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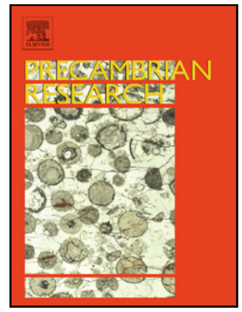

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Re-Os geochronology of the Neoproterozoic – Cambrian Dalradian Supergroup of Scotland and Ireland: Implications for Neoproterozoic stratigraphy, glaciations and Re-Os systematics

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Abstract

New Re-Os geochronology for the Ballachulish Slate Formation of the Dalradian Supergroup, Scotland yields a depositional age of 659.6 ± 9.6 Ma. This age represents the first successful application of the Re-Os system to rocks that have extremely low Re and Os abundances (<1 ppb and <50 ppt, respectively). The Re-Os age represents a maximum age for the glaciogenic Port Askaig Formation and refutes previous chemostratigraphic and lithostratigraphic studies which correlated the Port Askaig Formation with a series of middle Cryogenian (ca. 715 Ma) glacials. Additionally, the Re-Os age strongly suggests that the Port Askaig Formation may be correlative with the ~ 650 Ma end-Sturtian glaciations of Australia. As a consequence, the correlation of the Ballachulish Limestone Formation with the ca. 800 Ma Bitter Springs anomaly is not tenable. Initial Os isotope data from the Ballachulish Slate Formation coupled with data from Australia reveals a radiogenic $^{187}Os/^{188}Os$ isotope composition (~0.8 to 1.0) for seawater during the Neoproterozoic, which is similar to that of modern seawater (1.06).

We also report a young, highly imprecise Re-Os age (310 ± 110 Ma) for the Early Cambrian Leny Limestone Formation which is constrained biostratigraphically by a polymerid and miomerid trilobite fauna. We suggest, based on the mineralogy of the Leny Limestone, (kaolinite, muscovite and a serpentine group mineral, berthierine), that the Re-Os systematics have been disturbed by post-depositional fluid flow associated with Palaeozoic igneous intrusions. However, it is evident from the Ballachulish Slate Formation results that anhydrous metamorphism does not disturb the Re-Os geochronometer.

Keywords: Re-Os, Dalradian, Neoproterozoic, Sturtian, Rodinia, Laurentia

1. Introduction

Neoproterozoic strata record a number of significant events such as the transition from stratified Proterozoic oceans with oxic surface waters and anoxic deep waters to a more-or-less fully oxygenated ocean (Anbar and Knoll, 2002; Knoll, 2003; Fike et al., 2006; Halverson and Hurtgen, 2007; Canfield et al., 2008). Major changes in biological systems and evolutionary developments occurred towards the end of the Proterozoic including the evolution of metazoans (Logan et al., 1995; 1997; Vidal and Moczydlowska-Vidal, 1997; Jensen et al., 2000; Martin et al., 2000; Narbonne and Gehling, 2003; Knoll et al., 2006; Macdonald, 2010a, b). Additionally, the Neoproterozoic was a time of major climatic fluctuation with a number of extreme glacial events recorded in the rock record (e.g. the "Snowball Earth" of Kirschvink, 1992; Hoffman et al., 1998; Hoffman and Schrag, 2002 or the "Slushball Earth" of Hyde et al., 2000). However, there is at present, no consensus as to the cause, extent, duration or number of these glacial events (Kennedy et al., 1998; Evans, 2000; Fairchild and Kennedy, 2007). The lack of precise and accurate geochronological data has severely hindered attempts to develop a chronological framework for the Neoproterozoic. In particular, understanding and constraining the extent and duration of these glacial events has relied upon lithostratigraphy and chemostratigraphy with only a few glaciogenic successions constrained by robust geochronological data (Hoffmann et al., 2004; Zhou et al., 2004; Kendall et al., 2004; 2006; 2009a; Condon et al., 2005; Bowring et al., 2007; Macdonald et al., 2010a).

During the Neoproterozoic, the continental masses of Laurentia, Baltica and Amazonia were juxtaposed as a result of various orogenic events to form the supercontinent Rodinia (e.g. Li et al., 2008 and references therein). During the break-up of Rodinia which commenced at ca. 750 Ma there was a period of intracontinental extension and basin genesis along the eastern margin of Laurentia (Harris et al., 1994; Soper, 1994; Cawood et al., 2007). Scotland occupied a unique position within the Rodinia supercontinent lying close to the junction of the Laurentian, Baltica and Amazonian continental blocks (Dalziel, 1994). The sedimentary basins that formed during the formation and breakup of Rodinia are preserved in Scotland as the Torridonian, Moine and Dalradian Supergroups (Anderton, 1982; 1985; Rainbird et al., 2001; Strachan et al., 2002; Cawood et al., 2003; 2004; 2007).

The Dalradian Supergroup of Scotland and Ireland is a metasedimentary succession that was deposited on the eastern margin of Laurentia during the late Neoproterozoic and Early Cambrian. Existing constraints imply the base is younger than 800 Ma and it extends to at least 510 Ma (Harris et al., 1994; Smith et al., 1999; Prave et al., 2009a). Despite its importance in regional and global studies of the Proterozoic, our understanding of the Dalradian sequence suffers from a lack of radiometric ages (Halliday et al., 1989; Dempster et al., 2002). In an attempt to improve the chronostratigraphy of the Dalradian, several workers have applied lithostratigraphic and chemostratigraphic tools with varying levels of success (Prave, 1999; Brasier and Shields, 2000; Condon and Prave, 2000; Thomas et al., 2004; McCay et al., 2006; Prave et al., 2009a; Sawaki et al., 2010). These studies have improved our knowledge of the Proterozoic ocean chemistry and the environmental conditions of deposition within the Dalradian sedimentary basin. However, chemostratigraphic tools cannot provide absolute ages and ultimately rely upon correlation with sequences which have robust radiometric and / or biostratigraphic age constraints (Melezhik et al., 2001; 2007; Fairchild and Kennedy, 2007; Jiang et al., 2007; Meert, 2007; Giddings and Wallace, 2009; Frimmel, 2010). As a result, obtaining precise and accurate radiometric ages remain a priority for resolving many of the issues regarding global correlations.

The rhenium-osmium (Re-Os) geochronometer has been shown to provide robust depositional ages even for sedimentary rocks that have experienced hydrocarbon maturation, greenschist metamorphism and flash pyrolysis associated with igneous intrusions (Creaser et al., 2002; Kendall et al., 2004; 2006; 2009a, b; Selby and Creaser, 2005; Rooney et al., 2010). Thus, the Re-Os system represents an accurate, precise and reliable geochronometer for providing depositional age data for the Dalradian metasediments and constructing a chronostratigraphic framework for the chemostratigraphic, tectonostratigraphic and lithostratigraphic datasets.

Here, we present new Re-Os age that constrain the depositional age of a sedimentary unit from the Dalradian Supergroup. The Re-Os data also provides an estimate for the osmium isotope composition of seawater in the Dalradian basin during the Neoproterozoic and ultimately provide a maximum depositional age for a key Neoproterozoic glacial horizon. A further aspect of this study involves the application of Re-Os geochronology to sedimentary units with low Re and Os abundances (<1 ppb Re and <50 ppt Os) to provide accurate and precise geochronology. Additionally, this work presents results from a sedimentary unit (Leny Limestone Formation) in which the Re-Os geochronometer has been disturbed as a result of post-depositional fluid flow. The results from this study provide us with new insights into the robustness of the Re-Os geochronometer.

2. Geological Setting

2.1. The Dalradian Supergroup

The Dalradian Supergroup of Scotland and Ireland consists of a thick (~25 km) metasedimentary succession and a minor amount of mafic volcanics deposited on the eastern margin of the Laurentian craton during the Neoproterozoic to Early Cambrian (Fig. 1; Harris et al., 1994 and references therein). This quoted thickness of the Dalradian Supergroup is a cumulative thickness from all subgroups and is not a true reflection of sediment thickness. Many aspects of basin genesis have proved controversial, with little consensus apparent even after more than a century of studies. Most models for Dalradian deposition invoke a long, shallow-marine, ensialic basin which underwent prolonged extension during the late Neoproterozoic, resulting in the eventual separation of Laurentia from western Gondwana at ca. 550 Ma (Hoffman, 1991; Soper, 1994; Dalziel and Soper, 2001). An alternative model proposes that the lower portions of the Dalradian represented a rapidly formed foredeep basin associated with the mid-Neoproterozoic (840 – 730 Ma) Knoydartian Orogeny (Prave, 1999). In both models extensional tectonics played a major role in the genesis of the upper portions of the Dalradian basin during the latest Neoproterozoic to Early Cambrian.

Lithostratigraphic correlation of the Dalradian Supergroup is hampered by the paucity of volcanic horizons suitable for U-Pb geochronology and the lack of biostratigraphically diagnostic fossils (Fig. 2). Additionally, many portions of the Dalradian sequence exhibit extreme facies variability along strike having experienced complex polyphase deformation and metamorphism (Harris et al., 1994, Strachan et al., 2002 and references therein). Despite these issues, a coherent lithostratigraphy has been established from western Ireland to the Shetland Islands, 200 km north of mainland Scotland (Harris et al., 1994).

The Dalradian Supergroup consists of four groups which are from oldest to youngest; the Grampian, Appin, Argyll and Southern Highland groups (Figs. 1 and 2).

The basal Grampian Group crops out primarily in the Central Highlands although possible correlatives exist on the north Grampian coast and on the Shetland Islands (Strachan et al., 2002). The Grampian Group consists of up to 7 km of predominantly marine, quartzo-feldspathic psammites and semi-pelites (Glover and Winchester, 1989; Harris et al., 1994). The Grampian Group sedimentary succession displays sharp lateral variations typical of a syn-rift origin (Soper and England, 1995; Banks et al., 2007). The overlying Appin Group is exposed in a broad zone throughout Scotland and Ireland as far north as the Shetland Islands. The Appin Group consists of up to 4 km of quartzite, semi-pelites and phyllites deposited as a post-rift, thermal subsidence sequence (Litherland, 1980; Glover et al., 1995; Soper and England, 1995; Glover and McKie, 1996). The overlying Argyll Group records rapid deepening of the basin following the shallow marine conditions of the Appin Group (Anderton, 1985). The Argyll Group consists of a thick heterogeneous succession of shelf sediments up to 9 km thick which passes upwards into deep water turbidite and basinal facies and associated mafic volcanics (Anderton, 1982). The marked change from a shelf setting to deep water sedimentation is widely ascribed to the onset of syn-depositional rifting. The basal subgroup (Islay Subgroup) of the Argyll Group is marked by a distinctive and persistent tillite horizon; the Port Askaig Formation, correlatives of which are traceable from Connemara in western Ireland to Banffshire in NE Scotland (Anderton, 1985; Harris et al., 1994). The Southern Highland Group (along with the newly defined Trossachs Group of Tanner and Sutherland, 2007) marks the top of the Dalradian succession and consists of ca. 4 km of coarse-grained turbiditic clastics and volcaniclastic strata (Anderton, 1985; Soper and England, 1995). The Southern Highland Group is considered to represent the change from a period of continental rifting and rupture to that of a thermally subsiding margin (Anderton, 1985).

2.1.1. Glaciogenic horizons within the Dalradian and possible global correlations

The Port Askaig Formation of the Argyll Group is a thick (~900 m) succession of diamictites interbedded with sandstone, conglomerate and mudstone (Kilburn et al., 1965; Spencer, 1971; Eyles, 1988; Arnaud and Eyles, 2002). The formation represents the most persistent and distinctive glaciogenic horizon within the Dalradian Supergroup (Fig. 2). A glaciogenic origin was first recognised in the late nineteenth century (Thomson, 1871; 1877), and is described in detail in the classic memoir of Spencer (1971). The most extensive outcrops of the Port Askaig Formation consists of ~400 m of coarse-grained and poorly sorted diamictite interbedded with sandstone, mudstone and conglomerate with some megaclasts in the diamictite exceeding 100 m in size (Spencer, 1971; Arnaud, 2004). Recent studies identified enriched $\delta^{13}C$ (+11.7‰) and unradiogenic $^{87}Sr/^{86}Sr$ (0.7067) in carbonate formations above and below the Port Askaig Formation (Brasier and Shields, 2000; Sawaki et al., 2010). These data have been used to correlate the glaciogenic horizon with the ca. 750 – 690 Ma global Sturtian glaciation (Brasier and Shields, 2000; Fanning and Link, 2004; McCay et al., 2006; Macdonald et al., 2010a). Two more stratigraphically limited glaciogenic units within the Dalradian Supergroup have also been identified; the Stralinchy “Boulder Bed” Formation and the Inishowen - Loch na Cille Ice Rafted Debris (IRD) Formations (Fig. 2; Condon and Prave, 2000; McCay et al., 2006). The Stralinchy Formation occurs in the Easdale Subgroup in Donegal in NW Ireland and has been correlated with the ~635 Ma global Marinoan glaciation (Hoffmann et al., 2004; Condon et al., 2005; McCay et al., 2006). The Loch na Cille and Inishowen glaciogenic formations occur within the uppermost Argyll Group and basal Southern Highland Group respectively, and have been correlated with the 580 Ma Laurentian Gaskiers glacial event (Condon and Prave, 2000; Bowring et al., 2003).

2.2. Current chronological constraints for the Dalradian Supergroup

With the exception of *Bonnia-Ollenellus* Zone Early Cambrian trilobites and inarticulate brachiopods of the upper Southern Highland Group, the Dalradian Supergroup is almost entirely devoid of fossils (Pringle, 1939; Fletcher and Rushton, 2007). In addition, absolute chronological constraints on the age of Dalradian sedimentation are also very sparse (Fig. 2). The oldest phase of volcanic activity in the Dalradian Supergroup occurs within correlatives of the Port Askaig Formation in NE Scotland (Chew et al., 2010). However, this thin tholeiitic pillow basalt has not been dated thus far. The lower part of the Southern Highland Group in SW Scotland is characterised by ca. 2 km of tholeiitic mafic volcanic rocks and sills (Tayvallich Volcanic Formation). The Tayvallich Formation is cross cut by a 595 ± 4 Ma (U-Pb SHIRIMP) keratophyre intrusion and a felsic tuff from this formation has yielded a U-Pb zircon age of 601 ± 4 Ma (Halliday et al., 1989; Dempster et al., 2002). Pegmatites from the Central Scottish Highlands has yielded a U-Pb monazite age of 806 ± 3 Ma although the stratigraphic position of these pegmatites remains controversial (Noble et al., 1996). These pegmatites have been suggested to intrude into Grampian Group rocks thus providing a minimum age for these sediments (Noble et al., 1996; Highton et al., 1999). However, other studies (e.g. Smith et al., 1999) propose that the pegmatites intrude into the Dava and Glen Banchor successions which lie unconformably below the Grampian Group and that therefore the Grampian Group is younger than 806 Ma (Smith et al., 1999; Strachan et al., 2002).

Numerous studies have utilised $\delta^{13}C$, $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ data from several different carbonate units of the Dalradian Supergroup with the aim of correlation with global chemostratigraphic curves (Brasier and Shields, 2000; Thomas et al., 2004; McCay et al., 2006; Halverson et al., 2007a; Prave et al., 2009a; Sawaki et al., 2010). A composite $\delta^{13}C$ profile for the Dalradian Supergroup has been used to tentatively correlate the Ballachulish Limestone of the Appin Group with the ca. 800 Ma Bitter Springs anomaly (Prave et al., 2009a; Fig. 2). Additional correlations include the pre-Marinoan Trezona anomaly and ca. 635 Ma Marinoan-equivalent cap carbonate sequence with units of the middle Easdale Subgroup and the terminal Proterozoic (ca. 600 – 551 Ma) Shuram-Wonoka anomaly in the Girlsta Limestone on Shetland (Melezhik et al., 2008; Prave et al., 2009a, b).

2.3. Metamorphism and deformation of the Dalradian Supergroup

The Dalradian Supergroup of Scotland is one of the classic areas for the study of regional and contact metamorphism (e.g., Barrow, 1893; Tilley, 1925; Baker, 1985; Voll et al., 1991; Dempster et al., 1992; Pattison and Harte, 1997). The main phases of regional metamorphism took place during the Grampian Orogeny. The Grampian Orogeny is understood to be related to the collision of Laurentia with an oceanic arc during the Early Ordovician and can be considered broadly equivalent to the Taconic Orogeny of the Appalachians (Dewey and Mange, 1999; Soper et al., 1999). Geochronological constraints for the Grampian Orogeny include U-Pb zircon ages from syn-tectonic intrusives of 475 – 468 Ma and Sm-Nd metamorphic garnet crystallisation ages of 473 – 465 Ma which date peak metamorphism (Friedrich et al., 1999; Baxter et al., 2002).

The Dalradian sedimentary succession also experienced contact metamorphism associated with the intrusion of numerous Late Caledonian (ca. 430 – 390 Ma; Oliver, 2001) granites throughout the Grampian Terrane of Scotland (Fig. 1). In addition to the granites there are also a number of minor Late Palaeozoic intrusive suites recorded in the Dalradian (Neilson et al., 2009 and references therein).

3. Samples for this study

Two localities were chosen for Re-Os geochronology analyses; the Ballachulish Slate Formation from the Ballachulish Subgroup of the Appin Group and the Leny Limestone Formation of the Southern Highland Group (Figs. 1 and 2). The Ballachulish Slate was chosen to provide a maximum age constraint on the depositional age of the Port Askaig Formation (Fig. 2). The Leny Limestone Formation was chosen as it contains the only biostratigraphically diagnostic fauna found in the Dalradian Supergroup (Pringle, 1939; Fletcher and Rushton, 2007). Additionally, the metasedimentary rocks of the Dalradian Supergroup represent an opportunity to further our understanding of the effects of regional and contact metamorphism on the Re-Os geochronometer.

3.1. Appin Group – Ballachulish Slate Formation

The Appin Group consists of three subgroups, the Lochaber, Ballachulish and Blair Atholl (Fig. 2). The Ballachulish Slate Formation consists of ca. 400 m of pyritiferous black slates and graphitic phyllites. Samples were collected on the eastern foreshore of Loch Linnhe at the entrance to Loch Leven (56° 42. 1’ N, 5° 11. 6’ W; Fig. 1). In this area, the top of the Ballachulish Slate Formation is estimated to be ca. 1 km below the equivalent of the Port Askaig Formation (Litherland, 1980; Harris et al., 1994). Regional metamorphic grade associated with the Grampian Orogeny varies from chlorite grade in the NW to garnet grade in the SE. Estimates of P-T conditions range from ca. 450 - 550° C from NW to SE, at ca. 6 kbar (Pattison and Voll, 1991). In addition to Grampian regional metamorphism, the Ballachulish Slates also experienced Late Caledonian (ca. 430 Ma) igneous activity and contact metamorphism primarily associated with the well characterised Ballachulish Igneous Complex (Pattison and Harte, 1997; Pattison, 2006).

The metamorphic aureole varies in width from ca. 400 to 1700 m, based upon the first appearance of cordierite in metapelites (Pattison, 2006). Regional P-T conditions at the time of intrusion are estimated at ca. 250 – 300° C at ca. 3 kbar. The age of the Ballachulish Igneous Complex is constrained by Re-Os molybdenite and U-Pb zircon ages of 433.5 ± 1.8 Ma and 428 ± 9.8 Ma, respectively (Conliffe et al., 2010; Rogers and Dunning, 1991, recalculated by Neilson et al., 2009). Fluid flow between the intrusion and the aureole was limited and there is no evidence for a large-scale hydrothermal circulation system or associated mineralogical changes connected to the intrusion (Harte et al., 1991; Pattison, 2006).

The slates analysed in this study were sampled ca. 2 km NNW of the NW contact of the Ballachulish Igneous complex and are hence outside the aureole. The slates sampled are black and massive with bedding occasionally still discernible and predominantly orientated parallel to cleavage. X-ray diffractometry (XRD) studies indicate that the Ballachulish Slates have a composition of quartz, mica, chlorite and feldspars (albite and occasionally orthoclase), typical of an argillaceous slate. The samples of Ballachulish slate used in this study are similar in composition to those described in greater detail by Walsh (2007).

3.2. Southern Highland Group – Leny Limestone

The Leny Limestone forms part of the Keltie Water Grit Formation of the Southern Highland Group. The formation consists of pale grey to white, siliceous grits, black graphitic slates and rare locally fossiliferous limestones (Tanner and Pringle, 1999). The limestones of this formation yield a fauna including polymerid and miomerid trilobites, brachiopods, sponges, hyoliths and bradoriids (Fletcher and Rushton, 2007). The miomerid trilobites indicate a stratigraphical age equivalent to the base of the paradoxidid Amgan Stage of Siberia traditionally regarded as Middle Cambrian (511 – 506 Ma, Ogg et al., 2008). However, the polymerid trilobites e.g., *Pagetides*, are forms from the *Bonnia-Olenellus* Zone and are thus regarded as Lower Cambrian (516.5 – 512 Ma; Ogg et al., 2008). An age of ca. 512 Ma has been adopted here as the age of the Leny Limestone Formation (Fletcher and Rushton, 2007).

Black graphitic slates of the Leny Limestone Formation were sampled on the south-easterly face of the Western Quarry (56° 15.5’ N, 4° 13.1 W; Fig. 1). The metamorphic grade during the Grampian Orogeny was low, with an estimated peak metamorphic temperature of 270˚C (Tanner and Pringle, 1999). Detrital biotite is preserved, albeit commonly partially altered to chlorite. The locality is also the locus of several phases of igneous activity such as intrusions of Devonian quartz-felsite dykes and Permo-Carboniferous quartz dolerite dykes (British Geological Survey, 2005; Fletcher and Rushton, 2007). The Devonian intrusion exhibits a 70 m fault offset, though this faulting is not seen in the Permo-Carboniferous dyke suggesting faulting occurred prior to this younger intrusive episode. XRD analysis of the Leny Limestone Formation slates reveal a composition of quartz, micas (mainly muscovite), kaolinite and a serpentine-group mineral with the chemical formula of $Fe_3Si_2O_5(OH)_4$ suggested to represent berthierine (Brindley, 1982).

4. Sampling and analytical methods

Sampling of the Ballachulish Slate and Leny Limestone Formations was limited to a vertical interval of ca. 50 cm of stratigraphy across a lateral interval of several tens of metres. Weathered material was removed from the outcrop prior to sampling of fresh surfaces. Large (~100 g) samples were selected to ensure homogenisation of Re-Os abundances in the samples (Kendall et al., 2009b). All samples were polished to remove cutting and drilling marks to eliminate any potential contamination. The samples were dried at 60 °C for ~12 hrs and then crushed to a fine powder of ~30 μm. The samples were broken into chips with no metal contact and powdered in a ceramic dish using a shatterbox.

Rhenium-osmium isotope analysis was carried out at Durham University's TOTAL laboratory for source rock geochronology and geochemistry at the Northern Centre for Isotopic and Elemental Tracing (NCIET). Sample digestion using a CrO_3-H_2SO_4 solution is the preferred method for Re-Os geochronology as it has been shown to preferentially liberate hydrogenous Re and Os, ultimately providing more precise ages (Selby and Creaser, 2003; Kendall et al., 2004). An inverse *aqua-regia* solution was also employed in an attempt to evaluate the contribution of detrital Re and Os in these samples. Previous work has shown that *aqua-regia* digestion liberates both non-hydrogenous (detrital and meteoritic) and hydrogenous Re and Os. This detrital Os component has been shown to represent a source of geological scatter that results in determination of imprecise and / or inaccurate depositional ages (Ravizza et al., 1991; Selby and Creaser, 2003; Kendall et al., 2004).

Approximately 1 g of sample powder was digested together with a mixed tracer (spike) solution of ^{190}Os and ^{185}Re in a Cr^{VI}-H_2SO_4 solution in a sealed carius tube at 220 °C for ~48 h (Selby and Creaser, 2003; Kendall et al., 2004). Through the use of the Cr^{VI}-H_2SO_4 digestion media it is possible to preferentially liberate the hydrogenous Re and Os components from the samples thus limiting any detrital component (Selby and Creaser, 2003; Kendall et al., 2004). For the inverse *aqua-regia* digestions approximately 1 g of sample powder was dissolved together with a spike solution of ^{190}Os and ^{185}Re in a 1:2 acid mixture of 3 ml 12 N HCl and 6 ml of 16 N HNO_3 in a sealed carius tube at 220 °C for ~48 h (Selby and Creaser, 2003).

Rhenium and Os were purified from the acid solution using solvent extraction ($CHCl_3$), micro-distillation and anion chromatography methods and analysed by negative thermal ionisation mass spectrometry as outlined by Selby and Creaser (2003), and Selby (2007). The purified Re and Os fractions were loaded onto Ni and Pt filaments, respectively (Selby et al., 2007), with the isotopic measurements conducted using a ThermoElectron TRITON mass spectrometer via static Faraday collection for Re and ion-counting using a secondary electron multiplier in peak-hopping mode for Os. Average procedural blanks for the Cr^{VI}-H_2SO_4 method during this study were 16.8 ± 0.06 pg and 0.43 ± 0.06 pg (1σ S.D., n = 3) for Re and Os respectively, with an average $^{187}Os/^{188}Os$ value of ~0.25 ± 0.11 (n = 3). For the inverse *aqua-regia* method procedural blanks for Re and Os were 1.9 ± 0.01 pg and 0.12 ± 0.06 pg, respectively (1σ S.D. n = 2) with an average $^{187}Os/^{188}Os$ value of ~0.4 ± 0.5 (1σ S.D., n = 2).

Uncertainties for $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ are determined by error propagation of uncertainties in Re and Os mass spectrometer measurements, blank abundances and isotopic compositions, spike calibrations and reproducibility of standard Re and Os isotopic values using methods identical to previous studies (e.g., Kendall et al., 2004; Selby and Creaser, 2005). The Re-Os isotopic data, 2σ calculated uncertainties for $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ and the associated error correlation function (rho) are regressed to yield a Re-Os date using *Isoplot V. 3.0* with a λ ^{187}Re constant of $1.666 \times 10^{-11} a^{-1}$ (Ludwig, 1980; Smoliar et al., 1996; Ludwig, 2003).

To ensure and monitor long-term mass spectrometry reproducibility, in-house standard solutions of Re and Os (Durham Romil Osmium Standard [DROsS]) are repeatedly analysed at NCIET. The Re standard analysed during the course of this study is made from 99.999% zone-refined Re ribbon and is considered to have an identical Re isotopic composition to that of the AB-1 Re standard (Creaser et al., 2002; Selby and Creaser, 2003; Kendall et al., 2004). The NCIET Re standard yields an average $^{185}Re/^{187}Re$ ratio of 0.59772 ± 0.00172 (1 SD, n = 114). This is in excellent agreement with the value reported for the AB-1 standard (Creaser et al., 2002). The Os isotope reference material (DROsS) yields an $^{187}Os/^{188}Os$ ratio of 0.106093 ± 0.00015 (1 SD, n = 36). The isotopic compositions of these solutions are identical within uncertainty to those reported by Rooney et al. (2010) and references therein.

5. Results

5.1. Ballachulish Slate Formation samples

The Ballachulish Slate samples have Re (0.3 – 1.9 ppb) and Os (25.5 – 52.2 ppt) abundances that are close to or less than that of average continental crustal values of ~1 ppb and 50 ppt, respectively (Table 1; Esser and Turekian, 1993; Peucker-Ehrenbrink and Jahn, 2001; Hattori et al., 2003; Sun et al., 2003). The $^{187}Re/^{188}Os$ ratios range from 56.5 to 311.7 and the $^{187}Os/^{188}Os$ ratios range from 1.660 – 4.478 (Table 1). Regression of the Re-Os isotope data yields a Re-Os age of 659.6 ± 9.6 Ma (2σ, n = 5, Model 1, Mean Square of Weighted Deviates [MSWD] = 0.01, initial $^{187}Os/^{188}Os$ = 1.04 ± 0.03; Fig. 3a).

Digestion of the Ballachulish samples using inverse *aqua-regia* yields elemental abundances of 0.3 – 1.8 ppb and 30.6 – 53.5 ppt for Re and Os, respectively, which are identical within uncertainty to the values from the samples digested using CrO_3-H_2SO_4 (Table 1). The $^{187}Re/^{188}Os$ ratios range from 41.4 to 308.2 and the $^{187}Os/^{188}Os$ ratios range from 1.472 to 4.364 (Table 1). Regression of the aqua regia derived Re-Os isotope data yields a Model 3 age of 655 ± 49 Ma (2σ, n = 5, MSWD = 16) with an initial Os isotope composition of 1.03 ± 0.16 (Fig. 3b).

5.2. Leny Limestone slate samples

The Leny Limestone slates are enriched in Re (46.2 – 66.1 ppb) and Os (419 – 633 ppt) in comparison to average continental crustal values of ~1 ppb and 50 ppt, respectively (Table 1). The $^{187}Re/^{188}Os$ ratios range from 898.4 to 1228.0 and the $^{187}Os/^{188}Os$ ratios range from 6.162 – 8.075 (Table 1). Regression of the Re-Os isotope data yields a Re-Os age of 310 ± 110 Ma (2σ, n = 9, Model 3, MSWD = 388, initial $^{187}Os/^{188}Os$ = 1.7 ± 2.0; Fig. 4).

6. Discussion

6.1. Effect of non-hydrogenous Re and Os in low abundance samples

The CrO_3-H_2SO_4 method has been shown to yield precise and accurate depositional age determinations for both Phanerozoic and Proterozoic sedimentary successions (Kendall et al., 2004; 2006; 2009a, c; Selby and Creaser, 2005; Anbar et al., 2007; Selby, 2007; Yang et al., 2009; Rooney et al., 2010). Data from the Ballachulish samples using the CrO_3-H_2SO_4 digestion method yields a Model 1 age with a low uncertainty (1.5 %) and a low degree of scatter about the isochron (MSWD <1). However, as these samples have Re and Os abundances comparable to that of average continental crust it is important to assess the effects of a detrital Re and Os component on the geochronology data. It has been shown that the incorporation of a detrital Os component could lead to a younger or older age depending on the isotopic composition of the detrital Os (Ravizza et al., 1991). The effects of a detrital Os component on Re-Os depositional ages have been assessed previously during the development of the CrO_3-H_2SO_4 method (Selby and Creaser, 2003; Kendall et al., 2004).

The results from the inverse *aqua-regia* digestion show Re and Os abundances that are comparable with the samples digested using CrO_3-H_2SO_4 (Table 1). The isotopic composition data highlights the impact of detrital Re and Os on the determination of depositional ages. All of the $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ values for the *aqua-regia* samples are lower than those of the samples digested using CrO_3-H_2SO_4 (15% and 9% lower, respectively; Table 1). This suggests that the *aqua-regia* digestion has liberated an unradiogenic detrital Os component. Both ages for the Ballachulish Slate Formation are very similar however, however the *aqua-regia* Re-Os data set have a much larger degree of scatter (MSWD = 16) and yield a less precise age (9% uncertainty; Fig 3b, c). The samples digested using the CrO_3-H_2SO_4 method yield a much more precise age with a lower degree of scatter (MSWD = 0.01; Fig. 3a). These variations in precision and geological scatter are very similar to those identified by previous studies which undertook digestion of samples in *aqua-regia* (Selby and Creaser, 2003; Kendall et al., 2004). Additionally, digesting samples in the CrO_3-H_2SO_4 solution at 80 °C instead of 220 °C has been shown to yield identical data supporting the notion that this method does not liberate non-hydrogenous Re and Os even at high temperatures (Kendall et al., 2009a).

The $^{187}Os/^{188}Os$ initial ratio (Os_i) data from the samples digested using the CrO_3-H_2SO_4 method are all very similar with a coefficient of variation of 0.3% in contrast to the Os_i data from the samples digested in *aqua-regia* which have a coefficient of variation of 5% (coefficient of variation = (SD/mean) x 100; Table 1). This suggests that there were variations in Os isotope composition and / or magnitude of the detrital Os flux into the Ballachulish Slate during deposition. Again, this is identical to the findings of Kendall et al. (2004) on the Old Fort Point Formation of Canada.

The low degree of scatter coupled with the precise age of 659.6 ± 9.6 Ma represents a depositional age for the Ballachulish Slate Formation and the initial $^{187}Os/^{188}Os$ isotope composition of 1.04 represents that of seawater at the time of deposition.

6.2. Implications for low Re and Os abundance geochronology

The Re-Os age for the Ballachulish Slate Formation indicate that samples with low Re and Os abundances (<1 ppb Re and <50 ppt Os) can be used to provide precise geochronological data (Fig. 3a; Table 1). These values are similar to abundances in average continental crust which range from 0.2 – 2 ppb and 30 – 50 ppt, respectively (Esser and Turekian, 1993; Peucker-Ehrenbrink and Jahn, 2001; Hattori et al., 2003; Sun et al., 2003).

Previous work on Re-Os geochronology has focused on sedimentary units greatly enriched in Re and Os with abundances >20 ppb and 500 ppt, respectively (Ravizza et al., 1989; Cohen et al., 1999, Creaser et al., 2002; Selby and Creaser, 2005; Selby, 2007; Rooney et al., 2010). However, some recent studies have successfully applied the Re-Os geochronometer to sedimentary rocks with low to moderate enrichments of Re and Os (1.7 – 50 ppb and 82 – 250 ppt, respectively; Kendall et al., 2004; 2006; 2009a, b; Yang et al., 2009). The Re-Os geochronology data for the Ballachulish Slate Formation represent successful application of the system to samples with very low Re and Os abundances provided that the system has not been disturbed as discussed below.

The low Re and Os abundances do not appear to impair the robustness of the system as the Ballachulish samples all have similar $^{187}Os/^{188}Os$ (Os_i) values, yield a large spread in present-day $^{187}Re/^{188}Os$ values (~260 units) and display positively correlated, radiogenic $^{187}Os/^{188}Os$ values indicative of a closed system (Table 1). This positive correlation indicates that the 659.6 ± 9.6 Ma age for the Ballachulish Slate Formation does not represent a mixing line. Additionally, if the systematics had been disturbed, any detrital Os component in these samples would represent a significant cause of geological uncertainty, resulting in an imprecise and geologically meaningless age. The highly precise age coupled with the low degree of scatter in the data, (659.6 ± 9.6 and MSWD = 0.01), suggests that this is a depositional age and the Os_i value of 1.04 represents the Os isotope composition of local seawater at the time of deposition. The results from the Ballachulish Slate Formation strongly suggest that the system can be applied to sedimentary units that have low Re and Os abundances. From this we can also propose that the system is robust enough to provide depositional ages for strata that have experienced complex and polyphase metamorphic histories.

6.3. *Age of the Ballachulish Slate Formation*

The Re-Os isotope data from the Ballachulish slates yield an age of 659.6 ± 9.6 Ma which represents the depositional age of the Ballachulish Slate Formation (Fig. 3a). Accordingly, this Re-Os age defines a maximum age constraint for the glaciogenic Port Askaig Formation (Fig. 2). Taken in the context of the previous geochronological constraints for the Dalradian, the Re-Os age for the Ballachulish Slate Formation strongly suggests that the Argyll Group was deposited within ~60 Ma, prior to the eruption of the Tayvallich volcanics at ca. 600 Ma. From these two geochronological constraints, combined with the possibility that correlatives of the ca. 635 Ma Marinoan cap carbonate sequence are found within units of the Easdale Subgroup (McCay et al., 2006) we suggest that the Port Askaig Formation records a low latitude glacial event that occurred at ca. 650 Ma.

Much of the recent work relating to the Dalradian Supergroup has focused on $\delta^{13}C$ carbonate and $^{87}Sr/^{86}Sr$ chemostratigraphy of the various carbonate units (Prave et al., 2009a and references therein; Sawaki et al., 2010). This focus on chemostratigraphy coupled with the lack of reliable geochronology data has resulted in several attempts at correlation of the Dalradian Supergroup with better constrained Neoproterozoic sequences (McCay et al., 2006; Prave et al., 2009a; Sawaki et al., 2010). The Ballachulish Limestone is ca. 200 m in thickness and passes upwards into the Ballachulish Slate (Anderton, 1982; Prave et al., 2009a). Work by Prave et al. (2009a) suggested that the Ballachulish Limestone possess $\delta^{13}C_{carbonate}$ values as low as -7‰ and was tentatively correlated with the ca. 800 Ma Bitter Springs anomaly of central Australia (Hill and Walter, 2000; Halverson et al., 2007b). However, the Re-Os data of 659.6 ± 9.6 Ma for the Ballachulish Slate Formation negates the possibility of this correlation (Fig. 2).

A 60 Ma duration for Argyll Group deposition suggested by the Re-Os data presented here contrasts with a duration of ca. 120 Ma required by chemostratigraphic and lithostratigraphic correlations of the Port Askaig Formation with a ca. 715 Ma "Sturtian" glacial (Prave, 1999; Brasier and Shields, 2000; Prave et al., 2009a;). A short duration for Argyll Group deposition is geologically more probable given that the Argyll Group represents a time of increased tectonic activity and syn-depositional faulting with rapid deposition taking place in subsiding fault-bounded sub-basins (Anderton, 1982; 1985). A short duration for Argyll Group deposition also negates the need for any putative regional-scale unconformity within the Argyll Group, which remains contentious (see Hutton and Alsop, 2004 and Tanner et al., 2005 for a review).

The new Re-Os geochronology data provide a more precise chronostratigraphic framework for understanding the tectonic evolution of the Dalradian basin and the onset of sedimentation within the basin. Furthermore, the Re-Os geochronology helps refine Neoproterozoic palaeogeographies related to the formation and breakup of the Rodinia supercontinent (e.g., Li et al., 2008; Li and Evans, 2010). Deposition of the Dalradian Supergroup occurred along the eastern margin of Laurentia, close to the triple junction of Baltica, Laurentia and Amazonia (Soper, 1994; Dalziel, 1994).

6.4. Implications for global correlations involving the glacial Port Askaig Formation

At present, global correlation schemes for Neoproterozoic glaciogenic deposits are dependent on correlation of two distinctive types of diamictite cap-carbonate pairs. These have been designated as "Sturtian" and "Marinoan" events after the type localities in southern Australia (Kennedy et al., 1998; Hoffman and Schrag, 2002; Halverson et al., 2005; Corsetti and Lorentz, 2006). The Sturtian glaciation however, is also used to define much older glacial events than the Sturtian *sensu stricto* of the Adelaide Rift Complex which has geochronological constraints of ca. 640 – 660 Ma (Preiss, 2000; Kendall et al., 2009a and references therein). These earlier glacial events assigned to the "Sturtian" have geochronological constraints which indicate low-latitude global glaciation at ca. 715 Ma based on U-Pb zircon ages (Bowring et al., 2007; Macdonald et al., 2010a). In this summary, they are referred to as middle Cryogenian (ca. 715 Ma) deposits to distinguish them from younger Sturtian (*sensu stricto)* glacial deposits on the Australian craton at ca. 640 – 660 Ma.

Early work on correlation of the Port Askaig Formation (Fig. 2) suggested a possible correlation with North Atlantic Varangerian tillite sequences which were originally constrained by a Rb-Sr diagenetic illite age of ca. 630 Ma (Hambrey, 1983; Fairchild and Hambrey, 1995; Gorokhov et al., 2001). Correlation of the Port Askaig Formation with the Varangerian tillite was also suggested by $^{87}Sr/^{86}Sr$ chemostratigraphy of Dalradian limestones that indicate that the base of the Dalradian Supergroup is younger than ca. 800 Ma and may be as young as ca. 700 Ma (Thomas et al., 2004). This correlation is difficult to support as the geochronological constraints for the Varangerian glaciation are based upon Rb-Sr illite geochronology, which is unlikely to represent a depositional age (Morton and Long, 1982; Ohr et al., 1991; Awwiller, 1994; Evans, 1996; Gorokhov et al., 2001; Selby, 2009).

Recent work has rejected the correlation of the Port Askaig Formation and the Varangerian glaciation. Instead, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ profiles from the underlying Islay Limestone and overlying Bonahaven Formation have been used to suggest a middle Cryogenian (ca. 715 Ma) age for the Port Askaig Formation (Brasier and Shields, 2000; Prave et al., 2009a). Further 'evidence' for a 715 Ma middle Cryogenian age for the Port Askaig Formation is the presence of younger glaciogenic units in the Dalradian, namely the Stralinchy-Reelan (a possible Marinoan correlative) and the Inishowen-Loch na Cille Formations (a possible Gaskiers correlative; Condon and Prave, 2000; McCay et al., 2006). However, the Re-Os age of 659.6 ± 9.6 Ma for the Ballachulish Slate Formation refutes the notion that the Port Askaig Formation is a component of a middle Cryogenian (ca. 715 Ma) glaciation. As reported above, the Re-Os age, coupled with existing geochronology constraints on the Tayvallich volcanics strongly suggest that the Port Askaig Formation records a glacial event on the eastern margin of Laurentia at ~650 Ma.

Palaeomagnetic constraints from Laurentia during the Neoproterozoic indicate that Laurentia (and hence the Port Askaig Formation) was at low latitudes from 723 – 614 Ma (see Trinidade and Macouin, 2007 and references therein). Similarly, the Sturtian (*sensu stricto*) glaciations on the Australian craton were also at low latitude and Re-Os geochronology of post-glacial rocks indicates an age of ~650 Ma for these glacial deposits. The Ballachulish Slate Formation Re-Os geochronology implies that the Port Askaig Formation could be correlated with the ~650 Ma Sturtian (*sensu stricto*) deposits of the Adelaide Rift Complex (Preiss, 2000; Kendall et al., 2006; 2009a). This suggestion is also supported by the Os_i data for the Ballachulish Slate, Upper Black River Dolomite and Tapley Hill formations as discussed below (Fig. 5; Kendall et al., 2006; 2009a; This study).

6.5. Os isotopic composition of seawater at 660 Ma

The initial Os_i values determined from the regression of the Re-Os isotope data (Table 1; Figs. 3 and 4) are interpreted to reflect the Os isotope composition of seawater at the time of deposition (Ravizza and Turekian, 1989; Cohen et al., 1999; Selby and Creaser, 2003). The Os isotope composition for seawater at the time of deposition of the Ballachulish Slate (1.04 ± 0.03) is identical, within uncertainty, to that of the present day Os isotopic composition of seawater (~1.06; Peucker-Ehrenbrink and Ravizza, 2000 and references therein; Rooney et al., unpublished data). The radiogenic Os_i value from the Ballachulish Slate Formation suggests that the contribution of radiogenic Os from riverine inputs and weathering of upper continental crustal material (present-day riverine inputs of $^{187}Os/^{188}Os$ ~1.5; Levasseur et al., 1999) dominated over the influx of unradiogenic Os from cosmic dust and hydrothermal alteration of oceanic crust and peridotites (present-day $^{187}Os/^{188}Os \sim 0.13$; Walker et al., 2002a, b).

The radiogenic values for the Os_i of the Ballachulish Slate Formation closely match values for the post-glacial Upper Black River Dolomite, Aralka and Tapley Hill Formations of southern Australia (1.04; 1.00; 0.82; 0.95, respectively; Kendall et al., 2006; 2009a). Although there are many contrasting palaeomagnetic reconstructions of the Laurentian and Australian cratons, most models indicate that during the Neoproterozoic these two cratons were both located at low latitudes and were separated by oceanic basins that formed as a result of rifting associated with the breakup of Rodinia (Li et al., 2008 and references therein; Li and Evans, 2010). We postulate that the very similar Os_i values reported from the pre-glacial Ballachulish and post-glacial Upper Black River Dolomite, Aralka and Tapley Hill Formations represent a possibly global Os isotope composition for the 660 – 640 Ma time interval (Kendall et al., 2006; 2009a). Additionally, this 'global' isotope composition for this interval is significantly more radiogenic than values for Mesoproterozoic seawater Os isotope composition (1.04 compared to 0.33 and 0.29; Rooney et al., 2010 and Kendall et al., 2009c). One possibility is that falling sea levels and the exposure of rifted margins associated with the breakup of Rodinia would expose older, more radiogenic continental crust to weathering. A further explanation for the increase in $^{187}Os/^{188}Os$ isotope composition for the Neoproterozoic is the increased oxygenation of deep waters during the late Neoproterozoic (Canfield and Teske, 1996; Anbar and Knoll, 2002; Canfield et al., 2007; 2008; Scott et al., 2008). This oxygenation of the oceans and atmosphere would result in increased chemical weathering of continental crust which, coupled with the breakup of Rodinia may result in an increase in seawater Os as seen for the Sr isotope composition of Neoproterozoic seawater (Jacobsen and Kaufman, 1999; Halverson et al., 2007a).

6.6. Systematics of Re-Os in Leny Limestone Formation

Although the Ballachulish Slate Formation experienced complex and polyphase metamorphism, these samples yield a precise depositional age with a low degree of scatter about the linear regression of the Re-Os data (659.6 ± 9.6 Ma, MSWD = 0.01). The results for the Ballachulish Slate samples imply that anhydrous metamorphism and dehydration reactions do not adversely affect Re-Os systematics. In contrast, the Leny Limestone Formation which has also experienced regional Grampian metamorphic events has been disturbed. We suggest that this Re-Os isotope disturbance is probably related to hydration and fluid-flow events associated with Carboniferous / Permian contact metamorphism as discussed below.

The Re-Os isotope data for the Leny Limestone Formation yield a highly imprecise age of 310 ± 110 Ma (MSWD = 338) that is significantly younger than the accepted age of ca. 512 Ma based upon the trilobite fauna found in the Leny Limestone (Fletcher and Rushton, 2007). In addition, the Os_i value of 1.7 ± 2.0 is much more radiogenic than known values for Cambrian seawater (~0.8; Mao et al., 2002) and all of the Phanerozoic.

The Re-Os geochronometer has been shown to be robust following hydrocarbon maturation events, greenschist-facies metamorphism and flash pyrolysis thus suggesting the system is robust even after temperatures as high as 650 °C and pressures as high as 3 kbar (Creaser et al., 2002; Kendall et al., 2004; 2006; 2009; Rooney et al., 2010). Disturbance of the Re-Os systematics by chemical weathering has been identified from outcrop studies on the Ohio Shale (Jaffe et al., 2002). The Leny Limestone Formation outcrop is not significantly weathered and the samples were taken in such a way as to avoid the effects of recent chemical weathering on the outcrop. The measures undertaken to ensure that fresh samples were used for Re-Os geochronology include; removal of surficial weathering prior to sampling of large (~200 g) samples extracted from the outcrop prior to cutting which meant that any evidence of weathering e.g., iron-staining or leaching and features such as quartz veins could be scrupulously avoided. Thus we do not consider these factors to have played a role in the Re-Os analysis of the Leny Limestone Formation.

Recent work has shown that the Re-Os geochronometer is susceptible to disturbance caused by hydrothermal fluid interaction with sedimentary units associated with the formation of a SEDEX deposit (Kendall et al., 2009c). The proximity of the Leny Limestone exposures to the Devonian and Permo-Carboniferous intrusions and associated interactions with hydrothermal fluids are likely causes of disturbance of the Re-Os systematics. In agreement with work by Kendall et al. (2009c) we suggest that the Re-Os age for the Leny Limestone represents a disturbed dataset. The negative Os_i values calculated at 512 Ma and the anomalously young age can be best explained by post-depositional mobilization of Re and Os resulting from hydrothermal fluid flow driven by the igneous intrusions found within the Leny Quarry. Possibly oxidising fluids generated by the intrusions may have leached Re and/or Os from the Leny Slate samples. The Leny Limestone slate samples all have $^{187}Re/^{188}Os$ values that plot to the right of the 512 Ma reference line suggestive of either Re gain or Os loss (Fig. 5). The occurrence of kaolinite, muscovite and berthierine from XRD analysis of the Leny Limestone Formation slates suggests that these minerals are the products of retrograde reactions involving chlorite, muscovite and an Fe-rich phase such as cordierite that was driven by reactions with hydrothermal fluids (Slack et al., 1992; Abad et al., 2010).

The lack of documented mineralisation (small [<1 cm thick] dolomite veins in the limestones notwithstanding) and identifiable accessory or index minerals renders it extremely challenging to gain a full understanding of the P-T conditions of contact metamorphism in the Leny Limestone Formation. However, given that the Grampian Orogeny would have generated local greenschist-facies conditions it is likely that hydrothermal fluid flow driven by the Palaeozoic igneous intrusions hydrated the Leny Limestone slates resulting in retrograde reactions and the disturbance of the Re-Os geochronometer.

7. Conclusions

New Re-Os geochronology for the Ballachulish Slate Formation yields a depositional age of 659.6 ± 9.6 Ma providing a maximum age constraint for the overlying glaciogenic Port Askaig Formation. The precise age coupled with the excellent linear fit of the Re-Os isotope data for the Ballachulish Slate Formation represents the first successful application of the Re-Os system in samples with Re and Os abundances comparable with, or lower than, average continental crustal values. Additionally, these results strongly suggest that meaningful Re-Os geochronology data can be obtained from sedimentary successions that have experienced polyphase contact and regional metamorphism provided that thermal alteration was anhydrous.

The Re-Os geochronology presented here indicates that the Port Askaig Formation is much younger than the middle Cryogenian glacial horizons bracketed at ca. 750 – 690 Ma, with which it was previously correlated. The new geochronology data for the Ballachulish Slate Formation also refutes a correlation of the underlying Ballachulish Limestone Formation with the ca. 800 Ma Bitter Springs anomaly of Australia (Hill and Walter, 2000; Halverson et al., 2007b; Prave et al., 2009a). The Re-Os geochronology provides a chronostratigraphic framework that indicates deposition of the Argyll Group occurred within a ~60 Ma interval prior to eruption of the Tayvallich Volcanics. The Re-Os data provide further support for the argument that Re-Os and U-Pb zircon geochronology are fundamental if we are to use chemostratigraphy to evaluate Neoproterozoic environments.

The Os_i value for seawater at the time of deposition of the Ballachulish Slate Formation is similar to that of the present-day value indicating that the dominant input of

Os to seawater was radiogenic input from the weathering of the continental crust. Additionally, the close similarity of Os_i values from the Ballachulish Slate Formation with Sturtian (*sensu stricto*) deposits from the Australian craton indicates that the dominant source of Os to the oceans was from weathering of an evolved upper continental crust.

Disturbance of Re-Os systematics in the Leny Limestone Formation is evident by a very imprecise and inaccurate age along with a negative value for the Os_i value (calculated at 512 Ma) for seawater in this biostratigraphically constrained Cambrian unit. These factors strongly suggest that the Re-Os system was disturbed in response to hydrothermal fluid flow associated with the intrusion of a number of igneous bodies during the Palaeozoic. The circulation of fluids through the Leny Limestone Formation is suggested to be the cause for the gain of Re and / or the loss of Os thus generating an imprecise age younger than the known depositional age.

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Figure Captions

Figure 1: Simplified geological and location map highlighting the fourfold division of the Dalradian Supergroup of the Grampian Terrane (modified from Harris et al., 1994; Thomas et al., 2004). Abbreviations of sampling locations: BA – Ballachulish Slate quarry; LQ - Leny Limestone quarry.

Figure 2: Generalised stratigraphic column of the Dalradian Supergroup with glaciogenic horizons and the purported Bitter Springs anomaly suggested by Prave et al., (2009) but refuted by the new Re-Os geochronology data. See text for details. BA – Ballachulish Slate Formation; LQ – Leny Limestone Formation. (1. Halliday et al., 1989; 2. Dempster et al., 2002; 3. This study; 4. Noble et al., 1996). Modified from Prave et al. (2009a).

Figure 3: Re-Os isochron diagram for the Ballachulish Slate Formation using various digestion mediums a) the CrO_3-H_2SO_4 digestion method, b) inverse *aqua-regia* digestion, c) both digestion analyses (CrO_3-H_2SO_4 solid line, inverse *aqua-regia* dashed line). Inset diagrams show the deviation of each point from the CrO_3-H_2SO_4 best-fit regression. A Model 1 isochron is accomplished by assuming scatter along the regression line is derived only from the input 2σ uncertainties for $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$, and ρ (rho).

Figure 4: Re-Os isochron diagram for the Leny Slate Member. The dashed line represents a 512 Ma reference line with the Os_i value of 0.8 representing Cambrian seawater (Mao et al., 2002; Jiang et al., 2003). The 512 Ma age assigned for the Leny Limestone is based on a trilobite fauna (Fletcher and Rushton, 2007). See text for discussion.

Figure 5: Graphic illustration of Re-Os geochronology data and Os_i values for Cryogenian and Sturtian (sensu stricto) pre and post glacial horizons. See text for discussion. Data from 1 = Ballachulish Slate Formation (this study); 2 = Aralka

Formation (Kendall et al., 2006); 3 = Tapley Hill Formation (Kendall et al., 2006); 4 = Black River Dolomite (Kendall et al., 2009a)

Tables

Table 1: Re-Os isotope data for the Ballachulish Slate and Leny Slate samples.

Re-Os geochronology of the Neoproterozoic – Cambrian Dalradian Supergroup of Scotland and Ireland: Implications for Neoproterozoic stratigraphy, glaciations and Re-Os systematics

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Abstract

New Re-Os geochronology for the Ballachulish Slate Formation of the Dalradian Supergroup, Scotland yields a depositional age of 659.6 ± 9.6 Ma. This age represents the first successful application of the Re-Os system to rocks that have extremely low Re and Os abundances (<1 ppb and <50 ppt, respectively). The Re-Os age represents a maximum age for the glaciogenic Port Askaig Formation and refutes previous chemostratigraphic and lithostratigraphic studies which correlated the Port Askaig Formation with a series of middle Cryogenian (ca. 715 Ma) glacials. Additionally, the Re-Os age strongly suggests that the Port Askaig Formation may be correlative with the ~ 650 Ma end-Sturtian glaciations of Australia. As a consequence, the correlation of the Ballachulish Limestone Formation with the ca. 800 Ma Bitter Springs anomaly is not tenable. Initial Os isotope data from the Ballachulish Slate Formation coupled with data from Australia reveals a radiogenic $^{187}Os/^{188}Os$ isotope composition (~0.8 to 1.0) for seawater during the Neoproterozoic, which is similar to that of modern seawater (1.06).

We also report a young, highly imprecise Re-Os age (310 ± 110 Ma) for the Early Cambrian Leny Limestone Formation which is constrained biostratigraphically by a polymerid and miomerid trilobite fauna. We suggest, based on the mineralogy of the Leny Limestone, (kaolinite, muscovite and a serpentine group mineral, berthierine), that the Re-Os systematics have been disturbed by post-depositional fluid flow associated with Palaeozoic igneous intrusions. However, it is evident from the Ballachulish Slate Formation results that anhydrous metamorphism does not disturb the Re-Os geochronometer.

Keywords: Re-Os, Dalradian, Neoproterozoic, Sturtian, Rodinia, Laurentia

1. Introduction

Neoproterozoic strata record a number of significant events such as the transition from stratified Proterozoic oceans with oxic surface waters and anoxic deep waters to a more-or-less fully oxygenated ocean (Anbar and Knoll, 2002; Knoll, 2003; Fike et al., 2006; Halverson and Hurtgen, 2007; Canfield et al., 2008). Major changes in biological systems and evolutionary developments occurred towards the end of the Proterozoic including the evolution of metazoans (Logan et al., 1995; 1997; Vidal and Moczydlowska-Vidal, 1997; Jensen et al., 2000; Martin et al., 2000; Narbonne and Gehling, 2003; Knoll et al., 2006; Macdonald, 2010a, b). Additionally, the Neoproterozoic was a time of major climatic fluctuation with a number of extreme glacial events recorded in the rock record (e.g. the "Snowball Earth" of Kirschvink, 1992; Hoffman et al., 1998; Hoffman and Schrag, 2002 or the "Slushball Earth" of Hyde et al., 2000). However, there is at present, no consensus as to the cause, extent, duration or number of these glacial events (Kennedy et al., 1998; Evans, 2000; Fairchild and Kennedy, 2007). The lack of precise and accurate geochronological data has severely hindered attempts to develop a chronological framework for the Neoproterozoic. In particular, understanding and constraining the extent and duration of these glacial events has relied upon lithostratigraphy and chemostratigraphy with only a few glaciogenic successions constrained by robust geochronological data (Hoffmann et al., 2004; Zhou et al., 2004; Kendall et al., 2004; 2006; 2009a; Condon et al., 2005; Bowring et al., 2007; Macdonald et al., 2010a).

During the Neoproterozoic, the continental masses of Laurentia, Baltica and Amazonia were juxtaposed as a result of various orogenic events to form the supercontinent Rodinia (e.g. Li et al., 2008 and references therein). During the break-up of Rodinia which commenced at ca. 750 Ma there was a period of intracontinental extension and basin genesis along the eastern margin of Laurentia (Harris et al., 1994; Soper, 1994; Cawood et al., 2007). Scotland occupied a unique position within the Rodinia supercontinent lying close to the junction of the Laurentian, Baltica and Amazonian continental blocks (Dalziel, 1994). The sedimentary basins that formed during the formation and breakup of Rodinia are preserved in Scotland as the Torridonian, Moine and Dalradian Supergroups (Anderton, 1982; 1985; Rainbird et al., 2001; Strachan et al., 2002; Cawood et al., 2003; 2004; 2007).

The Dalradian Supergroup of Scotland and Ireland is a metasedimentary succession that was deposited on the eastern margin of Laurentia during the late Neoproterozoic and Early Cambrian. Existing constraints imply the base is younger than 800 Ma and it extends to at least 510 Ma (Harris et al., 1994; Smith et al., 1999; Prave et al., 2009a). Despite its importance in regional and global studies of the Proterozoic, our understanding of the Dalradian sequence suffers from a lack of radiometric ages (Halliday et al., 1989; Dempster et al., 2002). In an attempt to improve the chronostratigraphy of the Dalradian, several workers have applied lithostratigraphic and chemostratigraphic tools with varying levels of success (Prave, 1999; Brasier and Shields, 2000; Condon and Prave, 2000; Thomas et al., 2004; McCay et al., 2006; Prave et al., 2009a; Sawaki et al., 2010). These studies have improved our knowledge of the Proterozoic ocean chemistry and the environmental conditions of deposition within the Dalradian sedimentary basin. However, chemostratigraphic tools cannot provide absolute ages and ultimately rely upon correlation with sequences which have robust radiometric and / or biostratigraphic age constraints (Melezhik et al., 2001; 2007; Fairchild and Kennedy, 2007; Jiang et al., 2007; Meert, 2007; Giddings and Wallace, 2009; Frimmel, 2010). As a result, obtaining precise and accurate radiometric ages remain a priority for resolving many of the issues regarding global correlations.

The rhenium-osmium (Re-Os) geochronometer has been shown to provide robust depositional ages even for sedimentary rocks that have experienced hydrocarbon maturation, greenschist metamorphism and flash pyrolysis associated with igneous intrusions (Creaser et al., 2002; Kendall et al., 2004; 2006; 2009a, b; Selby and Creaser, 2005; Rooney et al., 2010). Thus, the Re-Os system represents an accurate, precise and reliable geochronometer for providing depositional age data for the Dalradian metasediments and constructing a chronostratigraphic framework for the chemostratigraphic, tectonostratigraphic and lithostratigraphic datasets.

Here, we present new Re-Os age that constrain the depositional age of a sedimentary unit from the Dalradian Supergroup. The Re-Os data also provides an estimate for the osmium isotope composition of seawater in the Dalradian basin during the Neoproterozoic and ultimately provide a maximum depositional age for a key Neoproterozoic glacial horizon. A further aspect of this study involves the application of Re-Os geochronology to sedimentary units with low Re and Os abundances (<1 ppb Re and <50 ppt Os) to provide accurate and precise geochronology. Additionally, this work presents results from a sedimentary unit (Leny Limestone Formation) in which the Re-Os geochronometer has been disturbed as a result of post-depositional fluid flow. The results from this study provide us with new insights into the robustness of the Re-Os geochronometer.

2. Geological Setting

2.1. The Dalradian Supergroup

The Dalradian Supergroup of Scotland and Ireland consists of a thick (~25 km) metasedimentary succession and a minor amount of mafic volcanics deposited on the eastern margin of the Laurentian craton during the Neoproterozoic to Early Cambrian (Fig. 1; Harris et al., 1994 and references therein). This quoted thickness of the Dalradian Supergroup is a cumulative thickness from all subgroups and is not a true reflection of sediment thickness. Many aspects of basin genesis have proved controversial, with little consensus apparent even after more than a century of studies. Most models for Dalradian deposition invoke a long, shallow-marine, ensialic basin which underwent prolonged extension during the late Neoproterozoic, resulting in the eventual separation of Laurentia from western Gondwana at ca. 550 Ma (Hoffman, 1991; Soper, 1994; Dalziel and Soper, 2001). An alternative model proposes that the lower portions of the Dalradian represented a rapidly formed foredeep basin associated with the mid-Neoproterozoic (840 – 730 Ma) Knoydartian Orogeny (Prave, 1999). In both models extensional tectonics played a major role in the genesis of the upper portions of the Dalradian basin during the latest Neoproterozoic to Early Cambrian.

Lithostratigraphic correlation of the Dalradian Supergroup is hampered by the paucity of volcanic horizons suitable for U-Pb geochronology and the lack of biostratigraphically diagnostic fossils (Fig. 2). Additionally, many portions of the Dalradian sequence exhibit extreme facies variability along strike having experienced complex polyphase deformation and metamorphism (Harris et al., 1994, Strachan et al., 2002 and references therein). Despite these issues, a coherent lithostratigraphy has been established from western Ireland to the Shetland Islands, 200 km north of mainland Scotland (Harris et al., 1994).

The Dalradian Supergroup consists of four groups which are from oldest to youngest; the Grampian, Appin, Argyll and Southern Highland groups (Figs. 1 and 2).

The basal Grampian Group crops out primarily in the Central Highlands although possible correlatives exist on the north Grampian coast and on the Shetland Islands (Strachan et al., 2002). The Grampian Group consists of up to 7 km of predominantly marine, quartzo-feldspathic psammites and semi-pelites (Glover and Winchester, 1989; Harris et al., 1994). The Grampian Group sedimentary succession displays sharp lateral variations typical of a syn-rift origin (Soper and England, 1995; Banks et al., 2007). The overlying Appin Group is exposed in a broad zone throughout Scotland and Ireland as far north as the Shetland Islands. The Appin Group consists of up to 4 km of quartzite, semi-pelites and phyllites deposited as a post-rift, thermal subsidence sequence (Litherland, 1980; Glover et al., 1995; Soper and England, 1995; Glover and McKie, 1996). The overlying Argyll Group records rapid deepening of the basin following the shallow marine conditions of the Appin Group (Anderton, 1985). The Argyll Group consists of a thick heterogeneous succession of shelf sediments up to 9 km thick which passes upwards into deep water turbidite and basinal facies and associated mafic volcanics (Anderton, 1982). The marked change from a shelf setting to deep water sedimentation is widely ascribed to the onset of syn-depositional rifting. The basal subgroup (Islay Subgroup) of the Argyll Group is marked by a distinctive and persistent tillite horizon; the Port Askaig Formation, correlatives of which are traceable from Connemara in western Ireland to Banffshire in NE Scotland (Anderton, 1985; Harris et al., 1994). The Southern Highland Group (along with the newly defined Trossachs Group of Tanner and Sutherland, 2007) marks the top of the Dalradian succession and consists of ca. 4 km of coarse-grained turbiditic clastics and volcaniclastic strata (Anderton, 1985; Soper and England, 1995). The Southern Highland Group is considered to represent the change from a period of continental rifting and rupture to that of a thermally subsiding margin (Anderton, 1985).

2.1.1. Glaciogenic horizons within the Dalradian and possible global correlations

The Port Askaig Formation of the Argyll Group is a thick (~900 m) succession of diamictites interbedded with sandstone, conglomerate and mudstone (Kilburn et al., 1965; Spencer, 1971; Eyles, 1988; Arnaud and Eyles, 2002). The formation represents the most persistent and distinctive glaciogenic horizon within the Dalradian Supergroup (Fig. 2). A glaciogenic origin was first recognised in the late nineteenth century (Thomson, 1871; 1877), and is described in detail in the classic memoir of Spencer (1971). The most extensive outcrops of the Port Askaig Formation consists of ~400 m of coarse-grained and poorly sorted diamictite interbedded with sandstone, mudstone and conglomerate with some megaclasts in the diamictite exceeding 100 m in size (Spencer, 1971; Arnaud, 2004). Recent studies identified enriched $\delta^{13}C$ (+11.7‰) and unradiogenic $^{87}Sr/^{86}Sr$ (0.7067) in carbonate formations above and below the Port Askaig Formation (Brasier and Shields, 2000; Sawaki et al., 2010). These data have been used to correlate the glaciogenic horizon with the ca. 750 – 690 Ma global Sturtian glaciation (Brasier and Shields, 2000; Fanning and Link, 2004; McCay et al., 2006; Macdonald et al., 2010a). Two more stratigraphically limited glaciogenic units within the Dalradian Supergroup have also been identified; the Stralinchy “Boulder Bed” Formation and the Inishowen - Loch na Cille Ice Rafted Debris (IRD) Formations (Fig. 2; Condon and Prave, 2000; McCay et al., 2006). The Stralinchy Formation occurs in the Easdale Subgroup in Donegal in NW Ireland and has been correlated with the ~635 Ma global Marinoan glaciation (Hoffmann et al., 2004; Condon et al., 2005; McCay et al., 2006). The Loch na Cille and Inishowen glaciogenic formations occur within the uppermost Argyll Group and basal Southern Highland Group respectively, and have been correlated with the 580 Ma Laurentian Gaskiers glacial event (Condon and Prave, 2000; Bowring et al., 2003).

2.2. Current chronological constraints for the Dalradian Supergroup

With the exception of *Bonnia-Ollenellus* Zone Early Cambrian trilobites and inarticulate brachiopods of the upper Southern Highland Group, the Dalradian Supergroup is almost entirely devoid of fossils (Pringle, 1939; Fletcher and Rushton, 2007). In addition, absolute chronological constraints on the age of Dalradian sedimentation are also very sparse (Fig. 2). The oldest phase of volcanic activity in the Dalradian Supergroup occurs within correlatives of the Port Askaig Formation in NE Scotland (Chew et al., 2010). However, this thin tholeiitic pillow basalt has not been dated thus far. The lower part of the Southern Highland Group in SW Scotland is characterised by ca. 2 km of tholeiitic mafic volcanic rocks and sills (Tayvallich Volcanic Formation). The Tayvallich Formation is cross cut by a 595 ± 4 Ma (U-Pb SHIRIMP) keratophyre intrusion and a felsic tuff from this formation has yielded a U-Pb zircon age of 601 ± 4 Ma (Halliday et al., 1989; Dempster et al., 2002). Pegmatites from the Central Scottish Highlands has yielded a U-Pb monazite age of 806 ± 3 Ma although the stratigraphic position of these pegmatites remains controversial (Noble et al., 1996). These pegmatites have been suggested to intrude into Grampian Group rocks thus providing a minimum age for these sediments (Noble et al., 1996; Highton et al., 1999). However, other studies (e.g. Smith et al., 1999) propose that the pegmatites intrude into the Dava and Glen Banchor successions which lie unconformably below the Grampian Group and that therefore the Grampian Group is younger than 806 Ma (Smith et al., 1999; Strachan et al., 2002).

Numerous studies have utilised $\delta^{13}C$, $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ data from several different carbonate units of the Dalradian Supergroup with the aim of correlation with global chemostratigraphic curves (Brasier and Shields, 2000; Thomas et al., 2004; McCay et al., 2006; Halverson et al., 2007a; Prave et al., 2009a; Sawaki et al., 2010). A composite $\delta^{13}C$ profile for the Dalradian Supergroup has been used to tentatively correlate the Ballachulish Limestone of the Appin Group with the ca. 800 Ma Bitter Springs anomaly (Prave et al., 2009a; Fig. 2). Additional correlations include the pre-Marinoan Trezona anomaly and ca. 635 Ma Marinoan-equivalent cap carbonate sequence with units of the middle Easdale Subgroup and the terminal Proterozoic (ca. 600 – 551 Ma) Shuram-Wonoka anomaly in the Girlsta Limestone on Shetland (Melezhik et al., 2008; Prave et al., 2009a, b).

2.3. Metamorphism and deformation of the Dalradian Supergroup

The Dalradian Supergroup of Scotland is one of the classic areas for the study of regional and contact metamorphism (e.g., Barrow, 1893; Tilley, 1925; Baker, 1985; Voll et al., 1991; Dempster et al., 1992; Pattison and Harte, 1997). The main phases of regional metamorphism took place during the Grampian Orogeny. The Grampian Orogeny is understood to be related to the collision of Laurentia with an oceanic arc during the Early Ordovician and can be considered broadly equivalent to the Taconic Orogeny of the Appalachians (Dewey and Mange, 1999; Soper et al., 1999). Geochronological constraints for the Grampian Orogeny include U-Pb zircon ages from syn-tectonic intrusives of 475 – 468 Ma and Sm-Nd metamorphic garnet crystallisation ages of 473 – 465 Ma which date peak metamorphism (Friedrich et al., 1999; Baxter et al., 2002).

The Dalradian sedimentary succession also experienced contact metamorphism associated with the intrusion of numerous Late Caledonian (ca. 430 – 390 Ma; Oliver, 2001) granites throughout the Grampian Terrane of Scotland (Fig. 1). In addition to the granites there are also a number of minor Late Palaeozoic intrusive suites recorded in the Dalradian (Neilson et al., 2009 and references therein).

3. Samples for this study

Two localities were chosen for Re-Os geochronology analyses; the Ballachulish Slate Formation from the Ballachulish Subgroup of the Appin Group and the Leny Limestone Formation of the Southern Highland Group (Figs. 1 and 2). The Ballachulish Slate was chosen to provide a maximum age constraint on the depositional age of the Port Askaig Formation (Fig. 2). The Leny Limestone Formation was chosen as it contains the only biostratigraphically diagnostic fauna found in the Dalradian Supergroup (Pringle, 1939; Fletcher and Rushton, 2007). Additionally, the metasedimentary rocks of the Dalradian Supergroup represent an opportunity to further our understanding of the effects of regional and contact metamorphism on the Re-Os geochronometer.

3.1. Appin Group – Ballachulish Slate Formation

The Appin Group consists of three subgroups, the Lochaber, Ballachulish and Blair Atholl (Fig. 2). The Ballachulish Slate Formation consists of ca. 400 m of pyritiferous black slates and graphitic phyllites. Samples were collected on the eastern foreshore of Loch Linnhe at the entrance to Loch Leven (56° 42. 1’ N, 5° 11. 6’ W; Fig. 1). In this area, the top of the Ballachulish Slate Formation is estimated to be ca. 1 km below the equivalent of the Port Askaig Formation (Litherland, 1980; Harris et al., 1994). Regional metamorphic grade associated with the Grampian Orogeny varies from chlorite grade in the NW to garnet grade in the SE. Estimates of P-T conditions range from ca. 450 - 550° C from NW to SE, at ca. 6 kbar (Pattison and Voll, 1991). In addition to Grampian regional metamorphism, the Ballachulish Slates also experienced Late Caledonian (ca. 430 Ma) igneous activity and contact metamorphism primarily associated with the well characterised Ballachulish Igneous Complex (Pattison and Harte, 1997; Pattison, 2006).

The metamorphic aureole varies in width from ca. 400 to 1700 m, based upon the first appearance of cordierite in metapelites (Pattison, 2006). Regional P-T conditions at the time of intrusion are estimated at ca. 250 – 300° C at ca. 3 kbar. The age of the Ballachulish Igneous Complex is constrained by Re-Os molybdenite and U-Pb zircon ages of 433.5 ± 1.8 Ma and 428 ± 9.8 Ma, respectively (Conliffe et al., 2010; Rogers and Dunning, 1991, recalculated by Neilson et al., 2009). Fluid flow between the intrusion and the aureole was limited and there is no evidence for a large-scale hydrothermal circulation system or associated mineralogical changes connected to the intrusion (Harte et al., 1991; Pattison, 2006).

The slates analysed in this study were sampled ca. 2 km NNW of the NW contact of the Ballachulish Igneous complex and are hence outside the aureole. The slates sampled are black and massive with bedding occasionally still discernible and predominantly orientated parallel to cleavage. X-ray diffractometry (XRD) studies indicate that the Ballachulish Slates have a composition of quartz, mica, chlorite and feldspars (albite and occasionally orthoclase), typical of an argillaceous slate. The samples of Ballachulish slate used in this study are similar in composition to those described in greater detail by Walsh (2007).

3.2. Southern Highland Group – Leny Limestone

The Leny Limestone forms part of the Keltie Water Grit Formation of the Southern Highland Group. The formation consists of pale grey to white, siliceous grits, black graphitic slates and rare locally fossiliferous limestones (Tanner and Pringle, 1999). The limestones of this formation yield a fauna including polymerid and miomerid trilobites, brachiopods, sponges, hyoliths and bradoriids (Fletcher and Rushton, 2007). The miomerid trilobites indicate a stratigraphical age equivalent to the base of the paradoxidid Amgan Stage of Siberia traditionally regarded as Middle Cambrian (511 – 506 Ma, Ogg et al., 2008). However, the polymerid trilobites e.g., *Pagetides*, are forms from the *Bonnia-Olenellus* Zone and are thus regarded as Lower Cambrian (516.5 – 512 Ma; Ogg et al., 2008). An age of ca. 512 Ma has been adopted here as the age of the Leny Limestone Formation (Fletcher and Rushton, 2007).

Black graphitic slates of the Leny Limestone Formation were sampled on the south-easterly face of the Western Quarry (56° 15.5' N, 4° 13.1 W; Fig. 1). The metamorphic grade during the Grampian Orogeny was low, with an estimated peak metamorphic temperature of 270˚C (Tanner and Pringle, 1999). Detrital biotite is preserved, albeit commonly partially altered to chlorite. The locality is also the locus of several phases of igneous activity such as intrusions of Devonian quartz-felsite dykes and Permo-Carboniferous quartz dolerite dykes (British Geological Survey, 2005; Fletcher and Rushton, 2007). The Devonian intrusion exhibits a 70 m fault offset, though this faulting is not seen in the Permo-Carboniferous dyke suggesting faulting occurred prior to this younger intrusive episode. XRD analysis of the Leny Limestone Formation slates reveal a composition of quartz, micas (mainly muscovite), kaolinite and a serpentine-group mineral with the chemical formula of $Fe_3Si_2O_5(OH)_4$ suggested to represent berthierine (Brindley, 1982).

4. Sampling and analytical methods

Sampling of the Ballachulish Slate and Leny Limestone Formations was limited to a vertical interval of ca. 50 cm of stratigraphy across a lateral interval of several tens of metres. Weathered material was removed from the outcrop prior to sampling of fresh surfaces. Large (~100 g) samples were selected to ensure homogenisation of Re-Os abundances in the samples (Kendall et al., 2009b). All samples were polished to remove cutting and drilling marks to eliminate any potential contamination. The samples were dried at 60 °C for ~12 hrs and then crushed to a fine powder of ~30 µm. The samples were broken into chips with no metal contact and powdered in a ceramic dish using a shatterbox.

Rhenium-osmium isotope analysis was carried out at Durham University's TOTAL laboratory for source rock geochronology and geochemistry at the Northern Centre for Isotopic and Elemental Tracing (NCIET). Sample digestion using a CrO_3-H_2SO_4 solution is the preferred method for Re-Os geochronology as it has been shown to preferentially liberate hydrogenous Re and Os, ultimately providing more precise ages (Selby and Creaser, 2003; Kendall et al., 2004). An inverse *aqua-regia* solution was also employed in an attempt to evaluate the contribution of detrital Re and Os in these samples. Previous work has shown that *aqua-regia* digestion liberates both non-hydrogenous (detrital and meteoritic) and hydrogenous Re and Os. This detrital Os component has been shown to represent a source of geological scatter that results in determination of imprecise and / or inaccurate depositional ages (Ravizza et al., 1991; Selby and Creaser, 2003; Kendall et al., 2004).

Approximately 1 g of sample powder was digested together with a mixed tracer (spike) solution of ^{190}Os and ^{185}Re in a Cr^{VI}-H_2SO_4 solution in a sealed carius tube at 220 °C for ~48 h (Selby and Creaser, 2003; Kendall et al., 2004). Through the use of the Cr^{VI}-H_2SO_4 digestion media it is possible to preferentially liberate the hydrogenous Re and Os components from the samples thus limiting any detrital component (Selby and Creaser, 2003; Kendall et al., 2004). For the inverse *aqua-regia* digestions approximately 1 g of sample powder was dissolved together with a spike solution of ^{190}Os and ^{185}Re in a 1:2 acid mixture of 3 ml 12 N HCl and 6 ml of 16 N HNO_3 in a sealed carius tube at 220 °C for ~48 h (Selby and Creaser, 2003).

Rhenium and Os were purified from the acid solution using solvent extraction ($CHCl_3$), micro-distillation and anion chromatography methods and analysed by negative thermal ionisation mass spectrometry as outlined by Selby and Creaser (2003), and Selby (2007). The purified Re and Os fractions were loaded onto Ni and Pt filaments, respectively (Selby et al., 2007), with the isotopic measurements conducted using a ThermoElectron TRITON mass spectrometer via static Faraday collection for Re and ion-counting using a secondary electron multiplier in peak-hopping mode for Os. Average procedural blanks for the Cr^{VI}-H_2SO_4 method during this study were 16.8 ± 0.06 pg and 0.43 ± 0.06 pg (1σ S.D., n = 3) for Re and Os respectively, with an average ^{187}Os/^{188}Os value of ~0.25 ± 0.11 (n = 3). For the inverse *aqua-regia* method procedural blanks for Re and Os were 1.9 ± 0.01 pg and 0.12 ± 0.06 pg, respectively (1σ S.D. n = 2) with an average ^{187}Os/^{188}Os value of ~0.4 ± 0.5 (1σ S.D., n = 2).

Uncertainties for ^{187}Re/^{188}Os and ^{187}Os/^{188}Os are determined by error propagation of uncertainties in Re and Os mass spectrometer measurements, blank abundances and isotopic compositions, spike calibrations and reproducibility of standard Re and Os isotopic values using methods identical to previous studies (e.g., Kendall et al., 2004; Selby and Creaser, 2005). The Re-Os isotopic data, 2σ calculated uncertainties for ^{187}Re/^{188}Os and ^{187}Os/^{188}Os and the associated error correlation function (rho) are regressed to yield a Re-Os date using *Isoplot V. 3.0* with a λ ^{187}Re constant of $1.666 \times 10^{-11} a^{-1}$ (Ludwig, 1980; Smoliar et al., 1996; Ludwig, 2003).

To ensure and monitor long-term mass spectrometry reproducibility, in-house standard solutions of Re and Os (Durham Romil Osmium Standard [DROsS]) are repeatedly analysed at NCIET. The Re standard analysed during the course of this study is made from 99.999% zone-refined Re ribbon and is considered to have an identical Re isotopic composition to that of the AB-1 Re standard (Creaser et al., 2002; Selby and Creaser, 2003; Kendall et al., 2004). The NCIET Re standard yields an average $^{185}Re/^{187}Re$ ratio of 0.59772 ± 0.00172 (1 SD, n = 114). This is in excellent agreement with the value reported for the AB-1 standard (Creaser et al., 2002). The Os isotope reference material (DROsS) yields an $^{187}Os/^{188}Os$ ratio of 0.106093 ± 0.00015 (1 SD, n = 36). The isotopic compositions of these solutions are identical within uncertainty to those reported by Rooney et al. (2010) and references therein.

5. Results

5.1. Ballachulish Slate Formation samples

The Ballachulish Slate samples have Re (0.3 – 1.9 ppb) and Os (25.5 – 52.2 ppt) abundances that are close to or less than that of average continental crustal values of ~1 ppb and 50 ppt, respectively (Table 1; Esser and Turekian, 1993; Peucker-Ehrenbrink and Jahn, 2001; Hattori et al., 2003; Sun et al., 2003). The $^{187}Re/^{188}Os$ ratios range from 56.5 to 311.7 and the $^{187}Os/^{188}Os$ ratios range from 1.660 – 4.478 (Table 1). Regression of the Re-Os isotope data yields a Re-Os age of 659.6 ± 9.6 Ma (2σ, n = 5, Model 1, Mean Square of Weighted Deviates [MSWD] = 0.01, initial $^{187}Os/^{188}Os$ = 1.04 ± 0.03; Fig. 3a).

Digestion of the Ballachulish samples using inverse *aqua-regia* yields elemental abundances of 0.3 – 1.8 ppb and 30.6 – 53.5 ppt for Re and Os, respectively, which are identical within uncertainty to the values from the samples digested using CrO_3-H_2SO_4 (Table 1). The $^{187}Re/^{188}Os$ ratios range from 41.4 to 308.2 and the $^{187}Os/^{188}Os$ ratios range from 1.472 to 4.364 (Table 1). Regression of the *aqua-regia* derived Re-Os isotope data yields a Model 3 age of 655 ± 49 Ma (2σ, n = 5, MSWD = 16) with an initial Os isotope composition of 1.03 ± 0.16 (Fig. 3b).

5.2. Leny Limestone slate samples

The Leny Limestone slates are enriched in Re (46.2 – 66.1 ppb) and Os (419 – 633 ppt) in comparison to average continental crustal values of ~1 ppb and 50 ppt, respectively (Table 1). The $^{187}Re/^{188}Os$ ratios range from 898.4 to 1228.0 and the $^{187}Os/^{188}Os$ ratios range from 6.162 – 8.075 (Table 1). Regression of the Re-Os isotope data yields a Re-Os age of 310 ± 110 Ma (2σ, n = 9, Model 3, MSWD = 388, initial $^{187}Os/^{188}Os$ = 1.7 ± 2.0; Fig. 4).

6. Discussion

6.1. Effect of non-hydrogenous Re and Os in low abundance samples

The CrO_3-H_2SO_4 method has been shown to yield precise and accurate depositional age determinations for both Phanerozoic and Proterozoic sedimentary successions (Kendall et al., 2004; 2006; 2009a, c; Selby and Creaser, 2005; Anbar et al., 2007; Selby, 2007; Yang et al., 2009; Rooney et al., 2010). Data from the Ballachulish samples using the CrO_3-H_2SO_4 digestion method yields a Model 1 age with a low uncertainty (1.5 %) and a low degree of scatter about the isochron (MSWD <1). However, as these samples have Re and Os abundances comparable to that of average continental crust it is important to assess the effects of a detrital Re and Os component on the geochronology data. It has been shown that the incorporation of a detrital Os component could lead to a younger or older age depending on the isotopic composition of the detrital Os (Ravizza et al., 1991). The effects of a detrital Os component on Re-Os depositional ages have been assessed previously during the development of the CrO_3-H_2SO_4 method (Selby and Creaser, 2003; Kendall et al., 2004).

The results from the inverse *aqua-regia* digestion show Re and Os abundances that are comparable with the samples digested using CrO_3-H_2SO_4 (Table 1). The isotopic composition data highlights the impact of detrital Re and Os on the determination of depositional ages. All of the $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ values for the *aqua-regia* samples are lower than those of the samples digested using CrO_3-H_2SO_4 (15% and 9% lower, respectively; Table 1). This suggests that the *aqua-regia* digestion has liberated an unradiogenic detrital Os component. Both ages for the Ballachulish Slate Formation are very similar however, however the *aqua-regia* Re-Os data set have a much larger degree of scatter (MSWD = 16) and yield a less precise age (9% uncertainty; Fig 3b, c). The samples digested using the CrO_3-H_2SO_4 method yield a much more precise age with a lower degree of scatter (MSWD = 0.01; Fig. 3a). These variations in precision and geological scatter are very similar to those identified by previous studies which undertook digestion of samples in *aqua-regia* (Selby and Creaser, 2003; Kendall et al., 2004). Additionally, digesting samples in the CrO_3-H_2SO_4 solution at 80 °C instead of 220 °C has been shown to yield identical data supporting the notion that this method does not liberate non-hydrogenous Re and Os even at high temperatures (Kendall et al., 2009a).

The $^{187}Os/^{188}Os$ initial ratio (Os_i) data from the samples digested using the CrO_3-H_2SO_4 method are all very similar with a coefficient of variation of 0.3% in contrast to the Os_i data from the samples digested in *aqua-regia* which have a coefficient of variation of 5% (coefficient of variation = (SD/mean) x 100; Table 1). This suggests that there were variations in Os isotope composition and / or magnitude of the detrital Os flux into the Ballachulish Slate during deposition. Again, this is identical to the findings of Kendall et al. (2004) on the Old Fort Point Formation of Canada.

The low degree of scatter coupled with the precise age of 659.6 ± 9.6 Ma represents a depositional age for the Ballachulish Slate Formation and the initial $^{187}Os/^{188}Os$ isotope composition of 1.04 represents that of seawater at the time of deposition.

6.2. Implications for low Re and Os abundance geochronology

The Re-Os age for the Ballachulish Slate Formation indicate that samples with low Re and Os abundances (<1 ppb Re and <50 ppt Os) can be used to provide precise geochronological data (Fig. 3a; Table 1). These values are similar to abundances in average continental crust which range from 0.2 – 2 ppb and 30 – 50 ppt, respectively (Esser and Turekian, 1993; Peucker-Ehrenbrink and Jahn, 2001; Hattori et al., 2003; Sun et al., 2003).

Previous work on Re-Os geochronology has focused on sedimentary units greatly enriched in Re and Os with abundances >20 ppb and 500 ppt, respectively (Ravizza et al., 1989; Cohen et al., 1999, Creaser et al., 2002; Selby and Creaser, 2005; Selby, 2007; Rooney et al., 2010). However, some recent studies have successfully applied the Re-Os geochronometer to sedimentary rocks with low to moderate enrichments of Re and Os (1.7 – 50 ppb and 82 – 250 ppt, respectively; Kendall et al., 2004; 2006; 2009a, b; Yang et al., 2009). The Re-Os geochronology data for the Ballachulish Slate Formation represent successful application of the system to samples with very low Re and Os abundances provided that the system has not been disturbed as discussed below.

The low Re and Os abundances do not appear to impair the robustness of the system as the Ballachulish samples all have similar $^{187}Os/^{188}Os$ (Os_i) values, yield a large spread in present-day $^{187}Re/^{188}Os$ values (~260 units) and display positively correlated, radiogenic $^{187}Os/^{188}Os$ values indicative of a closed system (Table 1). This positive correlation indicates that the 659.6 ± 9.6 Ma age for the Ballachulish Slate Formation does not represent a mixing line. Additionally, if the systematics had been disturbed, any detrital Os component in these samples would represent a significant cause of geological uncertainty, resulting in an imprecise and geologically meaningless age. The highly precise age coupled with the low degree of scatter in the data, (659.6 ± 9.6 and MSWD = 0.01), suggests that this is a depositional age and the Os_i value of 1.04 represents the Os isotope composition of local seawater at the time of deposition. The results from the Ballachulish Slate Formation strongly suggest that the system can be applied to sedimentary units that have low Re and Os abundances. From this we can also propose that the system is robust enough to provide depositional ages for strata that have experienced complex and polyphase metamorphic histories.

6.3. *Age of the Ballachulish Slate Formation*

The Re-Os isotope data from the Ballachulish slates yield an age of 659.6 ± 9.6 Ma which represents the depositional age of the Ballachulish Slate Formation (Fig. 3a). Accordingly, this Re-Os age defines a maximum age constraint for the glaciogenic Port Askaig Formation (Fig. 2). Taken in the context of the previous geochronological constraints for the Dalradian, the Re-Os age for the Ballachulish Slate Formation strongly suggests that the Argyll Group was deposited within ~60 Ma, prior to the eruption of the Tayvallich volcanics at ca. 600 Ma. From these two geochronological constraints, combined with the possibility that correlatives of the ca. 635 Ma Marinoan cap carbonate sequence are found within units of the Easdale Subgroup (McCay et al., 2006) we suggest that the Port Askaig Formation records a low latitude glacial event that occurred at ca. 650 Ma.

Much of the recent work relating to the Dalradian Supergroup has focused on $\delta^{13}C$ carbonate and $^{87}Sr/^{86}Sr$ chemostratigraphy of the various carbonate units (Prave et al., 2009a and references therein; Sawaki et al., 2010). This focus on chemostratigraphy coupled with the lack of reliable geochronology data has resulted in several attempts at correlation of the Dalradian Supergroup with better constrained Neoproterozoic sequences (McCay et al., 2006; Prave et al., 2009a; Sawaki et al., 2010). The Ballachulish Limestone is ca. 200 m in thickness and passes upwards into the Ballachulish Slate (Anderton, 1982; Prave et al., 2009a). Work by Prave et al. (2009a) suggested that the Ballachulish Limestone possess $\delta^{13}C_{carbonate}$ values as low as -7‰ and was tentatively correlated with the ca. 800 Ma Bitter Springs anomaly of central Australia (Hill and Walter, 2000; Halverson et al., 2007b). However, the Re-Os data of 659.6 ± 9.6 Ma for the Ballachulish Slate Formation negates the possibility of this correlation (Fig. 2).

A 60 Ma duration for Argyll Group deposition suggested by the Re-Os data presented here contrasts with a duration of ca. 120 Ma required by chemostratigraphic and lithostratigraphic correlations of the Port Askaig Formation with a ca. 715 Ma "Sturtian" glacial (Prave, 1999; Brasier and Shields, 2000; Prave et al., 2009a;). A short duration for Argyll Group deposition is geologically more probable given that the Argyll Group represents a time of increased tectonic activity and syn-depositional faulting with rapid deposition taking place in subsiding fault-bounded sub-basins (Anderton, 1982; 1985). A short duration for Argyll Group deposition also negates the need for any putative regional-scale unconformity within the Argyll Group, which remains contentious (see Hutton and Alsop, 2004 and Tanner et al., 2005 for a review).

The new Re-Os geochronology data provide a more precise chronostratigraphic framework for understanding the tectonic evolution of the Dalradian basin and the onset of sedimentation within the basin. Furthermore, the Re-Os geochronology helps refine Neoproterozoic palaeogeographies related to the formation and breakup of the Rodinia supercontinent (e.g., Li et al., 2008; Li and Evans, 2010). Deposition of the Dalradian Supergroup occurred along the eastern margin of Laurentia, close to the triple junction of Baltica, Laurentia and Amazonia (Soper, 1994; Dalziel, 1994).

6.4. Implications for global correlations involving the glacial Port Askaig Formation

At present, global correlation schemes for Neoproterozoic glaciogenic deposits are dependent on correlation of two distinctive types of diamictite cap-carbonate pairs. These have been designated as "Sturtian" and "Marinoan" events after the type localities in southern Australia (Kennedy et al., 1998; Hoffman and Schrag, 2002; Halverson et al., 2005; Corsetti and Lorentz, 2006). The Sturtian glaciation however, is also used to define much older glacial events than the Sturtian *sensu stricto* of the Adelaide Rift Complex which has geochronological constraints of ca. 640 – 660 Ma (Preiss, 2000; Kendall et al., 2009a and references therein). These earlier glacial events assigned to the "Sturtian" have geochronological constraints which indicate low-latitude global glaciation at ca. 715 Ma based on U-Pb zircon ages (Bowring et al., 2007; Macdonald et al., 2010a). In this summary, they are referred to as middle Cryogenian (ca. 715 Ma) deposits to distinguish them from younger Sturtian (*sensu stricto)* glacial deposits on the Australian craton at ca. 640 – 660 Ma.

Early work on correlation of the Port Askaig Formation (Fig. 2) suggested a possible correlation with North Atlantic Varangerian tillite sequences which were originally constrained by a Rb-Sr diagenetic illite age of ca. 630 Ma (Hambrey, 1983; Fairchild and Hambrey, 1995; Gorokhov et al., 2001). Correlation of the Port Askaig Formation with the Varangerian tillite was also suggested by $^{87}Sr/^{86}Sr$ chemostratigraphy of Dalradian limestones that indicate that the base of the Dalradian Supergroup is younger than ca. 800 Ma and may be as young as ca. 700 Ma (Thomas et al., 2004). This correlation is difficult to support as the geochronological constraints for the Varangerian glaciation are based upon Rb-Sr illite geochronology, which is unlikely to represent a depositional age (Morton and Long, 1982; Ohr et al., 1991; Awwiller, 1994; Evans, 1996; Gorokhov et al., 2001; Selby, 2009).

Recent work has rejected the correlation of the Port Askaig Formation and the Varangerian glaciation. Instead, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ profiles from the underlying Islay Limestone and overlying Bonahaven Formation have been used to suggest a middle Cryogenian (ca. 715 Ma) age for the Port Askaig Formation (Brasier and Shields, 2000; Prave et al., 2009a). Further 'evidence' for a 715 Ma middle Cryogenian age for the Port Askaig Formation is the presence of younger glaciogenic units in the Dalradian, namely the Stralinchy-Reelan (a possible Marinoan correlative) and the Inishowen-Loch na Cille Formations (a possible Gaskiers correlative; Condon and Prave, 2000; McCay et al., 2006). However, the Re-Os age of 659.6 ± 9.6 Ma for the Ballachulish Slate Formation refutes the notion that the Port Askaig Formation is a component of a middle Cryogenian (ca. 715 Ma) glaciation. As reported above, the Re-Os age, coupled with existing geochronology constraints on the Tayvallich volcanics strongly suggest that the Port Askaig Formation records a glacial event on the eastern margin of Laurentia at ~650 Ma.

Palaeomagnetic constraints from Laurentia during the Neoproterozoic indicate that Laurentia (and hence the Port Askaig Formation) was at low latitudes from 723 – 614 Ma (see Trinidade and Macouin, 2007 and references therein). Similarly, the Sturtian (*sensu stricto*) glaciations on the Australian craton were also at low latitude and Re-Os geochronology of post-glacial rocks indicates an age of ~650 Ma for these glacial deposits. The Ballachulish Slate Formation Re-Os geochronology implies that the Port Askaig Formation could be correlated with the ~650 Ma Sturtian (*sensu stricto*) deposits of the Adelaide Rift Complex (Preiss, 2000; Kendall et al., 2006; 2009a). This suggestion is also supported by the Os_i data for the Ballachulish Slate, Upper Black River Dolomite and Tapley Hill formations as discussed below (Fig. 5; Kendall et al., 2006; 2009a; This study).

6.5. Os isotopic composition of seawater at 660 Ma

The initial Os_i values determined from the regression of the Re-Os isotope data (Table 1; Figs. 3 and 4) are interpreted to reflect the Os isotope composition of seawater at the time of deposition (Ravizza and Turekian, 1989; Cohen et al., 1999; Selby and Creaser, 2003). The Os isotope composition for seawater at the time of deposition of the Ballachulish Slate (1.04 ± 0.03) is identical, within uncertainty, to that of the present day Os isotopic composition of seawater (~1.06; Peucker-Ehrenbrink and Ravizza, 2000 and references therein; Rooney et al., unpublished data). The radiogenic Os_i value from the Ballachulish Slate Formation suggests that the contribution of radiogenic Os from riverine inputs and weathering of upper continental crustal material (present-day riverine inputs of $^{187}Os/^{188}Os$ ~1.5; Levasseur et al., 1999) dominated over the influx of unradiogenic Os from cosmic dust and hydrothermal alteration of oceanic crust and peridotites (present-day $^{187}Os/^{188}Os$ ~ 0.13; Walker et al., 2002a, b).

The radiogenic values for the Os_i of the Ballachulish Slate Formation closely match values for the post-glacial Upper Black River Dolomite, Aralka and Tapley Hill Formations of southern Australia (1.04; 1.00; 0.82; 0.95, respectively; Kendall et al., 2006; 2009a). Although there are many contrasting palaeomagnetic reconstructions of the Laurentian and Australian cratons, most models indicate that during the Neoproterozoic these two cratons were both located at low latitudes and were separated by oceanic basins that formed as a result of rifting associated with the breakup of Rodinia (Li et al., 2008 and references therein; Li and Evans, 2010). We postulate that the very similar Os_i values reported from the pre-glacial Ballachulish and post-glacial Upper Black River Dolomite, Aralka and Tapley Hill Formations represent a possibly global Os isotope composition for the 660 – 640 Ma time interval (Kendall et al., 2006; 2009a). Additionally, this 'global' isotope composition for this interval is significantly more radiogenic than values for Mesoproterozoic seawater Os isotope composition (1.04 compared to 0.33 and 0.29; Rooney et al., 2010 and Kendall et al., 2009c). One possibility is that falling sea levels and the exposure of rifted margins associated with the breakup of Rodinia would expose older, more radiogenic continental crust to weathering. A further explanation for the increase in $^{187}Os/^{188}Os$ isotope composition for the Neoproterozoic is the increased oxygenation of deep waters during the late Neoproterozoic (Canfield and Teske, 1996; Anbar and Knoll, 2002; Canfield et al., 2007; 2008; Scott et al., 2008). This oxygenation of the oceans and atmosphere would result in increased chemical weathering of continental crust which, coupled with the breakup of Rodinia may result in an increase in seawater Os as seen for the Sr isotope composition of Neoproterozoic seawater (Jacobsen and Kaufman, 1999; Halverson et al., 2007a).

6.6. Systematics of Re-Os in Leny Limestone Formation

Although the Ballachulish Slate Formation experienced complex and polyphase metamorphism, these samples yield a precise depositional age with a low degree of scatter about the linear regression of the Re-Os data (659.6 ± 9.6 Ma, MSWD = 0.01). The results for the Ballachulish Slate samples imply that anhydrous metamorphism and dehydration reactions do not adversely affect Re-Os systematics. In contrast, the Leny Limestone Formation which has also experienced regional Grampian metamorphic events has been disturbed. We suggest that this Re-Os isotope disturbance is probably related to hydration and fluid-flow events associated with Carboniferous / Permian contact metamorphism as discussed below.

The Re-Os isotope data for the Leny Limestone Formation yield a highly imprecise age of 310 ± 110 Ma (MSWD = 338) that is significantly younger than the accepted age of ca. 512 Ma based upon the trilobite fauna found in the Leny Limestone (Fletcher and Rushton, 2007). In addition, the Os_i value of 1.7 ± 2.0 is much more radiogenic than known values for Cambrian seawater (~0.8; Mao et al., 2002) and all of the Phanerozoic.

The Re-Os geochronometer has been shown to be robust following hydrocarbon maturation events, greenschist-facies metamorphism and flash pyrolysis thus suggesting the system is robust even after temperatures as high as 650 °C and pressures as high as 3 kbar (Creaser et al., 2002; Kendall et al., 2004; 2006; 2009; Rooney et al., 2010). Disturbance of the Re-Os systematics by chemical weathering has been identified from outcrop studies on the Ohio Shale (Jaffe et al., 2002). The Leny Limestone Formation outcrop is not significantly weathered and the samples were taken in such a way as to avoid the effects of recent chemical weathering on the outcrop. The measures undertaken to ensure that fresh samples were used for Re-Os geochronology include; removal of surficial weathering prior to sampling of large (~200 g) samples extracted from the outcrop prior to cutting which meant that any evidence of weathering e.g., iron-staining or leaching and features such as quartz veins could be scrupulously avoided. Thus we do not consider these factors to have played a role in the Re-Os analysis of the Leny Limestone Formation.

Recent work has shown that the Re-Os geochronometer is susceptible to disturbance caused by hydrothermal fluid interaction with sedimentary units associated with the formation of a SEDEX deposit (Kendall et al., 2009c). The proximity of the Leny Limestone exposures to the Devonian and Permo-Carboniferous intrusions and associated interactions with hydrothermal fluids are likely causes of disturbance of the Re-Os systematics. In agreement with work by Kendall et al. (2009c) we suggest that the Re-Os age for the Leny Limestone represents a disturbed dataset. The negative Os_i values calculated at 512 Ma and the anomalously young age can be best explained by post-depositional mobilization of Re and Os resulting from hydrothermal fluid flow driven by the igneous intrusions found within the Leny Quarry. Possibly oxidising fluids generated by the intrusions may have leached Re and/or Os from the Leny Slate samples. The Leny Limestone slate samples all have $^{187}Re/^{188}Os$ values that plot to the right of the 512 Ma reference line suggestive of either Re gain or Os loss (Fig. 5). The occurrence of kaolinite, muscovite and berthierine from XRD analysis of the Leny Limestone Formation slates suggests that these minerals are the products of retrograde reactions involving chlorite, muscovite and an Fe-rich phase such as cordierite that was driven by reactions with hydrothermal fluids (Slack et al., 1992; Abad et al., 2010).

The lack of documented mineralisation (small [<1 cm thick] dolomite veins in the limestones notwithstanding) and identifiable accessory or index minerals renders it extremely challenging to gain a full understanding of the P-T conditions of contact metamorphism in the Leny Limestone Formation. However, given that the Grampian Orogeny would have generated local greenschist-facies conditions it is likely that hydrothermal fluid flow driven by the Palaeozoic igneous intrusions hydrated the Leny Limestone slates resulting in retrograde reactions and the disturbance of the Re-Os geochronometer.

7. Conclusions

New Re-Os geochronology for the Ballachulish Slate Formation yields a depositional age of 659.6 ± 9.6 Ma providing a maximum age constraint for the overlying glaciogenic Port Askaig Formation. The precise age coupled with the excellent linear fit of the Re-Os isotope data for the Ballachulish Slate Formation represents the first successful application of the Re-Os system in samples with Re and Os abundances comparable with, or lower than, average continental crustal values. Additionally, these results strongly suggest that meaningful Re-Os geochronology data can be obtained from sedimentary successions that have experienced polyphase contact and regional metamorphism provided that thermal alteration was anhydrous.

The Re-Os geochronology presented here indicates that the Port Askaig Formation is much younger than the middle Cryogenian glacial horizons bracketed at ca. 750 – 690 Ma, with which it was previously correlated. The new geochronology data for the Ballachulish Slate Formation also refutes a correlation of the underlying Ballachulish Limestone Formation with the ca. 800 Ma Bitter Springs anomaly of Australia (Hill and Walter, 2000; Halverson et al., 2007b; Prave et al., 2009a). The Re-Os geochronology provides a chronostratigraphic framework that indicates deposition of the Argyll Group occurred within a ~60 Ma interval prior to eruption of the Tayvallich Volcanics. The Re-Os data provide further support for the argument that Re-Os and U-Pb zircon geochronology are fundamental if we are to use chemostratigraphy to evaluate Neoproterozoic environments.

The Os_i value for seawater at the time of deposition of the Ballachulish Slate Formation is similar to that of the present-day value indicating that the dominant input of

Os to seawater was radiogenic input from the weathering of the continental crust. Additionally, the close similarity of Os_i values from the Ballachulish Slate Formation with Sturtian (*sensu stricto*) deposits from the Australian craton indicates that the dominant source of Os to the oceans was from weathering of an evolved upper continental crust.

Disturbance of Re-Os systematics in the Leny Limestone Formation is evident by a very imprecise and inaccurate age along with a negative value for the Os_i value (calculated at 512 Ma) for seawater in this biostratigraphically constrained Cambrian unit. These factors strongly suggest that the Re-Os system was disturbed in response to hydrothermal fluid flow associated with the intrusion of a number of igneous bodies during the Palaeozoic. The circulation of fluids through the Leny Limestone Formation is suggested to be the cause for the gain of Re and / or the loss of Os thus generating an imprecise age younger than the known depositional age.

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Figure Captions

Figure 1: Simplified geological and location map highlighting the fourfold division of the Dalradian Supergroup of the Grampian Terrane (modified from Harris et al., 1994; Thomas et al., 2004). Abbreviations of sampling locations: BA – Ballachulish Slate quarry; LQ - Leny Limestone quarry.

Figure 2: Generalised stratigraphic column of the Dalradian Supergroup with glaciogenic horizons and the purported Bitter Springs anomaly suggested by Prave et al., (2009) but refuted by the new Re-Os geochronology data. See text for details. BA – Ballachulish Slate Formation; LQ – Leny Limestone Formation. (1. Halliday et al., 1989; 2. Dempster et al., 2002; 3. This study; 4. Noble et al., 1996). Modified from Prave et al. (2009a).

Figure 3: Re-Os isochron diagram for the Ballachulish Slate Formation using various digestion mediums a) the CrO_3-H_2SO_4 digestion method, b) inverse *aqua-regia* digestion, c) both digestion analyses (CrO_3-H_2SO_4 solid line, inverse *aqua-regia* dashed line). Inset diagrams show the deviation of each point from the CrO_3-H_2SO_4 best-fit regression. A Model 1 isochron is accomplished by assuming scatter along the regression line is derived only from the input 2σ uncertainties for $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$, and ρ (rho).

Figure 4: Re-Os isochron diagram for the Leny Slate Member. The dashed line represents a 512 Ma reference line with the Os_i value of 0.8 representing Cambrian seawater (Mao et al., 2002; Jiang et al., 2003). The 512 Ma age assigned for the Leny Limestone is based on a trilobite fauna (Fletcher and Rushton, 2007). See text for discussion.

Figure 5: Graphic illustration of Re-Os geochronology data and Os_i values for Cryogenian and Sturtian (sensu stricto) pre and post glacial horizons. See text for discussion. Data from 1 = Ballachulish Slate Formation (this study); 2 = Aralka

Formation (Kendall et al., 2006); 3 = Tapley Hill Formation (Kendall et al., 2006); 4 = Black River Dolomite (Kendall et al., 2009a)

Tables

Table 1: Re-Os isotope data for the Ballachulish Slate and Leny Slate samples.

Table 1

Re-Os isotope data for the Ballachulish Slate and Leny Limestone Formations

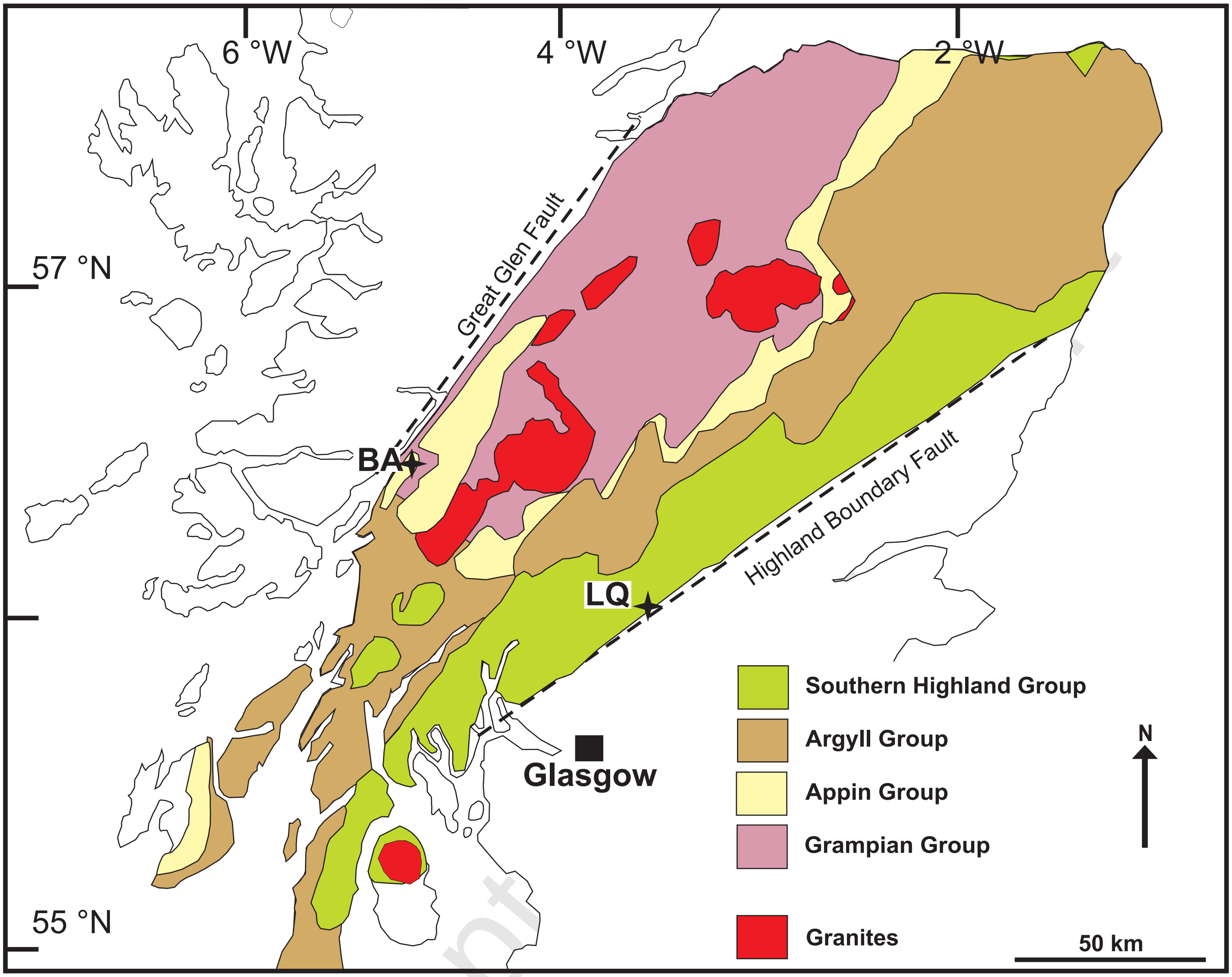
Sample [a]	Re (ppb)	±	Os (ppt)	±	^{192}Os (ppt)	±	^{187}Re/^{188}Os	±	^{187}Os/^{188}Os	±	rho[b]	Os_i[c]
Ballachulish Slate samples												
Balla 2B	1.20	0.01	46.0	0.5	13.9	0.2	172.6	2.3	2.944	0.044	0.731	1.04
Balla 2B ar	1.08	0.00*	43.8	0.4	13.3	0.2	161.3	1.9	2.876	0.042	0.763	1.09
Balla 2C	1.85	0.01	52.2	0.5	14.5	0.2	253.8	3.2	3.841	0.055	0.758	1.04
Balla 2C ar	1.77	0.01	53.5	0.5	15.3	0.2	230.8	2.6	3.564	0.050	0.745	1.01
Balla 3	1.69	0.01	40.9	0.5	10.8	0.2	311.7	4.6	4.478	0.072	0.813	1.04
Balla 3 ar	1.68	0.01	40.9	0.5	10.9	0.1	308.2	4.1	4.364	0.067	0.805	0.96
Balla 5B	0.29	0.01	29.2	0.3	10.1	0.2	56.5	1.4	1.660	0.029	0.482	1.04
Balla 5B ar	0.30	0.00*	30.6	0.3	10.6	0.1	55.6	0.8	1.593	0.026	0.767	0.98
Balla 6	0.39	0.02	25.5	0.7	8.4	0.5	93.3	6.4	2.060	0.142	0.645	1.03
Balla 6 ar	0.30	0.01	41.4	0.6	16.7	0.6	41.4	1.3	1.472	0.050	0.511	1.01
Leny Slate Samples												
L1	55.8	0.2	487.7	3.1	107.1	0.5	1036.8	5.6	6.874	0.033	0.716	-1.97
L2	55.4	0.2	431.0	3.0	89.8	0.4	1228.0	7.2	7.649	0.041	0.756	-2.83
L3	49.4	0.2	430.6	3.0	92.2	0.5	1065.8	6.2	7.239	0.038	0.759	-1.85
L4	50.9	0.2	419.2	3.0	85.0	0.4	1192.4	7.2	8.075	0.045	0.778	-2.10
L5	49.6	0.2	424.1	3.0	88.4	0.5	1117.0	6.7	7.642	0.042	0.771	-1.89
L6	51.2	0.2	443.0	3.0	92.1	0.4	1107.2	6.3	7.691	0.039	0.755	-1.76
L7	66.1	0.2	633.1	4.1	146.3	0.6	898.4	4.5	6.162	0.031	0.583	-1.50
L8	46.2	0.2	447.0	3.2	99.7	0.5	921.5	5.4	6.650	0.040	0.682	-1.21
L9	57.7	0.2	515.9	3.3	114.5	0.5	1001.9	5.2	6.716	0.031	0.680	-1.83

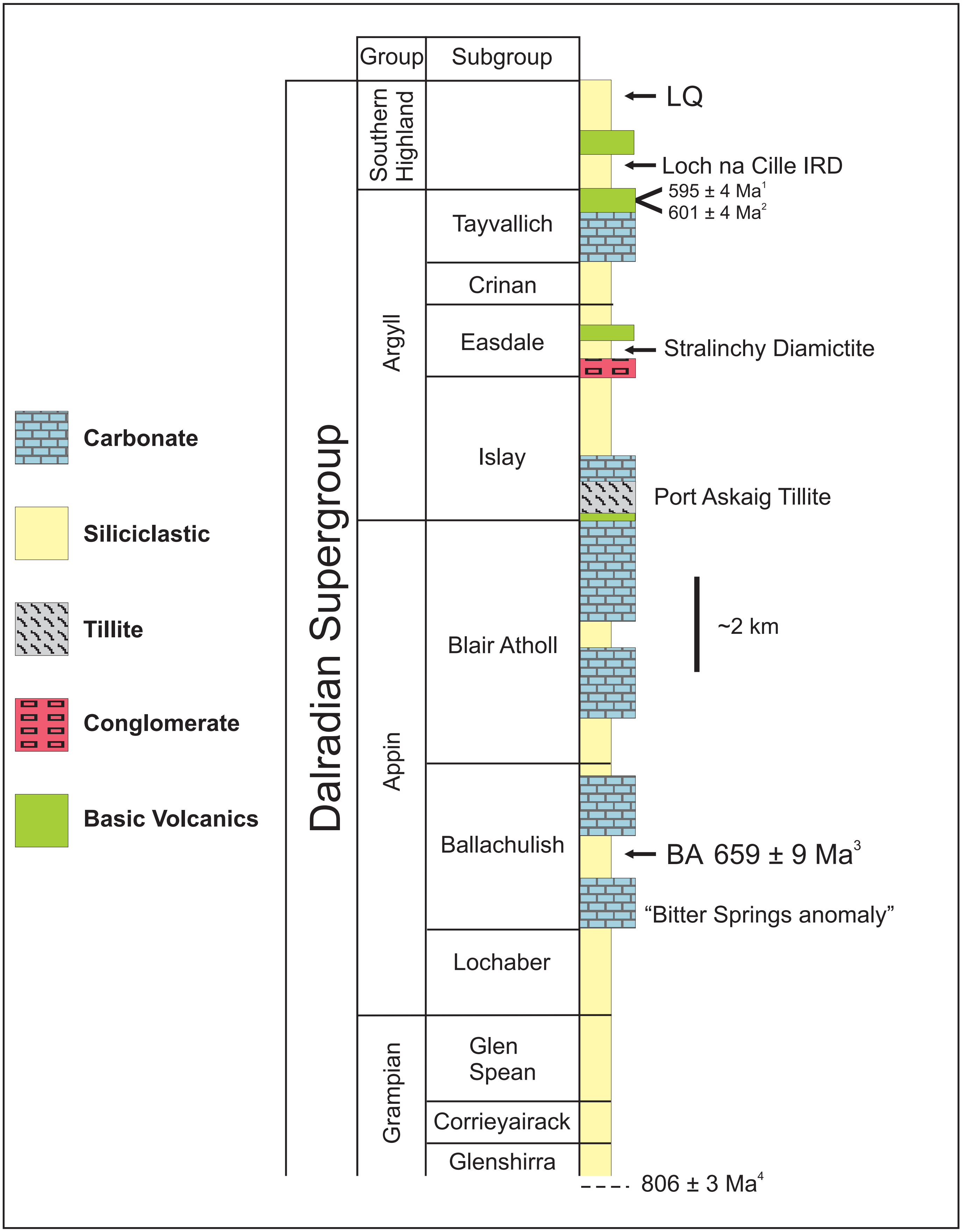
[a] "ar" denotes inverse aqua regia digestion

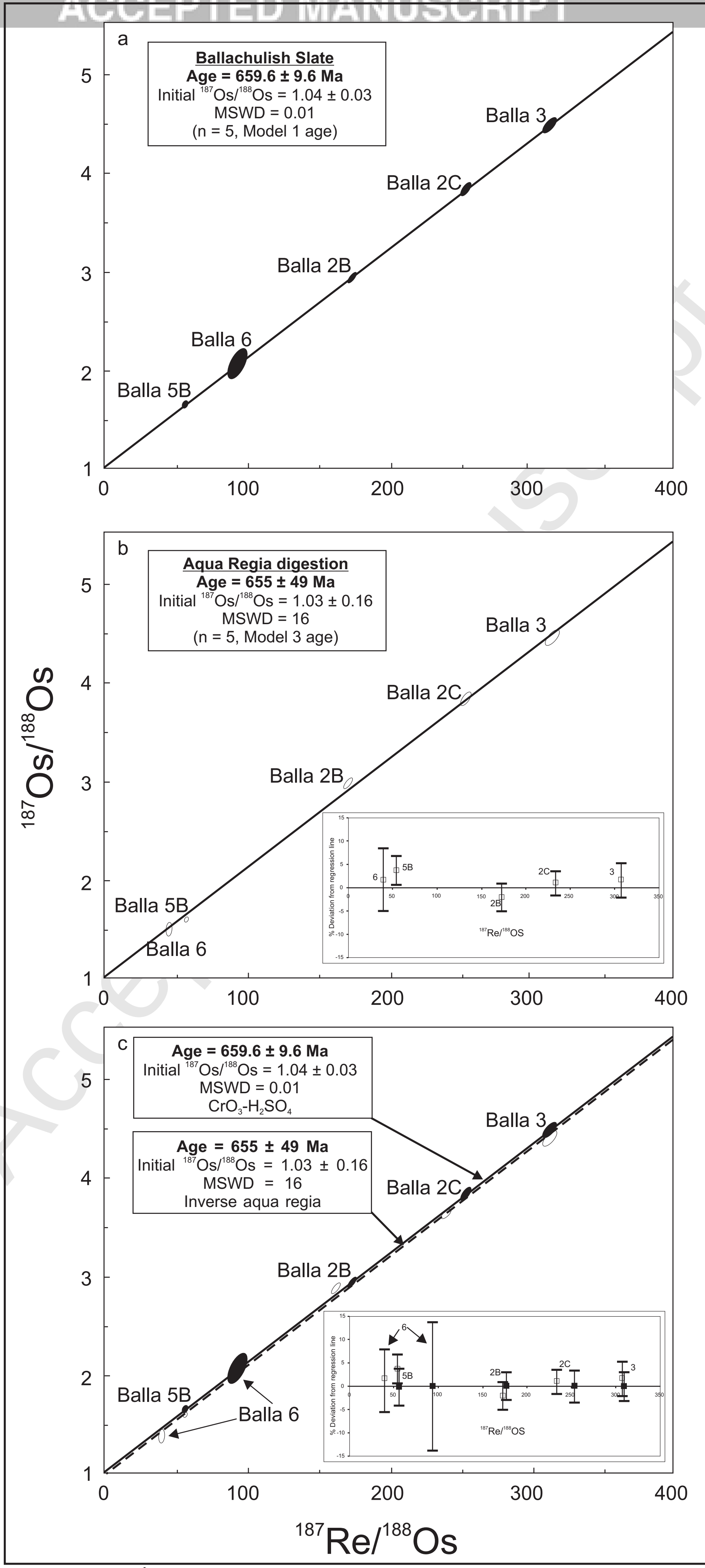
[*] Uncertainty is less than 0.01

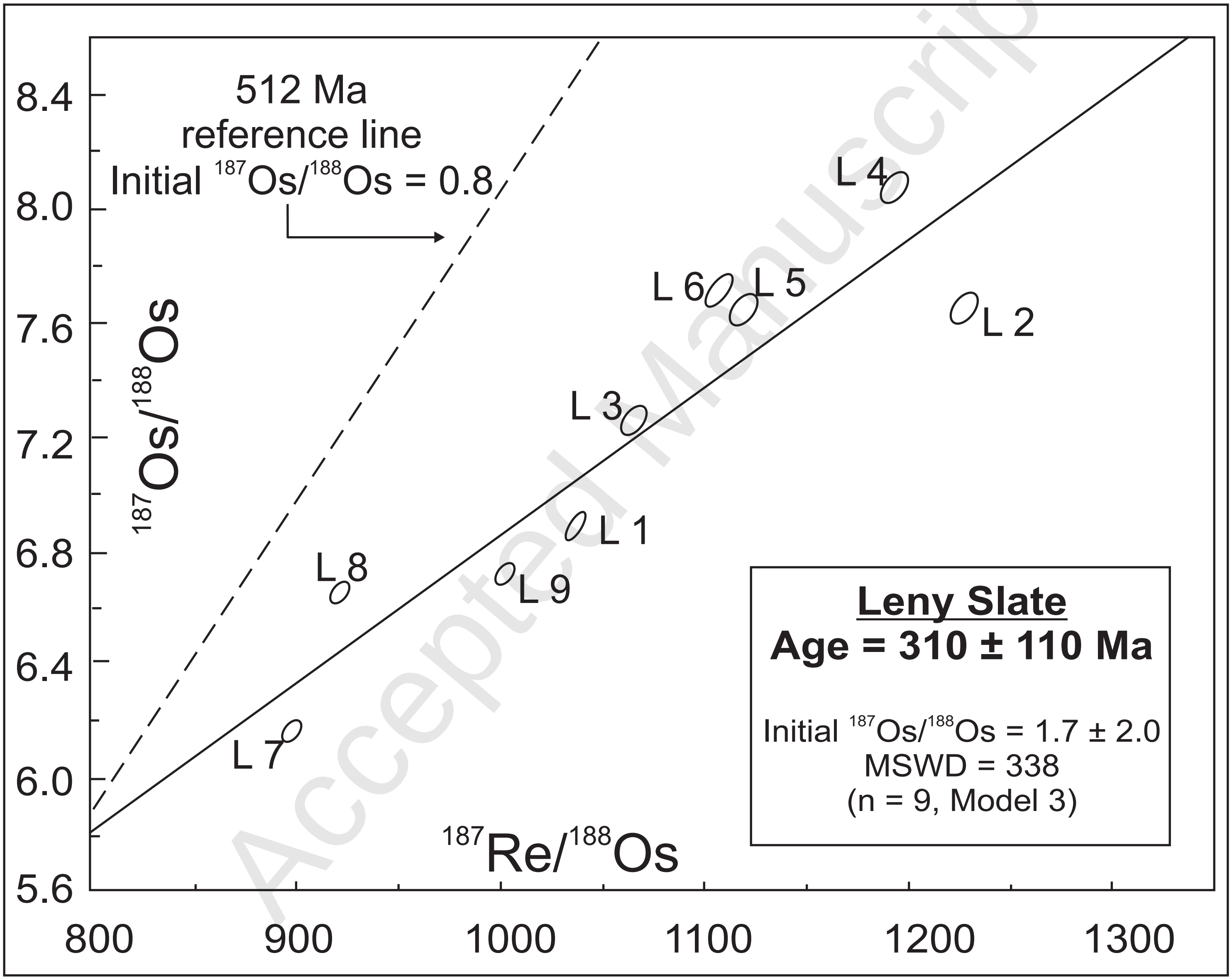
[b] Rho is the associated error correlation (Ludwig, 1980).

[c] Osi = initial ^{187}Os/^{188}Os isotope ratio calculated at 659 Ma for the Ballachulish Slate samples and at 512 Ma for the Leny Slate samples

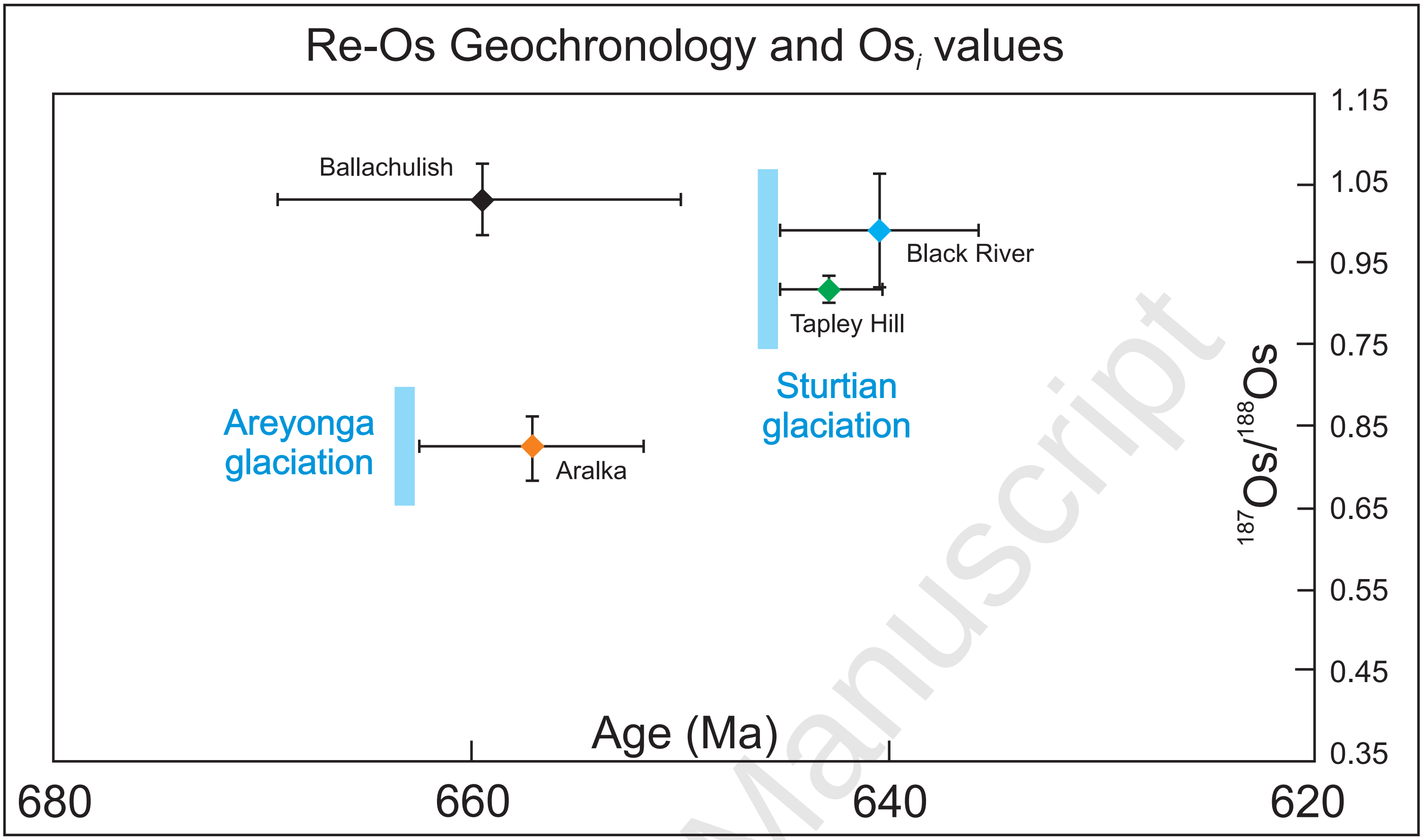

6 °W
4 °W
2 °W
57 °N
55 °N
Great Glen Fault
Highland Boundary Fault
BA
LQ
Glasgow
Southern Highland Group
Argyll Group
Appin Group
Grampian Group
Granites
N
50 km


Group
Subgroup
Southern Highland
Argyll
Appin
Grampian
Dalradian Supergroup
Tayvallich
Crinan
Easdale
Islay
Blair Atholl
Ballachulish
Lochaber
Glen Spean
Corrieyairack
Glenshirra
LQ
Loch na Cille IRD
595 ± 4 Ma1
601 ± 4 Ma2
Stralinchy Diamictite
Port Askaig Tillite
~2 km
BA 659 ± 9 Ma3
"Bitter Springs anomaly"
806 ± 3 Ma4
Carbonate
Siliciclastic
Tillite
Conglomerate
Basic Volcanics


a
Ballachulish Slate
Age = 659.6 ± 9.6 Ma
Initial $^{187}Os/^{188}Os$ = 1.04 ± 0.03
MSWD = 0.01
(n = 5, Model 1 age)
Balla 3
Balla 2C
Balla 2B
Balla 6
Balla 5B
b
Aqua Regia digestion
Age = 655 ± 49 Ma
Initial $^{187}Os/^{188}Os$ = 1.03 ± 0.16
MSWD = 16
(n = 5, Model 3 age)
Balla 3
Balla 2C
Balla 2B
Balla 5B
Balla 6
% Deviation from regression line
$^{187}Re/^{188}OS$
c
Age = 659.6 ± 9.6 Ma
Initial $^{187}Os/^{188}Os$ = 1.04 ± 0.03
MSWD = 0.01
CrO_3-H_2SO_4
Age = 655 ± 49 Ma
Initial $^{187}Os/^{188}Os$ = 1.03 ± 0.16
MSWD = 16
Inverse aqua regia
Balla 3
Balla 2C
Balla 2B
Balla 5B
Balla 6
% Deviation from regression line
$^{187}Re/^{188}OS$
$^{187}Os/^{188}Os$
$^{187}Re/^{188}Os$



512 Ma
reference line
Initial $^{187}Os/^{188}Os$ = 0.8
$^{187}Os/^{188}Os$
$^{187}Re/^{188}Os$
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
800
900
1000
1100
1200
1300
L 1
L 2
L 3
L 4
L 5
L 6
L 7
L 8
L 9
Leny Slate
Age = 310 ± 110 Ma
Initial $^{187}Os/^{188}Os$ = 1.7 ± 2.0
MSWD = 338
(n = 9, Model 3)


Re-Os Geochronology and Os$_i$ values
Ballachulish
Black River
Tapley Hill
Sturtian glaciation
Areyonga glaciation
Aralka
Age (Ma)
680
660
640
620
^{187}Os/^{188}Os
1.15
1.05
0.95
0.75
0.85
0.65
0.55
0.45
0.35