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Late Precambrian U–Pb titanite age for peak regional metamorphism and deformation (Knoydartian orogeny) in the western Moine, Scotland

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Abstract: There has been controversy over the number and timing of orogenies in the Precambrian Moine block in the Scottish Caledonides since the earliest radiometric dating in the 1960s. This work challenges a recent hypothesis, that this sector of the Laurentian margin was subjected to continuous crustal extension between >900 and 470 Ma. U–Pb dating (thermal ionization mass spectrometry) of titanite from a calc-silicate pod in the Moine (Morar Group) of the western Highlands gives an age of 737 ± 5 Ma. The titanite grew from Fe–Ti-bearing detrital minerals during the main progressive, syn-D_2, amphibolite-facies (sillimanite zone) regional metamorphism, thus demonstrating that a Neoproterozoic contractional tectonothermal event (Knoydartian orogeny) affected the Moine block following the rift-related emplacement of the West Highland granite gneiss at 873 Ma. We conclude that the Sgurr Beag Thrust, a major tectonic break separating the Morar and Glenfinnan groups of the Moine, is mainly of Neoproterozoic, not Caledonian, age. The early tectonothermal event was succeeded by the Grampian Phase (Caledonian orogeny) at 460–470 Ma.

Keywords: Caledonides, Moine, U–Pb, absolute age, titanite.

A major problem in studying the tectonic evolution of Precambrian crustal blocks lies in demonstrating whether the many structural and metamorphic events that have been identified belong to a single orogeny, or to two or more superimposed orogenies. A classical example of this dilemma is provided by the Neoproterozoic Moine block in the Caledonides of western Scotland (Fig. 1), where pioneering radiometric dating in the 1960s appeared to demonstrate the presence of a Precambrian orogeny at >700 Ma (Giletti *et al*. 1961; Long & Lambert 1963), overprinted by a much younger Caledonian orogenic event. This model was considerably refined during the 1980s (Piasecki & van Breemen 1983; Barr *et al*. 1985, 1986; Roberts *et al*. 1987), but more recent work has led to an apparently irreconcilable difference of opinion between those who support this hypothesis (Bluck *et al*. 1997; Vance *et al*. 1998; Bluck 2000, 2001), and those who contend that all of the regionally important structural and metamorphic events that have affected the Moine are of early Ordovician (*c*. 470 Ma) age (Soper & England 1995; Soper & Harris 1997; Soper *et al*. 1999; Dalziel & Soper 2001).

To break this impasse we report a U–Pb age for titanite grains, which are shown here to have grown in small bodies of calc-silicate in the Moine metasediments, during amphibolite-facies regional metamorphism. Growth of titanite took place during the metamorphic climax in rocks from the kyanite and sillimanite (Barrovian) zones. It occurred at about the time of the second deformation (D_2), and contemporaneous with the initiation of a major ductile fault, the Sgurr Beag Thrust (Powell *et al*. 1981).

Geological setting: the Moine rocks of the western Highlands

The Moine Supergroup consists of a thick (>10 km) sequence of highly deformed and metamorphosed psammite, semi-pelite and pelite, which occurs NW of the Great Glen Fault (Fig. 1). The Supergroup is divided into three major lithostratigraphical units: the Morar, Glenfinnan and Loch Eil groups (Johnstone *et al*. 1969; Holdsworth *et al*. 1994) (Fig. 2). Soper *et al*. (1998), building on earlier work by Strachan (1986) and Glendinning (1988), have proposed that the Moine sequence was deposited in a pair of contiguous NNE-trending half-graben that faced to the SE.

The basal member of the Moine Supergroup has traditionally been taken to be the conglomerate found in contact with the Lewisian-like rocks along the western side of the Glenelg–Attadale inlier (Clough, in Peach *et al*. 1910; Ramsay 1958). If this interpretation is correct, then the Sm–Nd garnet–whole-rock ages of *c*. 1000 Ma obtained from the basement rocks at Glenelg by Sanders *et al*. (1984) provide a maximum age for the onset of Moine deposition. Although Temperley & Windley (1997) interpreted all of the contacts between the Moine and Lewisian as being extensional detachments, J. G. Ramsay (pers. comm. 2001) has recently confirmed the unconformable basement–cover relationship between the Western Lewisian and the westernmost Moine in the Glenelg area.

Evidence for a *c*. 1000 Ma event in the Moine basement at Glenelg is compatible with U–Pb ages on detrital zircons from the Morar Group in the western Highlands of 1032–2713 Ma (Friend *et al*. 2003), and of 947–1889 Ma from the Loch Eil–Glenfinnan groups in the same area (including inherited grains present in the West Highland granite gneiss (Friend *et al*. 1997, 2003). Only six grains dated in these studies have ages of <1000 Ma. The top of the Moine sequence is not seen, and correlation with rocks south of the Great Glen Fault, such as the ‘Central Highland Complex’ (Piasecki 1980) or ‘basement rocks’ (Smith *et al*. 1999) is not proven.

The Morar Group is carried by the Moine Thrust, and is separated from the structurally overlying Glenfinnan and Loch Eil groups by the Sgurr Beag Thrust (Figs 2 and 3) (Tanner *et al*. 1970; Tanner 1971).

In the western Highlands the entire Moine sequence has been affected by three main phases of deformation (D_1–D_3) (Powell 1974; Baird 1982); later deformation (D_4) resulted in the formation of some large folds but these are of more localized

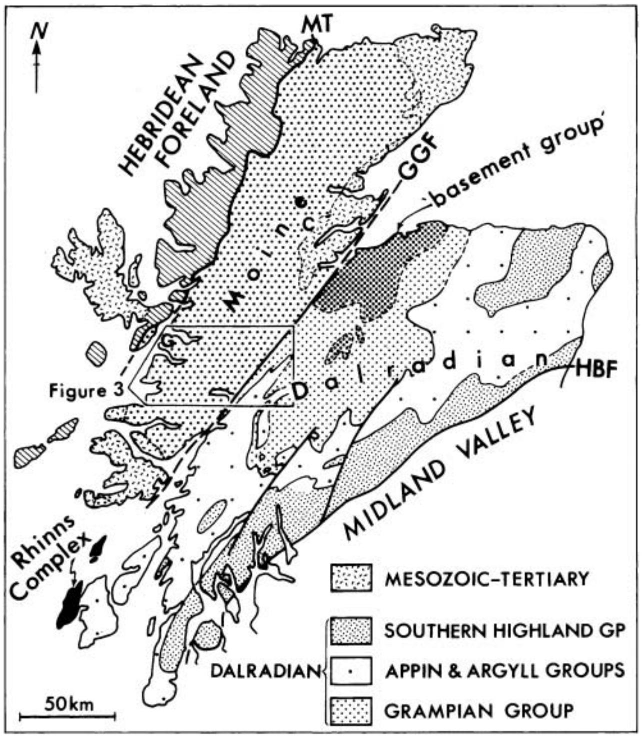

Fig. 1. Outline geological map showing the location of the main Precambrian blocks in Scotland (after Tanner & Bluck 1999). The 'Moine block' includes inliers of Lewisian and Lewisian-like rocks; the location of one of these at Glenelg is indicated (G). C, Carn Chuinneag; GGF, Great Glen Fault; HBF, Highland Boundary Fault; MT, Moine Thrust. The outcrop labelled 'Rhinns Complex' includes the Colonsay Group. Inset shows the location of Figure 3.

LOCH EIL GROUP GLENFINNAN GROUP		Sgurr Beag Nappe
	Sgurr Beag Thrust	
MORAR GROUP	Upper Morar Psammite Morar Pelite § Lower Morar Psammite Basal Pelite and local conglomerate	Moine Nappe

Fig. 2. Outline stratigraphy of the Moine Supergroup in the western Highlands of Scotland.

occurrence. It has been long considered that $D_1 + D_2$ in the Moine are of Precambrian age (Holdsworth & Roberts 1984), with D_3 as the main Caledonian (now Grampian) reworking event.

Regional metamorphism affecting the Moine ranges from greenschist to upper amphibolite facies, with widespread migmatization affecting the eastern part of the outcrop. The regional metamorphic peak was reached during the D_2 event (MacQueen & Powell 1977). Barrovian index minerals in pelites, such as kyanite and staurolite, are rare, and the mapping of isograds is largely dependent upon the mineral assemblages found in thin layers of calcareous psammite (calc-silicate pods) (Kennedy 1949; Winchester 1974; Tanner 1976; Fettes 1979).

Moine pegmatites

These pegmatites played a key role in early attempts to obtain a minimum age for the polyphase deformation and metamorphism that have affected the Moine. Giletti *et al*. (1961) and Long & Lambert (1963) obtained the first Precambrian ages of around 740 Ma from the Moine by Rb–Sr dating of large (up to 30 cm across) muscovite crystals from pegmatites from the Knoydart mica mine (location A, Fig. 3), Sgurr Breac and Loch Eilt (both shown in Fig. 3). These results fostered the conclusion that the rocks had been affected by a 'Knoydartian' (Bowes 1968), or 'Morarian' (Lambert 1969), orogenic event.

U–Pb dating of zircon from the Loch Eilt pegmatite (Fig. 4) subsequently yielded an age of 740 ± 30 Ma, which was concordant with a Rb–Sr muscovite age of 730 ± 5 Ma (van Breemen *et al*. 1974, 1978). U–Pb dating of zircon and monazite from the Sgurr Breac pegmatite (location B, Fig. 3) gave older ages of 770–815 Ma (van Breemen *et al*. 1974), confirmed by a more recent U–Pb (monazite) age of 784 ± 1 Ma (Rogers *et al*. 1998). A similar discordant pattern is seen in the Ardnish pegmatite (Fig. 4). Powell *et al*. (1983) reported Rb–Sr muscovite ages of 746–776 Ma, whereas U–Pb dating of monazite from the same pegmatite has given a considerably older age of 827 ± 2 Ma (Rogers *et al*. 1998). In addition, Piasecki & van Breemen (1983) reported *c*. 750 Ma Rb–Sr ages on muscovite books from pegmatitic segregations in shear zones from a number of localities in the Central Highlands, and in the western Moine at Kinloch Hourn.

The above pegmatites and muscovite-bearing segregations are all deformed but there is a dispute over their structural age. One group of workers argues that they were intruded after the country rocks had been deformed for the first time (Powell *et al*. 1983; Rogers *et al*. 1998; Bluck 2000, 2001), and hence provide a minimum age for an early (>750 Ma) orogenic event in the Moine, whereas Soper & Harris (1997) consider that the pegmatites formed in an extensional regime, and conclude that the 750 Ma ages have been partially reset from original *c*. 870 Ma ages.

Younger pegmatites, which give both Rb–Sr and U–Pb (zircon and monazite) ages of *c*. 445–470 Ma, are also found at Loch Eilt (van Breemen *et al*. 1974).

West Highland granite gneiss

An important feature of the western Moine is the West Highland granite gneiss (Dalziel & Soper 2001, and references therein). It consists of a deformed and metamorphosed complex of granitic sheets or sills, known locally as the Ardgour Gneiss, Fort Augustus Gneiss, etc., which are broadly concordant with the regional stratigraphy, and occur at about the Glenfinnan–Loch Eil boundary (Fig. 3). The complex can be traced intermittently for *c*. 80 km across the western Moine, with individual bodies reaching 5 km across. It is thought to have originated as a series of anatectic granites formed by the partial melting of Moinian rocks (see Barr *et al*. 1985, for summary and discussion).

Early attempts to date these intrusions using the Rb–Sr whole-rock isochron method gave ages around 1000 Ma (Brook *et al*. 1976). Together with Rb–Sr isochrons yielding *c*. 1000 Ma ages from the country rocks, these results were interpreted as evidence that the Grenville orogeny had affected the Moine rocks (Brook *et al*. 1977; Brewer *et al*. 1979; Roberts *et al*. 1987). However,

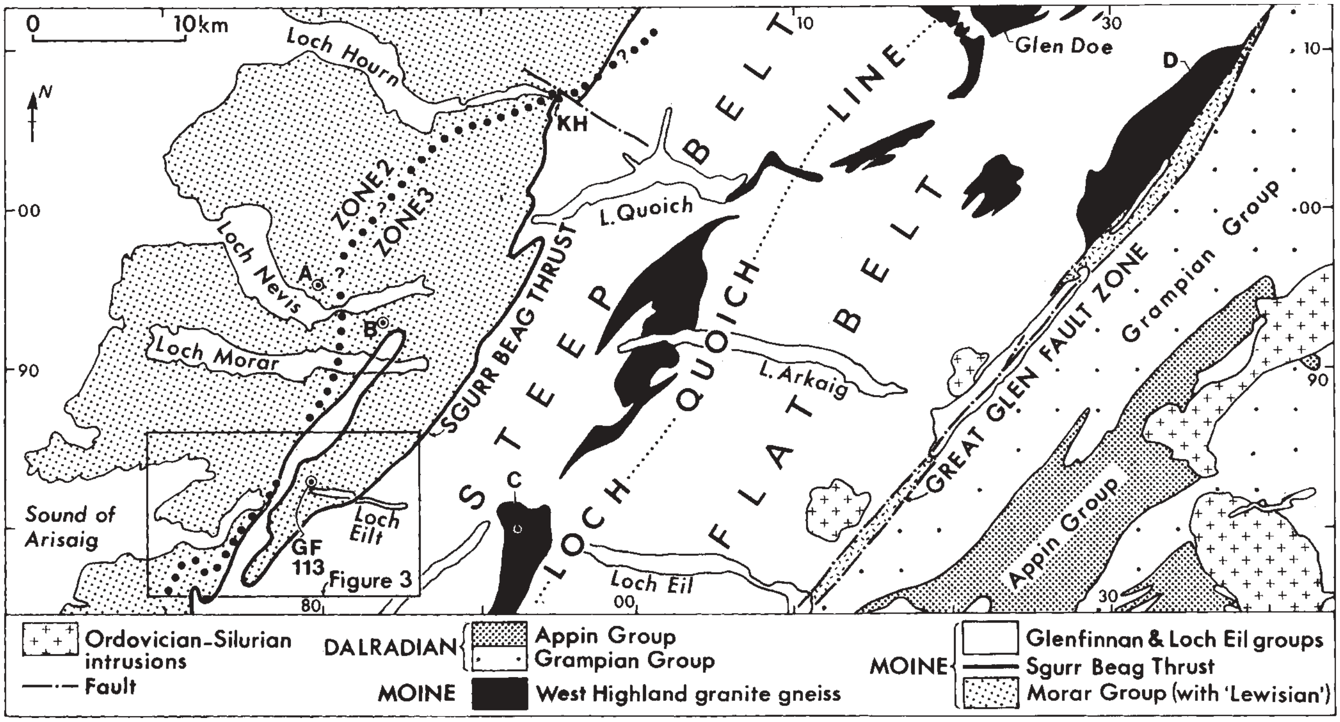

Fig. 3. Geology of part of the western Highlands of Scotland. The line marked by large filled circles separates Zones 2 and 3 defined by regional metamorphic calc-silicate assemblages. The location of analysed sample GF 113 is shown. Other locations of radiometrically dated rocks are: A, Knoydart mica mine; B, Sgurr Breac; C, Fort Augustus granite gneiss; D, Ardgour granite gneiss. (See text for explanation.) KH, Kinloch Hourn.

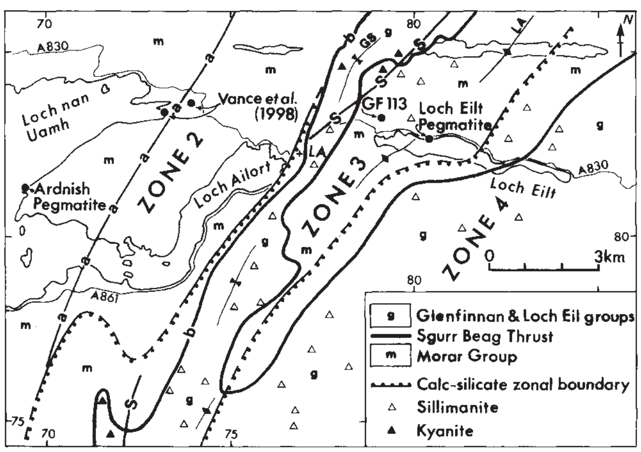

Fig. 4. Outline geological map (after Powell *et al.* 1981; Powell 1988) showing the relationship between metamorphic zones 2–4 defined by calc-silicate assemblages and the distribution of Barrovian index minerals kyanite and sillimanite in pelites. ●, locations of radiometrically dated samples. Line marked by 'a' indicates the western limit of microdiorite intrusions metamorphosed to the amphibolite facies; line marked by 'b' indicates the western outcrop of the Sgurr Beag Thrust, which defines approximately the western limit of regional migmatization; line marked by 'S' indicates sillimanite isograd. The positions of the pair of late folds (GS, Glenshian Syncline; LA, Loch Eilt Antiform) responsible for the repeated outcrop of the Sgurr Beag Thrust are shown schematically.

recent U–Pb studies on single zircon grains from the granite gneiss have yielded a consistent age of *c.* 873 Ma for the igneous protolith at Glenfinnan (location C, Fig. 3; Friend *et al.* 1997) and Fort Augustus (location D, Fig. 3; Rogers *et al.* 2001), and for the associated metagabbro at Glen Doe (Fig. 3; Millar 1999). This date places a secure upper bound on the sedimentation of the Moine but, as with the pegmatites, there is a dichotomy of opinion regarding the structural significance of this date. One school considers the granite protolith was emplaced during a period of crustal extension that preceded any deformation of the country rocks, the other concludes that intrusion postdated orogenesis and high-grade metamorphism of the Moine (Bluck 2001; Dalziel & Soper 2001; Rogers *et al.* 2001).

The 'Caledonian' event in these rocks is represented by a U–Pb titanite age of 470 ± 2 Ma from the West Highland granitic gneiss at Fort Augustus (Rogers *et al.* 2001) and two ages from the granite gneiss at Glenfinnan: a U–Pb monazite age of 455 ± 3 Ma (Aftalion & van Breemen 1980) and a lower intercept U–Pb zircon age of 450 Ma (Friend *et al.* 1997).

Although it is generally agreed that the West Highland granite gneiss and associated dyke-like basic sheets have seen all of the deformation episodes that affected the country rocks (Dalziel & Johnson 1963; Soper & Harris 1997; Millar 1999), two conflicting models have been proposed to explain their tectonic setting: either (1) the granites formed during high-grade regional metamorphism at *c.* 870 Ma, which accompanied the earliest orogenic event to affect the Moine (Friend *et al.* 1997), or (2) they formed during an anorogenic, rift-related event at *c.* 870 Ma, which predated the first contractional orogeny by over 400 Ma (Dalziel & Soper 2001; Ryan & Soper 2001).

The Sgurr Beag Thrust

The Sgurr Beag Thrust (formerly 'Slide') was first recognized at Kinloch Hourn (Fig. 3), where a very thin slice of Lewisianoid rock occurs between the Morar and Glenfinnan groups of the Moine (Tanner 1965, 1971). Correlation south from Kinloch

Hourn into the present study area around Lochailort is less certain because of the absence of the Lewisianoid 'marker' horizon. The criteria for locating the thrust contact at Lochailort are two-fold: the lithostratigraphical correlation of the Morar and Glenfinnan groups in this area with those elsewhere in the western Moine; and the presence at interface between these two groups of steeply inclined zones of highly sheared rocks some hundreds of metres thick (see Rathbone & Harris 1979, fig. 6; Rathbone *et al*. 1983).

Tanner (1971) concluded that movement on the Sgurr Beag Thrust at Kinloch Hourn took place before the peak of the regional metamorphism. This conclusion followed from the observation that metamorphic isograds based on the calc-silicate assemblages appear to cross the line of the Slide (Fig. 3) (Tanner 1976; Fettes 1979, fig. 3), as do swarms of axial planar pegmatites related to the D_2 (not D_3, Powell 1974) Sgurr nan Eugallt fold (Tanner 1971). Subsequently, Powell *et al*. (1981) presented a detailed model to explain the relationship between the calc-silicate isograds and the Thrust, and deduced that thrusting had taken place synchronously with peak (broadly syn-D_2) regional metamorphism. Finally, later workers such as Baird (1982) and Rathbone *et al*. (1983) have concluded that the thrust movement occurred after the metamorphic climax, and is Caledonian in age.

Regional metamorphic pattern

The model erected by Moine workers in the 1980s for the western Moine was of a Pre-Caledonian greenschist- to amphibolite-facies regional metamorphism (I) (Rathbone *et al*. 1983; Roberts *et al*. 1987), associated with Precambrian nappe structures ($D_1 + D_2$) being overprinted by Caledonian deformation accompanied by greenschist- to amphibolite-facies regional metamorphism (II). In this model, ductile thrusting (Sgurr Beag and Knoydart thrusts) occurred during the second amphibolite-facies event, followed by the formation of upright Caledonian D_3 folds. Critical to the recognition of the Caledonian age of the D_3 structures was the observation that the Glen Dessary syenite, dated by U–Pb on unabraded bulk zircon separates at 456 ± 5 Ma by van Breemen *et al*. (1979), cuts the $D_1 + D_2$ structures, but is deformed by D_3 (Roberts *et al*. 1984). Caledonian deformation has resulted in the subdivision of the SW Moine outcrop into a western 'Steep Belt,' characterized by upright D_3 folds, and an eastern 'Flat Belt' with recumbent Precambrian structures (Fig. 3). These two belts are separated by the 'Loch Quoich Line' (Roberts & Harris 1983).

The regional metamorphic scenario presented by these workers does not, however, accord with the sequence of prograde mineral assemblages, and sequence of internal fabrics in garnet porphyroblasts, seen in the western Moine. Study of the calc-silicate assemblages (Tanner 1976; Powell *et al*. 1981) shows that a single, progressive metamorphic event has affected the Morar and Glenfinnan groups between the west coast at Arisaig and the area around Loch Eilt (Figs 3 and 4). Metamorphic grade increases continuously from west to east, with grain size, An content of the plagioclase in the calc-silicate pods, and the morphology of the garnet porphyroblasts and their inclusion patterns, changing in a systematic manner. There is no evidence for the superimposition of two entirely separate high-grade metamorphic regimes either in the calc-silicate rocks or in the associated pelites (MacQueen & Powell 1977). Although appreciating that the superimposition of two amphibolite-facies metamorphisms (I and II) would be difficult to recognize, it would also be extremely fortuitous if the two separate greenschist- to upper amphibolite-facies zonal patterns were in such close agreement that the overprint could pass undetected (Fig. 4). Lack of suitable index minerals combined with subsequent retrogression may, however, have blurred this distinction.

The only direct attempt to date the prograde regional metamorphic assemblages in the western Moine was by Vance *et al*. (1998), who carried out Sm–Nd dating of garnet from the Morar Schists at four localities in the Morar area, including two near Lochailort (Fig. 4). These pelitic schists contain subhedral to euhedral garnet porphyroblasts with internal fabrics and well-defined compositional zoning (Anderson & Olimpio 1977; MacQueen & Powell 1977); all localities lie within Zone 2 of the calc-silicate assemblages. Vance *et al*. (1998) obtained ages of 814–823 Ma from the cores of garnets from all four localities, and 788 ± 4 Ma from the middle zone of a garnet from Polnish (Fig. 4), but were unable to date the narrow outermost garnet zone. By combining the age data with geothermobarometry they concluded that the garnets began growth between D_1 and D_2 at approximately 540 °C and 5 kbar, some 823 Ma ago, with garnet growth continuing for >34 Ma, by which time the temperature had risen to *c*. 700 °C, and pressure to >11 kbar. The results of this work have been criticized by Dalziel & Soper (2001), who implied that the Sm–Nd ratios are a 'chemical artefact', presumably meaning that the analysed garnet fractions have been contaminated by inclusions carrying REE. This criticism was countered by Bluck (2000), who, referring to the unpublished work of Hyslop, pointed out that large muscovites from the Moine similar to those that have yielded *c*. 750 Ma ages (i.e. Piasecki & van Breemen 1983) contain inclusions of regional metamorphic garnet that have a similar chemistry and growth history to the Morar examples.

Evidence of a later metamorphic (?Caledonian) event is possibly seen in retrogression of the Zone 4 calc-silicate assemblages east of the area shown in Fig. 4, where bytownite–anorthite is replaced by andesine (Tanner 1976; Fettes 1979). In addition, gently inclined and warped microdiorite dykes that cut across the upright D_3 folds are metamorphosed to amphibolite-facies assemblages in the same part of the area (Fig. 4) (Smith 1979; Talbot 1983).

The arguments that have been presented to support the separation of metamorphisms (I) and (II), and hence the relative timing of events in the model discussed above, can be clearly seen to be incorrect. For example, Barr *et al*. (1986) used the results of reconnaissance thermobarometry to show that the Sgurr Beag Thrust in the western Highlands has, in general, brought slightly hotter (*c*. 640 °C) rocks of the Glenfinnan Group in the east over cooler rocks (585–610 °C) of the Morar Group to the west. These workers (Barr *et al*. 1986, p. 760) agreed with Powell *et al*. (1981) that 'syn-sliding amphibolite facies metamorphism' had accompanied movement on the Sgurr Beag Thrust, and also concluded that the thrust 'juxtaposed rocks from which *pre-Caledonian P–T* estimates were obtained' (i.e. different portions of the already crystalline basement affected by regional metamorphism (I)). The *P–T* estimates in question were derived from coexisting garnet–biotite in pelites in which the garnet undergoes textural changes from west to east, as reported by Anderson & Olimpio (1977) and MacQueen & Powell (1977). However, the self-same assemblages that Barr *et al*. equated with regional metamorphism (I) are contemporaneous with those recorded from the calc-silicate rocks and used by Powell *et al*. (1981) to demonstrate syn-Caledonian movement on the Sgurr Beag Thrust during regional metamorphism II. Hence we can clearly identify a circular argument in which one set of isograds and reactions is assigned to two different events.

Petrogenesis of titanites in the calc-silicate pods

Small bodies of calc-silicate rock with a distinctive field appearance are present in all three groups of the Moine. They occur as pale-coloured lenses and ellipsoidal bodies that are generally 1–3 cm thick, exceptionally reaching 8 cm, and can be seldom traced for more than a metre or two along strike. Reddish brown garnets a few millimetres across are accompanied by scattered crystals or aggregates of biotite, hornblende or pyroxene crystals, and set in a white, pale grey or cream-coloured matrix.

The calc-silicate pods are of sedimentary origin, and occur in both pelitic and psammitic host rocks. They consisted originally of calcite-rich sandstone, and either formed during diagenesis, as concretions that are locally seen to overgrow features such as cross-bedding (Tanner 1976), or make up part of a bedded sequence. In the latter case, the calc-silicate bands form rhythmical sequences with psammite and pelite (Richey & Kennedy 1939), or are seen as lensoid or elliptical bodies that are wrapped by a thin band of psammite and enclosed in pelite.

Kennedy (1949) identified four key regional metamorphic assemblages in the calc-silicate pods of the western Highlands, which define a series of broadly north–south-trending zones, with metamorphic grade increasing from west to east, and further work by Tanner (1976) led to the modified prograde zonal classification shown in Table 1. Tanner & Miller (1980) studied the calc-silicate suite in the Mallaig–Loch Eil area and showed that there is a progressive loss of H_2O, CO_2, Na and K from these rocks during prograde metamorphism, climaxing in the production of an anhydrous anorthite–garnet–pyroxene-bearing rock virtually devoid of both Na and K. They defined the calc-silicate rocks as having a CaO/Al_2O_3 ratio of 0.3–0.7. Based upon microprobe analysis of plagioclase compositions in members of this suite, Powell *et al*. (1981) concluded that anorthite composition in the calc-silicate rocks was independent of whole-rock composition and controlled by metamorphic grade, thus validating the zonal scheme.

The peak metamorphic assemblages post-date D_1 in these rocks and are syn-D_2 in the Zone 3 assemblages (Tanner 1976; MacQueen & Powell 1977; Tanner & Miller 1980; Powell *et al*. 1981). Many of the calc-silicate lenses carry a strong, steeply plunging L > S fabric (?L_2) defined by aggregates of biotite and/or hornblende.

Titanite makes up 1–4% of the rock in the Zone 1–3 assemblages (Tanner 1976), and our recent work has shown that the following changes in titanite morphology occur with increasing metamorphic grade.

Table 1. *Regional metamorphic mineral assemblages in calc-silicate pods that define Zones 1–4 in the Moine of the western Highlands of Scotland, after Tanner (1976)*

	Calc-silicate assemblage	Equivalent Barrovian zone in pelite (approximate)
Zone 1	*albite–zoisite–calcite*–biotite	Garnet
Zone 2	*oligoclase/andesine–zoisite*–biotite ± hornblende	Staurolite/kyanite
Zone 3	*bytownite/anorthite–hornblende*	Kyanite/sillimanite
Zone 4	*bytownite/anorthite–pyroxene*	Sillimanite

The minerals diagnostic of each zone are shown in italics. All assemblages contain quartz and almandine-rich garnet (with up to 30–40% grossular). K-feldspar is absent throughout and accessory minerals include titanite, opaque Fe–Ti-oxide minerals, rutile, zircon, graphite, and apatite.

Zone 2

(1) Small opaque grains of (?) ilmenite (to 300–500 μm across) are commonly found in the lower-grade, zoisite-bearing calc-silicate assemblages. They are of detrital origin and can be seen in thin section to form bedding-parallel trails in a number of samples. In some rocks the opaque grains have a corona of titanite but in the majority of cases the opaques have been extensively, or completely, replaced by titanite.

(2) In several samples, where the trails of detrital (?) ilmenite grains are preserved in large garnet porphyroblasts, a progressive change is seen from unaltered grains in the centre of the garnet, to grains rimmed with titanite in the outer part of the porphyroblast, to grains completely replaced by titanite outside the garnet (Fig. 5a).

(3) Titanite forms either isolated crystals (100–300 μm across) or clusters of smaller, linked crystals; in both cases many of the individual titanites enclose grains of an opaque mineral (? ilmenite) or rutile (generally 10–30 μm across). Both the isolated titanite crystals and the clusters have highly irregular external shapes and show clear evidence of marginal intergrowth with quartz, feldspar and zoisite grains of the enclosing matrix (Fig. 5b).

(4) Minute detrital zircon, rutile and apatite grains, many times smaller (10–20 μm across) than the titanite crystals, are found scattered throughout the rock as well as enclosed within the titanite crystals.

Zone 3

(5) The titanite grains occur as shoals of single, well-formed individual grains with euhedral, rhomboid to elongate, rounded outlines (Fig. 5c). They show the same size range (150–300 μm in the longest dimension) as those in the Zone 2 rocks, but are more regularly distributed throughout the rock than in the latter.

(6) The titanites rarely contain inclusions of opaque grains or rutile, and Fe–Ti-oxides are seldom seen in the matrix, where the opaques are graphite or, in rare instances, sulphide minerals.

Some titanites enclose minute detrital grains of zircon, 10–30 μm long.

Taken together, features (1)–(7) show that the titanite is secondary in origin and has grown during prograde regional metamorphism by the partial or complete alteration of detrital grains of Fe–Ti-bearing minerals such as ilmenite and rutile. The titanite grains from Zones 1 and 2 show marginal growth interstitial to newly grown crystals of metamorphic minerals such as plagioclase, biotite and zoisite. Although this does not preclude the possibility that there were a few, minute, titanite grains of detrital origin in the original rock, they would be insignificant in amount compared with that of the newly grown titanite. Further breakdown of the Fe–Ti-bearing detrital minerals to form titanite took place during the formation of the Zone 3 assemblages: recrystallization of irregularly shaped titanite grains and aggregates gave rise to clear, subhedral to euhedral, rhomboid titanite crystals containing fewer inclusions.

For the above reasons, the well-formed titanite crystals in the Zone 3 assemblages would seem to provide an ideal target for U–Pb dating to determine the time at which peak regional metamorphism took place. A drawback is that the U content of the titanites is very low, making radiometric dating difficult. Thus small batches of selected grains have to be analysed by thermal ionization mass spectrometry (TIMS).

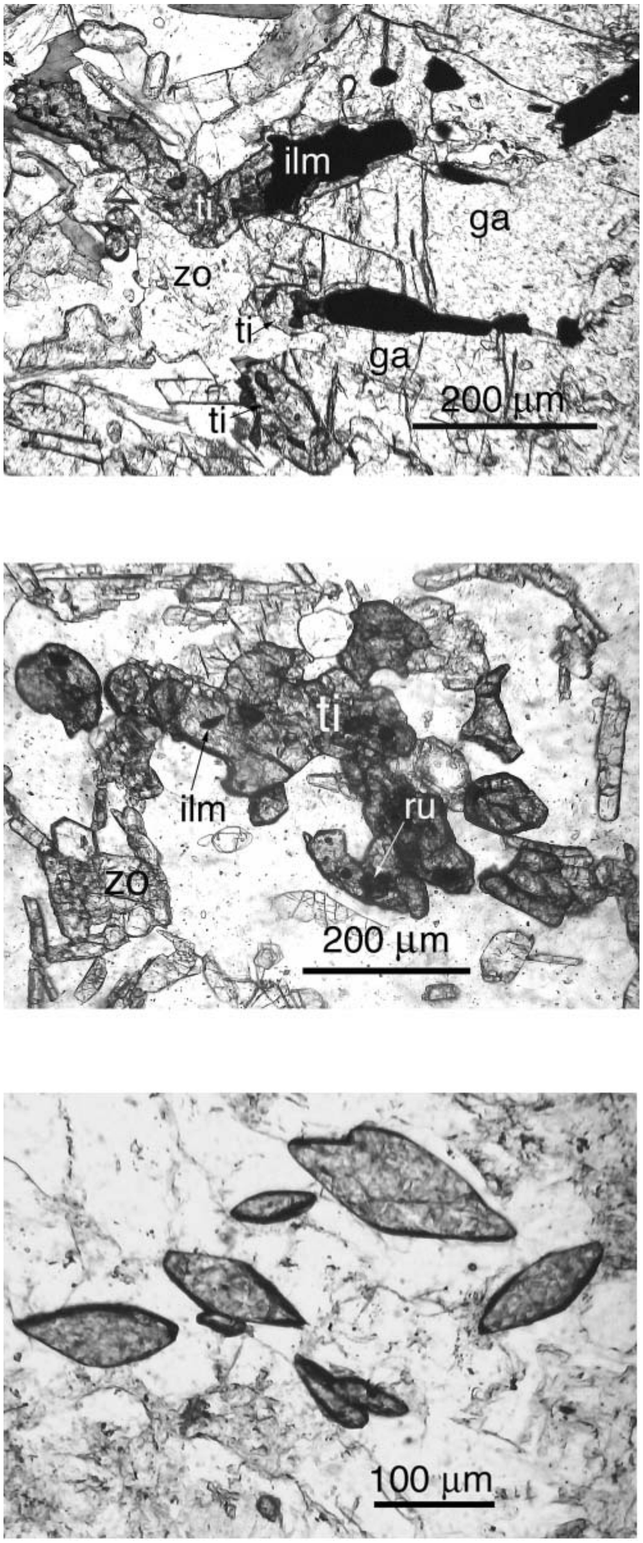

Fig. 5. (**a**) Photomicrograph showing the alteration of detrital ilmenite (ilm) enclosed in garnet (ga) to titanite (ti), where it protrudes into the quartz–feldspar–zoisite (zo)-bearing matrix. Sample GF 80. (**b**) Photomicrograph showing the morphology of titanite grains typically found in Zone 2 calc-silicate assemblages. The relict cores of ilmenite and rutile should be noted. Sample GF 90. (**c**) Photomicrograph showing the morphology of titanite grains (enclosed in a quartz–feldspar matrix) typically found in Zone 3 calc-silicate assemblages. Analysed sample GF 113.

Significance of U–Pb ages of metamorphic titanites

Titanite ($CaTiSiO_5$) is a common accessory mineral in metamorphic rocks, especially those with a high Ca/Al ratio such as limestones and calc-silicate rocks. It forms by a variety of reactions from the breakdown of detrital ilmenite, rutile and other Fe–Ti phases, as well as occurring as a primary detrital mineral. Reactions that are possibly relevant to the present study include

$$\text{ilmenite} + \text{calcite} + \text{Mg} - \text{biotite} = \text{titanite} + CO_2 + \text{Fe} - \text{biotite}$$

$$\text{rutile} + \text{calcite} + \text{quartz} = \text{titanite} + CO_2$$
(Hunt & Kerrick 1977)

$$\text{rutile} + 2\text{zoisite} + \text{quartz} = \text{titanite} + 3\text{anorthite} + H_2O$$
(Hunt & Kerrick 1977)

$$\text{Al(OH)titanite} + \text{ilmenite} + \text{quartz} = \text{Ti} - \text{titanite} + \text{anorthite} + \text{actinolite}$$
(Frost *et al*. 2000).

As titanite forms by means of a number of different reactions, some of them divariant, a precise knowledge of the blocking temperature (at which diffusion ceases, and radiometric daughter products begin to accumulate) for this mineral is important. This is particularly relevant in the present case, where we are dealing with a prograde metamorphic event that climaxed in the upper amphibolite facies, at temperatures in excess of 600 °C.

Early work suggested that the blocking temperature for titanite might be as low as *c*. 500 °C (Gascoyne 1986, and references therein), but a number of more recent studies, both theoretical and field-based, are in close agreement that it is >660–700 °C (Cherniak 1993; Schärer *et al*. 1994; Scott & St-Onge 1995; Pidgeon *et al*. 1996; Verts *et al*. 1996; Zhang & Schärer 1996; Essex *et al*. 1997; Hawkins & Bowring 1999; Essex & Gromet 2000; Frost *et al*. 2000). Scott & St-Onge (1995) studied the effect of grain size upon closure temperature, following the theoretical study of Cherniak (1993), and concluded that the effective radius for diffusion in titanite is <50 µm. However, Hawkins & Bowring (1999) found an age difference of 14 Ma for grains with radii of 19–105 µm, for an estimated temperature range of 530–590 °C.

These studies demonstrate that U–Pb dating of titanite crystals such as those in the Moine calc-silicates, which grew under amphibolite-facies conditions at <660 °C and had an effective diffusion radius of >110 µm, will record their age of crystallization, not the time of cooling of the metamorphic complex.

Analytical methods

Samples of about 1 kg were jaw crushed and disc milled and the <400 µm fraction was sieved out. Heavy mineral concentrates were obtained using a Gemini table, followed by a superpanner. A >3.3 density separate was recovered using Di-iodomethane and then the minerals were separated magnetically using a Frantz LB-1 magnetic separator. Titanites occurred predominantly in the <125 µm size fraction and in the magnetic fractions between 0.7 and 1.8 amp, and were hand picked under alcohol. Some fractions were abraded, as indicated in Table 2. Sample dissolution followed the method of Krogh (1973) and chemical separations followed Parrish *et al*. (1992).

Samples were analysed on a VG 354 mass spectrometer at the NERC Isotope Geosciences Laboratory following Noble *et al*.

Table 2. *U–Pb titanite data from a calc-silicate band (GF 113) in the Morar Group (Moine) of the western Highlands of Scotland (see Fig. 3 for location)*

Code	Description	Sample wt (µg)	U (ppm)*	Pb (ppm)*	Common Pb (pg)	^{206}Pb/^{204}Pb†	^{208}Pb/^{206}Pb‡	^{206}Pb/^{238}U‡	±% 2σ	^{207}Pb/^{235}U‡	± % 2σ	^{207}Pb/^{206}Pb§	±% 2σ	^{207}Pb/^{206}Pb age	±Ma 2σ	Rho‖
1	*c.* 30 grains, mag @ 1.5	32.4	47.49	7.5	78	167	0.046	0.1162	1.04	1.0247	1.20	0.06398	0.57	741	12	0.88
2	*c.* 30 grains, d mag @ 1.5	30.0	72.60	14.8	214	87	0.084	0.1085	0.72	0.9587	0.87	0.06411	0.49	745	10	0.83
3	*c.* 30 grains, mag @ 1.5	109.6	59.71	8.0	200	246	0.036	0.1101	1.12	0.9672	1.15	0.06371	0.24	732	5	0.98
4	*c.* 30 grains, mag @ 1.5	70.7	62.47	7.4	119	252	0.031	0.0984	0.79	0.8700	0.83	0.06412	0.25	746	5	0.95
5	*c.* 30¶ grains, mag @ 1.8	80.4	58.67	8.9	220	165	0.069	0.1090	0.39	0.9590	0.46	0.06383	0.24	736	5	0.85
6	*c.* 30¶ grains, mag @ 1.8	85.6	51.44	7.1	153	223	0.030	0.1116	0.45	0.9844	0.48	0.06396	0.18	740	4	0.93
7	*c.* 50¶ grains, mag @ 1.5	55.2	78.30	11.2	185	175	0.039	0.1065	0.21	0.9339	0.46	0.06359	0.39	728	8	0.54
8	*c.* 50 grains, mag @ 1.5	61.5	62.17	8.5	140	206	0.036	0.1080	0.21	0.9472	0.35	0.06363	0.26	730	5	0.66
9	*c.* 50 grains, mag @ 1.5	93.1	58.42	7.6	165	240	0.038	0.1061	0.21	0.9323	0.32	0.06375	0.23	733	5	0.70

*Sample weights, and hence U and Pb concentrations, are reliable to ±50%.
†Measured ratios are corrected for fractionation, common Pb, and spike.
‡Corrected for fractionation, spike, laboratory blank and initial common Pb using Stacey & Kramers (1975) (at 740 Ma).
§Errors for the measured ratios are propagated through data reduction and quoted at the 2σ percent level.
‖Correlation coefficients of ^{207}Pb/^{235}Pb and ^{206}Pb/^{238}U are calculated using procedures and algorithms of Ludwig (1993).
¶Abraded grains.

(1993). Uranium blanks were <0.1 pg U. All results and errors were calculated following Ludwig (1993, 1994) and the Pb isotope ratios were corrected for initial common Pb in excess of laboratory blank (taken as 5 pg) using the Stacey & Kramers (1975) model. Ages were calculated using the decay constants of Jaffey *et al*. (1971).

Results

Calc-silicate sample GF 113 was taken from a band of 5.5 cm thickness in the Morar Pelite *c*. 500 m NE of Arieniskill [NM 7914.8318]. It contains the assemblage qtz–calcic plag–ga–hb–bi–chl–mu–czo–titanite–rutile–zircon. Large sieved crystals of dark green hornblende (to 4 mm long) and spongy garnet (2–4 mm across) are set in a matrix of quartz and calcic plagioclase (>An_{70}), with minor amounts of biotite, chlorite, white mica, and rare secondary clinozoisite. Titanite occurs as rhomb-shaped grains 50–200 µm long, some 60% of which contain one or two minute opaque inclusions (10–25 µm across), probably of ilmenite, with some rutile and zircon. The titanite grains are very abundant and estimated at *c*. 10 grains per square millimetre of thin section. Those separated from GF 113 were clear, smooth surfaced and homogeneous-looking. When examined by back-scattered imaging, a sample of these grains showed no evidence of compositional zoning nor of the presence of inherited cores of possible detrital origin.

The selected titanite populations had ^{206}Pb/^{204}Pb ratios between 80 and 250 and are variably discordant, defining a discordia line with an upper intercept age of 737 ± 5 Ma (MSWD = 4.4) when anchored through a lower intercept of 0 ± 10 Ma (Fig. 6). Both abraded and unbraded fractions sit on the line.

Interpretation

We consider that the U–Pb age of 737 ± 5 Ma for the dated titanite grains is their age of crystallization for the following reasons. First, the titanites formed from detrital Fe–Ti-oxide minerals during the regional metamorphism that gave rise to the calc-silicate zones, and show no discernible evidence of older inheritance. The youngest published U–Pb age on detrital zircon from the Moine is 926 Ma (Friend *et al*. 2003). Second, the

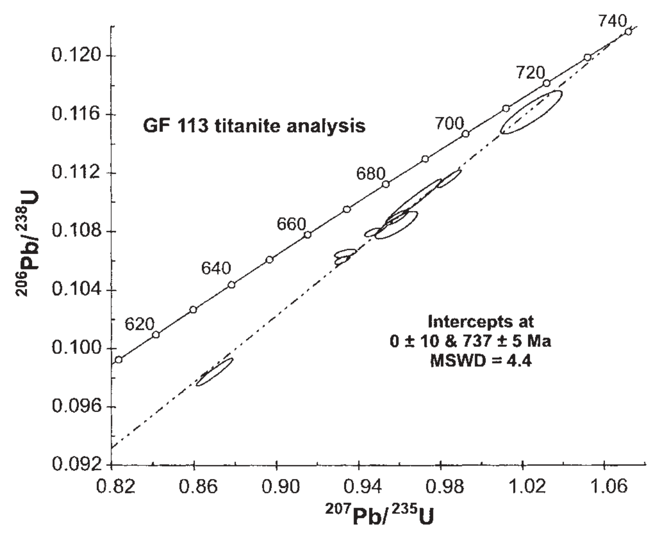

Fig. 6. U–Pb concordia diagram for nine separates of metamorphic titanite from sample GF 113.

maximum temperature reached during the regional metamorphism in the sillimanite-bearing pelites (Zone 3) in this area was probably <650 °C (Barr *et al*. 1985), and is lower than the inferred blocking temperature for titanite. The U–Pb age is therefore likely to date crystallization, not cooling or resetting.

This interpretation supports previous evidence that a Precambrian tectonothermal event has affected the Morar Group, as given by: (1) the U–Pb zircon age of 740 ± 30 Ma (van Breemen *et al*. 1978) from the deformed, garnet-bearing, Loch Eil pegmatite 1.5 km to the ESE of the GF 113 titanite locality (Fig. 4); (2) the *c*. 750 Ma ages on muscovite books from nearby minor shear zones in the same group of rocks (Piasecki 1984); (3) Sm–Nd ages on garnet ranging from 814–823 Ma (cores) to 788 ± 4 Ma (rim) (Vance *et al*. 1998) from metamorphic Zone 2, 5–6 km west of the GF 113 locality (Fig. 4).

Discussion

This study has demonstrated that the Morar Group has been affected by a Neoproterozoic contractional orogenic event, albeit with a so far unexplained difference in age given by different radiometric dating methods. The 737 Ma event has only been shown to affect the Morar Group, no comparable radiometric data being available at present for the Glenfinnan and Loch Eil groups that constitute the overlying Sgurr Beag Nappe.

Before considering how the new radiometric age relates to the timing of movement on the Sgurr Beag Thrust, it should be noted that there is some uncertainty in the identification of the line of the thrust south of Kinloch Hourn (Grant & Harris 2000, p. 196). This problem will remain until the position of the Thrust is mapped in detail in the remote ground between there and Lochailort, as the only published record is provided by the Arisaig Sheet (61) published by the British Geological Survey in 1971. It is important to resolve this problem as the spatial relationship between the line of the Thrust and the metamorphic isograds has been used to constrain the relative age of the slide movement (Powell *et al*. 1981), and hence its absolute age. Meanwhile, conclusions based upon the present correlation should remain provisional.

There are two current hypotheses for the age of the Sgurr Beag Thrust: (1) it is a post-peak-metamorphic, early Caledonian ductile structure, which has carried already gneissose Glenfinnan Group rocks over lower-grade Morar Group rocks to the west (Rathbone *et al*. 1983; Barr *et al*. 1986); (2) the main movement on the Sgurr Beag Thrust occurred during the regional metamorphism that affected both the Glenfinnan and Morar group rocks for the first time (Powell *et al*. 1981).

In hypothesis (1) the Thrust formed part of foreland-directed crustal duplex lying above the Moine Thrust (Grant & Harris 2000), and was subsequently deformed by upright D_3 folds (Barr *et al*. 1986, 1988; Roberts *et al*. 1987). From a study of microtextures and *c*-axis fabrics in the Sgurr Beag Thrust zone, Grant & Harris (2000) recognized two distinct stages in its development: foreland-directed thrusting under amphibolite-facies conditions, followed by a reworking event at lower temperatures, which was accompanied by localized dip-slip movement.

In hypothesis (2) the Moine Nappe (Morar Group) and Sgurr Beag Nappe have shared the same history, for the calc-silicate zones and western limit of migmatization are imprinted across the line of the Sgurr Beag Thrust that separates them (Tanner 1971; Powell *et al*. 1981). If the main regional metamorphic event (broadly syn-D_2) in the Moine Nappe is at *c*. 737 Ma then the main movement on the Sgurr Beag Thrust occurred during the Neoproterozoic, not the Caledonian, orogeny. The first of the two movements on the Sgurr Beag Thrust documented by Grant & Harris (2000) could therefore be Neoproterozoic in age, with the later movement occurring during the early phase (pre-D_4) of the Caledonian deformation. Thus early movement on the Thrust could have been synchronous with the prograde regional metamorphism and D_2 deformation, with the later movement causing some displacement of these isograds and deformation of the metamorphic rocks. This would explain the observation that garnet-bearing regional metamorphic rocks have been deformed within the thrust zone at Kinloch Hourn (Roberts & Barr 1988).

The revised history of events in the Moine block may be summarized as follows.

Extensional event (Ardgourian)

The West Highland granite suite was emplaced at *c*. 873 Ma. It is restricted to the Sgurr Beag Nappe (Loch Eil & Glenfinnan groups) but deformed pegmatites as old as 827 Ma (Rogers *et al*. 1998) are found within the Moine Nappe (Morar Group). Evidence for deformation predating the intrusion of the granite gneiss protolith has been disputed, and a pre-orogenic extensional setting for this body seems most likely.

Neoproterozoic orogeny (Knoydartian)

The 1980s model for the structural history of the Moine may now be resurrected. The D_1 and D_2 structures, the main regional metamorphic event in the Moine, and the major, early, displacement on the Sgurr Beag Thrust are all of Neoproterozoic age and together constitute a major episode of crustal thickening. This orogenic event was accompanied by the widespread development of *c*. 750 Ma micas in shear zones, including the Sgurr Beag Thrust at Kinloch Hourn (Piasecki & van Breemen 1983). It was followed by the intrusion of a suite of microdiorite dykes.

Early Palaeozoic orogeny (Caledonian)

The Grampian Phase of the Caledonian orogeny at *c*. 470 Ma (McKerrow *et al*. 2000) is represented by D_3 and D_4 in the Moine and associated with a regional metamorphism that is at lower grade than the Knoydartian in the west, and reached the amphibolite facies only in the eastern part of the western Highlands. It resulted in the local development of 470 Ma pegmatites, the growth of titanite in the 870 Ma granite gneiss at Fort Augustus, regional metamorphism of the post-Knoydartian microdiorite suite, and a proliferation of 470–440 Ma Rb–Sr mica ages in the Moine block.

There are a number of problems that arise from the recognition of a Knoydartian orogeny in the Moine block. First, the anomaly of a local contractional event along a part of the margin of Laurentia that was elsewhere undergoing extension until the early Ordovician has been fully aired elsewhere (Dalziel & Soper 2001) and is not discussed further here except to point out that it has been suggested that the Moine block could be a suspect terrane (Bluck *et al*. 1997) exotic to both the Hebridean foreland to the NW and to the Dalradian block to the SE. Second, within the Northern Highlands terrane the putative 590 Ma Carn Chuinneag Granite was intruded into, and hornfelsed, Moine rocks that had not been previously deformed or metamorphosed (Peach *et al*. 1912; Soper & Harris 1997). This problem has also been discussed elsewhere, and the relationships seen at Carn Chuinneag used to argue against the presence of a Precambrian event in the Moine (Soper & Harris 1997). The solution, although difficult to substantiate, would appear to be that the

Neoproterozoic tectonothermal event confirmed here in the western Highlands was localized and not sufficiently widespread to develop a penetrative pre-Caledonian fabric in the Moine rocks at Carn Chuinneag, 150 km to the NE (Fig. 1).

The results reported here are being tested by carrying out further radiometric dating of titanites from calc-silicate assemblages in both the Moine Nappe and the Sgurr Beag Nappe. The present data, however, exclude the possibility that, at a Scottish promontory on the Laurentian margin, there was a long-continued extensional regime from 870 Ma to Cambrian–Ordovician time, followed by a short-lived orogeny at 470 Ma (Dalziel 2001; Dalziel & Soper 2001).

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