions and granitic pegmatites.
‡ Includes three hornfelsed samples.
§ Values are for age at time of deposition (470 Ma to 441 Ma).

volcanic rocks of the Tayvallich Volcanic member of the Dalradian, Scotland, as these have been shown to be related to a rifting event at ~600 Ma rather than original development of Laurentian continental crust (Halliday *et al*. 1989).

Dalradian Supergroup rocks in Ireland and Scotland display characteristically strong negative $\varepsilon_{Nd(t)}$ values (Table 2), with median and mean $\varepsilon_{Nd(t)}$ values generally between − 7 and − 20 (O'Nions, Hamilton & Hooker, 1983; Frost & O'Nions, 1985; M. D. Jagger, unpub. Ph.D. thesis, Univ. Glasgow, 1985; Fitches *et al.* 1996; Menuge & Daly, 1990; R. P. Scanlon, unpub. M.Sc. thesis, University Coll. Dublin, 1998; Stone & Evans, 1999). Dalradian units in North Mayo, Connemara and Scotland, which span all parts of the known Dalradian stratigraphy, show wide overlap with respect to $\varepsilon_{Nd(t)}$. Two studies of $\varepsilon_{Nd(t)}$ in the Clew Bay Complex metasediments show that the Killadangan and Ballytoohy formations, which crop out on the southern shore of Clew Bay and on Clare Island, respectively (Harkin *et al*. 1996), have similar Nd composition to the Clew Bay Complex on Achillbeg (Chew, 2003). Clew Bay Complex samples are in general slightly more negative than the Dalradian averages, with a range from ~ − 13 to − 24 and median and mean values between − 15.9 and − 19.4 (Table 2; Harkin *et al*. 1996; Chew, 2003).

Because samples from the South Mayo Trough have yielded $\varepsilon_{Nd(t)}$ values below − 14, the maximum average $\varepsilon_{Nd(t)}$ value of the continental crust involved in petrogenesis must be lower than this. We have chosen to perform mass balance calculations using the range of $\varepsilon_{Nd(t)}$ values obtained for metasediments of the Clew Bay Complex, with − 15 as the upper bound, to represent the Laurentian end-member (from − 15 to − 24; Table 2). Clew Bay Complex metasediments are interpreted as the accretionary prism to the pre-collisional Lough Nafooey arc (Dewey & Ryan, 1990), and thus are the most direct representation of Laurentian-derived material that contributed to arc magmatism at this particular location along the subduction zone. The use of Clew Bay Complex $\varepsilon_{Nd(t)}$ values minimizes error that would arise from along-strike variability in Laurentian isotopic composition. $\varepsilon_{Nd(t)}$ values from the Clew Bay Complex do overlap well with the general Dalradian and Laurentian basement values (Table 2), and similar results would be obtained if North Mayo Dalradian values (as low as − 19.2), Connemara Dalradian values (as low as − 18.2), or Scottish Dalradian values (as low as − 22.6) were used instead.

4.c. Recycling of Laurentian continental material in arc magmatism

Using an $\varepsilon_{Nd(t)}$ value of + 8.90 to represent primitive arc melt and a range from − 15 to − 24 to represent Laurentian crust, binary mixing calculations can be used to estimate the relative proportions of each in the South Mayo Trough stratigraphy. We assume that Nd is approximately seven times more concentrated in Laurentian crust than in the primitive arc melt. This assumption is based upon REE analyses from North Mayo Dalradian and Clew Bay Complex samples (Menuge & Daly, 1990; Harkin *et al*. 1996; Chew, 2003) and from 21 analyses of the Bohaun Volcanic

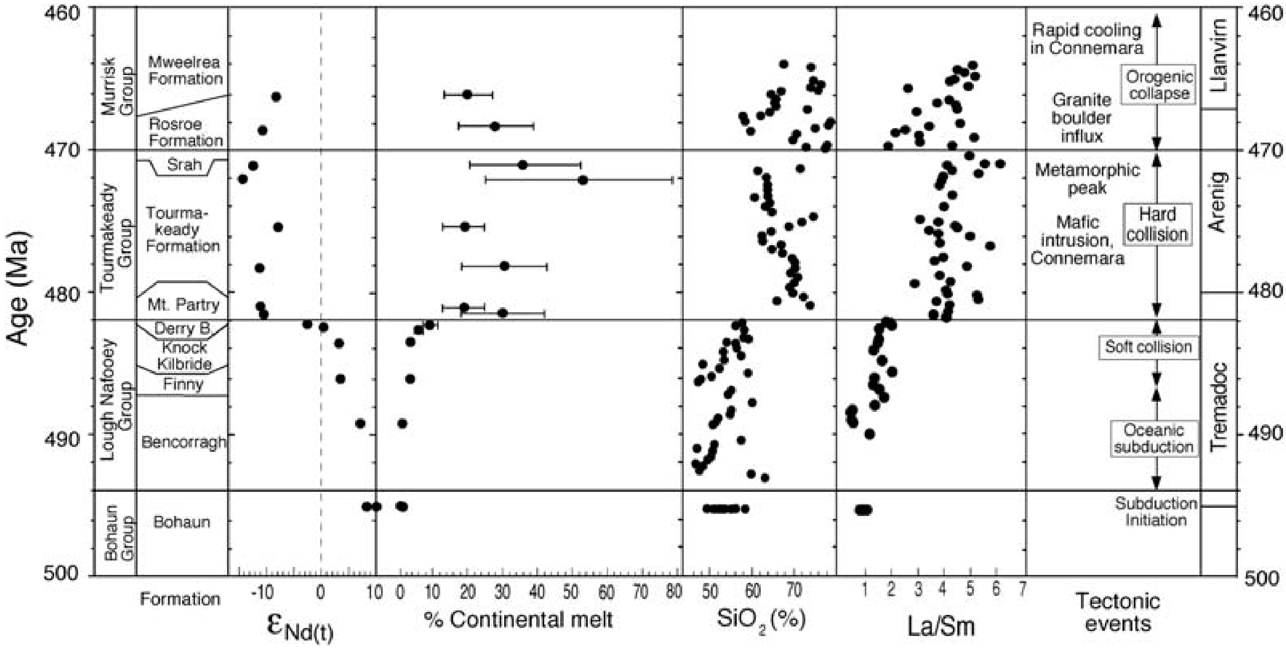

Figure 4. Nd isotopic stratigraphy of the South Mayo Trough, with corresponding calculated proportions of continental crust in the melt at each stage. For comparison, silica content and La/Sm ratios (a measure of LREE enrichment) are also shown (from Draut & Clift, 2001); the up-section enrichment of both properties is apparent. The proportion of continental material is calculated assuming binary mixing between one end-member with the composition of primitive intra-oceanic arc melt (with an $\varepsilon_{Nd(t)}$ value of +8.9, the average of the two Bohaun Volcanic Group samples analysed for this study) and with the other end-member as Laurentian crust. To represent the Laurentian end-member, we have used the Clew Bay Complex, accretionary prism to the Lough Nafooey Arc, which is composed of Laurentian-derived metasediments with a range of $\varepsilon_{Nd(t)}$ values from −15 to −24. The age of each sample is derived from a combination of biostratigraphic datums using the time scale of Tucker & McKerrow (1995) for Ordovician fauna. Tectonic events on the far right side of the diagram are based on the work of Friedrich *et al*. (1999), Draut & Clift (2001) and Draut *et al*. (2002).

Group, a combination of the two analysed for this study and 19 presented by Clift & Ryan (1994). The $\varepsilon_{Nd(t)}$ value that would result from mixing melt of these two compositions is calculated using the relationship:

$$\varepsilon_{mix} = \frac{7\varepsilon_L P_L + \varepsilon_A P_A}{7P_L + P_A} \quad (1)$$

where ε_L is the $\varepsilon_{Nd(t)}$ value of the Laurentian crust (in this case, the range found in the Clew Bay Complex), ε_A is that of the intra-oceanic arc (the Bohaun Volcanic Group) and ε_{mix} is the $\varepsilon_{Nd(t)}$ value that results from mixing these two end-members. P_L is the proportion of Laurentian melt in the mix, and P_A the proportion of arc melt. Because

$$P_A = 1 - P_L \quad (2)$$

equation (1) can be more simply written in terms of P_L:

$$\varepsilon_{mix} = \frac{7\varepsilon_L P_L + \varepsilon_A(1 - P_L)}{6P_L - 1} \quad (3)$$

and (3) can be rearranged to find the proportion of continent-derived melt from known values of ε_{mix}, the South Mayo volcanic rocks:

$$P_L = \frac{\varepsilon_A - \varepsilon_{mix}}{6\varepsilon_{mix} - 7\varepsilon_L + \varepsilon_A} \quad (4)$$

Figure 4 shows the results of these calculations, and the inferred proportions of continental crust throughout the South Mayo volcanism. Stages of arc–continent collision listed in Figure 4 are those inferred by Draut & Clift (2001) on the basis of combined lithological, geochemical and isotopic evidence from Connemara and South Mayo (see also Friedrich *et al*. 1999). A corresponding tectonic synthesis (Draut *et al*. 2002) is shown in Figure 5.

The oldest volcanic units within the Lough Nafooey Group imply little involvement of continent-derived melt in arc volcanism; basalts of the Bencorragh Formation indicate less than ~1 % continental material, with a strongly positive $\varepsilon_{Nd(t)}$ value of +7.25. This compares well with ~0.5 % continental sediment involvement estimated for the modern Tonga Arc (Ewart & Hawkesworth, 1987). Toward the top of the Lough Nafooey Group, subduction had apparently brought the arc and continent in such close proximity that significant Laurentian sediment was being recycled through the subduction zone and incorporated into the arc volcanism (Fig. 5). The top of the Knock Kilbride Formation within the Lough Nafooey Group contains ~4.7–2.3 % continental material, while the Derry Bay Formation (the youngest unit of the Lough Nafooey Group) shows further continental involvement, with

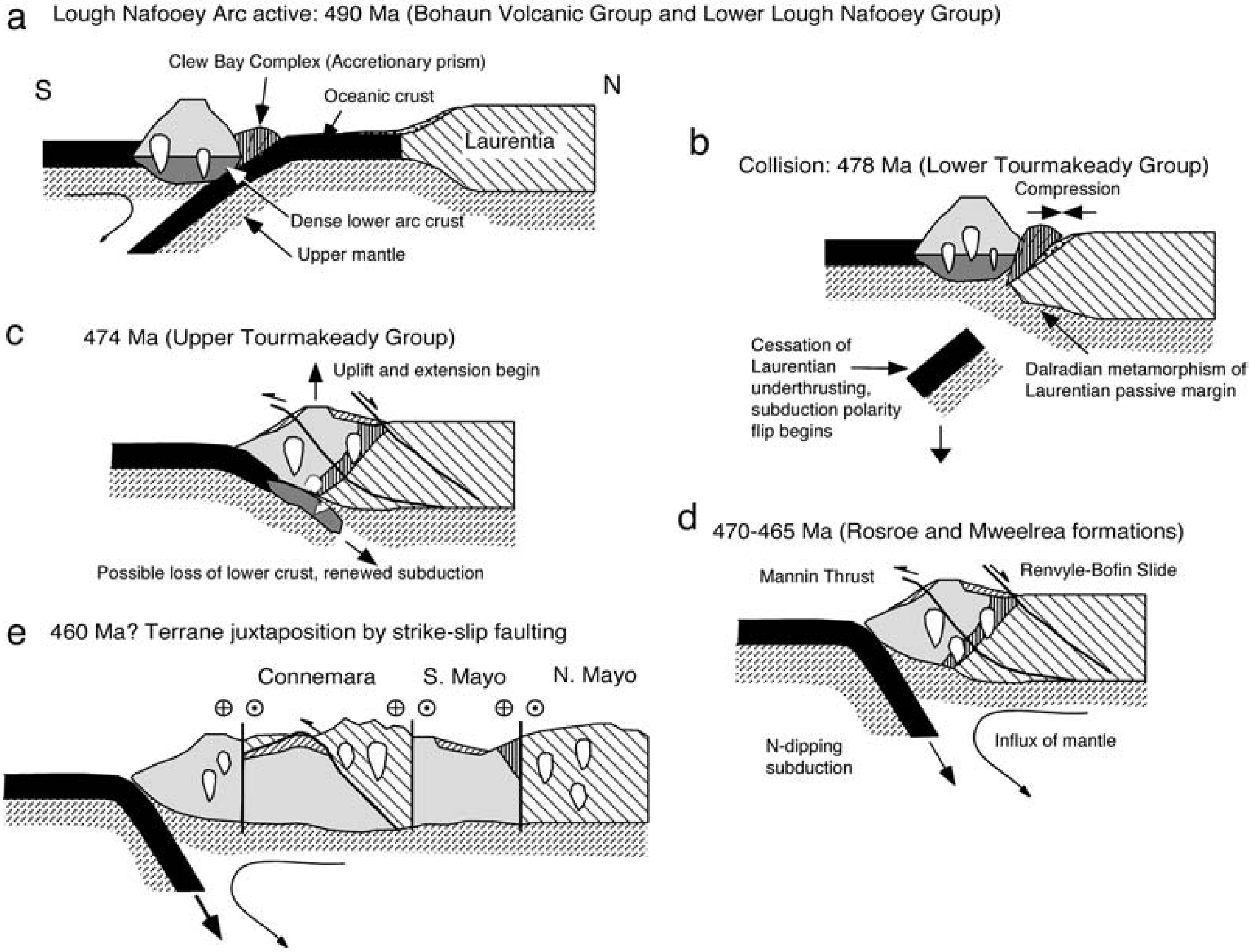

Figure 5. Tectonic interpretation of the Grampian Orogeny in western Ireland (see Draut *et al*. 2002). (a) The Lough Nafooey Arc was active above a S-dipping subduction zone in Late Cambrian to Early Ordovician time, approaching Laurentia as the Iapetus Ocean closed. Metasediments of the accretionary prism comprise the Clew Bay Complex. (b) By 478 Ma, while the Lower Tourmakeady Group was erupted in South Mayo, arc–continent collision had begun. (c) During Upper Tourmakeady eruption ($\sim$ 474 Ma), S-dipping subduction had ceased. Northward subduction began to be initiated, which may have facilitated the loss of the dense mafic–ultramafic lower crust below the orogen. (d) By 470 Ma, Rosroe Formation and Murrisk Group tuffs were erupted in South Mayo. Separation and loss of the lower crustal cumulates may have occurred (Draut *et al*. 2002); compressional and extensional faulting occurred simultaneously (e.g. Mannin Thrust and Renvyle-Bofin Slide in Connemara). A subduction-zone chemical signal in the Mweelrea Formation of South Mayo's Murrisk Group implies that N-dipping subduction under Laurentia was active by that time. (e) Subsequent strike-slip faulting ordered North and South Mayo and Connemara in their present relative positions.

7.1–21.7 % Laurentian material. Given that the eruption of volcanic units in the Lough Nafooey Group precedes metamorphism and orogenesis in the Irish Caledonides, we suggest that the primary mechanism for introducing continental material to the area of melt production in the arc was by subduction of distal Laurentian slope sediment (e.g. Elburg *et al*. 2002) and possibly of blocks of extended continental crust close to the continent-ocean transition (e.g. Hilton *et al*. 1992).

Within the Tourmakeady Volcanic Group, whose eruption coincided with major deformation, orogeny and mafic intrusion in Connemara ('hard' collision between the arc and continent), lower $\varepsilon_{Nd(t)}$ values than in the Lough Nafooey Group lead to a wider range of possible proportions of continental melt. A sample of rhyolitic breccia from the Tourmakeady Volcanic Group yielded an $\varepsilon_{Nd(t)}$ value of -14.11, which corresponds to 25.0–28.8 % continental material in the melt. This implies that during hard collision, volcanic products of the arc contained Laurentian crust as a major, and possibly dominant, component.

Assimilation of the Laurentian crust through which the arc was erupting following collision is assumed to be the dominant mechanism of continental melt incorporation by this advanced stage of collision. Wallrock assimilation during eruption of the Tourmakeady Volcanic Group is supported by high Zr content in these volcanic units relative to earlier Bohaun Group and Lough Nafooey Group volcanism (Draut & Clift, 2001). Elevated Zr is interpreted to result from incorporation of zircon into the melt. The most plausible mechanism for introducing Zr into the Tourmakeady Volcanic Group melt is the assimilation of zircon from crustal wallrock along the melt ascent path. Chemical data from many continental arc studies indicate that continental crust plays a significant role in petrogenesis (e.g. DePaolo, 1981; Hilton *et al*. 1992; Pearce & Parkinson, 1993). The apparently significant influence of continental wallrock assimilation on Tourmakeady Volcanic Group chemistry implies that by the time of the Tourmakeady Volcanic Group eruption (∼481–470 Ma), the volcanism was that of a continental arc built on the newly active Laurentian margin.

It is noteworthy that even within the new continental arc represented by the youngest stratigraphic units considered, the Rosroe and Mweelrea formations, our calculations suggest that mantle-derived material would still have contributed the majority of the melt produced at that arc. The late syn- and post-collisional Rosroe and Mweelrea formations indicate approximately 14–39 % Laurentian melt in volcanism after 470 Ma. Previous work has indicated rapid cooling of the orogen at that time (Friedrich *et al*. 1999) and inferred gravitational collapse (Clift *et al*. 2003). It has also been proposed that the dense lower crust had been lost from the base of the orogen in the final stages of the Grampian Orogeny, which would have brought an influx of new mantle material under the arc in place of the detached lower crust (Fig. 5; Draut *et al*. 2002; Clift *et al*. 2003). Influx of new mantle, which would ascend without substantial incorporation of continental wallrock as the arc reached maturity, may account for the slightly higher $\varepsilon_{Nd(t)}$ values of the Rosroe and Mweelrea samples relative to those of the Tourmakeady Volcanic Group. We suggest that by the time of eruption of these post-collisional tuffs, the proportions of Laurentian and mantle-derived melt within the mature continental arc had reached a steady state in which approximately 14–39 % of Nd in the volcanic product was Laurentian in origin.

4.d. Implications for petrogenesis at continental arcs

These results demonstrate that, although continental material contributed significantly to melt production during and after arc–continent collision, there was still a strong, and possibly dominant, mantle-derived melt component. At the point in the South Mayo stratigraphy when continental involvement was greatest (within the Tourmakeady Volcanic Group, during peak Dalradian metamorphism), the *minimum* proportion of mantle-derived melt at that stage is calculated to be 21 %. Subsequently, during 'steady-state' continental arc conditions represented by the upper Rosroe and Mweelrea tuffs, mantle-derived magmatism appears to be dominant, contributing ∼60–85 % of the melt that formed the volcanic units. In contrast to earlier studies (e.g. Frost & O'Nions, 1985), this indicates that recycling of continental crust is apparently overshadowed by the addition of new melt at this continental arc.

Reworking of the accreted oceanic arc crust may contribute somewhat to this apparently low degree of crustal contamination after the Grampian Orogeny. Because the igneous crust of the accreted arc is very 'oceanic' in its isotopic character, remelting of this crust cannot be easily separated from new contributions derived directly from the mantle. Our estimates of crustal involvement following the Grampian Orogeny are thus minimum estimates and only reflect the degree of old Laurentian crustal contamination. This behaviour is similar to that seen in the western Himalayas following the mid-Cretaceous collision of the Dras–Kohistan Arc to the southern margin of Asia. In this example, continental arc volcanism is more chemically enriched than the preceding oceanic volcanism, but Pb and Nd isotopes continued to show relatively oceanic signatures, interpreted to reflect the location of the new continental arc founded on the roots of the accreted oceanic structure (Clift *et al*. 2002).

It is noteworthy that, although their isotopic signature indicates dominant derivation from the mantle or remelted oceanic arc crust, the Rosroe and Mweelrea tuffs exhibit chemical characteristics typical of average continental crust (Fig. 4): andesitic to rhyolitic composition ($SiO_2 > 60$ %), high LREE enrichment, and a relative Nb depletion (Clift & Ryan, 1994; Draut & Clift, 2001). Thus, crystal fractionation, which led to the highly enriched composition of these units (Draut *et al*. 2002), has enabled magmas derived dominantly from mantle sources to assume the chemical characteristics of typical continental crust.

5. Conclusions

Mass-balance calculations from volcanic units that span arc–continent collision, subduction polarity reversal, and establishment of a continental arc along the Laurentian margin in Early Ordovician time (480–465 Ma) show that recycling of old continental crust does not dominate melt production in this setting. This finding has important implications for the growth of the continental crust. Arc magmatism can acquire a more 'continental' chemistry (becoming silica- and LREE-enriched) during arc–continent collision without the need to recycle large volumes of existing crust. Syn- and post-collisional volcanic units in South Mayo have a Nd isotopic signature dominated by a mantle or remelted oceanic crustal source, yet have evolved to such an extent that they are andesitic to rhyolitic in composition and are LREE-enriched, characteristics of the continental crust. These results therefore support the idea that new continental crust may be produced through arc magmatism associated with accretion of oceanic arcs.

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