Temperature–time evolution of the Assynt Terrane of the Lewisian Gneiss Complex of Northwest Scotland from zircon U-Pb dating and Ti thermometry

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**A B S T R A C T**

The Lewisian Gneiss Complex of Northwest Scotland is a classic Precambrian basement gneiss complex. The Lewisian is divided into a number of terranes on the basis of structural, metamorphic and geochronological evidence. The most well-studied of these is the Assynt Terrane, which forms the central part of the Lewisian outcrop on the Scottish mainland. Field evidence shows that it has a complex tectono-thermal history, the early stages of which remain poorly constrained. This paper sets out to better understand the chronology and thermal evolution of the Assynt Terrane through zircon U-Pb dating and Ti-in-zircon thermometry, the latter applied to the Lewisian for the first time. This is placed in context by integration with detailed field mapping, sample petrography, zircon cathodoluminescence (CL) imaging and rare earth element (REE) analysis.

Zircons from six tonalite-trondhjemite-granodiorite (TTG) gneiss samples and two metasedimentary gneiss samples were analysed. The TTG gneisses were predominantly retrogressed to amphibolite-facies; zircons showed a range of CL zoning patterns and REE profiles were similar to those expected for magmatic zircon grains. Zircons from the metasedimentary gneisses also displayed a range of CL zoning patterns and are depleted relative to chondrite in heavy REEs due to the presence of garnet.

Zircon analysis records a spread of concordant U-Pb ages from ~2500 to 3000 Ma. There is no evidence of ages with location in the crystal or with CL zoning pattern. A weighted average of 207 Pb/206 Pb ages from the oldest igneous zircon cores from the TTG gneiss samples gives an age of 2958 ± 7 Ma, interpreted to be a magmatic protolith crystallisation age. A weighted average of 207 Pb/206 Pb ages of the youngest metamorphic rims yields an age of 2482 ± 6 Ma, interpreted to represent the last high-grade metamorphism to affect these rocks. Ti-in-zircon thermometry records minimum temperatures of 710–834 °C, interpreted to reflect magmatic crystallisation.

REE profiling enabled the zircons in the metasedimentary rocks to be linked to the presence of metamorphic garnet, but resetting of U-Pb systematics precluded the determination of either protolith or metamorphic ages. Zircons from the metasedimentary gneisses generally record higher minimum temperatures (803–847 °C) than the TTG gneisses, interpreted to record zircon crystallisation in an unknown protolith.

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1. Introduction

The Lewisian Gneiss Complex of Northwest Scotland (Fig. 1a) is a classic example of a basement gneiss complex and is an important location for understanding the processes of metamorphism and deformation in lower crustal rocks. Field relationships and metamorphic mineral assemblages allowed Peach et al. (1907)
and Sutton and Watson (1951) to determine a relative chronology of tectonothermal events in the Lewisian, providing a framework for the large number of geochemical and geochronological investigations that have been carried out since then (summarised in Kinny et al., 2005; Wheeler et al., 2010; Goodenough et al., 2013). The dominant lithologies in the Lewisian Gneiss Complex are tonalite-trondhjemite-granodiorite (TTG) gneisses, with subordinate mafic and ultramafic gneisses and rare metasedimentary rocks (e.g. Sutton and Watson, 1951; Davies, 1974; Tarney and Weaver, 1987; Johnson and White, 2011; Zirkler et al., 2012). In the area around the village of Scourie (Fig. 1b), three major sets of structures and associated metamorphic assemblages have been recognised in the TTG gneisses and attributed to three tectonothermal events. Sutton and Watson (1951) used the heterogeneous preservation of these structures and assemblages to subdivide the mainland outcrop of the LGC into three regions (Fig. 1a). The area around Scourie was termed the Central Region, bounded to the north and south by the Northern and Southern Regions.

In parts of the Central Region, such as around Scourie, field evidence for all three tectonothermal events is preserved. The earliest event is expressed as strong gneissic layering, which represents the gneissification of the TTG magmatic protoliths. In areas with little subsequent deformation, granulite-facies metamorphic assemblages are preserved, and this metamorphic event is named the Badcallian (Park, 1970). The Badcallian event is also characterised by ultra-high temperatures and partial melting (Johnson et al., 2012, 2013; Rollinson, 2012; Rollinson and Gravestock, 2012). Field evidence for partial melting is clearest in the mafic gneisses where bands of felsic melt permeate these bodies (Johnson et al., 2012, 2013). Geochemical evidence for partial melting comes from whole rock and mineral trace element patterns of TTG and mafic gneisses. Rollinson and Gravestock (2012) determined that light Rare Earth Element (REE) enrichment in clinopyroxenes in mafic gneisses could not be a primary magmatic feature and must have been generated by interaction with a felsic partial melt. Rollinson (2012) built on these partial melting studies to show that the Lewisian TTG protoliths were generated from a LIL- and HFSE-depleted basaltic source.

The subsequent Inverian event is characterised by an amphibolite-facies hydrous static retrogression of dry Badcallian granulite-facies assemblages and localised shear zones up to a few kilometres wide (e.g. Canisp (Evans, 1965; Jensen, 1984; Attfield, 1987)). The Inverian event was followed by the intrusion of the mafic Scourie Dyke Swarm, an important chronological marker. Heterogeneous deformation of the dykes enabled recognition of pre- and post-dyke tectonothermal events. Post-dyke, deformation associated with the Laxfordian amphibolite-facies event heterogeneously overprinted earlier assemblages and structures (Sutton and Watson, 1951). Around Scourie, the Laxfordian event is represented by discrete shear zones a few metres wide, and by widespread static overprinting of earlier granulate-facies assemblages. In the Northern and Southern regions, the Laxfordian deformation and metamorphism is generally more pervasive. The terms Badcallian, Inverian and Laxfordian are used here to refer to the structures and mineral assemblages and the tectonothermal activity they represent; the attributes of each are summarised in Table 1.

As well as the dominant TTG gneisses, parts of the Lewisian Gneiss Complex, including areas around Scourie, contain typically garnetiferous brown-weathering, mica-rich rocks interpreted to be sedimentary in origin (Beach, 1973; Davies, 1974; Okeke et al., 1983; Goodenough et al., 2013). The relationship of these metasedimentary rocks to the rest of the TTG gneisses is not wholly clear. They tend to be spatially associated with mafic and ultramafic gneisses, interpreted to represent an ocean floor supracrustal package (e.g. Davies, 1974; Cartwright et al., 1985; Cartwright and Barnicoat, 1987). Based on structural relationships, Davies (1974) suggested that the mafic–ultramafic and metasedimentary assemblage was juxtaposed against the TTG gneisses prior to the Badcallian tectonothermal event. In support of this, detailed petrographic analysis by Zirkler et al. (2012) indicated partial melting of the metasedimentary rocks in the Badcallian. However, Rollinson and Gravestock (2012) interpreted that due to their dispersed nature within the TTG gneisses, the mafic and ultramafic gneisses, and hence the associated metasedimentary rocks, were intruded by the TTG gneisses and represent the oldest assemblage in the area. Additionally, Friend and Kinny (1995) obtained a magmatic crystallisation age of ~2960 Ma from a TTG gneiss sample which cross-cuts a mafic–ultramafic body at Scourie; hence the mafic–ultramafic and metasedimentary assemblages pre-date crystallisation of the TTG protoliths.

Early workers such as Peach et al. (1907) and Sutton and Watson (1951) assumed that the LGC was one block of crust of a single age and the three tectonothermal events had concurrently affected each of the three regions. Radiometric dating was initially applied with the aim of attributing precise ages to protolith formation and tectonothermal events. However, a large suite of high spatial

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**Fig. 1.** (a) Location of the outcrop area of the Lewisian Gneiss Complex in Northwest Scotland, inset map shows location in the British Isles; mainland outcrop regions are after Peach et al. (1907). (b) Localities where zircons analysed in this study were taken from. (c) The terrane model of Kinny et al. (2005) showing the different terranes interpreted to make up the Lewisian.
resolution ion microprobe U-Pb zircon dating from across the LGC has illustrated the complexity of its history, and led to a new interpretation of its formation and tectonothermal evolution (Friend and Kinny, 1995, 2001; Kinny and Friend, 1997; Love et al., 2004, 2010; Kinny et al., 2005). Significant debate continues over the link between radiometric dates and events that can be recognised in the field.

The ages of the younger, Palaeoproterozoic events are generally agreed. Davies and Heaman (2014) dated the main Scourie Dyke Swarm intrusion episode at ~2418–2375 Ma while Corfu et al. (1994) and Kinny and Friend (1997) attributed U-Pb titanite ages of ~1750 Ma to the Laxfordian event. However, dating of protoliths and the pre-Scourie Dyke metamorphic events has proved more controversial. Corfu et al. (1994) obtained U-Pb zircon ages of ~2710 Ma and ~2490 Ma from gneisses near Badcall Point (Fig. 1b) which they attributed to the Badcallian and Inverian respectively. Subsequently, U-Pb zircon ages from the Central Region led Friend and Kinny (1995) to suggest a magmatic protolith age for the LGC of 2960–3030 Ma with a major metamorphic event at ~2490 Ma; they did not find a significant age cluster at ~2710 Ma. This led them to interpret that the granulite-facies Badcallian event actually occurred at ~2490 Ma with the Inverian occurring soon after but not recorded in the zircons.

Following this, magmatic protolith ages of 2680–2840 Ma were obtained from the Northern Region, with no record of metamorphism at ~2490 Ma (Kinny and Friend, 1997). The difference in age profile for magmatic protolith formation and subsequent tectonothermal activity led to the conclusion that the Northern Region and Central Region were separate crustal blocks. Friend and Kinny (2001) found that different parts of the Outer Hebrides also had different magmatic protolith formation and tectonothermal activity ages. Similarly, Love et al. (2004) found different ages for magmatic protoliths and tectonothermal activity in the southern part of the Central Region. These findings were formalised into a model of discrete terranes with different magmatic protolith ages and tectonothermal histories, which then accreted during or before the Laxfordian event (Kinny et al., 2005) (Fig. 1c). Further work by Love et al. (2010) indicated that the Southern Region was also composed of multiple terranes with varying histories. The Central Region around Scourie was re-named the Assynt Terrane, and the Northern Region the Rhiconich Terrane (Fig. 1c) (Kinny et al., 2005). However, Crowley et al. (2014) was able to distinguish temporarily precise ages of both ~2500 Ma and ~2700 Ma from the Assnyt Terrane using an innovative CA-ID-TIMS approach. Goodenough et al. (2010) investigated field relationships in the Laxford Shear Zone (Fig. 1a), the boundary between the Assynt and Rhiconich Terranes, and suggested that the two terranes were accreted during the Inverian event at ~2480 Ma (Goodenough et al., 2013).

There have been many previous studies attempting to constrain the thermal history of the Assynt Terrane. Early work used ion exchange geothermometers such as garnet-pyroxene in mafic and ultramafic gneisses, and determined peak metamorphic conditions in the Badcallian between 600 °C and >1000 °C (O’Hara and Yarwood, 1978; Barnicoat, 1983; Sills and Rollinson, 1987). Sills (1983) suggested Inverian retrogression occurred at ~600 °C based on a range of ion exchange thermometers and tentatively estimated >500 °C for Laxfordian metamorphism from muscovites in shear zones. Droop et al. (1999) estimated ~530–630 °C for peak Laxfordian metamorphism from metapelites from the Loch Maree Group in the Southern Region of the Lewisian Gneiss Complex.

More recent attempts to constrain thermal conditions in the Assynt Terrane have involved mineral equilibria modelling. Johnson and White (2011) constructed pseudosections in THERMOCALC (Holland and Powell, 1998) for the bulk composition of a metagabbro and a metapyroxenite from near Scourie. They calculated peak metamorphic temperatures for the Badcallian of 875–975 °C. Zirklar et al. (2012) followed a similar approach in combining mineral equilibria modelling with petrographic observation to determine peak Badcallian metamorphic temperatures of >900 °C from metasedimentary rocks at Stoer, also in the Assynt Terrane. Petrographic characterisation of the metasediments by Zirklar et al. (2012) showed that there was hydrous retrogression of the peak granulite-facies assemblage, evidenced by retrograde growth of hornblende, biotite and other hydrous minerals. This retrogressive assemblage indicated temperatures of 520–550 °C, interpreted to reflect the Inverian tectonothermal event.

Understanding the formation and tectonothermal evolution of the Lewisian Gneiss Complex continues to present challenges. There is ongoing debate into whether the Badcallian tectonothermal event occurred at ~2500 Ma or ~2700 Ma. Crowley et al. (2014) have interpreted both ages to represent high-grade metamorphism from their CA-ID-TIMS measurements but which of these ages relates to the granulite-facies mineral assemblage and structures observed in the field remains debated (Friend and Kinny, 1995; Kinny et al., 2005; Park, 2005; Park et al., 2005; Whitehouse and Kemp, 2010; Goodenough et al., 2013; Crowley et al., 2014). In this contribution, we conduct zircon U-Pb dating and Ti-in-zircon thermometry, the latter applied to the Lewisian for the first time, to investigate the chronology and thermal evolution of the Assynt Terrane. This is placed in context by integration with detailed field mapping, sample petrography, zircon cathodoluminescence (CL) imaging and rare earth element (REE) analysis.

### 2. Sample characterisation

Zircon grains were collected from eight samples, six from the TTG gneisses which dominate the Assynt Terrane, and two from metasedimentary rocks. The samples of TTG gneiss were collected at two localities that were mapped in detail, Badcall Point and Duartmore Point (Figs. 1b and 2a and b). These samples were chosen to reflect the tectonothermal history of the Assynt Terrane. At Badcall Point, Badcallian gneissic layering is the dominant structure but the Badcallian granulite-facies metamorphic assemblage has been retrogressed, as is typical across much of the Assynt Terrane. Sillie-textured hornblende and quartz have replaced pyroxenes; plagioclase is the other main mineral. Sample JMO9/BP02 was taken from this lithology. The Badcallian gneissic layering is the dominant structure but the Badcallian granulite-facies metamorphic assemblage has been retrogressed, as is typical across much of the Assynt Terrane. Sillie-textured hornblende and quartz have replaced pyroxenes; plagioclase is the other main mineral. Sample JMO9/BP02 was taken from this lithology. The Badcallian gneissic layering is the dominant structure but the Badcallian granulite-facies metamorphic assemblage has been retrogressed, as is typical across much of the Assynt Terrane.
Fig. 2. Field maps showing structures, mineral assemblages and sample localities: (a) Badcall Point, with context map (left) and detail map (right); (b) Duartmore Point; (c) Sithean Mor.
amphibolite-facies hornblende + plagioclase + quartz assemblage. At Duartmore Point (Fig. 2b), the Badcallian layered gneiss retains amphibolite-facies clinopyroxene but orthopyroxene has largely been replaced by epidote and biotite: plagioclase and quartz are the other major minerals. Sample JM09/DP03 was taken from this lithology. The Badcallian gneissic layering is cross-cut by an intrusion of the Scourie Dyke Swarm which is in turn cross-cut and deformed by a ~15 m wide Laxfordian shear zone. The shear zone has moderately to strongly planar and linear fabrics and an amphibolite-facies hornblende + plagioclase + quartz assemblage. On either side of the shear zone is a zone where amphibolite-facies gneissic layering is preserved but has been statically retrogressed to amphibolite-facies. Sample JM09/DP01 was taken from this zone.

Two samples were taken from the body of metasedimentary rocks at Sithean Mor (Figs. 1b and 2c). The metasedimentary package is internally heterogeneous with biotite- and garnet-rich zones, and more quartzose areas. The biotite- and garnet-rich zones are interpreted to be relict muddy sediments. These grade into the more quartzose zones that by association are interpreted to be relict quartz-rich sediments. This is in agreement with the interpretations of Okeke et al. (1983) and Beach (1973). This outcrop of metasedimentary rocks is surrounded by TTG gneisses with Badcallian gneissic layering. The strike of the layering runs into the metasedimentary outcrop and continues in the form of a moderately-developed planar fabric comprising biotite-rich and biotite-poor layers. Sample JM08/22 has a garnet + biotite + plagioclase + quartz assemblage. The garnet is highly fractured and partially replaced with biotite and quartz. Sample JM08/23 is composed of: lensoid- or arcuate-shaped quartz aggregates, 2–3 mm long and composed of equant 0.5 mm-diameter crystals, possibly porphyroclasts; large partially sericิตised plagioclase crystals, possibly also porphyroclasts; a very fine matrix of quartz, feldspar and muscovite; and very high relief kyanite. The kyanite is variably accicular or euhedral in shape when viewed in thin section, with the different shapes representing different sections through the crystals.

In addition to the zircon-bearing samples, a further sample (JM09/SM09) was taken from Scourie Mor (Fig. 1b) at NC 14146 44175. This sample is representative of the pristine granulite-facies Badcallian assemblage, not seen at the Duartmore Point or Badcall Point localities. It has a granoblastic texture with orthopyroxene, clinopyroxene, plagioclase, quartz and accessory rutile, but does not contain zircon.

3. Zircon analysis

3.1. Analytical methods

Zircons were labelled according to the sample name, followed by “Z” and the zircon number. A prefix of “GM” indicates a zircon on a grain mount; the absence of this prefix indicates a zircon on a thin or thick section. “Ch” before the zircon number indicates a zircon from a thick section. For example, GMBP042Z6 is zircon 6 from sample JM09/BP04 and was on a grain mount; BP06ChZ1 denotes zircon 1 from the thick section of sample JM09/BP06.

Internal chemical zoning in zircons was revealed by cathodoluminescence (CL) imaging carried out in a Philips XL30 scanning electron microscope at the University of Liverpool. The zircons were then analysed by ion microprobe at the Edinburgh Ion Microprobe Facility (EIMF) at the University of Edinburgh. U-Pb isotope analysis was conducted using a Cameca IMS 1270 ion microprobe and analytical procedures follow those of Kelly et al. (2008). U/Pb ratios were calibrated against the 91,500 (Wiedenbeck et al., 1995), SL1 (Maas et al., 1992) and Plesovice (Slama et al., 2008) zircon standards. Plesovice was the primary standard and yielded a mean 206Pb/238U ratio of 0.05359 ± 0.00023 (MSWD = 2.4; 95% conf., 206Pb/238U age = 340.5 ± 4.8 Ma; n = 62). A common Pb correction was also applied in-house. Common Pb surface contamination was reduced by rastering the sample with the ion microprobe beam immediately prior to isotope measurement and by production of flat-bottom analysis pits through carefully tuned beam conditions. Correction for in situ common Pb was made using measured 206Pb counts above that of the detector background (typically ~0.2–1.5 ppb). In the analyses for this project, measured common Pb was generally in the range of <5 ppb, although occasionally analyses were much higher than this, likely the result of contamination on the sample surface and in exposed cracks; such analyses were discarded. Uncertainties on all isotopic ratios and ages are quoted at the 2σ level. Plots and age calculations have been made using the computer program ISOPLOT (Ludwig, 2003).

Following U-Pb analysis, trace elements (REEs and Ti) were measured using a Cameca 4f ion microprobe, following the analytical procedures of Kelly and Harley (2005). Analytical reproducibility during the analytical session was tested by regular measurement of REEs and Ti in the 91,500 zircon standard (Wiedenbeck et al., 1995) and NIST SRM610 glass standard. The analyses from the 91,500 zircon show an increase in chondrite-normalised values of trivalent REEs as ionic radius decreases from La to Lu, together with large positive Ce anomaly and small negative Eu anomaly. Good agreement is obtained between the SIMS measurements for zircon 91,500 presented here and those of Whitehouse and Platt (2003) and Hoskin (1998) although there is some variation in REE concentrations in the analyses of 91,500, also encountered by Hoskin (1998). For most REEs (particularly the heavier ones), the average analytical error is <10% (2σ) but for some of the lighter REEs which have lower concentrations, it can be significantly higher. This is interpreted to be partly due to a lack of reproducibility from the spectrometer but also to heterogeneity in the 91,500 standard as noted above. Error on Ti is ~10% (2σ). Analytical reproducibility against the NIST SRM610 glass standard was <6% (2σ) for the elements analysed. Raw data were reduced using the jCION6 software written by John Caven at the University of Edinburgh. REE data were chondrite-normalised against the values of McDonough and Sun (1995).

3.2. Zircon cathodoluminescence

When imaged by cathodoluminescence (CL), the population of zircons showed a range of chemical zoning patterns typical of complex zircons from high-grade metamorphic rocks (Fig. 3). Surrounding cores, both CL-bright and CL-dark, are found in many crystals. Some cores have distinctive oscillatory zoning patterns (e.g. GMBP042Z6 and BP06ChZ1 in Fig. 3, both from samples of TTG gneiss in the Laxfordian shear zone at Badcall Point), indicative of growth from a magma (Corfu et al., 2003). Other cores are homogeneous in CL response (e.g. BP01ZG in Fig. 3, from the statically retrogressed shear zone margin TTG gneiss at Duartmore Point) or may show some irregular zoning. Cores are typically surrounded by rims which are usually CL-bright (e.g. GMDP01ZZ and BP06ChZ1 in Fig. 3, from the statically retrogressed shear zone margin TTG gneiss at Duartmore Point and Laxfordian shear zone TTG gneiss at Badcall point, respectively) and may in some cases have medium or low CL response (CL-dark). The rims are generally homogeneous in CL response and are interpreted to have formed during metamorphism (Corfu et al., 2003). This may have been through solid-state recrystallization of pre-existing magmatic zircon (Hoskin and Black, 2000) or through growth during the partial melting which occurred in the Badcallian tectono-thermal event (Johnson et al., 2012, 2013; Rollinson, 2012; Rollinson and Gravestock, 2012). Some whole grains do not have any discernible
| Sample/spot | CL zoning pattern | U (ppm) | Th (ppm) | Pb (ppm) | Th/U | 204Pb/206Pb (ppb) | 203Pb/206Pb | 2σ | 203Pb/206Pb 2σ | 205Pb/206Pb 2σ | 205Pb/206Pb 2σ | Error Corr. | % Disc. | 207Pb/206Pb age | 2σ |
|-------------|------------------|---------|----------|----------|------|-------------------|-------------|-----|----------------|----------------|----------------|------------|--------|-----------------|-----|
| GMBP04Z1-1  | r (br)           | 35.34   | 48.52    | 24.83    | 1.41 | 0.524             | 0.189       | 0.006 | 13.421         | 0.576           | 0.515           | 0.015      | 0.669  | 2.08             | 2734|
| GMBP04Z1-2  | r (br)           | 35.24   | 49.49    | 27.80    | 1.44 | 0.420             | 0.213       | 0.005 | 16.677         | 0.565           | 0.568           | 0.015      | 0.776  | 0.90             | 2927|
| GMBP04Z2-1  | r (br)           | 23.51   | 24.05    | 13.66    | 1.05 | 0.627             | 0.167       | 0.005 | 10.594         | 0.434           | 0.460           | 0.012      | 0.628  | 3.54             | 2528|
| GMBP04Z2-2  | r (br)           | 35.08   | 32.89    | 20.40    | 0.96 | 1.47              | 0.168       | 0.003 | 10.807         | 0.326           | 0.468           | 0.010      | 0.742  | 2.33             | 2533|
| GMBP04Z3-1  | c (bc)           | 16.46   | 21.09    | 10.03    | 1.31 | 0.49              | 0.173       | 0.007 | 10.886         | 0.583           | 0.457           | 0.015      | 0.615  | 6.02             | 2583|
| GMBP04Z3-2  | c (bc)           | 21.05   | 25.57    | 13.85    | 1.25 | 0.394             | 0.173       | 0.005 | 11.932         | 0.450           | 0.501           | 0.013      | 0.709  | 1.41             | 2583|
| GMBP04Z4-1  | r (br)           | 23.11   | 29.88    | 13.83    | 1.33 | 0.10              | 0.168       | 0.004 | 10.430         | 0.364           | 0.449           | 0.011      | 0.702  | 5.89             | 2541|
| GMBP04Z4-2  | r (br)           | 21.63   | 26.78    | 13.27    | 1.27 | 0.243             | 0.160       | 0.004 | 10.352         | 0.366           | 0.468           | 0.011      | 0.650  | 0.66             | 2459|
| GMBP04Z4-3  | c (dc)           | 127.60  | 55.92    | 66.72    | 0.45 | 4.59              | 0.163       | 0.001 | 10.516         | 0.239           | 0.469           | 0.010      | 0.948  | 0.10             | 2482|
| GMBP04Z5-1  | h                | 20.13   | 24.51    | 15.47    | 1.25 | 1.53              | 0.201       | 0.008 | 15.977         | 0.997           | 0.577           | 0.027      | 0.738  | -3.69            | 2832|
| GMBP04Z5-2  | h                | 28.26   | 24.28    | 18.60    | 0.88 | 1.17              | 0.190       | 0.008 | 13.890         | 0.750           | 0.531           | 0.016      | 0.572  | -0.32            | 2738|
| GMBP04Z6-1  | r (br)           | 15.38   | 14.55    | 9.58     | 0.96 | 0.76              | 0.179       | 0.007 | 12.277         | 0.625           | 0.499           | 0.016      | 0.623  | 1.24             | 2640|
| GMBP04Z6-2  | r (ozp)          | 34.99   | 49.14    | 28.31    | 1.44 | 1.73              | 0.211       | 0.009 | 16.985         | 0.888           | 0.584           | 0.019      | 0.634  | -1.83            | 2912|
| GMBP04Z7-1  | h                | 18.32   | 19.41    | 10.71    | 1.09 | 1.69              | 0.167       | 0.004 | 10.582         | 0.431           | 0.459           | 0.014      | 0.753  | 3.61             | 2582|
| GMBP04Z7-2  | h                | 12.54   | 9.84     | 7.24     | 0.81 | 2.17              | 0.164       | 0.003 | 10.849         | 0.362           | 0.481           | 0.012      | 0.775  | -1.45            | 2494|
| GMBP04Z7-3  | h                | 16.48   | 18.01    | 10.64    | 1.12 | 4.32              | 0.167       | 0.005 | 11.649         | 0.536           | 0.505           | 0.018      | 0.791  | -4.19            | 2530|
| GMBP04Z7-4  | h                | 30.80   | 41.16    | 21.78    | 1.37 | 2.11              | 0.191       | 0.005 | 13.705         | 0.512           | 0.521           | 0.014      | 0.720  | 1.54             | 2747|
| GMBP04Z8-2  | h                | 13.39   | 8.05     | 7.78     | 0.62 | 2.27              | 0.206       | 0.009 | 13.864         | 0.861           | 0.487           | 0.021      | 0.800  | 11.02            | 2976|

Table 3
Ion microprobe U-Th-Pb data for zircons analysed in this study. CL zoning pattern identifiers as Table 2.
internal zoning patterns – these are termed homogeneous (e.g. GMBP04Z5 and GMBP02Z1 in Fig. 3, from the Laxfordian shear zone TTG gneiss sample and statically retrogressed TTG gneiss samples, respectively, both from Badcall Point), although it cannot be ruled out that they contain distinct zones beneath the level of polishing. A number of crystals are irregular in their CL zoning pattern – they have no recognisable core or rim structures and cannot be clearly assigned to any particular formation mechanism (e.g. GM23Z2 and BP06Z3 in Fig. 3, from a metasedimentary gneiss sample from Sithean Mor and a Laxfordian shear zone TTG gneiss sample at Badcall Point, respectively). For the purposes of analysing zircon U-Pb and Ti to gain further insight into the temperature-time history of the Assynt Terrane, the CL zoning patterns were divided into four groups: cores (oscillatory-zoned, homogeneous or heterogeneous zoning, CL-bright or CL-dark); rims (CL-bright or CL-dark); homogeneous zircons; and irregular zonation. Zircons from each sample have a range of zoning patterns (Tables 2 and 3).

3.3. Zircon rare earth elements

Rare earth element (REE) profiling of zircons was carried out as it can link distinct CL domains to metamorphic assemblages in the host rock, therefore giving a better constraint to petrogenetic information recorded by zircon (e.g. Whitehouse and Kamber, 2003; Kelly and Harley, 2005).

103 spot analyses of REE were made, covering all zircon CL zonation types (Table 2). The majority of zircon analyses from Badcall Point and Duartmore Point show a typical magmatic zircon REE profile of increasing chondrite-normalised La-Lu with a positive Ce anomaly and a negative Eu anomaly (Fig. 4a–d). Yb/Gd ratio (an easy way of assessing the relative concentrations of heavy REEs to middle REEs) is generally 8–15 (Table 2). There is no clear distinction in REE profile between the different CL zoning pattern categories (Fig. 4b and d). A few analyses from both localities deviate from the typical pattern. Four analyses from an irregularly-zoned zircon from sample JM09/BP06, from the Laxfordian shear zone at Badcall Point, are relatively depleted in light and middle REEs and have very high Yb/Gd ratios of 72–323 (Fig. 4a and d). A single analysis from an irregularly-zoned zircon from sample JM09/BP01 (Inverian zone, Badcall point), in the Inverian shear zone at Badcall Point, has a flat heavy REE profile (Yb/Gd = 1.87) (Fig. 4a and b) while one core analysis from statically retrogressed sample JM09/DP01 at Duartmore Point also has a relatively flat heavy REE profile (Yb/Gd = 3.28) (Fig. 4b and e).

Most zircon REE profiles from the metasedimentary rocks at Sithean Mor (samples JM08/22 and JM08/23) have relatively flat REE profiles: all bar 2 of the 15 analyses have Yb/Gd of <7 (Table 2, Fig. 4c and f). The highest two Yb/Gd values are from a homogeneous zircon while the two analyses from zircon rims have Yb/Gd of <1. Zircon cores and irregularly-zoned zircons have a range of Yb/Gd values of ~1–7 (Table 2, Fig. 4c and f). There is no clear correlation between Yb/Gd ratio and CL zoning pattern as rims, irregularly-zoned crystals and a core analysis all have Yb/Gd ratio of <3.

3.4. Zircon U-Th-Pb

In order to investigate the chronological history of the Assynt Terrane, a total of 103 U-Th-Pb spot analyses were conducted on the same analytical spots as the REE profiles. U contents range from 2 to 440 ppm while Th ranges from 1 to 360 ppm, although the majority of analyses are 10–100 ppm for both Th and U (Table 3). There is a wide range in Th and U contents within each sample although zircons from the metasedimentary rocks from Sithean Mor (samples JM08/22 and JM08/23) cluster towards the top of the range for Th and U (Fig. 5a; Table 3). There is no correlation between CL zoning pattern and Th or U contents; each of the four zoning pattern types records a wide range in Th and U (Fig. 5b; Table 3). Th/U is generally in the range 0.5–2, although some analyses from an irregularly-zoned zircon from sample JM09/BP06 (TTG gneiss in Laxfordian shear zone, Badcall Point) are as low as 0.04 (Fig. 5a and b; Table 3).

As well as a range in Th and U concentrations, there is also a range in \(^{207}\text{Pb}^{206}\text{Pb}\) ages from 2384 ± 46 Ma to 3017 ± 56 Ma across all the analysed zircons (Table 3). It would be expected that zircon cores record the oldest ages and rims record younger ages but in fact there is no such relationship in this population. Age, U content and Th/U do not correlate with sample history nor CL zoning pattern (Fig. 5c–f; Table 3). Each sample records a range of \(^{207}\text{Pb}^{206}\text{Pb}\) ages as do the different CL zoning patterns (Fig. 6a and b). The ages are mainly concordant (~2% to +5%) although some are more discordant (Table 3) and the data define a spread along concordia with no obvious clustering representing protolith or metamorphic ages (Fig. 6c and d).

3.5. Zircon Ti

Ti contents of zircons were measured along with U-Th-Pb and REEs so that Ti-in-zircon thermometry (Watson and Harrison,
Fig. 4. Matsuda plots of zircon rare earth element profiles for: (a) Badcall Point colour-coded by sample; (b) Badcall Point colour-coded by cathodoluminescence zoning pattern; (c) Duartmore Point colour-coded by sample; (d) Duartmore Point colour-coded by cathodoluminescence zoning pattern; (e) Sithean Mor colour-coded by sample; (f) Sithean Mor colour-coded by cathodoluminescence zoning pattern; values normalised against chondrite values of McDonough and Sun (1995). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)
Fig. 5. U-Th-Pb chemistry of zircons from this study plotted as: Th concentration (ppm) vs. U concentration (ppm) colour-coded by sample (a) and by cathodoluminescence zoning pattern (b); U concentration (ppm) vs. $^{207}$Pb/$^{206}$Pb age colour-coded by sample (c) and by cathodoluminescence zoning pattern (d); Th/U ratio vs. $^{207}$Pb/$^{206}$Pb age colour-coded by sample (e) and by cathodoluminescence zoning pattern (f). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)
Fig. 6. Spread of $^{207}\text{Pb}/^{206}\text{Pb}$ ages recorded by zircons in this study: (a) $^{207}\text{Pb}/^{206}\text{Pb}$ ages with 2σ errors colour-coded by sample; (b) $^{207}\text{Pb}/^{206}\text{Pb}$ ages with 2σ errors colour-coded by cathodoluminescence zoning pattern; (c) Wetherill concordia plot of zircon Pb/U ratios colour-coded by sample; (d) Wetherill concordia plot of zircon Pb/U ratios colour-coded by cathodoluminescence zoning pattern. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

2005; Watson et al., 2006) could be applied for the first time to further the understanding of the temperature history of the Assynt Terrane. The abundance of Ti in zircon in equilibrium with rutile and quartz is proportional to temperature and therefore provides a crystallisation thermometer for the zircon and its host rock. It was hypothesised that the Ti thermometer would record the magmatic protolith crystallisation temperatures and/or the temperature of the Badcallian or Inverian metamorphism. Ti contents ranged from 6 to 27 ppm (Table 2). Zircons from metasedimentary samples from Sithean Mor had higher average Ti concentrations than Badcall Point and Duartmore Point although there was no clear distinction between the two samples from this locality (Fig. 7a). Zircons from Duartmore Point and Badcall Point had a similar range of Ti concentrations and again there was no clear distinction between samples with different tectonothermal histories at each locality. There was also no clear correlation between CL zoning pattern category and Ti content (Fig. 7b), nor between Ti content and $^{207}\text{Pb}/^{206}\text{Pb}$ age (Fig. 7c and d). Some intragranular variation in Ti content was observed (e.g. between core and rim in zircon GM03P321, granulite-facies TTG gneiss, Duartmore Point) and also intradomain variation (e.g. in the core of zircon BP06Ch22, TTG gneiss in Laxfordian shear zone, Badcall Point) but these variations were minor and restricted to a small number of grains (Table 2).

4. Discussion

4.1. REE patterns

The relative abundance of the different REE in zircon has been shown to vary according to the environment in which the zircon formed or was modified (e.g. Bea et al., 1994; Rubatto, 2002; Whitehouse and Kamber, 2003; Rubatto and Hermann, 2006). For
example, zircon grown from a felsic-intermediate magma typically has a steeply HREE-enriched chondrite-normalised La-Lu profile due to a preference for the smaller ionic radius heavier REEs over the larger lighter REEs (Murali et al., 1983; Hinton and Upton, 1991; Hoskin and Ireland, 2000; Whitehouse and Kamber, 2003) but with a positive Ce anomaly (Ce/Ce*) and negative Eu anomaly (Eu/Eu*). Zircon formed or modified during metamorphism, however, may deviate from this pattern (e.g. Kelly and Harley, 2005). The REE composition of zircon that grows or is modified during metamorphism will be affected by concurrent growth or resorption of other REE-sequestering minerals such as garnet, which preferentially incorporates heavy REEs (Rubatto, 2002; Whitehouse and Platt, 2003), monazite, which contains light REEs (Bea and Montero, 1999; Schaltegger et al., 1999; Rubatto et al., 2001), or amphibole, which incorporates middle REEs (Davidson et al., 2007). Rollinson and Gravestock (2012) showed that some clinopyroxenes in Lewisian pyroxenites exerted a strong influence in light REEs while orthopyroxene preferentially incorporated heavy REEs.

In the TTG gneisses, zircon Yb/Gd ratios are generally 8–15 (Table 2) which is lower than that measured by Kelly and Harley (2005) for magmatic zircon (Yb/Gd = 20–30). The lack of variation in REE profile between the different CL zoning pattern categories (Fig. 4b and d) suggests that zircon did not exchange REEs with metamorphic minerals such as garnet and monazite, which strongly influence the REE profile in zircon, even if they were present in the rocks. Analyses which deviate from the typical pattern may have been influenced by the presence of other minerals. The four analyses from an irregularly-zoned zircon from sample JM09/BP06, from the Laxfordian shear zone at Badcall Point, are relatively depleted in light and middle REEs and have very high Yb/Gd ratios of 72–323 (Fig. 4a and d). Monazite sequesters light REEs (Bea and Montero, 1999) but monazite has not been recorded in the TTG gneisses of the LGC. Amphibole sequesters middle REEs (Davidson et al., 2007) but amphibole is abundant in the TTG gneisses in the Inverian and Laxfordian assemblages and does not appear to have had a similar effect on the REE pattern of any of the other zircon grains analysed from this shear zone sample.

The analyses with the flat heavy REE profiles (an irregularly-zoned zircon from sample JM09/BP01, in the Inverian zone at Badcall Point, and a core from statically retrogressed sample JM09/DP01 at Duartmore Point) indicate those zircon domains may have formed their current REE profile in the presence of a
metamorphic mineral that sequesters the HREE such as garnet. However, garnet has not been documented in the TTG gneisses of the Assynt Terrane, and is not stable in compositionally similar tonalites at pressures less than 15 kbar (Knudsen and Andersen, 1998); this pressure is greater than almost all of the peak pressures calculated in the Assynt Terrane and significantly higher than the most recent reliable estimate (Johnson and White, 2011).

The prevalence of relatively low Yb/Gd ratios and relatively flat chondrite-normalised heavy REE profiles in zircons from the metasedimentary rocks at Sīthean Mor (samples JMO8/22 and JM08/23) suggests that REE abundance in these zircons has been affected by garnet. Garnet is present in sample JMO8/22, and although it was not found in sample JM08/23, it is widely distributed at this locality. The zircon REE link with garnet has the potential to allow zircon CL zones to be correlated with the tectonothermal evolution of the Assynt Terrane (Rubatto, 2002; Whitehouse and Platt, 2003). Petrological inspection and phase equilibria modelling by Zirkler et al. (2012) showed that garnet in similar metasedimentary rocks from elsewhere in the Assynt Terrane was present in both Badcallian and Inverian assemblages. This suggests that the zircon CL zones from Sīthean Mor with relatively flat heavy REE profiles re-equilibrated in the presence of garnet during the either the Badcallian or Inverian tectonothermal events. The temperature estimates of Zirkler et al. (2012) for Inverian metamorphism (520–550 °C) are considered too low for zircon to equilibrate with its surrounding minerals, therefore the zircon rims with flat heavy REE profiles from Sīthean Mor are suggested to have formed in the Badcallian tectonothermal event. Partial melting of these metasedimentary rocks in the Badcallian (Johnson et al., 2012, 2013; Rollinson, 2012; Rollinson and Gravestock, 2012) is also likely to have led to zircon rim growth from anatectic melt.

4.2. U-Th-Pb

Through zircon dating, this study sought to determine the age of TTG protolith formation of the Assynt Terrane and to attempt to distinguish ages for the Badcallian and Inverian metamorphic events. Our hypothesis was that zircons would yield ages reflecting the tectonothermal histories of their host samples (i.e. inside and outside Laxfordian shear zones, layered gneisses preserving Badcallian granulite-facies assemblages or statically retrogressed in the Inverian and/or Laxfordian). However, the ~500 Myr spread of concordant SIMS ages obtained did not correlate with sample tectonothermal history (Fig. 6). In order to obtain a protolith age for the TTG gneisses of the Assynt Terrane, a starting point is to look for the oldest age in the zircon populations from Badcall Point and Duartmore Point. The oldest age is 3017 ± 56 Ma, although this age is reversely discordant by 6%. This degree of reverse discordance is interpreted to be beyond the level of an analytical artefact affecting the U/Pb ratio calibration so this particular age may be overestimated. An alternative approach used by Whitehouse and Kemp (2010) to determine a protolith age is to assume that there is a single magmatic age and that the spread of ages has been caused by later Pb-loss. Successive rejection of the youngest ages is performed until the mean square of weighted deviates (MSWD) of the weighted average age of the population falls below a limit, below which analytical error can account for the observed scatter. This objective approach does not take account of the CL zoning pattern. The oldest age in the TTG gneiss zircon population is from a rim which is unlikely to reflect protolith formation whereas cores are much more likely to reflect the early stages of zircon history, possibly growth from a protolith magma (Corfu et al., 2003). Taking the threshold MSWD to be 1 (Whitehouse and Kemp, 2010), the oldest three cores yield a mean age of 2958 ± 7 Ma (MSWD = 1.00, probability = 0.37). Including the next youngest core increases the MSWD to only 1.3 which is still acceptable and yields a mean age of 2957 ± 14 Ma. These four oldest cores are all oscillatory zoned and thus are likely to have formed by crystallisation from a magma (Corfu et al., 2003). Cores with younger ages do not all show oscillatory zoning, and also greatly increase the MSWD. This age of 2957 ± 14 Ma is within error of the 2960 Ma age suggested by Friend and Kinny (1995) for the formation of the protolith to the Assynt Terrane. However, it is ~100 Myr older than the protolith age suggested by Whitehouse and Kemp (2010) and Crowley et al. (2014) who interpret that ages >~2850 Ma are inherited from an older magma.

Attempts to pick out ages for the Badcallian and Inverian metamorphic events from the zircon population in this study are hampered by the spread of concordant ages. In this study, no clustering of ages was found in any sample (Fig. 6a) or CL zoning pattern category (Fig. 6b). The fact that not all of the oldest ages in the population are from cores as might be expected, coupled with the spread of concordant ages of ~500 Myr in the different CL zoning pattern categories, makes interpretation of the chronological history of the Assynt Terrane extremely difficult. The youngest age in this population (2384 ± 46 Ma) is from a zircon rim from sample JM09/BP06 but is 46 Myr younger than the next youngest age and is reversely discordant by 2%. Adopting the approach used above to determine a protolith formation age, but rejecting the oldest ages until a MSWD threshold is reached, the youngest ten ages (those <2500 Ma) yield a mean age of 2479 ± 12 Ma (MSWD = 3.1, probability 0.001). As more ages are excluded, the MSWD only increases but by rejecting the 2384 ± 46 Ma and taking the next nine youngest ages, the MSWD drops to 1.3. Only by rejecting the second youngest age (2430 ± 44 Ma) as well, however, does the MSWD drop below 1 – the next eight youngest ages (ranging from 2459 ± 46 Ma to 2494 ± 28 Ma) yield a mean age of 2482 ± 6 Ma (MSWD = 0.69, probability = 0.68). This is considered to represent the age of a high-grade metamorphic event in the Assynt Terrane, as recognised by Friend and Kinny (1995) and Whitehouse and Kemp (2010). However, even our exhaustive study of the characteristics of individual zircon grains does not allow us to confirm whether this high-grade metamorphic event was at granulite facies (Badcallian) or amphibolite facies (Inverian).

Friend and Kinny (1995) also interpreted that a high-grade metamorphic event occurred at ~2500 Ma, the younger end of their spread of concordant SIMS data, which heterogeneously reset the zircon U-Pb systematics causing the spread of ages. They suggested this high grade event was the Badcallian, thus making it ~200 Myr younger than previously thought (Corfu et al., 1994). Whitehouse and Kemp (2010) agreed that there must have been a high-grade event at ~2500 Ma but could not disprove the idea that there was another high grade event at ~2700 Ma, something not considered by Friend and Kinny (1995). Using an incremental CA-ID-TIMS approach, Crowley et al. (2014) were able to distinguish age clusters at ~2700 Ma and ~2500 Ma, which they interpreted as pertaining to the Badcallian and Inverian respectively. Goodenough et al. (2013) obtained an age of ~2480 Ma from zircons from microgranite sheets with field relationships suggesting they were formed in the Inverian tectonothermal event. While the TIMS approach does not appear able to resolve a tectonothermal event at ~2700 Ma, our age of 2482 ± 6 Ma from the TTG gneisses is very close to that of Goodenough et al. (2013) obtained from granite sheets which suggests this age represents a high-grade tectonothermal event, possibly the Inverian. It is also possible that the high grade metamorphism followed by slow cooling (Johnson and White, 2011) has allowed intragranine Pb diffusion which has obscured the age of the Badcallian event. Further investigation of the process of Pb remobilisation may shed further light on this.

Dating of zircons from the metasedimentary rocks at Sīthean Mor allows the possibility of constraining the timing of their deposition. When using zircons to constrain the depositional ages of
metasedimentary rocks, the youngest core age (interpreted to be detrital) is the maximum depositional age while the oldest rim age (interpreted to be metamorphic) is the minimum depositional age. At Sithean Mor, the youngest core age is 2506±18 Ma and the oldest rim age is 2726±28 Ma. This reversal of the expected pattern – metamorphic rims giving older ages than magmatic cores – indicates that the zircons from the metasedimentary rocks have had their Pb isotope systematics reset as well as those in the TTG gneisses. As a result, it is not possible to constrain the timing of deposition of the metasedimentary rocks at Sithean Mor. Goodenough et al. (2013) had a similar outcome from their attempts to date zircons from a different outcrop of metasedimentary rocks elsewhere in the Assynt Terrane.

REE profiling can enable zircon U-Pb ages to be linked to major metamorphic indicator minerals in the host rocks (e.g. Rubatto, 2002; Whitehouse and Platt, 2003; Kelly and Harley, 2005; Harley and Kelly, 2007). However, the TTG gneisses in this study showed limited variation in their REE profiles (Fig. 6) and together with the resetting of Pb isotope systematics this made it difficult to link ages to metamorphic minerals. In the metasedimentary rocks, low Yb/Gd ratios indicated that zircon had re-equilibrated in the presence of garnet, or a garnet-bearing partial melt, likely during partial melting in the Badcallian (Zirkler et al., 2012) but this occurred in all CL zoning categories, not just metamorphic rims as would be expected.

Ultimately, it is difficult to confidently assign zircon U-Pb ages from this study to magmatic or metamorphic events due to the resetting of Pb isotope systematics. Friend and Kinny (1995) and Whitehouse and Kemp (2010) referred to major and heterogeneous Pb-loss but the mechanism behind this phenomenon is elusive. MacDonald et al. (2013) conducted Electron Backscatter Diffraction analysis on the zircon population in this study; they found that very few zircons had lattice distortion which can facilitate element movement and those that did were not included in this study. Metamict zircons were not analysed in this study.

Although several metamorphic events can be recognised in the Assynt terrane of the Lewesian Gneiss Complex on the basis of field evidence, it is evident from our dataset – and from that of Whitehouse and Kemp (2010) – that these events cannot be recognised in the zircon age systematics of the TTG gneisses through SIMS analysis. Recent work by Crowley et al. (2014) using TIMS rather than SIMS was able to distinguish age populations, which were attributed to the Badcallian and Inverian events. However, the phase equilibria modelling of Zirkler et al. (2012) gave a temperature estimate of only 520–550 °C for the Inverian, although they acknowledge this may not be the peak temperature. This is still well below temperatures (∼750–800 °C) considered to enable zircon to equilibrate with its surroundings (e.g. Hoskin and Schaltegger, 2003) suggesting the Inverian event may have been too cold to be recorded in zircon systematics. While Friend and Kinny (1995) favoured an age of ∼2500 Ma for the granulate-facies Badcallian tectonothermal event, Crowley et al. (2014) indisputably showed evidence for a major event recorded in zircon U-Pb systematics at ∼2700 Ma. Field evidence for two granulate-facies events is not present but Whitehouse and Kemp (2010) also suggested this as a possibility. Direct dating of metamorphic minerals or magmatic rocks that can be linked directly to tectonothermal events may in future provide definitive ages.

4.3. Ti-in-zircon thermometry

Several previous studies have attempted to constrain the thermal history of the Assynt Terrane using a variety of palaeothermometers (e.g. O’Hara and Warwood, 1978; Savage and Sills, 1980; Barnicoat, 1987; Sills and Rollinson, 1987). In this study, we apply the relatively new Ti-in-zircon thermometer (Watson et al., 2006). SIMS spot measurement of Ti concentration in zircon offers the possibility of determining the crystallisation temperature of magmatic cores and metamorphic rims, and therefore potentially the temperatures of the Lewesian protolith formation and subsequent metamorphic events. Ti content in zircon is proportional to the crystallisation temperature; this forms the basis of the Ti-in-zircon geothermometer derived by Watson et al. (2006). As the metamorphic conditions of the Inverian (520–550 °C, although potentially not peak temperature (Zirkler et al., 2012)) and Laxfordian (510–660 °C (Droop et al., 1999)) tectonothermal events are too low to be recorded in zircon trace element chemistry (e.g. Hoskin and Schaltegger, 2003), it is considered here that Ti-in-zircon thermometry will record minimum temperatures of the TTG protolith crystallisation and/or Badcallian metamorphism.

The accuracy of the temperatures calculated with the Ti-in-zircon thermometer is controlled by TiO2 – the presence of rutile in the rock indicates that TiO2 = 1 and Ti content in zircon formed with the rutile is buffered. In this situation, the calculated temperatures will be accurate. However, Ferry and Watson (2007) calibrated the thermometer equation to take into account sub-unity TiO2; the lowest temperatures are calculated if zircon is assumed to be in equilibrium with rutile (TiO2 = 1) while temperature increases as TiO2 decreases. If there is no rutile present during zircon crystallisation, the system is not buffered and the calculated temperature will be a minimum. Rutile has been reported in felsic intrusive sheets (Rollinson, 1979, 1980) and some metasedimentary rocks (e.g. Zirkler et al., 2012) in the Assynt Terrane, but these rock compositions have not been studied in this contribution. Only sample JM09/SM09 (typical pristine Badcallian granulite-facies gneiss with granoblastic texture and an opt+ cpx+ plag + qtz assemblage) has rutile in its mineral assemblage, allowing the assumption of TiO2 = 1 during metamorphic zircon equilibration. As all the other samples in this study lack rutile the calculated zircon-Ti temperatures are minima.

In the TTG gneisses, the calculated minimum temperature range is 710–834 °C but the majority are ∼780–800 °C (Table 4 and Fig. 7). There is no clear distinction in minimum temperature between magmatic cores and metamorphic rims (Fig. 7). This could be explained in three ways: (1) Ti distribution between cores and rims was unaffected by the Badcallian metamorphism; (2) magmatic crystallisation temperatures from zircon cores were overprinted during Badcallian metamorphism, or (3) cores represent minimum magmatic crystallisation temperatures and rims represent Badcallian metamorphic temperatures. The first scenario is unlikely as zircon rims are interpreted to have grown from anatectic melt during the Badcallian and so should record minimum Badcallian temperatures. The second scenario is also unlikely as fine CL zoning is preserved in many magmatic cores; Cherniak and Watson (2007) showed that higher temperatures and longer timescales are required to initiate diffusion of Ti than REEs such as Dy which precludes this hypothesis. We therefore interpret that despite the overlapping temperature ranges the cores represent minimum magmatic crystallisation temperatures (710–834 °C) and rims represent minimum Badcallian metamorphic temperatures (769–841 °C). The fact that core-rim textures are preserved in CL indicates temperature–time conditions were not sufficient to remodelise CL-controlling REEs. As remobilisation of Ti requires higher temperatures and longer timescales (Cherniak and Watson, 2007), the Ti in the zircon cores is interpreted not to have been remodelised and therefore still records minimum protolith crystallisation temperatures. Typical modern tonalites crystallise over a wide temperature range of ∼700–1100 °C (e.g. Lambert and Wyllie, 1974; Shimura et al., 1992; Ishihara, 2005; Harrison et al., 2007) so the temperatures from cores fall within this range. The recent peak Badcallian temperature estimate by Johnson and White (2011) of 875–975 °C based on phase equilibria modelling of granulite-facies
Table 4
Ti-in-zircon minimum temperatures calculated using the thermometer of Watson et al. (2006). CL zoning pattern identifiers as Table 2.

| Sample/spot | Cl zoning pattern | Ti (ppm) | $T$ (°C) at $f_{H_2O} = 1$ | $2\sigma$ |
|-------------|-------------------|----------|--------------------------|----------|
| JM09/BP02   |                   |          |                          |          |
| GMBP02Z1-1  | h                 | 15.43    | 788                      | 28       |
| GMBP02Z2-1  | h                 | 15.90    | 791                      | 28       |
| GMBP02Z2-2  | r                 | 17.75    | 803                      | 30       |
| GMBP02Z2-2  | r                 | 16.89    | 798                      | 29       |
| JM09/BP02 average |       |          |                          | 795      |
| JM09/BP01   |                   |          |                          |          |
| BP01Z1-1    | r                 | 18.66    | 808                      | 30       |
| GMBP01Z1-1  | r                 | 14.53    | 782                      | 27       |
| JM09/BP01 average |       |          |                          | 795      |
| JM09/BP06   |                   |          |                          |          |
| BP06ChZ2-1  | r (br)            | 17.13    | 799                      | 29       |
| BP06ChZ2-2  | c (ozp)           | 14.64    | 783                      | 27       |
| BP06ChZ2-2  | c (ozp)           | 15.84    | 791                      | 28       |
| BP06ChZ2-2  | c (ozp)           | 14.53    | 782                      | 27       |
| BP06ChZ2-3  | r                | 18.16    | 805                      | 30       |
| BP06ChZ2-6  | r (dr)            | 19.42    | 812                      | 31       |
| BP06ChZ2-7  | r                 | 12.15    | 765                      | 26       |
| BP06ChZ2-9  | r (dr)            | 17.58    | 802                      | 30       |
| BP06Z3-1    | r                 | 12.61    | 768                      | 26       |
| BP06Z3-2    | r                 | 16.84    | 797                      | 29       |
| BP06Z3-3    | r                 | 10.52    | 751                      | 24       |
| BP06Z3-4    | r                 | 14.23    | 780                      | 27       |
| BP06Z3-5    | r                 | 14.81    | 784                      | 28       |
| GMBP06Z1-1  | r (br)            | 18.62    | 808                      | 30       |
| GMBP06Z1-2  | r (br)            | 17.87    | 804                      | 30       |
| GMBP06Z1-3  | c (bc)            | 15.66    | 790                      | 28       |
| GMBP06Z2-1  | r (emb)           | 16.72    | 797                      | 29       |
| GMBP06Z2-2  | c (ozp)           | 18.75    | 809                      | 30       |
| GMBP06Z2-3  | r (br)            | 15.39    | 788                      | 28       |
| GMBP06Z2-3  | r (br)            | 14.84    | 784                      | 28       |
| GMBP06Z3-3  | c (dc)            | 16.38    | 794                      | 29       |
| GMBP06Z4-1  | r                 | 15.00    | 785                      | 28       |
| GMBP06Z5-1  | c (bc)            | 15.78    | 791                      | 28       |
| GMBP06Z6-3  | c (bc)            | 13.78    | 777                      | 27       |
| GMBP06Z6-4  | r                 | 14.48    | 782                      | 27       |
| GMBP06Z6-5  | r (br)            | 15.83    | 791                      | 28       |
| GMBP06Z5-2  | c (dc)            | 14.60    | 783                      | 27       |
| GMBP06Z6-1  | r                 | 23.72    | 834                      | 33       |
| JM09/BP06 average |       |          |                          | 791      |
| JM09/BP04   |                   |          |                          |          |
| GMBP04Z1-1  | r (br)            | 17.26    | 800                      | 29       |
| GMBP04Z2-1  | r (br)            | 18.30    | 806                      | 30       |
| GMBP04Z2-1  | r (br)            | 16.95    | 798                      | 29       |
| GMBP04Z2-2  | r (br)            | 11.89    | 762                      | 25       |
| GMBP04Z2-3  | c (bc)            | 16.13    | 793                      | 29       |
| GMBP04Z2-3  | c (bc)            | 16.25    | 794                      | 29       |
| GMBP04Z2-4  | r (br)            | 13.81    | 777                      | 27       |
| GMBP04Z2-4  | r (br)            | 14.81    | 784                      | 28       |
| GMBP04Z2-4  | c (dc)            | 8.58     | 732                      | 22       |
| GMBP04Z2-5  | h                 | 17.10    | 799                      | 29       |
| GMBP04Z2-5  | h                 | 17.30    | 800                      | 29       |
| GMBP04Z2-6  | r (br)            | 18.91    | 809                      | 30       |
| GMBP04Z2-6  | c (ozp)           | 19.13    | 811                      | 31       |
| GMBP04Z2-7  | h                 | 21.06    | 821                      | 32       |
| GMBP04Z2-7  | h                 | 18.59    | 808                      | 30       |
| GMBP04Z2-7  | h                 | 20.74    | 819                      | 32       |
| GMBP04Z2-8  | h                 | 19.12    | 811                      | 31       |
| GMBP04Z2-8  | h                 | 16.61    | 796                      | 29       |
| GMBP04Z6-1  | h                 | 16.60    | 796                      | 29       |
| GMBP04Z9-2  | h                 | 14.82    | 784                      | 28       |
| JM09/BP04 average |       |          |                          | 795      |
| JM09/DP03   |                   |          |                          |          |
| GMDP03Z1-1  | r (br)            | 13.09    | 772                      | 26       |
| GMDP03Z1-2  | r (br)            | 12.66    | 769                      | 26       |
| GMDP03Z1-3  | c (ozp)           | 6.71     | 710                      | 20       |
| GMDP03Z1-4  | r (br)            | 14.07    | 779                      | 27       |
| GMDP03Z1-5  | r (br)            | 13.03    | 771                      | 26       |
| GMDP03Z2-1  | c (ozp)           | 19.64    | 813                      | 31       |
| DP03Z2-1    | h                 | 19.41    | 812                      | 31       |
| JM09/DP03 average |       |          |                          | 775      |
Table 4 (Continued)

| Sample/spot | CL zoning pattern | Ti (ppm) | $T$ (°C) at $\alpha_{TiO_2} = 1$ | $2\sigma$ |
|-------------|-------------------|----------|--------------------------------|---------|
| JM09/DP01-1 | h                 | 17.78    | 803                            | 30      |
| DP0124-2    | h                 | 16.39    | 794                            | 29      |
| DP0126-1    | r (br)            | 17.14    | 799                            | 29      |
| DP0126-2    | r (br)            | 15.90    | 791                            | 28      |
| DP0126-3    | c (dc)            | 15.09    | 786                            | 28      |
| DP0126-4    | r (br)            | 17.78    | 803                            | 30      |
| DP0126-5    | r (br)            | 18.59    | 808                            | 30      |
| DP01210-1   | r (br)            | 20.28    | 817                            | 31      |
| DP01210-2   | r (br)            | 19.81    | 814                            | 31      |
| GM0122-2    | c (dc)            | 14.87    | 785                            | 28      |
| GM0122-4    | c (dc)            | 14.15    | 780                            | 27      |
| GM0122-5    | r (br)            | 15.15    | 786                            | 28      |
| GM0123-3    | h                 | 20.75    | 819                            | 32      |
| GM0124-1    | h                 | 9.95     | 745                            | 24      |
| GM0124-2    | h                 | 12.78    | 769                            | 26      |
| GM0125-1    | c (dc)            | 10.81    | 753                            | 24      |
| GM0125-2    | r (br)            | 17.20    | 800                            | 29      |
| GM0126-1    | r (br)            | 13.70    | 776                            | 27      |
| GM0126-2    | r (br)            | 14.19    | 780                            | 27      |
| GM0126-3    | c (dc)            | 13.87    | 778                            | 27      |
| GM0127-1    | h                 | 19.31    | 812                            | 31      |
| GM0128-1    | r (br)            | 15.34    | 788                            | 28      |
| GM0129-3    | r                 | 13.42    | 774                            | 27      |
| JM09/DP01 average |             |          | 787                            | 28      |
| Average all TTG |             |          | 790                            |         |
| JM08/22    | c (ozp)           | 21.31    | 822                            | 32      |
| GM2221-1    | c (bc)            | 19.97    | 815                            | 31      |
| GM2221-2    | c (ozp)           | 22.97    | 830                            | 33      |
| GM2222-1    | c (ozp)           | 19.39    | 812                            | 31      |
| GM2223-1    | c (ozp)           | 19.84    | 815                            | 31      |
| JM08/22 average |             |          | 819                            | 32      |
| JM08/23    | ir                | 17.80    | 803                            | 30      |
| GM2321-1    | ir                | 19.54    | 813                            | 31      |
| GM2322-1    | ir                | 24.39    | 837                            | 34      |
| GM2324-1    | r (br)            | 24.32    | 837                            | 34      |
| GM2324-2    | r (br)            | 25.19    | 841                            | 34      |
| GM2325-1    | h                 | 20.55    | 818                            | 31      |
| GM2325-2    | h                 | 17.94    | 804                            | 30      |
| GM2326-1    | h                 | 26.69    | 847                            | 35      |
| GM2326-2    | ir                | 22.06    | 826                            | 32      |
| GM2326-3    | ir                | 24.48    | 838                            | 34      |
| JM08/23 average |             |          | 826                            | 32      |
| Average all metasediments |          |          | 823                            |         |

assemblages in mafic gneiss is higher than the range of Ti temperatures from metamorphic rims but as these Ti-temperatures are minima, the results are at least consistent with granulite metamorphic conditions. In addition, Roberts and Finger (1997) showed that zircon would grow or recrystallize after peak metamorphism in granulite-facies gneiss. The fact that the zircon temperatures in this study are slightly lower than the peak metamorphic assemblage temperatures calculated by Johnson and White (2011) is in accord with this phenomenon. This suggests that the Ti-in-zircon thermometer could be recording a post-peak Badcalladian temperature.

Zircon from the metasedimentary rocks at Sithean Mor records higher Ti-in-zircon temperatures than from the TTG gneisses from Badcall Point and Duartmore Point. At $\alpha_{TiO_2} = 1$, the average temperature is 823 °C compared to 790 °C in the TTG gneisses and the minimum recorded temperature from Sithean Mor of 803 °C is much higher than the lowest from the TTG gneisses (710 °C) (Table 4 and Fig. 7). Cores with magmatic CL patterns are interpreted to be detrital and have an average minimum temperature of 820 °C, higher than magmatic cores from the TTG gneisses. As the metasedimentary rocks are interpreted to predate the TTG gneisses (Rollinson and Gravestock, 2012), this temperature is tentatively interpreted to represent zircon crystallisation in a pre-Lewisian rock. The two zircons with convincing metamorphic rims yield an average temperature of 839 °C, lower than the temperature estimate of Johnson and White (2011) for peak Badcallian metamorphism but at least consistent with granulite conditions for zircon rim equilibration. The higher minimum temperature for Badcallian metamorphism calculated from these zircons relative to those in the TTG gneisses is interpreted to reflect greater availability of Ti.

4.4. Overall history of the Assynt Terrane

This contribution has sought to determine the chronological and thermal histories of the Assynt Terrane of the Lewisian Gneiss Complex. A single study cannot provide a complete picture of this and so in this section we place our results in the context of previous work to construct an overall temperature–time history of the Assynt Terrane during Archaean to Palaeoproterozoic times (Table 5). A key remaining issue in the history of the Assynt Terrane is the absolute age of the Badcalladian tectono thermal event. Initial U-Pb zircon
Table 5
Summary table of the temperature-time history of the Assynt Terrane combining data from this study and previously published work.

| Event                                      | Timing                           | Temperature                      |
|--------------------------------------------|----------------------------------|----------------------------------|
| TTG protolith formation                    | 2958 ± 7 Ma (this study), 2960–3030 Ma (Friend and Kinny, 1995), ~2843 Ma (Goodenough et al., 2013), ~2850 Ma (Whitehouse and Kemp, 2010), all from U-Pb zircon dating | Minimum 710–834 °C (this study) from Ti-in-zircon thermometry |
| Badcallian tectothermal event              | 2482 ± 6 Ma (this study), ~2500 Ma (Friend and Kinny, 1995) or ~2700 Ma (Corfu et al., 1994; Whitehouse and Kemp, 2010; Crowley et al., 2014), all from TTG gneisses, all from U-Pb zircon dating | Minimum 769–841 °C (this study) from Ti-in-zircon thermometry, ~875–975 °C (Johnson and White, 2011) from TTG gneisses, >900 °C (Zirkler et al., 2012) from metasedimentary rocks, both from mineral equilibria modelling |
| Inverian tectothermal event                | 2482 ± 6 Ma (this study), ~2480 Ma (Corfu et al., 1994; Goodenough et al., 2013) from microgranite sheets/pegmatite, ~2500 Ma (Corfu et al., 1994; Whitehouse and Kemp, 2010; Crowley et al., 2014) from TTG gneisses, all from U-Pb zircon dating | ~520–550 °C (Zirkler et al., 2012) from mineral equilibria modelling of metasedimentary rocks but not necessarily peak metamorphism, ~600 °C (Sills, 1981) from ion-exchange thermometers on TTG gneisses |
| Intrusion of Scourie Dyke Swarm            | ~2418–2375 Ma (Davies and Heaman, 2014) from U-Pb dating of zircon and baddeleyite | No absolute estimates |
| Arc magmatism                              | ~1880 Ma (Goodenough et al., 2013) from U-Pb zircon dating of alkaline granites | No absolute estimates |
| Laxfordian tectothermal event              | ~1790–1670 Ma (Corfu et al., 1994; Kinny et al., 2005), from U-Pb dating of zircon and titanite in TTG gneisses | ~530–630 °C (Droop et al., 1999) from ion exchange thermometry on the Loch Maree Group in southern LGC (not in Assynt Terrane) |

dating by Corfu et al. (1994) suggested it occurred at ~2710 Ma but ion microprobe dating by Friend and Kinny (1995) led them to interpret it occurred at ~2500 Ma. A novel approach of sequential CA-ID-TIMS zircon U-Pb dating by Crowley et al. (2014) has recently indicated there is a high-grade metamorphic event at ~2700 Ma which they have attributed to the Badcallian. Furthermore, an age of ~2480 Ma was obtained for microgranite sheets with field relationships indicating they were formed in the Inverian tectothermal event (Goodenough et al., 2013). Similarly, Corfu et al. (1994) dated a pegmatite cross-cut by a Scourie Dyke at ~2480 Ma. This would suggest that the ~2500 Ma age from the TTG gneisses interpreted by Friend and Kinny (1995) to be the Badcallian is actually the Inverian. However, it should be noted that the temperature estimate from a mineral assemblage interpreted to be Inverian in age by Zirkler et al. (2012) of 520–550 °C is well below the closure temperature of the U-Pb system in zircon (Cherniak and Watson, 2001). It is therefore possible that a second high-grade, potentially granulite-facies, tectothermal event occurred at ~2500 Ma, although there is no field evidence for this. Alternatively, the mineral assemblage analysed by Zirkler et al. (2012) may not in fact be peak-Inverian. It seems likely that the most effective way to date the Badcallian event will be to date magmatic rocks that are clearly associated with this event, rather than attempting further to identify metamorphic ages in the complex TTG gneisses.

5. Conclusions

Zircons from a range of TTG gneisses and metasedimentary rocks from the Assynt Terrane, a significant part of the Precambrian Lewisian Gneiss Complex of Northwest Scotland, have been analysed for U-Th-Pb and Ti, with the intention of constraining the temperature-time history. This contribution has presented the first application of Ti-in-zircon thermometry (Watson et al., 2006) to the Lewisian. Furthermore, analysis of these trace elements and isotopes in the context of field and petrographic characterisation and zircon cathodoluminescence imaging/REE profiling of internal chemical zoning has raised the following key points about the history of the Assynt Terrane:

- The oldest three cores yield a mean age of 2958 ± 7 Ma (MSWD = 1.00, probability = 0.37). This is older than the magmatic protolith ages interpreted by Whitehouse and Kemp (2010) and Crowley et al. (2014) but is close to that derived by Friend and Kinny (1995) for the formation of the protolith to the Assynt Terrane.
- A high-grade tectothermal event occurred at 2482 ± 6 Ma. This age is very close to the age of 2480 Ma obtained by Goodenough et al. (2013) from granite sheets that have field relationships indicating they are Inverian in age. However, the best available temperature estimate for the Inverian tectothermal event (520–550 °C Zirkler et al., 2012) is below the temperature at which zircon trace element systems are likely to be reset. We recognise a spread of concordant ages from the protolith crystallisation age of 2958 ± 7 Ma to 2482 ± 6 Ma, which are likely to encompass the Badcallian and Inverian metamorphic events. It remains possible that there were two granite-facies tectothermal events at ~2700 Ma and ~2500 Ma. It is clear that resolving the ages of these events by SIMS is difficult within these complex zircon systematics (as recognised by Whitehouse and Kemp (2010)), but identification of associated magmatism or novel approaches such as that of Crowley et al. (2014) will lead to this.
- Zircons in the metasedimentary rocks have relatively flat chondrite-normalised heavy REE profiles (low Yb/Gd ratios), which suggest they equilibrated with Badcallian metamorphic garnet. However, a range of U-Pb ages are recorded in these zircons and therefore a definitive age for the Badcallian cannot be determined from these zircons.
- Ti-in-zircon thermometry (Watson et al., 2006) records temperatures of 710–834 °C for zircon cores in the TTG gneisses, interpreted to record the minimum crystallisation temperature of the magmatic protolith. Zircon rims record minimum temperatures of 769–841 °C, interpreted to represent minimum temperatures for Badcallian metamorphism and post-peak Badcallian anatectic zircon growth.
- Zircons in the metasedimentary rocks record generally higher minimum temperatures, with an average of 823 °C compared to 790 °C in the TTG gneisses. The zircon cores in the metasedimentary rocks are interpreted to be detrital and the calculated temperatures are interpreted to record zircon crystallisation in a magmatic protolith that predates the Lewisian Gneiss Complex. Zircon rims record temperatures that are lower than the estimates of Johnson and White (2011) for peak Badcallian metamorphism but are consistent with metamorphism of the sediments under granulite facies conditions in that event.
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