Interrogating the provenance of large river systems: Multi-proxy *in situ* analyses in the Millstone Grit, Yorkshire

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Running title: Provenance of large river systems

Abstract: Establishing the source(s) of sedimentary material is critical to many geological applications, but is complicated by the ability of some minerals to be recycled. To test the relative utility of current proxies for determining a unique provenance, new samples have been collected from the Namurian Millstone Grit Group of Yorkshire, England. Two K-feldspar ²⁰⁶Pb/²⁰⁴Pb isotope populations between 12.5 and 15.5 and c. 18.4 are consistent with Archaean–Proterozoic basement and Caledonian granites, respectively. Zircon U–Pb age populations at c. 2700, 2000–1000 and 430 Ma reflect a mixture of Archaean basement, overlying Proterozoic sediments and intrusive Caledonian granites, while εHf values in zircons of all ages indicate crystallization from reworked crust. Garnet major element compositions are relatively rich in Fe and low in Ca, indicative of derivation from a granulitic or charnockitic source. Rutile Cr/Nb ratios indicate source rocks were dominantly metapelitic, while Zr-in-rutile thermometry records two populations representing lower (c. 650°C) and higher (c. 800°C) metamorphic grade material. Combining these results with published monazite and muscovite data suggests overall derivation from the Greenland Caledonides, with additional contributions from NE Scotland and western Norway, highlighting the power of multi-proxy provenance work, especially in tectonically and geologically complicated regions.

Keywords: provenance, K-feldspar, zircon, garnet, rutile

Supplementary material: Sample details, full analytical methods, data tables and references for compilation figures in the text are available at www.geolsoc.org.uk/SUP000000.

Sedimentary rocks and modern sediments sample wide areas of the crust, which in turn preserves units that vary greatly in age and composition. Techniques that investigate their source(s), collectively known as sedimentary provenance studies (e.g. Arribas *et al.* 2007), have a wide range of applications. These include establishing palaeogeography during key parts of the Earth's history, such as during supercontinent formation events, identifying changes in sea level or climate, and correlation of unfossiliferous sequences, particularly

those with hydrocarbon reservoir potential. Dramatic improvements in the precision and accuracy of geochemical and isotopic measurements have driven the development of single-mineral studies, while the rise of *in situ* techniques has promoted rapid characterisation of individual growth zones using ever-smaller volumes of material (e.g. Sylvester 2008). Of particular utility are heavy minerals such as garnet, zircon, apatite, and titanite, as well as rock-forming minerals like feldspar.

The ability to link multiple minerals, especially those with different chemical or isotopic signatures, to the same source rock or tectonic event is critical to many geological studies, because no one mineral documents the complete evolution of source area. Some minerals, like zircon, are sufficiently robust that they may survive multiple sedimentary cycles, unless structurally damaged (i.e. metamict zircons), so minerals from completely unrelated sources may end up in the same sedimentary basin even in small drainage systems (e.g. Dickinson *et al.* 2009). Others, such as K-feldspar, can break down rapidly during sedimentary transport due to their susceptibility to chemical weathering (e.g. Nesbitt *et al.* 1997). Studies which rely on detrital age distributions to reconstruct palaeogeography or establish provenance may therefore reach incorrect interpretations if polycyclic populations are not correctly identified.

Recent work in Triassic basins to the west of Shetland suggests that recycled zircon populations may be identified through the absence of any corresponding first-cycle K-feldspar population (Tyrrell *et al.* 2009). However, our ability to determine the source area of any given proxy is still limited by the availability of published data to which it can be compared, and identifying the source of well-documented proxies, such as detrital zircon age distributions, is complicated when similar populations have been identified across a wide area. This paper seeks to compare the relative utility of different isotopic and geochemical proxies for a) establishing whether recycling has occurred in potentially polycyclic minerals, and b) which proxies are most capable of pinpointing a unique source area at current levels of precision. To these ends, samples were collected from the Upper Carboniferous Millstone Grit Group of northern England, which is also suggested to contain a mixture of first- and polycyclic detritus and contains a wide range of minerals used as provenance proxies (e.g. Hallsworth & Chisholm 2000, 2008; Tyrrell *et al.* 2012a).

Regional setting

The North Atlantic region incorporates four major land areas, whose tectonic components have repeatedly accreted, separated and collided over several billion years, creating

continental belts of similar compositions and ages on both sides of the Atlantic Ocean (e.g. Starmer 1996; Woodcock & Strachan 2000). Figure 1 depicts the region during Carboniferous times, and summarises current understanding of the basement ages and common Pb isotopic ratios within these terranes. In brief, North America contains the oldest extant continental crust, the Hadean–Eoarchaeon Slave Craton, and abundant material of Archaean and Palaeo- to Mesoproterozoic age (*c.* 1800–1000 Ma), with Caledonian/Acadian units (*c.* 400–360 Ma) stretching from Newfoundland into the north-eastern US (e.g. Spooner & Fairbairn 1970).

Greenland also contains Eoarchaeon basement, best studied in the Isua area on the west coast, as well as significant basement of Palaeoproterozoic age (2000–1800 Ma; Kalsbeek *et al.* 1993). Caledonian metamorphism and granite intrusives (*c.* 430 Ma) are confined to the north-eastern seaboard, where they intrude older (meta-)sedimentary units and Archaean basement (e.g. Kalsbeek *et al.* 2008b). Considerable uncertainty remains over the nature of basement located under the Inland Ice, although cratonic blocks are thought to extend across the island (e.g. Kalsbeek *et al.* 1993).

Scandinavia is constructed around two Meso- to Neoarchaeon cratons (Murmansk and Karelia), with Palaeoproterozoic (2000–1800 Ma) basement to the south along the Baltic Sea and Mesoproterozoic (1500–1000 Ma) and Caledonian (*c.* 460–420 Ma) metamorphic belts forming the western coast of Norway (e.g. Slagstad *et al.* 2011).

The Britain and Ireland were created by the closure of the Iapetus Ocean, which brought together Laurentian (Archaean/Palaeo- to Mesoproterozoic) and Ganderian/Avalonian (Neoproterozoic and younger) basement (e.g. Woodcock & Strachan 2000). Caledonian granites (*c.* 440–390 Ma) are widely distributed throughout the northern parts of these islands, as in Greenland largely intruding older metasedimentary rocks (e.g. Pidgeon & Aftalion 1978). The Rockall High, now underwater off the coasts of Scotland and Ireland, was exposed during the Carboniferous, and is mostly of Palaeoproterozoic (*c.* 2.1–1.7 Ga) age (Dickin 1992).

The Pennine Basin of northern England consists of Carboniferous sedimentary rocks deposited unconformably upon Caledonian basement, tilted during the Variscan orogeny, then partially overlapped by Permo-Triassic sedimentary rocks (Aitkenhead *et al.* 2002). The Namurian Millstone Grit Group comprises a fluvio-deltaic sequence of upward-coarsening mudstones, siltstones and sandstones with thin coal seams, and is divided into six substages based on the dominant ammonoid genus and/or marine bands between them. These units now young to the SE (Figure 2), decreasing in age from Pendleian in the west to Yeadonian in the

east. Precise U–Pb ages are only available for global stages in the Carboniferous. Of these, the transition from the Viséan to the Serpukhovian stage at 330.9 Ma corresponds to the beginning of the Pendleian substage, the transition from the Serpukhovian to the Bashkirian stage at 323.2 Ma falls during the Sabdenian substage, and the transition from the Bashkirian to the Moscovian stage at 315.2 Ma corresponds to the Westphalian B to C substage transition (Richards 2013). Gilligan (1919) first recognized a northern source area for these sedimentary rocks based on gross palaeocurrents to the SW, a hypothesis supported by later facies analysis (e.g. Collinson 1988; Leeder 1988).

More recently, research has concentrated on specific mineral and isotopic provenance fingerprints, all indicating a northern derivation but disagreeing on specific sources. Heavy mineral analysis determined that the Millstone Grit is monazite-rich, chrome spinel-poor and garnet-bearing, and with varying proportions of garnet recording the effects of diagenesis rather than variations in provenance (Hallsworth & Chisholm 2000, 2008). These authors excluded any substantial contribution from any part of Scotland or Scandinavia. Bulk rock Sm–Nd analysis yielded strongly negative $\epsilon_{\text{Nd}_{320}}$ values between -11 and -7, requiring a source area dominated by Proterozoic rocks (Glover *et al.* 1996; Leng *et al.* 1999). Although monazite is the most likely host of Nd in these rocks, U–Pb ages from monazite were dominated by Scandian grains of 420 ± 7 Ma, interpreted to record input from a single pluton (Evans *et al.* 2001). Ar/Ar ages from mica formed two peaks at *c.* 440 and 420 Ma, most consistent with derivation from Scotland (Stuart *et al.* 2001).

U–Pb dating of detrital zircon (TIMS and SHRIMP) revealed distinct Archaean (3546–2765 Ma), Mesoproterozoic (1573–1103 Ma) and Caledonian (456–362 Ma) age populations (Cliff *et al.* 1991; Hallsworth *et al.* 2000), although the youngest ages are here considered to have suffered Pb loss. K-feldspar common Pb analyses throughout the sequence identified two populations, one strongly unradiogenic and the other much more radiogenic (Tyrrell *et al.* 2006; Tyrrell *et al.* 2012a). Based on the peaks in the published zircon U–Pb ages, these K-feldspar peaks were interpreted to reflect first-cycle material from Archaean–Proterozoic basement and Scottish Southern Upland granites, respectively, while the Proterozoic U–Pb ages record detrital zircons recycled from Southern Upland metasedimentary rocks.

Since published work is predominantly from the youngest stages of the Millstone Grit, samples (11LYK) were collected throughout the sequence in a north-to-south transect to investigate variations in age profiles across the gross palaeoflow direction (Figure 2). Additional analyses were obtained from samples (ST03) investigated by Tyrrell *et al.* (2006)

to ensure the detection of minor components (e.g. Andersen 2005). The oldest stage, the Pendleian, is represented by the basal Pendle Grit (11LYK05) and the Grassington Grit (ST03/111), followed by the Arnsbergian Marchup (11LYK04) and Middleton (11LYK02) grits. Sabdenian units were not sampled due to their limited exposure. The Kinderscoutian Addingham Edge Fm. (11LYK01) underlies the Marsdenian Huddersfield White Rock (ST03/118 and 124), while the youngest samples were collected from the Yeadonian Rough Rock (ST03/126, 127, 129, 132 and 133).

Analytical methods

Detailed methods can be found in the Supplementary material, and are summarised here. Thin (30 µm) and thick (300 µm) sections were prepared for each sample from the same rock chip. Point counting (500 spots) on each thin section was conducted using a standard petrographic microscope. Individual grains of K-feldspar were identified in thick section by backscattered electron (BSE) imaging on a Hitachi TM-1000 desktop SEM at University College Dublin (UCD). Each grain of sufficient size was then analyzed for common Pb by laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) at UCD using a ThermoScientific Neptune and a New Wave Research UP-193 Excimer laser after Tyrrell *et al.* (2012b). Pb isotopic ratios were corrected for fractionation using the $^{203}\text{Tl}/^{205}\text{Tl}$ measured in NIST 612 glass.

Zircon mounts were prepared using a minimum of steps to reduce the influence of operator bias on analytical results (Sláma & Košler 2012). Samples were crushed to < 500 µm and passed through methylene iodide to collect the heavy fraction. Grains were then cast into mounts, without picking, and polished to half height so that each zircon could be photographed in BSE (UCD) and cathodoluminescence (CL; Portsmouth) imaging to identify growth zoning and contaminating features such as cracks and inclusions. Because refractory minerals such as zircon are not easily destroyed by normal crustal processes, they frequently preserve two or more growth events within their structures. Since these growth events may be separated by millions of years, it is important to identify individual growth zones so that meaningless data arising from inadvertent mixtures are avoided.

U–Pb ages were measured by laser ablation quadrupole mass spectrometry (LA-Q-ICP-MS) after Jeffries *et al.* (2003), using an Agilent 7500cs coupled to either a New Wave Research UP-213 Nd:YAG or Resonetics RESolution SE Excimer laser at the University of Portsmouth. A 15–30 µm spot was rastered along a line to minimise the depth:width ratio and avoid fractionation. Ratios were calculated using sample-standard bracketing, and zircons

were analysed in a ribbon pattern to avoid pre-selecting ‘nice’ grains (e.g. Mange & Maurer 1992). The amount of ^{204}Pb in these analyses was below the detection limit, and no common Pb correction was performed. All uncertainties were propagated in quadrature. Only ages whose 2σ error envelopes overlapped concordia, were measured in the youngest growth zone and avoided irregular features such as cracks and inclusions, were used. $^{206}\text{Pb}/^{238}\text{U}$ ages are quoted if younger than 1200 Ma, and $^{207}\text{Pb}/^{206}\text{Pb}$ ages if older, due to the differential decay rates of the parent isotopes.

Hafnium ratios were measured by LA-MC-ICP-MS at UCD after Hawkesworth and Kemp (2006). Only grains with a concordant U–Pb age were analysed, drilling 30–40 μm spots directly through the U–Pb tracks. Data were normalised to JMC-475 after applying an exponential $^{173}\text{Yb}/^{171}\text{Yb}$ mass bias correction using an in-house spreadsheet. ϵHf values and model ages were calculated based on a two-stage model, using the bulk Earth (chondritic uniform reservoir; CHUR) $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios from Bouvier *et al.* (2008), depleted mantle (DM) $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios from Griffin *et al.* (2002), and the Lu decay constant from Söderlund *et al.* (2004). A bulk crustal $^{176}\text{Lu}/^{177}\text{Hf}$ value of 0.015 is assumed (Griffin *et al.* 2002).

Garnet major element compositions were determined by electron microprobe analysis at Aberdeen University. Grains were mounted on double-sided adhesive tape, coated with carbon, and analysed using a Link Systems AN10000 energy-dispersive X-ray analyser attached to a Cambridge Instruments Microscan V electron microprobe. Each stoichiometrically-determined formula corresponds to ideal garnet compositions, which are expressed in terms of the relative abundance of the Mg, Fe^{2+} , Ca and Mn end members (all Fe calculated as Fe^{2+}). Previous work has established that this method does not create a bias towards rim compositions (Morton 1985).

Rutile trace element compositions were determined by LA-Q-ICP-MS at Cardiff University. Grains were analysed using a Thermo Elemental X(7) series coupled to a New Wave Research UP-213 Nd:YAG laser. Thermo Elemental Plasmalab time-resolved analysis data acquisition software was used for initial data reduction, with post-processing completed in Excel. Source rock lithologies were inferred from Cr/Nb ratios according to Meinhold *et al.* (2008), and Zr-in-rutile temperatures were calculated following Watson *et al.* (2006) as this method does not require an estimate of pressure conditions during growth, something that is impossible to determine in detrital grains.

Results

Petrography and heavy mineral analysis

Compositions for each sample are presented in Supplementary Table 1. Grain sizes in all samples are generally ≤ 1 mm, occasionally 2–3 mm, and rarely up to 5 mm in ST03/111 (Grassington Grit, Pendleian). Quartz is the dominant constituent, with up to 20% K-feldspar and plagioclase. Orthoclase is more abundant than microcline in all samples except ST03/127 (Rough Rock, Yeadonian), but the proportions grade towards unity up sequence. Heavy minerals include zircon, rutile, garnet, monazite and apatite, with no discrete bands observed (Supplementary Table 2). Ratios of key index minerals, including monazite:zircon and garnet:zircon (GZi), are consistent with previous work in the area (Hallsworth *et al.* 2000; Hallsworth & Chisholm 2008), and extend these profiles back to the Pendleian (Table 1).

Garnet major element chemistry was determined for four samples (Supplementary Table 3), all of which reported a similar range of high-pyropes, low-grossular compositions, with only a few spessartine-rich ($X_{Mn} > 5\%$) grains (Figure 3). These compositions are consistent with derivation from granulitic or charnockitic source rocks, such as those found in the Lewisian basement of Scotland, the west coast of Norway and the east coast of Greenland (Morton *et al.* 2004). The exception is 11LYK01 (Kinderscout Grit, Kinderscoutian), which contains a discrete population of spessartine-rich grains (open circles, Figure 3), clearly distinct from the spessartine-poor, more pyrope-rich population (filled circles). Although the GZi ratio in this sample is quite low, which is consistent with dissolution due to deep burial, neither samples with similar GZi ratios lower in the sequence, nor those higher in the sequence with higher GZi ratios, record the same discrete populations, suggesting it is a true provenance signal.

Rutile Cr/Nb ratios from five samples (Supplementary Table 4; Figure 4) indicate that grains derived from metapelitic lithologies predominate (Meinhold *et al.* 2008). The exception once again is 11LYK01 (Kinderscout Grit, Kinderscoutian), which records almost equal numbers from metapelitic and metamafic units. Metapelitic grains appear to record two temperature peaks, one at 600–650°C (amphibolite/eclogite facies) and the other at 800–850°C (granulite facies). The small number of grains from metamafic units makes any clear determination difficult, but the dominant population in sample 11LYK01 is 600–650°C. This population appears to be echoed in the other samples apart from ST03/126 (Rough Rock, Yeadonian), with an apparent peak nearer 800–850°C. Recent papers have documented variations in Zr-in-rutile temperatures at the thin-section scale (e.g. Luvizotto *et al.* 2009; Kooijman *et al.* 2012), but even if these temperatures are considered minimum temperature

estimates it is clear that they record growth in high temperature regimes, providing constraints on possible source areas.

Pb in K-feldspar

All data are presented in Supplementary Table 5. Eleven samples yielded uniform and strongly bimodal Pb isotope distributions, with two dominant $^{206}\text{Pb}/^{204}\text{Pb}$ populations between 12.5–15.5 and 18–19, and a small number of analyses in between (Figure 5). Analyzed grains measure from 120 to 2500 μm in length, with a majority between 200 and 1500 μm . No correlation is observed between grain size and reported isotopic ratios. These results are consistent with those of Tyrrell *et al.* (2006), which required a larger analytical volume and yielded a maximum of 13 analyses per sample. Neither population disappears, nor is a third population introduced, suggesting a relatively stable drainage area with two predominant source units: one old and very unradiogenic, and the other much younger and more radiogenic. The only significant variation between samples is in the most unradiogenic grains ($^{206}\text{Pb}/^{204}\text{Pb} < 13$), which are primarily restricted to the three more northerly Rough Rock samples (ST03/126–129).

U–Pb and Hf in zircon

Grains are typically <300 μm in length, while those >450 μm are limited to ST03/111 (Grassington Grit, Pendleian). Colours range from purple to colourless, while internal appearance in CL varies from unzoned to multiple layers of sector and/or oscillatory zoning (Supplementary Figure 1). Most analyses were made on rims, as these document the final growth event preserved by the zircon, and therefore are most likely to identify the source area. Each was *c.* 20 μm thick, displaying either sector or oscillatory zoning. Zircon U–Pb ages (Figure 5; Supplementary Table 6 and Figure 2) range from 3640 Ma to 400 Ma, with a single 297 ± 6 Ma age (11LYK04) most likely the result of cryptic Pb loss. Sharp peaks are recorded at *c.* 2700 Ma and *c.* 430 Ma, while a broad smear of ages between 2000 Ma and 1000 Ma is dominated by older grains in most samples. There is no correspondence between U–Pb ages and colour, size, U/Th ratios or U and Th concentrations. Although the age distributions agree with previous work (Cliff *et al.* 1991; Hallsworth *et al.* 2000), there is some variation in the proportion of analyses comprising each peak. However, this variation is consistent with the observations of Sláma and Košler (2012), who demonstrated that while analysing a minimum number of grains ensures even small populations are detected, their measured proportions may vary within 10% of their true values.

Only a small number of Hf analyses (Supplementary Table 7) were possible due to the typical size of zircon rims, but taken together the resulting ϵHf values form a distribution familiar around the North Atlantic region (Figure 6). Older grains record the same pattern of ϵHf values identified in all parts of the N Atlantic region, although the data available for comparison are heavily biased towards a handful of ‘classic’ field areas (Lancaster *et al.* 2015). For instance, Mesoproterozoic zircons from this study with positive ϵHf are consistent with derivation from Baltica, but those with strongly negative ϵHf do not resemble any known basement. As a result, Hf isotopes cannot currently resolve any questions of provenance and will not be discussed further. Zircons crystallized at *c.* 430 Ma from this study have slightly more positive ϵHf values than those from NE Scotland (Appleby *et al.* 2010). However, it is interesting that these Silurian zircons are associated with Proterozoic model ages, indicating reworking of either Proterozoic basement or zircon-bearing sedimentary rocks (zircon being the predominant host of Hf), mirroring the results of monazite and bulk rock Nd work. In addition, only the oldest layers (Pendleian and Arnsbergian) record traces of juvenile crust (ϵHf values $\approx$ DM), extracted and crystallized at *c.* 1200 and 1700 Ma. Further work is clearly needed to determine the significance of this pattern, if any.

Discussion

Isotopic provenance

Perhaps the most striking feature when comparing the isotopic data from this study is the identification of three populations in the zircon U–Pb data, but only two in the K-feldspar common Pb distributions (grey bars, Figure 5). If the hypothesis of Tyrrell *et al.* (2009) is correct, then the Archaean and Caledonian peaks in the K-feldspar distribution indicate that the zircon peaks at similar ages also represent first-cycle detritus, presumably from the same source, while the broad Proterozoic zircon age peak represents recycled material. However, large river systems like the one feeding the Pennine Basin potentially mix material from a very wide drainage area, in this case one with large expanses of isotopically similar crust. Independent examination of each line of evidence is crucial before any conclusions about shared provenance and degree of recycling can be drawn.

Our ability to identify unique sources for detrital material is limited by our characterisation of known basement in the likely source areas. While there is reasonably good understanding of U–Pb ages around the North Atlantic region, published Hf and Pb isotope

data are concentrated in the oldest (Archaean–Palaeoproterozoic) and youngest (Palaeozoic) areas, and often do not overlap each other geographically (Figure 1; Figure 3 of Lancaster *et al.* 2015). However, if labile minerals (such as K-feldspar) survive the journey from source to sink, then more resistant minerals (such as zircon) from the same source area are more likely to also reach that sink.

Plotting common Pb isotopic ratios against each other (Figure 7), rather than in isolation, provides a better means of discrimination between the two K-feldspar populations and potential source areas by exploiting the different decay rates of the parent isotopes. Starting with the least radiogenic population ($^{206}\text{Pb}/^{204}\text{Pb} < 15.5$), only K-feldspars from Archaean–Palaeoproterozoic units in West Greenland, and their eastern correlatives, record the full range of $^{206}\text{Pb}/^{204}\text{Pb}$ values observed in the Millstone Grit. Contributions from certain parts of North America, Baltica and Scotland would be indistinguishable from Greenland, although only Baltica and Scotland were suitably located to contribute detritus into the Millstone Grit system based on palaeogeographic reconstructions (e.g. Nance *et al.* 2012). K-feldspars with slightly more radiogenic $^{207}\text{Pb}/^{204}\text{Pb}$ ratios may indicate a slightly higher μ source rock, as is noted in K-feldspar from the Slave Province and the Karelian.

The most radiogenic analyses ($^{206}\text{Pb}/^{204}\text{Pb} > 18$) overlap published data in Caledonian basement from all four areas, making a visual assessment impossible. However, statistical tools designed to handle large geological datasets have recently been developed for the R programming environment (Vermeesch & Garzanti 2015) which calculate the distances between data points to create a ‘best fit’ pattern. Multi-dimensional scaling (MDS) analysis can compare multiple large datasets of the same type (i.e. zircon U–Pb ages), or different types either with (isotopic) or without (QFL, heavy mineral analysis) associated uncertainties in what is called a Procrustes analysis. As a result, all lines of evidence can now be assessed together, rather than in isolation, providing better grounds for comparison between samples from the same suite or potential source areas, assuming representative records are available.

Since the radiogenic K-feldspars in the Millstone Grit form a single tight cluster with $^{206}\text{Pb}/^{204}\text{Pb}$ ratios between 18 and 19, they are more likely to record a single source area, and so can be compared to published data via MDS (Figure 8a). Although the assumption of representation is unsound for some source areas (e.g. the Southern Upland granites (S2) are represented by only three data points), some broad conclusions can still be drawn. Compatible sources lie within the solid oval, with only Eastern Greenland (G) and Norway (N) outside. However, if Norway is subdivided into component K-feldspar and galena profiles, the K-feldspar data plot within the field, while the galena data remain without.

Because neither mineral accepts appreciable amounts of U into its crystal structure, both are considered to preserve their common Pb isotopic ratios from the time of crystallisation, and therefore their Pb isotopic ratios should be directly comparable. This observation suggests that galena and K-feldspar from the same locality may not preserve the same record of Caledonian evolution, perhaps due to later resetting, or that there is greater heterogeneity along the belt than current data distributions can detect. Since up to half of the published Pb data from N Atlantic region were measured in galena, potential source areas with limited or no published K-feldspar data, such as NW Scotland and the Grampian Highlands, may not be represented correctly in this analysis. However, the impact of any irregularities in one line of evidence should be reduced when multiple traits are considered simultaneously.

The ages of potential Caledonian source units in the region are resolvable within precision, providing a point of comparison with the MDS Pb analysis. Figure 8b considers all zircon ages between 400 and 500 Ma from this study and the Caledonian age compilation of Slagstad *et al.* (2011), using the same groupings where possible. Norway (N) remains outside the compatible region, while Greenland (G) and NE Canada (C) have moved inside and the Southern Uplands of Scotland (S2) and Ireland (I) have moved outside. Apart from Norway and NE Canada, which have nearly 100 data points each, all populations in this comparison have a similar numbers of values, making the comparison fairer than for K-feldspar. As such, the area from eastern Greenland, through northern Scotland and into NE Canada is considered the most likely source of the Caledonian zircons.

If the Caledonian material is first-cycle detritus, then combining the two data sets in a special class of MDS, termed a Procrustes analysis, can identify the most likely source of both the K-feldspar and zircon. The resulting plot (Figure 8c) indicates that compatible areas are restricted to the Southern Uplands and East Greenland. They plot at almost identical distances from the samples in this study, indicating that they are equally likely to be the source of detritus in the Millstone Grit. Without a larger basement dataset for comparison, therefore, it is impossible to determine whether one area is more consistent than the other, or establish the proportion of contribution from each.

It is more problematic to test the Archaean zircons in the same manner, as the Archaean peak in the K-feldspar distributions is much broader, making a single source less likely. However, the zircon U–Pb peak (2.4–3.2 Ga) can be compared to published ages from around the margin (Figure 8d), which are nearly all located in Greenland and NW Scotland. Based on this analysis, Scotland (with the Outer Hebrides) provides a better fit for the samples in this study. Tyrrell *et al.* (2012a) first proposed the Lewisian basement as the

source of the Archaean peaks in the Millstone Grit, but during the Caledonian Orogeny it was covered by Proterozoic and Cambro-Ordovician sedimentary rocks (in turn chiefly derived from Greenland), and remained covered apart from small inliers until the Triassic (e.g. Johnstone & Mykura 1989; Cawood *et al.* 2007; Tyrrell *et al.* 2009).

However, Kalsbeek *et al.* (1993) established the chronology of crustal generation, intrusion and reworking in the Ammassalik complex of SE Greenland, which closely matches that of the Lewisian complex in Scotland. The correspondence was much weaker with nominal correlatives on the western coast of Greenland, from which the majority of the zircon ages available for comparison were derived. Although covered by locally-derived sedimentary rocks in the Devonian and Lower Carboniferous, unconformities above these sequences record the removal of material during Viséan and Namurian times, in places down to the basement, before deposition resumed in the Westphalian (Stemmerik *et al.* 1991). As such, while either the Lewisian or the Ammassalik complexes could have provided the Archaean grains, Greenland is considered more likely based on the availability of material at the time of deposition.

While the consistent interpretation deduced from the Archaean and Caledonian material strongly suggests that they are both first cycle, the same cannot be said for the Proterozoic zircons, which lack a matching K-feldspar population. Mesoproterozoic to Silurian supracrustal sequences are found in Scotland, Greenland and Norway (Figure 5). The combined Millstone Grit samples record a broad distribution of ages between 2000–1000 Ma with an emphasis towards older ages, as is also observed in the Torridonian Supergroup of NW Scotland, the Eleonore Bay and Krummedal sequences of eastern Greenland and the Svaerholt succession in western Norway (Kalsbeek *et al.* 2000; Dhuime *et al.* 2007; Kirkland *et al.* 2007; Lancaster *et al.* 2011). The opposite emphasis is observed in the Southern Uplands of Scotland (Waldron *et al.* 2008) and the two Pendleian samples from Yorkshire, suggesting the latter two may record a more local derivation than the rest of the sequence, whether directly from the Southern Uplands or recycled via the Old Red Sandstone. Although intrusive units of 1000–900 Ma are known in eastern Greenland, they are very limited in areal extent (Henriksen & Higgins 2008), consistent with the paucity of such material in the Millstone Grit. Likewise, material between 900–500 Ma is rare in the Millstone Grit, but common in intrusive units which crosscut the Norwegian sedimentary rocks. Therefore, while small contributions from these or either Scottish source up sequence cannot be ruled out, none could be a dominant contributor without significantly skewing the stable K-feldspar distribution in the Millstone Grit.

Further lines of evidence come from published detrital monazite and muscovite studies. Evans *et al.* (2001) identified a single monazite population of 420 ± 7 Ma in northerly-derived samples, plus a single grain aged 2040 ± 1.4 Ma, and concluded both ages were more consistent with derivation from east Greenland than either Norway or Scotland. Likewise, muscovite forms first-cycle detritus, but as a light platy mineral is more likely to remain suspended than heavy minerals such as zircon (Hoang *et al.* 2010). Stuart *et al.* (2001) investigated the Ar/Ar age distribution of detrital muscovite from Devonian–Carboniferous samples in the northern UK. Only the Devonian samples recorded ages < 400 Ma, which are well documented in published muscovite data from Scandinavia and east Greenland. All Carboniferous samples, including four from the Namurian (Kinderscoutian–Yeadonian), yielded two peaks at *c.* 420 and 440 Ma. These ages are consistent with cooling ages in northern Scotland (455–425 Ma), as documented by detrital rutiles from the Moine and Dalradian sediments (Small *et al.* 2013).

Together, these observations are most consistent with derivation of detritus from a region stretching from the Caledonide belt of eastern Greenland to northern Scotland, and are not distinguishable isotopically using data currently available for potential sources. The matching Archaean and Caledonian populations in the K-feldspar and zircon distributions indicate that these are both first-cycle detritus, while recycled Proterozoic sedimentary rocks contributed the third zircon population. However, current understanding of basement exposure during the Carboniferous, particularly that of Archaean age, suggests Greenland may be the dominant contributor. Muscovite and, at least in the Pendleian, zircon data suggest some material from Scotland is present, and small amounts of K-feldspar and/or zircon from either the Southern Uplands or the NW Highlands would not be distinguishable from that derived from Greenland.

Compositional and heavy mineral provenance

While the isotopic data provide some constraints, finer detail may come from more traditional compositional and heavy mineral work. In Greenland, K-rich Caledonian granites intrude both quartzofeldspathic basement and overlying Proterozoic sedimentary rocks (Kalsbeek *et al.* 2008a). These young granites typically contain 20–45% K-feldspar (microcline in post-tectonic granites but more typically orthoclase in syn-tectonic units) and up to 0.5% rutile, zircon and apatite, while the sedimentary rocks they intrude contain K-feldspar, rutile, monazite and garnet (Haller 1971; Caby & Bertrand-Sarfati 1988). The Archaean–Palaeoproterozoic basement is tonalitic to granitic in composition, consisting chiefly of

quartz, plagioclase and K-feldspar, with minor garnet, zircon and apatite (Kalsbeek 1995). It is also associated with medium- to ultra high-pressure eclogites which contain garnet and rutile (e.g. Gilotti 1993; Gilotti & Ravna 2002). By contrast, granites in both the Grampian Highlands and Southern Uplands of Scotland typically contain microcline and plagioclase; rutile is only reported in the surrounding metasedimentary units (e.g. Pidgeon & Aftalion 1978; Hutton & Murphy 1987). Archaean Lewisian basement is exposed only in the north-west of Scotland and the Outer Hebrides, and has a similar mineralogy to contemporaneous basement in Greenland (e.g. Park 2009). Caledonian intrusions in southern Norway are typically mafic to ultramafic in composition, which are K-feldspar poor; further north and offshore, granites and granodiorites are more abundant, although the nature of the K-feldspars is not reported (e.g. Slagstad *et al.* 2011).

Garnet and rutile preserve major and minor element distributions that can be diagnostic of their crystallisation environment, and so their chemistry is as useful for provenance work as their absence or presence in a sample. Complementing the four samples studied for garnet chemistry in this study, detailed work in the upper three stages of the sequence has identified a very distinctive garnet composition that is higher-pyrope and lower-grossular than garnets in Westphalian samples (Hallsworth *et al.* 2000). In the N Atlantic region, similar garnets are only found in South Harris and Huntly-Portsoy (Scotland), Stavanger (Norway) and east Greenland (Morton & Whitham 2002; Morton *et al.* 2004). Dalradian-sourced garnets are considerably more spessartine-, almandine- and grossular-rich than those observed in Yorkshire, apart from sample 11LYK01, ruling out contributions from the Dalradian metasedimentary rocks directly, or via the Southern Uplands and ORS sedimentary rocks of the Midland Valley (Morton *et al.* 2004; Hallsworth & Chisholm 2008).

There is a slight change in the range of pyrope–almandine compositions recorded through the sequence, suggesting either some heterogeneity in the source area or the introduction of material from another source. In particular, detrital garnets collected from a river draining the Rogaland anorthosite norite complex just outside Stavanger are similarly high in pyrope, but include more grossular-rich compositions (Morton *et al.* 2004). A small amount of higher-grossular garnet is observed in the Millstone Grit samples, and since Ca-bearing garnet is the least stable composition during storage and diagenesis, contamination by such material might not always be apparent (Haughton & Farrow 1989). However, Stavanger is the opposite end of Norway from the Svaerholt metasedimentary rocks which could contribute the correct distribution of Proterozoic zircon ages, as discussed above, with no suitable material available further south. As such, the dominance of the higher-pyrope

population most likely indicates a primary source area within the Greenland Caledonide belt, since no other basement region in the N Atlantic margins appears able to generate the garnet populations observed in the Millstone Grit.

Both Scotland and Greenland preserve rutile-bearing units of the correct lithologies, but each records a different pattern of peak temperatures which can be exploited in provenance work. The Grampian metasedimentary rocks and metamafic units include the Barrovian type locality, which reached greenschist–amphibolite facies (~550–650°C) conditions in the Ordovician (e.g. Baxter *et al.* 2002). Rutiles preserving similar temperatures were identified by Lundmark *et al.* (2014) in Palaeozoic sedimentary rocks from the North Sea, but temperatures below 600°C are rare in the study area and are found chiefly in 11LYK01, which contains garnets similar to those supplied by the Dalradian. By contrast, the Southern Uplands reached only the prehnite-pumpellyite facies (<350°C), although many of its Ordovician successions are thought to derive from a Barrovian metamorphic terrane (Oliver & Leggett 1980). In eastern Greenland, eclogites and the Krummedal metasedimentary rocks reached peak temperatures of 750–850°C, while surrounding garnet-clinopyroxene units, which are lower in Na than true eclogites and so do not contain omphacite, reached 600–650°C (Gilotti 1993; Gilotti & Ravna 2002). These same peaks, as well as a dominantly metapelitic source lithology, were identified by Morton and Chenery (2009) in Jurassic–Palaeocene sedimentary rocks from the Norwegian Sea, interpreted to reflect derivation from Greenland due to the lack of suitable sources in Norway.

One last consideration is how consistent the Millstone Grit is over the course of its depositional history. Since there is no *a priori* reason any of these minerals must be from the same source, and there is only limited published data available for comparison, it is much harder to apply statistical tools to these data. However, it is possible to compare all the samples from this study, drawing together all lines of evidence in a Procrustes plot (Figure 8e). Garnet composition and rutile thermometry are not available for enough samples to be included, but zircon U–Pb ages, Pb ratios in K-feldspar, heavy mineral distributions and bulk petrology can be combined for eight of the twelve samples, covering all five substages. The similarity between most of the samples is striking, with only the two Pendleian samples (11LYK05 and ST03/111) and ST03/124 (Marsdenian) separate from the rest.

Vermeesch and Garzanti (2015) observed that on Procrustes plots, petrological data such as heavy mineral and QFL counts control the Y axis, while isotopic data control the X axis. Low zircon and high garnet counts were observed in the heavy mineral analysis of sample ST03/124, but otherwise it is indistinguishable from the rest, suggesting that this

observation is correct. 11LYK01 (Kinderscoutian), which stands out in the rutile thermometry, here blends in with the dominant trend, suggesting such fluctuations are due to slight changes in transport and/or storage conditions, rather than a fundamental shift in source area. While grain size, and hence hydraulic sorting, could have an effect on the appearance of Procrustes distributions, similar size distributions in all samples from this study make rigorous comparisons difficult. It is interesting to note, however, that of the three samples separated from the main population in Figure 8e, the largest grain sizes were observed in 11LYK01, which plots closest to the main group, while ST03/124 and 11LYK05 have very similar grain size distributions to the main group but plot further away. Together, these observations suggest that grain size did not have much influence on the distribution of the data collected in this study.

Every line of evidence examined in this study is independently compatible with derivation from eastern Greenland, suggesting that it is a significant source of Millstone Grit detritus. However, contributions from southwest Norway and northern Scotland cannot be ruled out, and in some cases (particularly during the Kinderscoutian) could dominate. While all minerals were derived from source areas affected by the Caledonian orogeny, Proterozoic zircon has been recycled through (meta-)sedimentary units, with the addition of first-cycle grains from local basement and Caledonian intrusive rocks. Monazite, garnet, and K-feldspar are resistant enough to travel long distances, but are less likely to survive more than one sedimentary cycle, so the ages or compositions they preserve most likely document the most recent source area. Rutile can survive sedimentary recycling, but is chemically consistent with crystallisation in first-cycle source areas. Muscovite, the lightest of these minerals, is only consistent with derivation from Scotland, and so has travelled the shortest distance, with any material from other source areas being destroyed before reaching Yorkshire. In short, comparing signals from several minerals with different behaviours can untangle even the most complicated of histories, and traditional methods can provide as much, or even more, information as modern isotopic techniques.

Regional context

It is notable that broadly similar U–Pb age distributions have been identified in sedimentary rocks deposited along the eastern edge of the UK from the Ordovician until the Carboniferous (Figure 5). Discontinuities in sequences from eastern Greenland correspond exactly with periods of deposition in Yorkshire, including a gap between Viséan and Westphalian sedimentary rocks when the Namurian Millstone Grit was deposited (Morton & Whitham

2002; Larsen *et al.* 2008). These changes occur on timescales of 10 to 20 myr, considerably longer than the 100 to 200 kyr glacio-eustatic sea level cycles controlling marine incursions (Collier *et al.* 1990; Larsen *et al.* 2008). Instead, these changes are thought to correspond to changes in the rates of spreading at mid-ocean ridges, particularly during plate reorganisation (Hallam 1963; Pitman 1978), or through compression of the crust and change in continental elevation (Whitehead & Clift 2009).

The Palaeozoic was a time of considerable tectonic activity in the north Atlantic. Avalonia slid into Baltica to close Tornquist's Sea in the Ordovician, which in turn collided with Laurentia to close the Iapetus Ocean and create the Caledonian metamorphic belt in the Silurian (Soper *et al.* 1992; Trench & Torsvik 1992). The transition from late Silurian to early Devonian saw the assembly of the Scottish Highlands from disparate blocks along the Caledonian front (Dewey & Strachan 2003). Extension in the Devonian and Carboniferous exhumed deep crustal rocks (HP–UHP) in Greenland and Norway and created new sedimentary basins in Scotland and Greenland, most likely the result of late orogenic collapse due to a change in plate motion (e.g. Larsen & Bengaard 1991; Gilotti & McClelland 2005). High-angle brittle faults are reported in Greenland starting in the Viséan, which could record the change to plate divergence and ultimately continental rifting (Gilotti & McClelland 2008).

While the Millstone Grit provides only a brief window into this regional evolution, the relative stability of all provenance signals throughout the sequence suggests that while eustatic sea level change drove cycles of deposition and marine incursion within the Pennine Basin (Aitkenhead *et al.* 2002), it was not controlling erosion in the source areas. One model which could explain these observations is if the large-scale tectonic shifts of the preceding *c.* 130 myr produced large areas of uplifted crust which eroded preferentially, not least due to the warm humid climate during the Carboniferous. Locally-derived detritus deposited in the earliest Pendleian was quickly overwhelmed by material from further afield as the river system developed. The consistent shift in provenance indicators during the Kinderscoutian may reflect brittle faulting in Greenland, or headwater drainage reorganization, which temporarily allowed a greater proportion of clearly Scottish detritus to enter the system, but further research is clearly required to untangle the full complexities of this region.

Conclusions

New data from the Millstone Grit of Yorkshire suggest derivation from the Greenland Caledonides, with generally minor contributions from Scotland and/or Norway. Strong

similarities between potential sources in this complicated region mean no one mineral or isotopic system can provide a unique provenance determination. Instead, comparing minerals with different stabilities and chemistries is necessary to untangle the full story. In particular, comparing labile and refractory records can identify primary (first-cycle) and secondary (polycyclic) provenance, and traditional methods may offer more insights than isotopic techniques. New statistical tools show great promise for comparing the ever-larger detrital datasets modern *in situ* analytical techniques are capable of producing, but are still limited by a patchy distribution of basement data to identify possible sources.

(Acknowledgements)

Reviews by Delia Rösel and an anonymous reviewer provided very helpful feedback on the submitted version of this paper. Shane Tyrrell is thanked for assistance with project development, fieldwork and analyses. PJL was funded by an IRC EMPOWER Postdoctoral Fellowship. The National Centre for Isotope Geochemistry (NCIG) at University College Dublin is a joint venture of University College Dublin, Trinity College Dublin, University College Cork and National University of Ireland, Galway, funded mainly by Science Foundation Ireland, including Grant No. 04/BR/ES0007/EC07 awarded to JSD.

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Figure captions:

Fig. 1: Map of the North Atlantic region during Carboniferous times, after Evans *et al.* (2001), Nance *et al.* (2012) and Woodcock and Strachan (2000). Ages of crustal units adapted from Cawood *et al.* (2007). References for published Pb data given in the Supplementary Material. K-feldspar and galena data are indicated with solid outlines; whole rock data corrected for radiogenic ingrowth have dashed outlines. Large grey arrow indicates gross palaeoflow direction during the Carboniferous. Locations of published garnet data indicated with grey circles.

Fig. 2: Left: Sketch map of the Pennine Basin in northern England with sample localities, based on the BGS 1:50 000 scale bedrock maps and the British National Grid. W - Westphalian; V - Viséan. Right: Stratigraphic column with samples, after Aitkenhead *et al.* (2002). Age for the onset of the Pendleian from Richards (2013).

Fig. 3: Major element compositions of detrital garnet from four samples in this study. X_{Fe+Mn} , X_{Mg} and X_{Ca} are the proportions of Fe + Mn, Mg and Ca, respectively, with all Fe determined as Fe^{2+} . Filled circles - $X_{Mn} < 5\%$. Open circles - $X_{Mn} > 5\%$. Samples: 11LYK05 (P); 11LYK01 (K); ST03/124 (M); ST03/126 (Y).

Fig. 4: Kernel density estimate (KDE) curves of Zr-in-rutile temperatures from five samples in this study, plotted using the Density Plotter tool of Vermeesch (2012) and the propagated 1σ uncertainties. Number of rutiles from each source given in pie charts to right. Source lithologies: Black - metamafic. Grey - metapelitic. Facies: gr-/bl-schist - green-/blueschist. amph/eclogite - amphibolite/eclogite.

Fig. 5: KDE curves of all isotopic data collected in this study, and published data from potential source areas. Grey bars indicate peaks within each data set. Left: $^{206}Pb/^{204}Pb$ ratios in K-feldspar from this study. n = number of analyses. Right: U-Pb ages from zircons analyzed in this study. n = (number of concordant analyses)/(total number of analyses). Right: Published zircon U-Pb data from the Millstone Grit, All Yorkshire (published Millstone Grit plus this study), Scotland (NW Highlands, Grampian Supergroup and

Southern Uplands), Norway (Svaerholt succession) and Greenland (Caledonide belt, Eleonore Bay and Krummedal), including detrital (curves) and local granite/basement ages (horizontal bars); references in the Supplementary Material. Age curves are log-transformed to take advantage of similar relative errors across geochronological datasets.

Fig. 6: Plot of ϵ_{Hf} values measured in concordant zircons from this study, plotted against published basement zircons from around the N Atlantic basin (compilation by Lancaster *et al.* (2015)). Typical 2SD uncertainties on both axes are smaller than symbols. Dashed lines represent the $^{176}\text{Hf}/^{177}\text{Hf}$ evolution of parent rocks extracted from the depleted mantle (DM) at the indicated times (model age), assuming a bulk crustal $^{176}\text{Lu}/^{177}\text{Hf}$ value of 0.015 (Griffin *et al.* 2002). CHUR - chondritic uniform reservoir.

Fig. 7: Plot of $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ for all K-feldspar data in this study, compared to published K-feldspar and galena from around the North Atlantic region (references in the Supplementary Material). Single-stage Pb evolution lines for $^{238}\text{U}/^{204}\text{Pb}$ (μ) = 8 and 9 after Stacey and Kramers (1975). Arch - Archaean; Prot - Proterozoic; Palaeo - Palaeozoic; Caled - Caledonian/Avalonian.

Fig. 8: Multi-dimensional scaling (MDS) maps created using the `provenance` package for R by Vermeesch and Garzanti (2015). a) Radiogenic K-feldspar $^{206}\text{Pb}/^{204}\text{Pb}$ ratios from this study compared to published data from around the N Atlantic craton (references in Supplementary Material). S1 - NW and Grampian Highlands, Scotland. S2 - Southern Uplands, Scotland. S3 - Midland Valley, Scotland. E - N England. I - Ireland. O - Shetland, Orkney, Isle of Man. G - Greenland. N - Norway. A - NE USA. C - NE Canada. b) Caledonian zircon U-Pb data from this study compared to published compilation by Slagstad *et al.* (2011). Sv - Svalbard. Other symbols as before. c) Procrustes plot combining the data in a) and b). S1 - NW Highlands, Scotland. S2 - Grampian Highlands, Scotland. Other symbols as before. d) Archaean zircon U-Pb data from this study compared to published data from around the N Atlantic craton (references in Supplementary Material). Symbols as in a). e) Procrustes plot combining all zircon U-Pb ages, heavy mineral distributions, K-feldspar $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, and bulk petrology for eight samples from this study.

gr-/bl- schist amphib/ ecl granulite

Y

M

K

A

P

a) Pb (18 < ²⁰⁶Pb/²⁰⁴Pb < 19)

b) U-Pb (400–500 Ma)

c) Pb + U-Pb

d) U-Pb (2.4–3.6 Ga)

e) Yorkshire