Chemical Geology 286 (2011) 222–228

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

# Geochronology of the Tardree Rhyolite Complex, Northern Ireland: Implications for zircon fission track studies, the North Atlantic Igneous Province and the age of the Fish Canyon sanidine standard

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## ARTICLE INFO

*Article history:*
Received 25 October 2010
Received in revised form 9 May 2011
Accepted 10 May 2011
Available online 16 May 2011

Editor: L. Reisberg

*Keywords:*
Tardree Rhyolite Complex
Geochronology
40Ar/39Ar, U–Pb, CA-TIMS
Standard
Zircon fission track
(U–Th)/He
North Atlantic Igneous Province
Fish Canyon sanidine standard

## ABSTRACT

The British–Irish Palaeogene Igneous Province (BIPIP) is part of the larger North Atlantic Igneous Province and includes the lava fields of Antrim, Mull, and Skye. The Tardree Rhyolite Complex (TRC) in Northern Ireland forms an important stratigraphic unit between the Lower and Upper Basalt Formations of the Antrim Lava Group (ALG). Previous zircon age determinations obtained from the TRC have been used as a standard in zircon fission track studies, but contradict several $^{40}$Ar/$^{39}$Ar sanidine and U–Pb zircon results. We provide new $^{40}$Ar/$^{39}$Ar sanidine and U–Pb CA-TIMS zircon ages which resolve this discrepancy. Two sanidine samples from the Sandy Braes vent and the columnar-jointed dome-forming rhyolites of Tardree Forest yield a weighted mean $^{40}$Ar/$^{39}$Ar age of 61.13 ± 0.42 Ma (2σ, internal error). Ten U–Pb CA-TIMS zircon analyses were undertaken, eight of which employed the CA-TIMS approach on both multi-grain fractions and single grains. Six of the CA-TIMS data yield a disequilibrium-corrected weighted mean $^{206}$Pb–$^{238}$U age of 61.32 ± 0.09 Ma (2σ). The consistency of the $^{40}$Ar/$^{39}$Ar ages with the CA-TIMS U–Pb zircon age, points to a closed system of both K and Ar since eruption. We propose that the crystallization age of the TRC be taken as 61.32 ± 0.09 Ma and that the currently used age of the zircon fission track standard (58.4 ± 0.7 Ma) be changed accordingly. This also places the eruption of the TRC in magnetochron C26r, which is consistent with the reversed polarity magnetic remanence observed in the ALG, and supports the conclusion of Ganerød et al. (2010) that the Lower Basalt Formation is older than the Vaigat Formation in Western Greenland. No resolvable zircon inheritance has been detected by the TIMS analyses, consistent with the fact that the temporal and geographic extent of rhyolitic magmatism within this sector of the BIPIP was very limited, and hence was unlikely to provide inherited magmatic zircons from slightly older magmas (antecrysts). Potentially older zircon xenocrysts would be derived from the underlying Caledonian basement (>400 Ma) or yet older rocks. These should be easily detectable if the Tardree zircon was to be employed as a U–Pb zircon standard. The paired $^{40}$Ar/$^{39}$Ar and $^{206}$Pb–$^{238}$U results from this study indicate an age of 28.393 ± 0.194 Ma for the widely used Fish Canyon sanidine standard and gives further support to the recent calibrations of Kuiper et al. (2008) and Renne et al. (2010).

## 1. Introduction and aims

The Antrim plateau in Northern Ireland (Fig. 1b) hosts the largest volcanic remnant of the British–Irish Palaeogene Igneous Province (BIPIP, Fig. 1a). The BIPIP is a sub-province of the larger North Atlantic Igneous Province (NAIP), which is composed of the Palaeogene volcanic rocks around the North Atlantic Ocean and the West Greenland–Baffin corridor. It precedes the onset of major breakup-related volcanism at around c. 55 Ma (Saunders et al., 1997). Constraining the eruption dynamics in a Large Igneous Province relies on precise age determinations of its constituent magmatic phases. However, using $^{40}$Ar/$^{39}$Ar geochronology, which is a widely employed method for dating basaltic rocks, precise age determinations can be difficult due to the low-potassium contents of magmatic plagioclase and its susceptibility to alteration, although groundmass dating can potentially circumvent this drawback (Koppers et al., 2000). Therefore, obtaining U–Pb zircon dates from key silicic

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doi:10.1016/j.chemgeo.2011.05.007

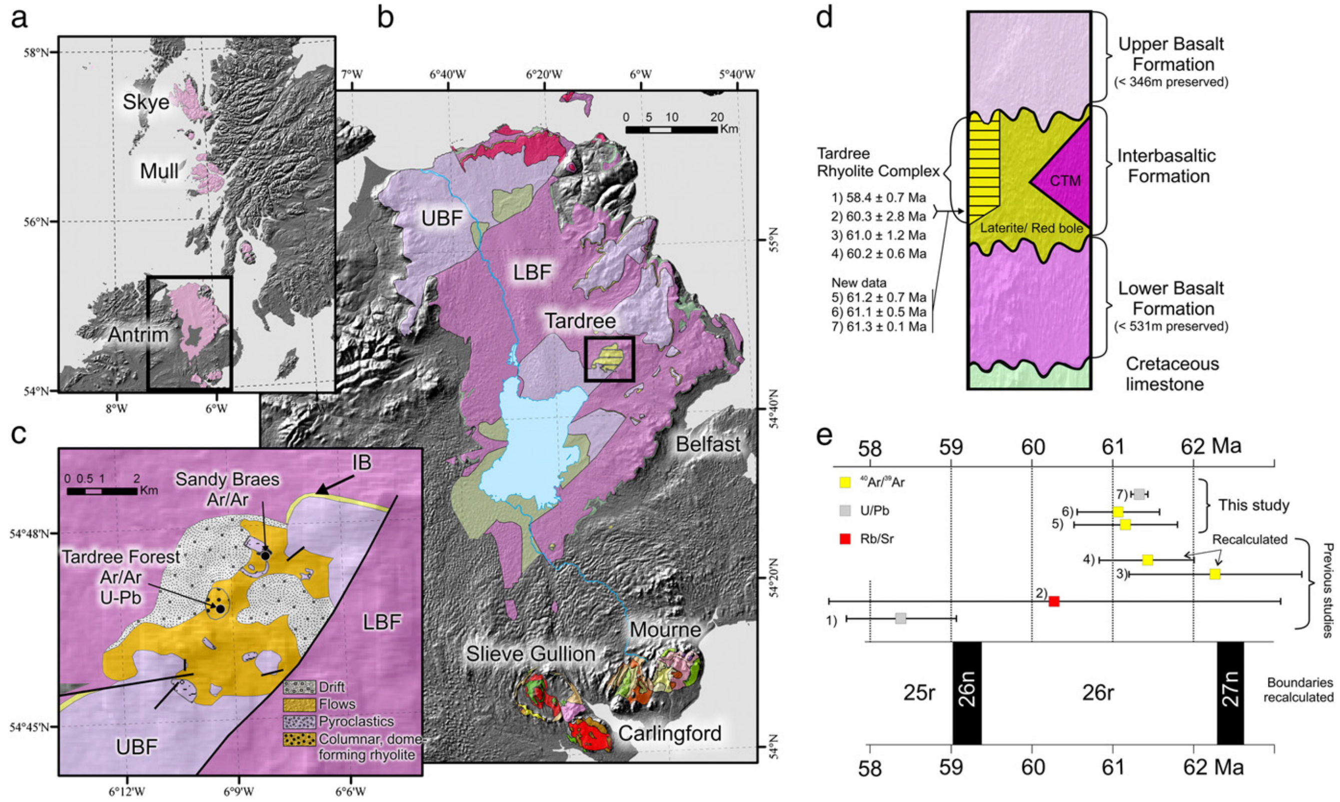

**Fig. 1.** a) Schematic geological map of the British–Irish Palaeogene Igneous Province and b) the Antrim plateau with the central complexes of Mourne, Slieve Gullion and Carlingford displayed. c) Geological map of the Tardree Rhyolite Complex after Old (1975). The samples were taken at two localities (black dots); at the columnar dome-forming rhyolite in Tardree Forest (54°46′44″N, 6°9′14″W) and in the Sandy Braes area (54°47′32″N, 6°8′2″W). LBF, IB and UBF denote Lower-, Inter- and Upper Basalt formations respectively. d) Simple stratigraphic column of the Antrim Lava Group. CTM denotes Causeway Tholeiite Member. Previous age determinations (at the 2σ level) are listed from the following sources: 1) U–Pb SIMS zircon age of Gamble et al. (1999), 2) Rb–Sr age of Meighan et al. (1988), 3) $^{40}$Ar/$^{39}$Ar sanidine age of Thompson (1985), 4) $^{40}$Ar/$^{39}$Ar sanidine age of Chambers (2000), ages 5, 6 and 7 are from this study. e) The GTS2004 geomagnetic polarity timescale (Ogg and Smith, 2004) with the data from d) illustrated. The chrons in GTS2004 are recalculated to conform to an age of 28.305 Ma for the Fish Canyon sanidine standard (Renne et al. 2010). Note that ages 3 and 4 are also shown, recalculated to conform with the age of 28.619 Ma for the Taylor Creek Rhyolite (Renne et al. 2010) and 17.48 Ma for the B4 biotite (Calculated from Table 3.2 in McDougall and Harrison (1999) using data in Renne et al. (2010)), which gives an age of 62.2 ± 1.2 Ma for age 3 and 61.4 ± 0.6 Ma for age 4. Full external errors for the $^{40}$Ar/$^{39}$Ar data are very similar to internal errors and therefore not shown.

horizons, where available, can provide crucial information to corroborate $^{40}$Ar/$^{39}$Ar dates from basaltic provinces. Basaltic volcanism in Northern Ireland commenced with the eruption of the voluminous basalt flows of the Lower Basalt Formation (LBF, Fig. 1d) of the Antrim Lava Group (ALG) onto early Upper Maastrichtian limestones (Mitchell, 2004). Following a period of volcanic dormancy, the landscape was subjected to massive lateritization (Fig. 1d), with development of a significantly weathered bole horizon on top of the LBF (Hill et al., 2000). This volcanic hiatus in the north of Northern Ireland was interrupted by eruption of the quartz tholeiite Causeway member (CTM) of the Interbasaltic Formation (Lyle and Preston, 1993). It consists of up to nine thick flows (Wilson and Manning, 1978), including the spectacular columnar-jointed lava flows of the Giant's Causeway. During this interval, silicic volcanic activity produced the rhyolites and pyroclastic flows of the Tardree Rhyolite Complex (TRC, Fig. 1) and presumably related isolated local intrusions (Old, 1975). Silicic volcanics are found elsewhere in the central complexes of Mourne, Carlingford and Slieve Gullion located south of the Antrim Plateau (Fig. 1). The subsequent second cycle of voluminous basaltic volcanism marks a return to primitive magmatism. This is represented by the olivine tholeiite lavas of the Upper Basalt Formation (Lyle, 1980, Fig. 1d). The TRC (Fig. 1c) consists of a suite of mainly rhyolite and pyroclastic deposits, with columnar-jointed dome-forming rhyolite encountered at Tardree Mountain (Fig. 1c) and varied pyroclastic formations such as the vent complex at Sandy Braes which includes a rare occurrence of obsidian (Old, 1975, Fig. 1c).

Zircon from the TRC is used as a standard in fission track geochronology. Fitch and Hurford (1977) reported a zircon fission track age of 65.2 ± 1.6 Ma[1] for Tardree Rhyolite zircon. This age determination employed the external detector method and a value of $6.85 \times 10^{-17}$ year$^{-1}$ for the decay constant ($\lambda_f$) as the ζ-calibration method (Hurford and Green, 1983) had not been adopted at that time. Tardree Rhyolite zircons often exhibit major U zonation, typically with a U-rich core and a U-poor rim (Tagami et al., 2003). Fig. 2 in Tagami et al. (2003) illustrates the typical spontaneous fission track distribution in a Tardree rhyolite zircon, with a high-track density core (corresponding to a U-rich domain) and a low-track density (U-poor) rim.

Hourigan et al. (2005) report LA-ICPMS U and Th elemental concentration profiles for TRC zircons. Similar to the data of Tagami et al. (2003), these concentration profiles demonstrate that the cores are enriched in uranium relative to the rims. The amount of U-enrichment in the cores is variable from grain to grain, and ranges from ~2× to ~40×. Uncorrected (U–Th)/He ages for the Tardree zircons are 56.2 ± 5.4 Ma (Tagami et al., 2003) and 57.8 ± 1.2 Ma (Dobson, 2006). Mean α-ejection corrected ages are irreproducible and significantly older due to the high U-cores and strong zoning in the zircons (Tagami et al., 2003, Dobson, 2006).

Both zircon fission track and (U–Th)/He zircon studies of the Tardree rhyolite use the U–Pb zircon age of 58.4 ± 0.7 Ma of Gamble et al. (1999) as the assumed eruption age for the complex (age 1 quoted in Fig. 1d, e). This age determination employed an ion micro-probe (SHRIMP), using the SL13 zircon standard. However,

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[1] Ages are reported at 2σ level throughout the paper.

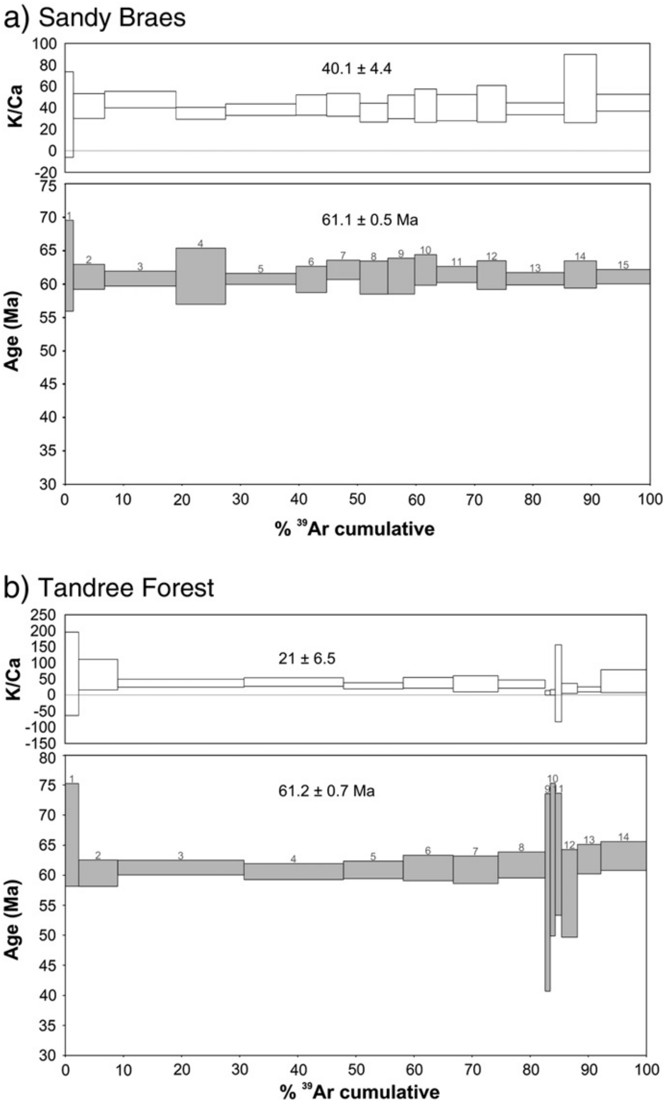

**Fig. 2.** $^{40}Ar/^{39}Ar$ age spectrums (below) and K/Ca ratios (above) for the two $^{40}Ar/^{39}Ar$ sanidine $CO_2$ laser step heating experiments from a) Sandy Braes and b) Tardree Forest. The error bars on each step, and for the calculated dates are shown at the 2σ level. The numbers above each bar resembles the experiment number (step) in A.1.

several other methods have yielded considerably older ages for the complex. Meighan et al. (1988) report an Rb–Sr whole rock isochron of 60.3 ± 2.8 Ma (age 2 quoted in Fig. 1d, e). Dates obtained by the $^{40}Ar/^{39}Ar$ method from step heating of sanidine include an age of 61.0 ± 1.2 Ma (Thompson, 1985; age 3 quoted in Fig. 1 d and e), a weighted mean age of 60.2 ± 0.6 Ma[2] obtained by Chambers (2000; age 4 quoted in Fig. 1 d, e) and the unpublished $^{40}Ar/^{39}Ar$ plateau age of 60.7 ± 1.2 Ma of Lux and Gibson, quoted in Meighan et al. (1988) (not shown in Fig. 1 d, e) for the eruption age for the Tardree rhyolite.

This study is intended to refine the age of the TRC by employing $^{40}Ar/^{39}Ar$ and U–Pb geochronology. In doing so, we provide precise age determinations on a stratigraphically important horizon which will a) refine the age of the Tardree Rhyolite zircon reference standard for fission track studies, and b) put the lava formations of Northern Ireland in a NAIP framework and c) test whether TRC sanidine behaved as a closed system since eruption. Regarding the last aim, paired $^{40}Ar/^{39}Ar$ and $^{206}Pb$–$^{238}U$ ages are used to calculate the age of the widely used Fish Canyon Tuff sanidine standard in $^{40}Ar/^{39}Ar$ geochronology.

## 2. New age determinations

Fresh samples of the rhyolite were taken at two localities; one in a disused quarry at the base of the columnar dome-forming rhyolite in Tardree Forest (54°46′44″N, 6°9′14″W, sampled for both $^{40}Ar/^{39}Ar$ and U–Pb analysis) and the other in the Sandy Braes area (54°47′32″ N, 6°8′2″W) sampled for $^{40}Ar/^{39}Ar$ analysis (Fig. 1c). Thin section examination reveals a porphyritic texture with fresh phenocrysts of quartz and sanidine feldspar (up to 20–25% in total). Phenocrysts are up to 5 mm across and larger crystals seem more abundant than smaller ones. The groundmass to the Tardree Forest dome rock is micro-crystalline with intergrown quartz and feldspar visible at high magnification (40×). The groundmass of the Sandy Braes sample, in turn, is glassy (i.e. no individual crystals visible even at high magnification) but with frequent perlitic cracks. Quartz and feldspar phenocrysts are not perfectly euhedral in either sample, frequently displaying rounded edges, but are surprisingly simple in respect to internal textures, with a striking absence of visible compositional zoning or abundant foreign crystal cores. Some sieve-textured quartz crystals and some feldspar glomerocrysts do occur, however. The phenocrysts in the Tardree Forest and the Sandy Braes samples look petrographically identical. Both $^{40}Ar/^{39}Ar$ analyses are from sanidines, and were obtained using the step heating technique which facilitates assessing whether Tardree Rhyolite Complex sanidine has remained a closed system since crystallization.

### 2.1. $^{40}Ar/^{39}Ar$ dating

#### 2.1.1. Methodology

Samples were crushed with a jaw crusher and sieved (mesh size 180–250 μm). Conventional mineral separation techniques were employed, including magnetic separation using a Frantz isodynamic magnetic mineral separator followed by heavy liquid separation with lithium polytungstate to separate feldspar from quartz. The mineral separates were washed in acetone several times and finally handpicked under a binocular microscope. Mineral grains with grain coatings or inclusions were avoided. The samples from Tardree Forest and Sandy Braes were packed in aluminum capsules together with the Taylor Creek Rhyolite (TCR) flux monitor standard along with pure (zero age) $K_2SO_4$ and $CaF_2$ salts. The samples were irradiated together at site 5C at the McMaster Nuclear Reactor (Hamilton, Canada) for 27 h (50MWH) with a nominal neutron flux of $4 \times 10^{13}$ n $cm^{-2}$ $s^{-1}$. The correction factors for the production of isotopes from Ca were determined to be $(^{39}Ar/^{37}Ar)_{Ca} = (1.057 \pm 0.00529) \cdot 10^{-3}$, $(^{36}Ar/^{37}Ar)_{Ca} = (5.49 \pm 0.02745)\ 10^{-4}$ and $(^{40}Ar/^{39}Ar)_K = (3.51102 \pm 0.01756)\ 10^{-2}$ for the production of K (errors quoted at 1σ). The samples were step heated using a defocused Merchantek $CO_2$ laser. The extracted gases were passed over SAES AP-10 getters for the first 2 min, then for 9 min in a separate part of the extraction line. They were analyzed with a MAP 215–50 mass spectrometer installed at the Geological Survey of Norway. The peaks were determined during peak hopping for 8 cycles (regressed back to zero inlet time) on the different masses ($^{41-35}Ar$) on a Balzers electron multiplier. Blanks were analyzed every 3rd measurement. After blank correction, a correction for mass fractionation, $^{37}Ar$ and $^{39}Ar$ decay and neutron-induced interference reactions produced in the reactor was undertaken using in-house software (AgeMonster written by M. Ganerød). It implements the equations of McDougall and Harrison (1999) and the newly proposed decay constant for $^{40}K$ after Renne et al. (2010). A $^{40}Ar/^{36}Ar$ ratio of 295.5 ± 0.5 from Steiger and Jäger (1977), based on the data from Nier (1950), was used for the atmospheric argon correction and mass fractionation calculation (power law). We calculated J-values relative to an age of 28.619 ± 0.034 Ma for the TCR sanidine flux

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[2] Ages come from Chambers' thesis. Weighted mean ages are calculated without the error on J, but added later.

monitor (Renne et al., 2010). Weighted mean ages are calculated by weighting on the inverse of the variance (analytical uncertainties).

### 2.1.2. Results

The age results are displayed in Table 1 while the raw experimental results can be found in Table A.1 (Supplemental data file). Both heating experiments yielded concordant apparent ages over the whole age spectrum (Fig. 2a and b), with each step overlapping at the 95% confidence level. The K/Ca ratios (calculated from $^{39}Ar_k/^{37}Ar_{Ca}$) are shown above the spectra (Fig. 2a and b). For the Sandy Braes and the Tardree Forest samples respectively, a weighted mean plateau age (WMPA) of 61.1 ± 0.51 Ma and 61.2 ± 0.74 Ma (internal errors) was obtained for plateaus comprising 100% of the total $^{39}Ar$ gas released. Analytical, internal and external errors are shown in Table 1. The inverse isochrons yield similar ages and the $^{40}Ar/^{36}Ar$ intercepts overlap with the atmospheric value (Table 1 and Figure A.2 a, b).

The K/Ca ratios obtained from the sanidines from the two localities are different, but their weighted mean plateau ages overlap at the 95% confidence level (including the experimental error on J) and therefore we treat them as isochronously emplaced units, and combing them we obtain a weighted mean age of 61.13 ± 0.42 Ma.

## 2.2. U–Pb CA-TIMS zircon dating

### 2.2.1. Methodology

Approximately 100 kg of sample was crushed and sieved to below 300 μm and a heavy mineral fraction was obtained using a Gemeni mineral separation table. An aliquot of this heavy fraction was separated using heavy liquids and a magnetic separator. No apatite was found in the non-magnetic fraction between 2.9 and 3.3 g/cm$^3$, but the >3.3 g/cm$^3$ non-magnetic fraction yielded abundant zircon. The zircon fraction is composed of prismatic grains up to 300 μm long with aspect ratios between 3:1 and 10:1, displaying pronounced normal idiomorphic growth zoning (Fig. 3) and generally free of irregular xenocrystic cores. A small aliquot of zircon was analyzed by isotope dilution thermal ionization mass spectrometry at the Department of Geosciences, University of Oslo. The zircon grains were either mechanically abraded (Krogh, 1982) or pre-treated using the chemical abrasion method ("CA-TIMS") modified from Mattinson (2005) for a single leaching step similar to the protocol of Mundil et al. (2004). This method employs high-temperature treatment of the zircon grains (in our case 900 °C for 72 h) to anneal zircon lattice radiation damage from natural alpha, alpha recoil, and spontaneous fission processes. The annealed zircon fraction is then subjected to a partial dissolution step in concentrated HF and $HNO_3$ at 194 °C for 16 h which removes still damaged zircon sub-domains with high U and Th concentrations. These sub-domains are generally variously discordant due to Pb loss, whereas the remaining portion of the zircon crystal tends to be free from Pb loss.

The zircon analyses follow a modified procedure of Krogh (1973); details of the routines in the Oslo laboratory are given in Corfu (2004). The ages are calculated using the decay constants of Jaffey et al. (1971), and the data are regressed using the program Isoplot (Ludwig, 2003).

### 2.2.2. Results

Ten zircon analyses were undertaken, two on mechanically abraded grains and the rest on chemically abraded grains, employing both multi-grain fractions and single grains (Fig. 3, Table A.3). The $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ data have been corrected for a deficit in $^{206}Pb$ resulting from an initial $^{230}Th$ deficit in the parent magma, assuming Th/U = 4, and using the equation of Schärer (1984). Six of the CA-TIMS data points (1–6 in Fig. 3) yield a Concordia age (Ludwig, 1998) of 61.31 ± 0.11 Ma (2σ, MSWD (of conc. and equiv.) = 1.4) and a corresponding weighted mean $^{206}Pb–^{238}U$ age of 61.32 ± 0.09 Ma (2σ). Four analyses (7–10 in Fig. 3), including the two mechanically abraded fractions (7 & 9 in Fig. 3), are slightly younger. These younger grains represent either a slightly younger magmatic population, or zircons that crystallized contemporaneously with the main magmatic population (grains 1–6) and that then underwent lead loss. As these young zircons include the mechanically abraded grains, it seems likely that this is a result of lead loss. Inclusion of the oldest three of the four youngest zircons (7–9 in Fig. 3) in the age calculation has only a marginal effect on the resulting age, increasing the MSWD to 2.1 and lowering the Concordia age to 61.24 ± 0.14 Ma and the corresponding weighted mean $^{206}Pb–^{238}Ub$ age to 61.18 ± 0.14 Ma. Data points 7–10 were tested against each of data points 1–6 to check for outliers using the $t_1 - t_2 \geq 1.96 \cdot \sqrt{\sigma_{t_1}^2 + \sigma_{t_2}^2}$ criteria (if quoted at 1σ level). All data points (7–10) were found to be distinct at the 95% confidence limit from at least two data points of the population 1–6. This justifies their exclusion from the weighted mean average calculation.

# 3. Discussion

## 3.1. Implications for Zircon Fission Track studies and the North Atlantic Igneous Province

U–Pb TIMS geochronology is referred to as the "gold standard" in geochronology (Renne et al., 1998), because it does not depend on the measurement of standards for its high degree of accuracy and involves two decay schemes ($^{235}U–^{207}Pb$ and $^{238}U–^{206}Pb$), allowing internal-reliability assessment. Secondly, the decay constants are precisely determined (Jaffey et al., 1971). The main source of inaccuracy is commonly the isotopic tracer. Our U–Pb tracer is calibrated against known reference solutions. Measurements of the 'Earthtime 100 Ma' solution yields an average (8 values) that is about 1‰ below that obtained with the ET535 tracer solution prepared by the Earthtime Initiative (see www.earth-time.org). This translates into a potential bias of less than 0.07 Ma, which is below the precision of our age. $^{40}Ar/^{39}Ar$ dating relies on one decay scheme and the analysis of standards of "known" age. Hence, in this study, where high-quality U–Pb and $^{40}Ar/^{39}Ar$ have been obtained from the same sample with an apparently simple thermal history, it can be assumed that the U–Pb age is more accurate and that any discrepancy may be a result of miscalibration of the $^{40}K$ decay constants. Adopting the decay constant and age value for the Taylor Creek Rhyolite monitor of Renne et al. (2010), we obtain a close match between the $^{40}Ar/^{39}Ar$ and U–Pb systems, with the weighted mean of the $^{40}Ar/^{39}Ar$ plateaux marginally younger by 0.35%. We

**Table 1**
$^{40}Ar/^{39}Ar$ results for $CO_2$ laser step heating experiments. Ages are in Ma. *Uncertainties are reported as analytical/internal/external errors, the weighted mean is reported as analytical/internal. The internal error includes the analytical error and the error on the J-value (analytical + fluence monitor uncertainty). External error also includes the uncertainty on the $^{40}K$ decay constant.

| Sample | Spectrum analysis | | | | | | Inverse isochron analysis | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $^{39}Ar\%$ (n) | Age | ±2σ* | MSWD | K/Ca | ±2σ | Age | ±2σ* | MSWD | Intercept |
| Sandy Braes | 100 (15) | 61.1 | 0.38/0.51/0.57 | 0.348 | 40.1 | 4.4 | 60.19 | 1.39/1.44/1.45 | 0.223 | 326.3 ± 46.6 |
| Tardree Forest | 100 (14) | 61.22 | 0.58/0.74/0.77 | 0.71 | 21 | 6.5 | 61.1 | 0.8/0.92/0.94 | 0.757 | 297.5 ± 9.4 |
| Weighted mean age | | 61.13 | 0.316/0.42 | | | | | | | |

plot the new dates obtained from this study together with previous results in Fig. 1e with the GTS2004 polarity time scale (Ogg and Smith, 2004) shown below. For direct comparison with the new $^{40}$Ar/$^{39}$Ar results, we apply the inter-calibrated ages for the TCR and the B4 biotite monitors from table 3.2 in McDougall and Harrison (1999), and recalculate the dates from Chambers (2000) and Thompson (1985) using the “ArArCalibration” routine (http://earthref.org/tools/ararcalc/index.html), shown in Fig. 1e.

The results show that all previous data, except those of Gamble et al. (1999) overlap at the 95% confidence level, suggesting that the age reported by Gamble et al. (1999) is likely to be inaccurate. This is probably a function of the standard zircon (SL13) employed in the SHRIMP analysis. The SL13 zircon has been shown to be a problematic standard (Compston, 2001) as it is composed of a mixture of domains, some of which have undergone Pb loss alongside other domains that are undisturbed. As a consequence, a prohibitively large number of standard analyses are required to define precisely the true standard age (Compston, 2001). As an independent control, we also observe that the new radiometric dates place the eruption of the TRC in magnetochron C26r (Ogg and Smith, 2004), consistent with the magnetic reversal stratigraphy for the Antrim Lava Group of Wilson (1963) and the recent reinvestigation of Ganerød et al. (2010). A C26r age for the Interbasaltic Formation is comparable with dates and magnetic polarity data obtained from the Mull Lava Group (Mussett, 1986, Ganerød et al. 2008) and the Small Isles (Chambers et al. 2005) in the British–Irish Palaeogene Igneous Province.

There is a general consensus (e.g. Chambers et al. 2005) that the oldest basaltic formation in the NAIP is the Vaigat Formation in Western Greenland, dated to 61.7 ± 0.5 Ma[3] (Storey et al., 1998). Riisager and Abrahamsen (1999) documented the presence of magnetochron C27n in the lower part of the Vaigat Formation. Ganerød et al. (2010) dated the basalt stratigraphy of the Antrim Lava Group in Northern Ireland by $^{40}$Ar/$^{39}$Ar and obtained 62.6 ± 0.6 Ma and 59.6 ± 0.6 Ma for the Lower and Upper Basalt formations respectively (LBF, UBF). The relative age difference (1.47 ± 0.73 Ma) between the TRC obtained here and LBF are sound given that the TRC is underlain by at least 19 m of laterite (Old, 1975), which would have required a significant length of time to form. The reverse polarity observed in the LBF (Wilson, 1963, Ganerød et al. 2010) and the new ages for the TRC tell us with more confidence that the LBF was erupted during magnetochron C27r and therefore is older than the Vaigat Formation in Western Greenland.

For the reasons discussed above, we propose the U–Pb CA-TIMS zircon weighted mean $^{206}$Pb–$^{238}$U age of 61.32 ± 0.09 Ma be adopted as the age of the TRC zircon. This age should also be adopted for zircon fission track studies.

Neither the ten analyses from this study nor the 22 zircon grains analyzed by Gamble et al. (1999), have documented any geochronological evidence for inherited zircons in the TRC. The search for cores during cathodoluminescence (CL) examination revealed just one small core, potentially inherited, inside a large crystal (Fig. 3d). Zircon morphologies and internal textures indicate that most zircons occur as simple crystals with pronounced, and very regular idiomorphic growth zonation, consistent with magmatic crystallization, commonly with an enrichment of U (CL-dark) in the centers with respect to the rim portions of the crystals. This zonation is likely a function of progressive depletion of U (and also Th) during progressive crystallization of zircon and co-magmatic

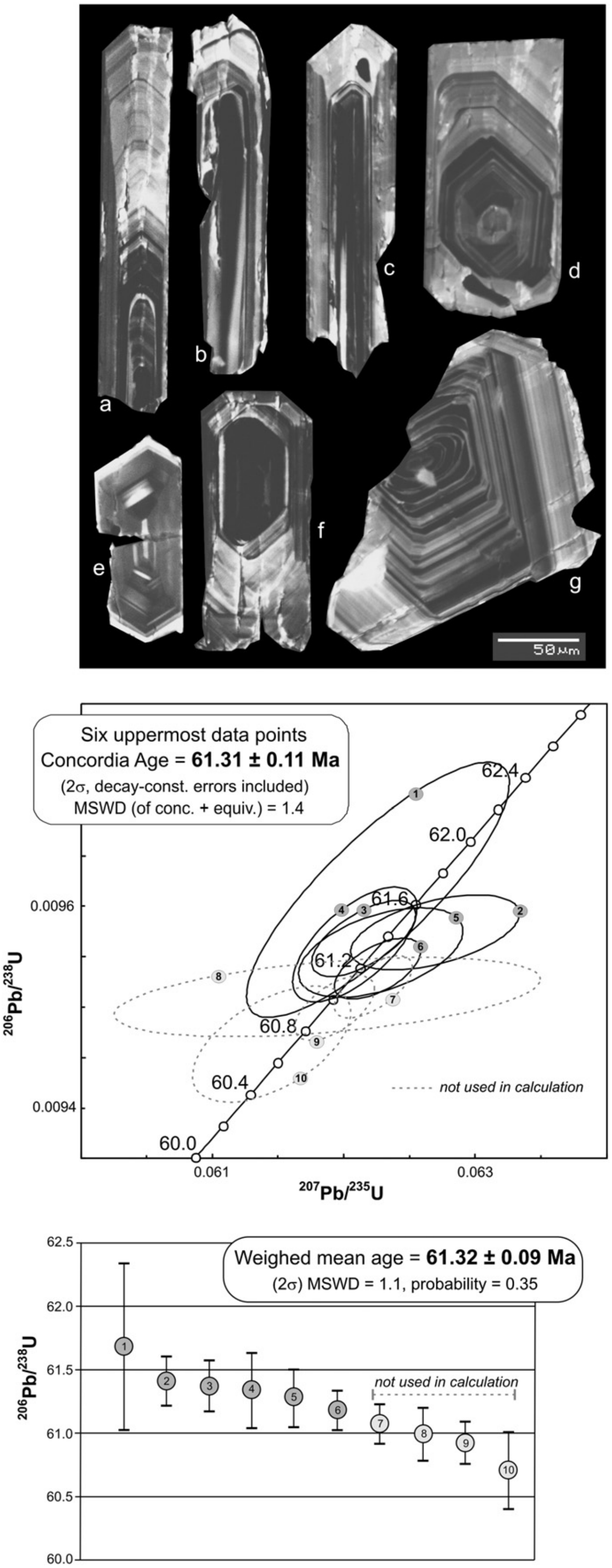

**Fig. 3.** The top portion of the figure shows cathodoluminescence (CL) images of Tardree zircon crystals. Note the pronounced idiomorphic growth zoning with only subordinate internal discontinuities, and the predominance of CL-dark zones in the interior compared to the rims of the crystals. The only potential core seen in this study (15 zircons examined) is contained inside grain d. The irregular, whitish, longitudinl striations in some of the crystals (e.g. a, b, f) reflect crystallographically oriented fracturing during polishing. The bottom part of the figure comprises a Concordia diagram and weighted mean $^{206}$Pb–$^{238}$U age chart using the U–Pb data of this study (Table A.3). The Concordia and weighted mean $^{206}$Pb–$^{238}$U age use the six oldest $^{206}$Pb–$^{238}$U ages (Table A.3). These six analyses also all employ the chemical abrasion method. Data points with gray error ellipses are not considered in the Concordia age or weighted mean $^{206}$Pb–$^{238}$U age calculations (see text for details).

allanite which will decrease the concentrations of these incompatible elements in the melt. The presence of allanite in TRC has been documented by Brooks et al. (1981) at Sandy Braes. However, any potential age variation between the U-rich rims and U-poor cores is unlikely to be temporally resolvable by an *in situ* geochronological technique. The typical 2σ uncertainty on the $^{206}$Pb–$^{238}$Ub TIMS zircon analyses in this study is c. 0.25 Ma; *in situ* analyses of core and rim domains by either SIMS or LA-ICPMS would most likely yield analytical uncertainties approximately an order of magnitude larger. However, given that the amount of older silicic magmatism in this sector of the BIPIP is very restricted, it is unlikely that the TRC contains any slightly older inherited zircon (antecrysts). Any zircon xenocrysts are therefore likely to have been derived from the underlying basement which comprises Neoproterozoic–Early Palaeozoic metasedimentary rocks of the Dalradian Supergroup and potentially Caledonian (ca. 400 Ma) granites. Inherited zircons from either of these two units should be easily detectable if the Tardree zircon was to be employed as a U-Pb zircon standard.

### 3.2. Implications for the age of the Fish Canyon sanidine standard

The $^{40}$Ar/$^{39}$Ar method is a relative geochronometer whose accuracy depends on accurate and precise knowledge of the age of the monitors used. Progress has recently been made in reducing the systematic errors in $^{40}$Ar/$^{39}$Ar geochronology, including revision of the $^{40}$K decay constant and the age of the widely used sanidine standard Fish Canyon (FCs). Based on orbital tuning of Miocene strata in the Melillia basin, Morocco, Kuiper et al. (2008) reported an age of 28.201 ± 0.046 Ma for FCs. Subsequently, using the procedures in Min et al. (2000) and Kwon et al. (2002), Renne et al. (2010) optimized both the age of FCs and the $^{40}$K decay constant using several optimal pairs of $^{40}$Ar/$^{39}$Ar and $^{206}$Pb/$^{238}$U data, which resulted in an age of 28.305 ± 0.036 Ma for FCs and a $^{40}$K total decay constant of 5.5492 (±0.093) $10^{-10}$ $a^{-1}$. Using these new values and the reduced systematic errors, $^{40}$Ar/$^{39}$Ar ages can now potentially be comparable with high precision U/Pb and astronomical tuning ages. Channell et al. (2010) found a discrepancy between independent $^{40}$Ar/$^{39}$Ar and astrochronological age estimates for the Matuyama-Brunhes (MB) boundary when adopting either the values of Kuiper et al. (2008) or Renne et al. (2010). The value of FCs that adjusted the $^{40}$Ar/$^{39}$Ar ages to the best fit astrochronological age is 27.93 Ma, which led them to conclude that there is a fundamental problem with the $^{40}$Ar/$^{39}$Ar or U/Pb or both systems.

The age of FCs can be calculated from samples where both $^{40}$Ar/$^{39}$Ar isotopic data and estimates of their true age from independent methods are available (e.g. Min et al., 2000, Kwon et al., 2002, Renne et al., 2010). Suitable age pairs for example are those where closed systems of K and Ar could be shown by $^{40}$Ar/$^{39}$Ar spectrum analysis, and $^{206}$Pb–$^{238}$U data are statistically coherent (Renne et al. 2010). The $^{40}$Ar/$^{39}$Ar spectrum analysis shown herein (Fig. 2) shows that the TRC is devoid of any reheating effects since its eruption and that there are no resolvable age differences between the samples and isotopic systems. Using the $^{206}$Pb–$^{238}$U age of 61.32 ± 0.09 Ma as the true age of the Tardree Rhyolite Complex (TRC) and the mean $^{40}$Ar/$^{39}$Ar age (61.13 ± 0.316 Ma, analytical error) as a standard, the relationship between the TRC and the age of the Fish Canyon ($t_{FC}$), can be expressed as (Eq. 5 in Renne et al. (1998)):

$$t_{FC} = \lambda^{-1}\, ln\left[\left(e^{\lambda t_{TRC}} - 1\right)\cdot \prod_{i=1}^{n} R_{i-1}^{i} + 1\right] \tag{1}$$

where $t_{TRC}$ is the $^{206}$Pb–$^{238}$U age, λ is the total decay constant of $^{40}K = 5.5492\,(\pm 0.093)\ 10^{-10}\,a^{-1}$ (Renne et al. 2010), and $\prod_{i=1}^{n} R_{i-1}^{i}$ is the product of all the intercalibration steps. The R value and its uncertainty can be calculated by applying Eq. 3 and 7 in Renne et al. (1998). We calculate $R_{TRC}^{TCR} = 0.4639495 \pm 0.0012536$, and $R_{TCR}^{FC} = 0.988924 \pm 0.000978$ (1σ) is simply the inverse of the value reported in Renne et al. (1998). This leads to $R_{TRC}^{TCR}\cdot R_{TCR}^{FC} \equiv R_{TRC}^{FC} = 0.4588108 \pm 0.0013201$ (1σ) where the combined uncertainty is calculated using $\sqrt{\sum_{i=1}^{n}\left(R_i^2\cdot\sigma_{R_i}^2\right)}$. Application of Eq. 1 above and Eq. 6 in Renne et al. (1998) yields $t_{FC} = 28.393 \pm 0.194$ Ma (2σ), where ~95% of the uncertainty is associated with the R term in Eq. 6. This is in agreement with recent calibrations (Kuiper et al. 2008, Renne et al. 2010) but does not overlap with the value suggested by Channell et al. (2010). However, any pairs of matching $^{40}$Ar/$^{39}$Ar and U/Pb ages will always be close to the standard value of FCs using this approach given that the intercalibration factors are accurate (in multistep intercalibration), so the age discrepancy suggested by Channell et al. (2010) remains unresolved. If the suggested age of FCs of Channell et al. (2010) more closely resembles its true age, and we recalculate the weighted mean $^{206}$Pb–$^{238}$U age from $FCs_{28.305–27.93}$, the data herein imply that the Jaffey et al. (1971) decay constant of $^{238}$U is inaccurate and too low by ~1.2% which seems very unlikely based on recent re-evaluations (Schön et al. 2004, Schoene et al., 2006). Another factor that could affect the U/Pb age reported herein is the correction for disequilibrium in the $^{238}$U to $^{206}$Pb decay chain, however, our correction of about 0.1 Ma is in this age range and it pushes the zircon points towards greater ages. Unless we make the highly implausible assumption that there existed zircons with very high initial Th, which were depleted in Th by the time of measurement, we cannot reduce the age with a negative correction.

## 4. Conclusions

The Tardree Rhyolite Complex in Northern Ireland forms an important stratigraphic marker between the Lower and Upper Basalt Formations of the Antrim Lava Group. Zircon from the complex has been used as a standard in zircon fission track studies. We report two $^{40}$Ar/$^{39}$Ar sanidine ages and one U–Pb CA-TIMS zircon age from two separate portions of this complex. A weighted mean age of 61.13 ± 0.42 Ma was obtained from the $^{40}$Ar/$^{39}$Ar sanidine analyses along with a U–Pb CA-TIMS zircon weighted mean $^{206}$Pb–$^{238}$Ub age of 61.32 ± 0.09 Ma. These high-precision results are in agreement with all previously published data from the Tardree Rhyolite Complex, with the exception of a SHRIMP age which is suggested to be too young due to the use of a heterogeneous standard. Available data (ten CA-TIMS analyses and 22 previously published SIMS analyses) suggest that the zircon population is devoid of inheritance from both the underlying (Caledonian) basement and crystals derived from a precursor magma (antecrysts). It is recommended that the U–Pb zircon age of 61.32 ± 0.09 Ma be adopted as the crystallization age of the Tardree Rhyolite Complex and hence also for the age of the fission track zircon reference material from Tardree. Tardree zircon may also prove to be a useful U–Pb zircon standard, although further single-crystal CA-TIMS analyses are required to evaluate this more fully. Tardree Rhyolite Complex erupted during magnetochron C26r and is time equivalent to the lower part of the Mull Lava Group and the Small Isles in the British–Irish Palaeogene Igneous Province. These new ages support the conclusion of Ganerød et al. (2010) that the Lower Basalt Formation in the Antrim Lava Group is older than the Vaigat Formation in Western Greenland. The $^{40}$Ar/$^{39}$Ar and $^{206}$Pb-$^{238}$U results from this study indicate simultaneous closure for the two systems and yield an age of 28.393 ± 0.194 Ma for the widely used Fish Canyon sanidine standard, which gives further support to the recent calibrations of Kuiper et al. (2008) and Renne et al. (2010). The TRC may serve to be an optimal sanidine standard for $^{40}$Ar/$^{39}$Ar geochronology in the future, a potential we are currently investigating.

## Acknowledgments

MG acknowledges the Norwegian Research Council and the Geologic Survey of Norway for funding this research. DC, VRT and FM acknowledge funding from Science Foundation Ireland and from the Irish Research Council for Science, Engineering and Technology.

We appreciate the effort and constructive comments of two anonymous reviewers and the editorial handling by Laurie Reisberg. We also greatly appreciate laboratory assistance from Bart Hendriks and Britt Vongraven of the Geologic Survey of Norway, discussion with John Gamble from University College Cork, Ireland, and Paul Renne, Berkley Geochronology Centre, for always lending insightful comments and discussion.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.chemgeo.2011.05.007.

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