

Petroleum generation and migration in the Cambro-Ordovician Laurentian margin succession of NW Scotland



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Abstract: Fluid inclusion and organic biomarker data show that there was formerly a hydrocarbon system in the Cambro-Ordovician Laurentian margin rocks of NW Scotland. Oil fluid inclusions occur in stylolitized Eriboll Formation sandstone, in K-feldspar cements with an ⁴⁰Ar/³⁹Ar age of 415 ± 5.5/5.8 Ma (2σ, analytical precision/full external precision). Organic extracts from Durness Group black limestones yield biomarker ratios characteristic of high thermal maturity. Organic maturation to yield oil probably occurred during orogenic deformation along the Moine Thrust Zone. The recognition of a hydrocarbon system in Scotland adds to a huge hydrocarbon province in Laurentian rocks including North America and Greenland.

Supplementary material: Technical data for Ar-Ar dating are available at <https://doi.org/10.6084/m9.figshare.c.3879616>

Received 3 May 2017; revised 27 July 2017; accepted 2 August 2017

Rocks of the Early Palaeozoic Laurentian margin are well exposed in NW Scotland, where they crop out along the Moine Thrust Zone from Durness to Skye (Fig. 1). The rocks have been intensively studied by generations of geologists because they are the focus of deformation along the Moine Thrust Zone, and are structurally repeated in several parts of the zone (Coward 1983). They are composed of transgressive Lower Cambrian siliciclastic deposits (Eriboll and An-t-Sron Formations; McKie 1990), passing upwards into shallow marine platform carbonates (Middle Cambrian to Llanvirn Durness Group; Huselbee & Thomas 1998).

The succession in Scotland represents a southeastern margin of Laurentia, on which carbonate platform deposits are widespread (Fig. 2; McKerrow *et al.* 1991). The carbonate rocks of Laurentia represent a vast hydrocarbon province. Oil production and oil showings occur from the southern USA to the Canadian Arctic and from western Canada to Newfoundland and Greenland (see below). The Scottish rocks have not previously been regarded as part of this province. The carbonates and shales contain detrital kerogen, but there have been no prior records for migrated hydrocarbons. Here we report evidence from fluid inclusion data and organic biomarker analysis of rock extracts to show that Scottish rocks do indeed belong to the same hydrocarbon province. Further, we constrain the timing of hydrocarbon migration by ⁴⁰Ar/³⁹Ar dating of an associated mineral phase.

Geological setting

The Laurentian succession passes up into Silurian and Devonian rocks elsewhere (see below), but its upper limit in Scotland is unknown because it is terminated by a thrust plane. The total Laurentian Lower Palaeozoic sequence preserved is up to 1.5 km (Swett 1969). Structural burial during the Caledonian Orogeny (Moine Thrust imbrication dated at *c.* 435–425 Ma; Freeman *et al.* 1998; Dewey 2005; Goodenough *et al.* 2011) may have been to a depth of ≥10 km (Coward 1983), and has left the succession thermally metamorphosed. Conodont alteration indices in the Durness region are about five, representing temperatures of up to

325°C (Johnson *et al.* 1985; Laubach & Diaz-Tushman 2009), acritarch thermal indices suggest temperatures of about 150–250°C, increasing northwards (Downie 1982), and illite crystallinity data along the whole outcrop indicate temperatures of 250–350°C, also with higher degrees of thermal alteration in the north (Allison & Ferguson 1997). Upon emplacement the base of the Moine Thrust sheet was probably at 450°C (Johnson *et al.* 1985). A further heat pulse focused along the Moine Thrust occurred in Permian time (Parnell *et al.* 2004). A mean fluid inclusion homogenization temperature of 175°C (trapping temperatures probably above 200°C) determined for calcite-rich breccias from the Kyle of Durness indicates a major thermal event, which in the Durness region has been dated palaeomagnetically as Permo-Triassic (Blumstein *et al.* 2005; Elmore *et al.* 2010). The incomplete sequence and the thermal impact of the orogeny mean that the burial and hydrocarbon generation histories are difficult to reconstruct.

Organic matter

If a hydrocarbon system existed in the Laurentian margin succession in Scotland, the most likely source rock in the succession is in the An-t-Sron Formation, immediately above the Eriboll Sandstone Formation (Fig. 1). This unit contains the marine dolomitic shales traditionally known as the Fucoid Beds. Total organic carbon (TOC) values for the shales are typically in the range up to 0.8%. As the rocks have a high thermal maturity, placing them at least in the window of gas generation, their TOC contents at the time of oil generation would have been higher. Assuming that the organic matter was oil-prone, hydrogen-rich, the carbon would be depleted to about 30% of the original values (Cornford 1998), which would thus have been up to 2.6%. Such values are characteristic of good source rocks. The highest present-day organic carbon content that we have measured in the An-t-Sron Formation is 3.35% in Assynt, which represents a very good source rock. Dark shales also occur in the Eriboll Formation (described as black shales in the Ullapool River; Cheeney 1988); these shales contain about 0.25% TOC, equivalent to original 0.83%, which is of marginal source rock value.

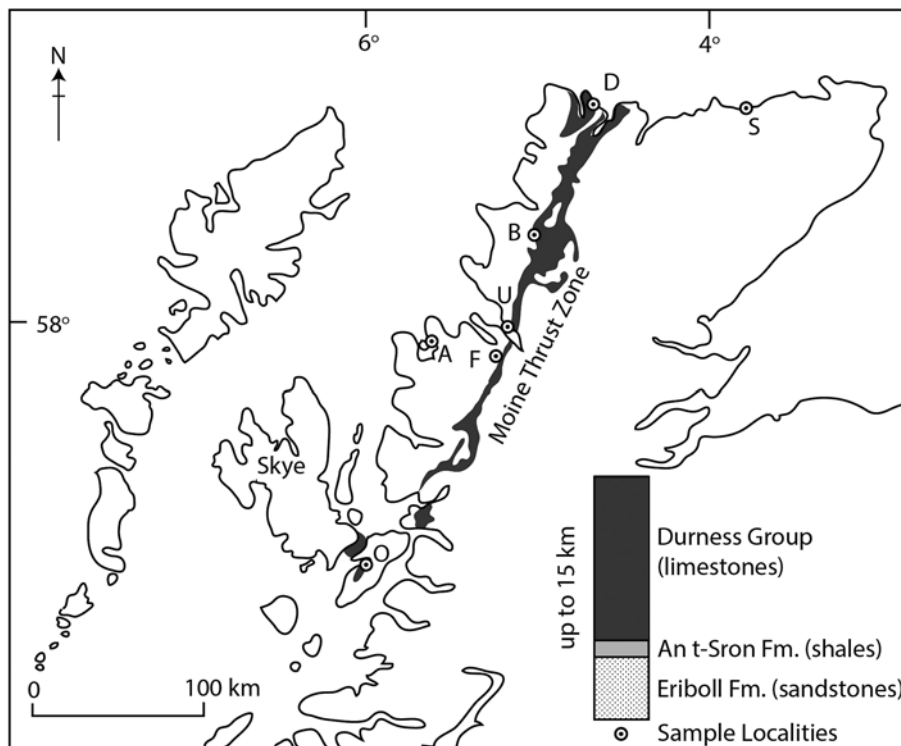


Fig. 1. Stratigraphic succession, and outcrop map of Durness Group limestones in NW Scotland, showing sample localities. A, Aultbea; B, Skiag Bridge, Assynt; D, Durness (Kyle of Durness and Balnakeil Bay); F, Dundonell Forest; O, Ord; S, Sandside Bay; U, Ullapool.

The Durness Group carbonates also contain widespread evidence for microbial remains at the microscopic scale and in stromatolitic morphologies (Brasier 1977; Wright 1997). Previous petrographic studies showed a range of levels of degradation of cyanobacterial mats, and Wright (1997) argued that the abundance of organic-rich sediments during Durness Group deposition gave rise to extensive dolomitization during diagenesis. Consequently, organic carbon commonly occurs as a matrix to dolomite crystals.

Black dolomites and limestones, reflecting the incorporation of organic carbon, occur in many beds, particularly within the Sailmhor Formation. Sailmhor Formation outcrops occur at several localities in the Durness region, in Assynt, and at Ord (Skye). In each locality

mottled dolomites are a mixture of black and pale phases (Fig. 3), termed the Leopard Stone by Peach & Horne (1930). Higher formations in the Durness Group are exposed only in the Durness region and in Skye. The Durness exposures of the Balnakeil, Croisaphuill and Durine Formations are partly black, and approximate correlatives of these rocks in Skye (Strath Suardal and Ben Suardal Dolostones) are also partly black but overprinted by the thermal effects of the Skye Tertiary igneous centre (Peach *et al.* 1910). The Sailmhor Formation is the equivalent of the Watts Bight Formation in western Newfoundland (Wright & Knight 1995): The Watts Bight Formation is similarly mottled black and pale, and is regarded as particularly prospective for petroleum (Fowler *et al.* 1995; Conliffe *et al.* 2009).

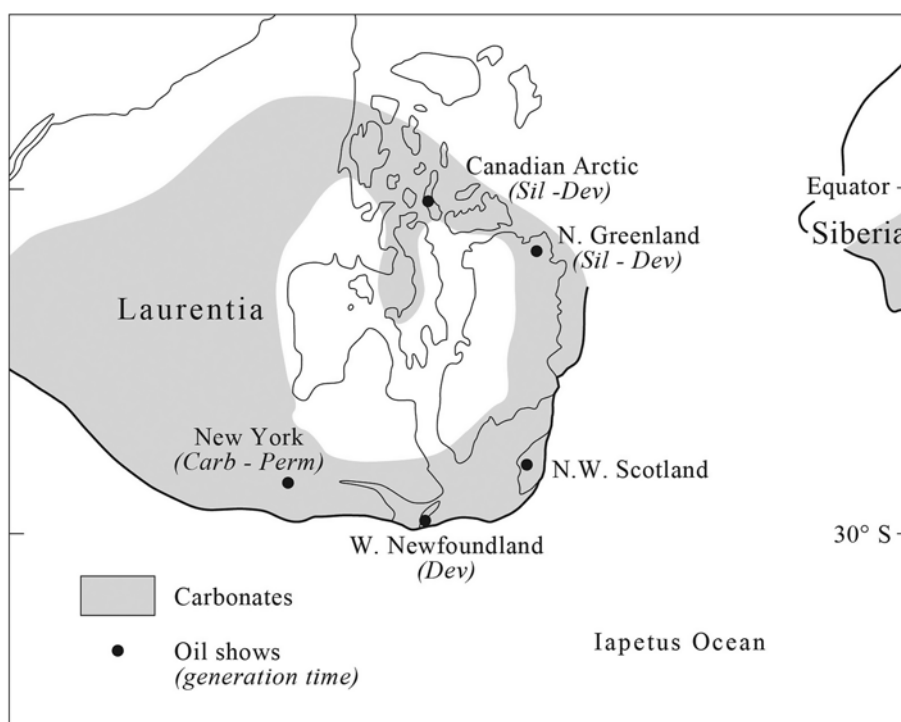


Fig. 2. Map of Laurentia (after McKerrow *et al.* 1991), showing location of Durness Group succession and other hydrocarbon-prospective regions, with timing of hydrocarbon generation as determined by previous studies (sources in text).

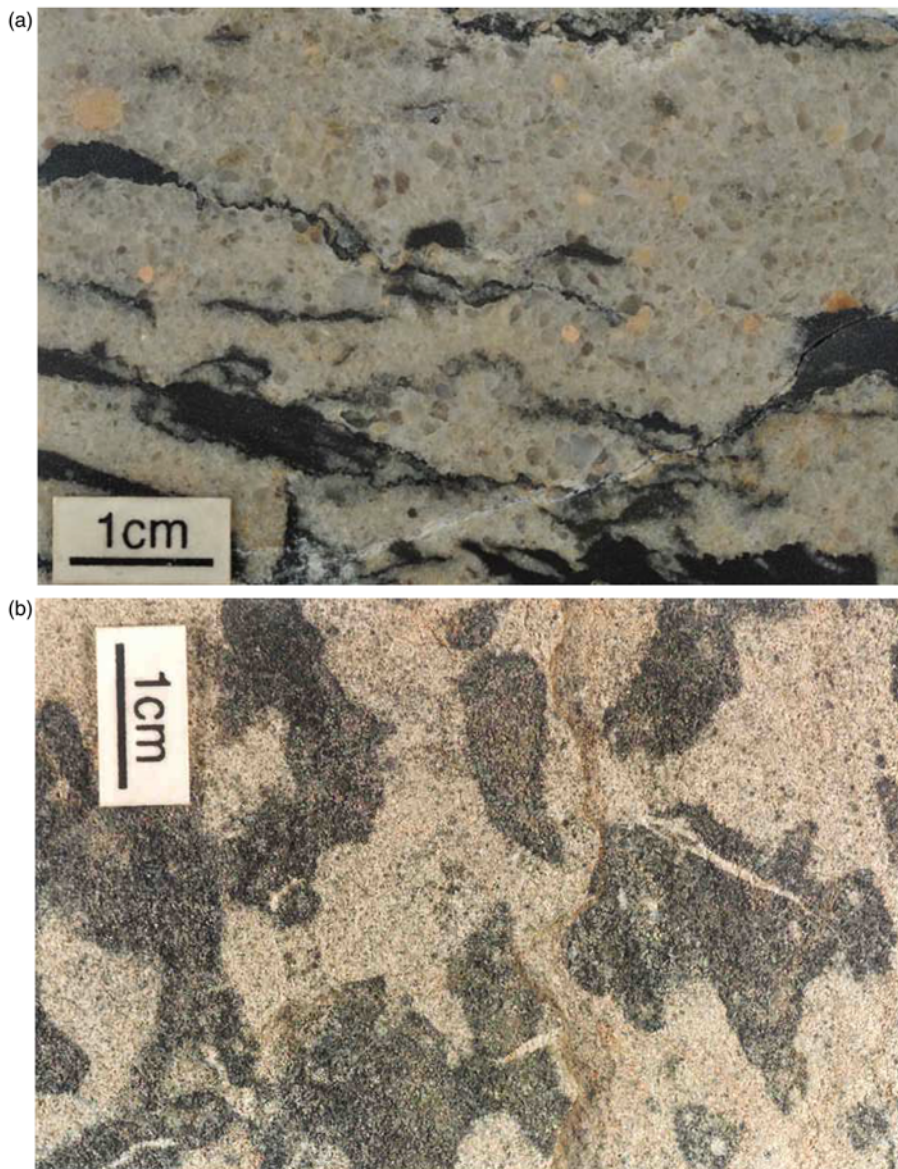


Fig. 3. Cambro-Ordovician rocks rich in organic matter. (a) Eriboll Formation sandstone with abundant stylolites, Ullapool; (b) Durness Group (Sailmhor Formation) limestone with mottled dark zones rich in organic matter (Leopard Rock, formally Leopard Stone), Durness.

Sampling localities

Samples were collected from localities shown in Figure 1. Samples from the Eriboll Formation including black stylolite-rich beds (Fig. 3) at Ullapool and Dundonell Forest were subject to fluid inclusion analysis and Ar–Ar dating. Ordovician limestone samples from along the 300 km length of the Moine Thrust from Skye to Durness were collected at Ord [NG 615132], the Skiag Bridge section in Assynt [NC 240239], Balnakeil Bay [NC 385688] and Kyle of Durness [NC 375637], for organic geochemistry. Coeval limestones from a mixed low-maturity–high-maturity succession in the Canadian High Arctic (Parnell *et al.* 2007) were used as reference samples. Devonian and Jurassic organic-rich source rocks from the region were also analysed for comparison.

Methods

Fluid inclusion analysis

Fluid inclusion wafers were examined using a Linkam THM600 heating and freezing stage attached to an Olympus BH-2 petrographic microscope, calibrated using standards of known melting point, including naphthalene, urea, benzanilide and distilled water. Oil inclusions, which fluoresce under ultraviolet light, were

photographed using a Nikon Eclipse 600 UV microscope fitted with a Nikon HB-10104AF mercury source.

$^{40}\text{Ar}/^{39}\text{Ar}$ dating

Samples for *in situ* UVLAMP $^{40}\text{Ar}/^{39}\text{Ar}$ dating were prepared as doubly polished fluid inclusion wafers using the approaches of Mark *et al.* (2005, 2006). All samples (wafers and separates) were cleaned in ethanol and de-ionized water. They were parcelled in high-purity Al discs for irradiation. Standards Fish Canyon sanidine (FCs) (28.294 Ma, Renne *et al.* 2011), GA1550 biotite (99.738 Ma, Renne *et al.* 2011) and Hb3gr hornblende (1081 Ma, Renne *et al.* 2011) were loaded adjacent to the samples to permit accurate characterization of the neutron flux (J parameter). Samples were irradiated for 3600 min in the Cd-lined facility of the CLICIT Facility at the OSU TRIGA reactor. Standards were analyzed on a MAP 215-50 system (described below briefly and in more detail by Ellis *et al.* 2012): FCs was analyzed by CO_2 laser total fusion as single crystals ($n = 20$); GA1550 ($n = 20$) was also analyzed by CO_2 laser total fusion; Hb3gr was step-heated using a CO_2 scanning laser ($n = 5$) (Barfod *et al.* 2014). Using GA1550, the J-parameter was determined to a precision approaching 0.1% uncertainty. Using the J-parameter measurements from GA1550, ages were determined for FCs and Hb3gr. The ages overlapped at the 68% confidence (1σ)

Table 1. Biomarker data for samples of Durness Group limestones

Locality	Pregnane/sterane	TAS	Sterane C ₂₉ $\alpha\alpha\alpha$ S/S + R	Sterane C ₂₉ $\alpha\beta\beta/\alpha\alpha\alpha + \alpha\beta\beta$	Ts/Ts + Tm	Hopane 30 $\beta\alpha/\alpha\beta$	MPI	MDR
Balnakiel Bay	0.61	0.49	0.49	0.53	0.43	0.14	0.67	3.5
Kyle of Durness	0.76	0.46	0.46	0.51	0.40	0.05	0.26	4.2
Assynt	0.54	0.42	0.57	0.46	0.44	0.11	0.57	3.4
Ord	0.76	0.42	0.60	0.55	0.40	0.06	0.23	6.4

with the ages reported by Renne *et al.* (2011), showing the J-parameters determined from GA1550 to be accurate.

Wafers were loaded into an ultrahigh-vacuum (UHV) laser cell with a SiO₂ window. *In situ* UVLAMP Ar extraction was conducted using a New Wave UP-213 nm UV laser system (described by Moore *et al.* 2011), and 50 × 50 × 5 µm (amounts of ablated material c. 12500 µm³) raster pits were made in mineral surfaces to extract the Ar isotopes. All gas fractions were subjected to 180 s of purification by exposure to two SAES GP50 getters (one maintained at room temperature, the other held at c. 450°C). A cold finger was maintained at -95.5°C using a mixture of dry ice (CO₂[s]) and acetone. Ion beam intensities (i.e. Ar isotope intensities and hence ratios) were measured using a MAP 215-50 mass spectrometer in peak jumping mode. Measurements were made using a Balzers SEV-217 electron multiplier. The system had a measured sensitivity of 1.13 × 10⁻¹³ mol V⁻¹ (mass spectrometer described by Mark *et al.* 2014, 2017). The extraction and cleanup, as well as mass spectrometer inlet and measurement protocols and data acquisition, were automated. Blanks (full extraction line and mass spectrometer) were made following every two analyses of unknowns. The average blank ± standard deviation (*n* = 28) from the entire blank run sequence was used to correct raw isotope measurements from unknowns. Mass discrimination was monitored by analysis of air pipette aliquots after every five analyses of unknowns (*n* = 9, 7.21 × 10⁻¹⁴ mol ⁴⁰Ar).

All Ar isotope data were corrected for backgrounds, mass discrimination and reactor-produced nuclides, and were processed using standard data reduction protocols (e.g. Mark *et al.* 2010a,b, 2011a) and reported according to the criteria of Renne *et al.* (2009). The atmospheric argon isotope ratios of Lee *et al.* (2006), which have been independently verified by Mark *et al.* (2011b), were employed. The optimization model of Renne *et al.* (2010) with the parameters of Renne *et al.* (2011) was used for age calculation. The BGC software (MassSpec) was used for data regression. All ages are presented as $X \pm Y/Z$, where *Y* is the 2σ analytical precision, and *Z* is the 2σ full external precision (unless stated otherwise). All raw data are presented in the Supplementary Material.

Organic geochemistry

Samples of Durness Group limestone were extracted using dichloromethane, then separated using thin layer chromatography, and hydrocarbon and aromatic fractions were analysed by gas chromatography–mass spectrometry. Measurements were directed on mass fragments that yield interpretable data at high thermal maturities; that is, steranes (*m/z* 217, 218), terpanes/hopanes (*m/z* 191), methylphenanthrenes (*m/z* 178 + 192), methylidibenzothiophenes (*m/z* 198) and triaromatic steroids (*m/z* 231). Analyses were performed using a Hewlett Packard HP5970 MSD attached to a HP5890 gas chromatograph. A 30 m SGE BPX5 column was used with 0.5 µm film thickness and 0.32 mm internal diameter. The gas chromatography temperature programme was 80°C for 2 min, heating at 4°C min⁻¹ up to 290°C, then holding for 30.5 min. Standard thermal maturity parameters were calculated from biomarker distributions (Peters *et al.* 2007). The C₂₁ + C₂₂ steranes/(C₂₁ + C₂₂ + C₂₉ $\alpha\alpha\alpha$ S & R steranes) parameter was measured using the short chain 5α(H)- and 20-methyl-5α(H)-pregnanes and the C₂₉

5α(H),14(H),17(H) 20S and 20R regular steranes. The C₂₀, C₂₁ and C₂₈ 20R triaromatic steroids (TAS) were used to calculate the C₂₀ + C₂₁ TAS/(C₂₀ + C₂₁ + C₂₈ R TAS) parameter. Other parameters used include the C₂₉ $\alpha\beta\beta/\alpha\alpha\alpha + \alpha\beta\beta$ sterane ratio, hopane Ts/Ts + Tm ratio, hopane 30 $\beta\alpha/\alpha\beta$ ratio, methylphenanthrene index (MPI) and methylidibenzothiophene ratio (MDR) (Table 1).

Data

Organic geochemistry, Durness Group limestones

Biomarkers were successfully extracted, quantitatively, from each of the four Durness Group limestones (Table 2; Figs 4 and 5). No yields were obtained from samples of Eriboll Formation sandstone used as controls.

The sterane ratio parameter has reached values of between 0.5 and 0.8. These values are typical of sequences that have reached peak hydrocarbon generation (the oil window) or beyond (Peters *et al.* 2007). The triaromatic steroid ratios (Fig. 6) range from 0.4 to 0.5, which is also at the high end of the range characteristic of peak hydrocarbon generation (Killops & Killops 1993). The values are consistent along the extent of the Moine Thrust Zone. The other parameters all give ratios that are consistent with peak hydrocarbon generation (Killops & Killops 1993; Peters *et al.* 2007).

Sterane compositions from the Durness Group limestone were also compared with compositions from known source rocks in other successions in the north of Scotland; that is, Jurassic at Aultbea and Devonian at Sandside Bay (Figs 1 and 7).

Fluid inclusion study, Eriboll Formation

Samples of Eriboll Formation from Ullapool and Dundonell Forest show similar petrography and fluid inclusion assemblages. At both localities, the rock consists of white quartz arenite (former Basal Quartzite), cut by dark stylolitic horizons approximately parallel to bedding (Fig. 8). The bulk quartz arenite is pervasively cemented by quartz. The stylolitic horizons additionally contain authigenic crystals of albite and K-feldspar. Overgrowths of albite and K-feldspar on detrital grains also occur in a zone about 1 mm around the stylolites. The stylolites additionally contain concentrations of heavy minerals, particularly zircon and apatite. The paragenetic sequence is quartz cementation, then stylolite formation, followed by albite cement and finally K-feldspar cement.

Primary two-phase fluid inclusions occur in each of the quartz, albite and K-feldspar overgrowths. They range in size from 2 to 15 µm. The inclusions in the quartz and albite are aqueous, whereas

Table 2. Extract data for samples of Durness Group limestones

Locality	Grid reference	EOM (% whole-rock)	Saturate (% extract)	Aromatic (% extract)
Balnakiel Bay	NC 385688	0.001	10	10
Kyle of Durness	NC 373635	0.001	50	33
Assynt	NC 240239	0.009	<10	<10
Ord	NG 615135	0.001	40	20

EOM, extractable organic matter.

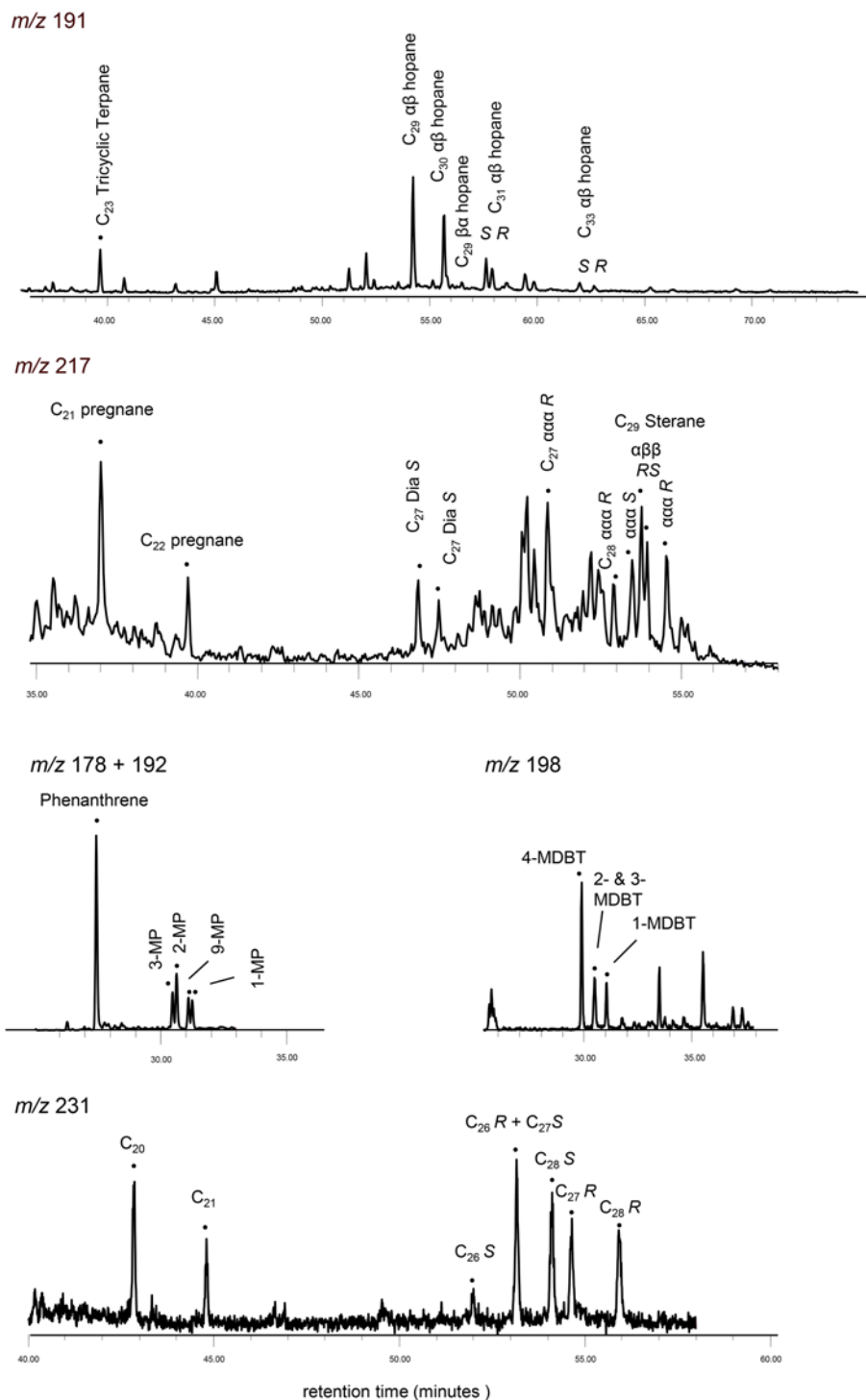


Fig. 4. Ion chromatograms for Durness Group sample from Assynt. (a) m/z 191. C_{23} tricyclic terpane = C_{23} 13 β (H),14 α (H) tricyclic terpane; C_{27} Ts = C_{27} 18 α (H)-22,29,30 trisnorneohopane; C_{27} Tm = 17 α (H)-22,29,30 trisnorhopane; C_{29} $\alpha\beta$ hopane = C_{29} 17 α (H),21 β (H) hopane; C_{31} $\alpha\beta$ S = C_{31} 17 α (H),21 β (H) (22S) hopane; C_{31} $\alpha\beta$ R = C_{31} 17 α (H),21 β (H) (22R) hopane. (b) m/z 217. C_{21} pregnane = 5 α (H)- and 20-methyl-5 α (H)-pregnane; C_{27} Dia S = C_{27} 13 β ,17 α (H) 20S diasterane; C_{27} $\alpha\alpha\alpha$ R = C_{27} 5 α ,14 α ,17 α (H) 20R sterane; (c) m/z 178 + 192. 3-MP = 3-methylphenanthrene; (d) m/z 198. 4-MDBT = 4-methyldibenzothiophene; 1-MDBT = 1-methyldibenzothiophene; (e) m/z 231. C_{20} = C_{20} triaromatic steroid; C_{26} S = C_{26} 20S triaromatic steroid.

there are both aqueous and hydrocarbon inclusions in the K-feldspar (Fig. 9). Hydrocarbon inclusions also occur in altered K-feldspar detrital grains. The hydrocarbon inclusions are sufficiently abundant to cause the stylolitic horizons to luminesce green–blue under UV illumination (Fig. 9). A later set of monophasic inclusions crosscuts all mineral phases. These secondary inclusions include some fluorescing oil.

The microthermometric data for the fluid inclusions are summarized in Table 3. Measurements were restricted to K-feldspar that appeared to be unaltered. The three cements yield homogenization temperatures (T_h) of 113–128°C (quartz), 104–111°C (albite) and 70–93°C (K-feldspar), from aqueous inclusions. The hydrocarbon inclusions were too small for reliable microthermometry.

In addition, petrographic studies of coarse black dolomites in the Durness Group limestones show that the dolomite crystals contain

fluid inclusions filled with liquid hydrocarbons, recognized by fluorescence under ultra-violet light. The inclusions are very small, typically of 1–2 μm width.

$^{40}\text{Ar}/^{39}\text{Ar}$ dating

$^{40}\text{Ar}/^{39}\text{Ar}$ ages were obtained from the K-feldspar cements. The data recovered define a normal distribution with ages ranging from 389.1 ± 11.3 Ma (1 σ , analytical precision) to 430.7 ± 10.3 Ma (1 σ , analytical precision) (Fig. 10; Supplementary Material). As such, we have calculated a weighted average $^{40}\text{Ar}/^{39}\text{Ar}$ age for the overgrowths of $415.3 \pm 5.5/5.8$ Ma (2 σ , analytical precision/full external precision); this age is interpreted to represent the growth of the K-feldspar overgrowths. Owing to the growth mechanism, authigenic K-feldspar has been demonstrated to have a relatively

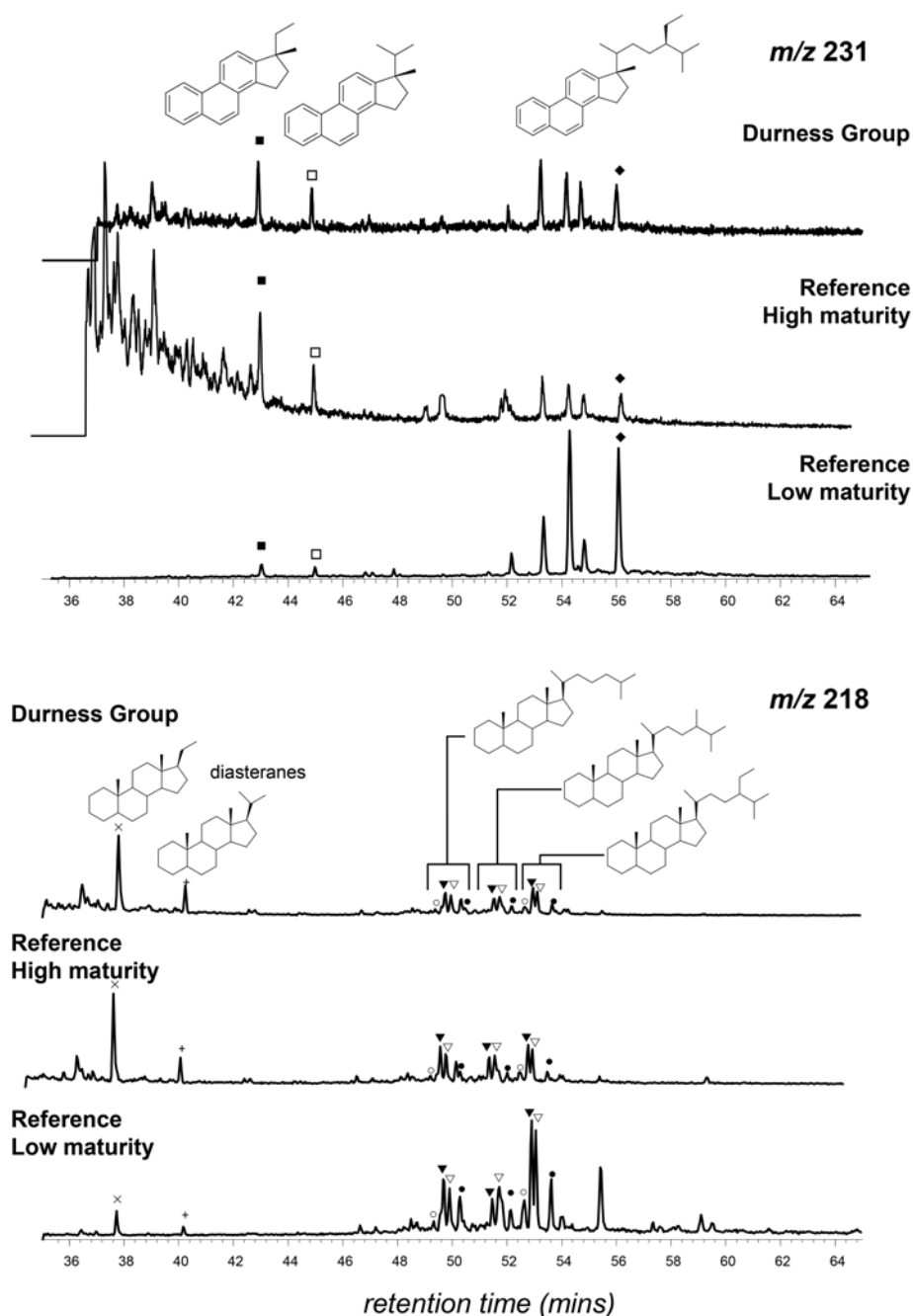


Fig. 5. Ion chromatograms for steranes (m/z 218) and triaromatic steroids (m/z 231) for Durness Group sample from Assynt, compared with reference low and high thermal maturity contemporary samples in Canadian High Arctic (Parnell *et al.* 2007). Durness Group data are more similar to reference high maturity data.

high closure temperature in excess of 250°C (Mark *et al.* 2007, 2008, 2010b). Radiogenic ^{40}Ar yields cluster between 88 and 92%, and hence when plotted on an isotope correlation plot the data do not define an isochron.

Discussion

Evidence for hydrocarbons in the Cambro-Ordovician succession

The hydrocarbon enrichment in the dolomites of the Durness Group exemplifies a hydrocarbon play that is found throughout the Cambro-Ordovician platform carbonates of the Laurentian continent (Fig. 2). The closest occurrences are bituminous dolomites in north Greenland (Christiansen 1989) and western Newfoundland (Fowler *et al.* 1995). Other regionally important deposits that have attracted oil exploration and production are in Ontario (Powell *et al.* 1984), the Williston Basin (Osadetz *et al.* 1989; Montgomery 1997) and the Canadian Arctic (Rayer 1981; Zhang 2008). The proportion

of mudrock facies, which might contain greater concentrations of organic matter, is very low in the Scottish outcrop. However, deeper water environments with an increase in mudrock facies are predicted to have existed to the east of the present outcrop (Swett & Smit 1972), and up-dip migration of hydrocarbons to the west is a possible scenario.

Sources for hydrocarbons

The other possible source rocks in the region are Devonian lacustrine rocks of the Orcadian Basin to the NE (Marshall *et al.* 1985) and Jurassic shales, which occur onshore in Skye and offshore from the mainland coast (Fyfe *et al.* 1993). The Jurassic units may have been deposited widely over NW Scotland, including the Moine Thrust Zone (Holford *et al.* 2010). The Devonian source rocks consistently contain high proportions of C_{28} $\alpha\alpha\alpha$ steranes (Fig. 7) and conspicuous amounts of gammacerane (a triterpane typical of hypersaline environments), both of which are absent from the Durness Group samples. Devonian sources are also unrealistic in

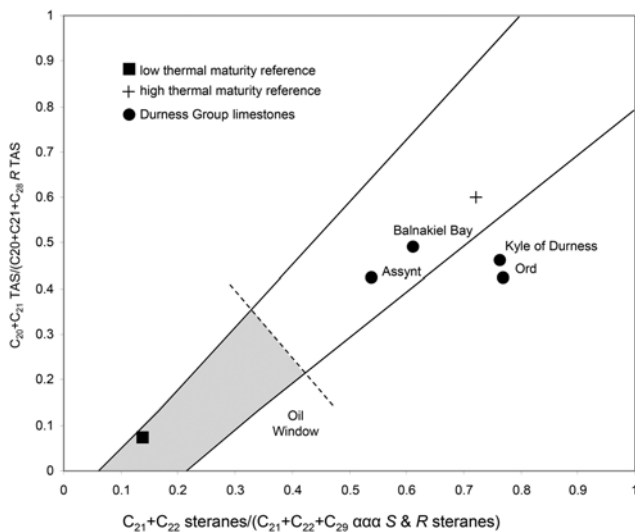


Fig. 6. Cross-plot of sterane and triaromatic steroid thermal maturity parameters. Durness Group data are compared with reference low and high thermal maturity samples and entire envelope of data from contemporary samples in Canadian High Arctic (Parnell *et al.* 2007).

the south of the Durness Group outcrop, where there is no evidence of any Devonian deposits. The Jurassic shales lack the prominent diasteranes found in the Durness Group samples. They are also immature in the region, except where thermally altered by the Skye Tertiary igneous centre (Thrasher 1992), and so have biomarker maturity ratios distinct from those of the Durness Group samples. Consequently, there is strong evidence for attributing the Durness Group hydrocarbons to an intraformational source.

In addition to the circumstantial evidence for an Early Palaeozoic source, a low abundance of C_{28} steranes in the Durness Group

samples (Fig. 7) is comparable with patterns measured from numerous other marine Early Palaeozoic sequences (e.g. Rullkötter *et al.* 1986; Grantham & Wakefield 1988). The high abundance of diasteranes (Fig. 7) is also a feature of other Ordovician sequences (e.g. Longman & Palmer 1987; Obermajer *et al.* 1999). C_{30} steranes are present, which are a general indicator of marine algae (Peters *et al.* 2007).

Thermal maturity

The biomarker thermal maturity parameters indicate heating into and beyond the oil window. This is consistent with the known thermal history of the region, and shows that the biomarkers extracted are genuine components of the rock, rather than modern contaminants from peat, etc.

The survival of hydrocarbons despite the orogenic heating at 250°C or higher adds to a growing body of evidence that hydrocarbons can persist at temperatures much greater than has conventionally been assumed. There are numerous examples of high carbon number biomarkers preserved in hydrocarbon reservoirs that have experienced over 200°C (e.g. Dutkiewicz *et al.* 2006; George *et al.* 2008), in some cases with compositions indicating low to moderate thermal maturity (Price 2000).

The persistence of biomarkers may also be partially explained by the residence of the hydrocarbons within fluid inclusions. The inclusions are sealed vessels that become overpressured during burial after entrapment. Hydrocarbon generation and organic chemical reactions are retarded by pressure (Dominé *et al.* 1990; Carr 1999), and biomarker ratios may become fixed at the value pertaining during entrapment in the inclusions. Previous studies have similarly recorded lower maturities in inclusion-hosted oils relative to present-day oils (George *et al.* 2007). Also, some organic matter sealed within Durness Group cherts during early diagenesis is pale brown in colour (Wright 1997), rather than the black colour typical of organic matter that has passed through the oil window.

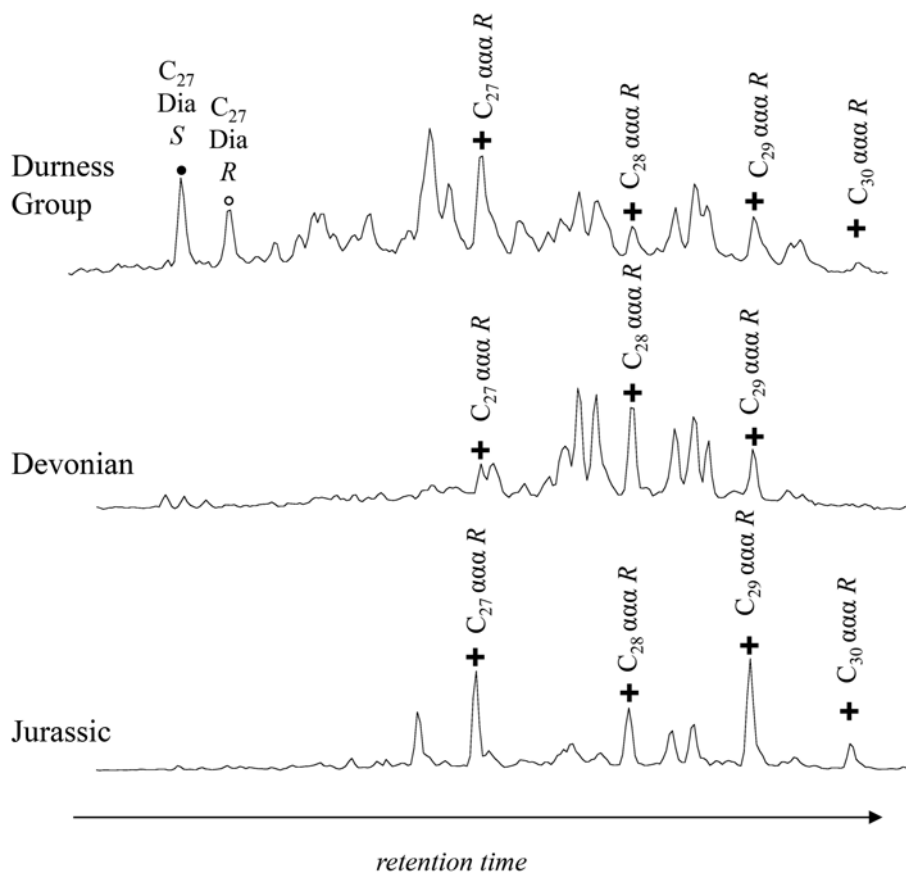


Fig. 7. Comparison of Durness Group sterane composition (m/z 217 ion chromatograms) with samples of known source rock in northern Scotland of Devonian and Jurassic age. C_{27} Dia $S = C_{27}$ $13\beta,17\alpha(H)$ $20S$ diasterane; $C_{27}\alpha\alpha R = C_{27}$ $5\alpha,14\alpha,17\alpha(H)$ $20R$ sterane. The high abundance of diasteranes in Durness Group sample, and C_{28} steranes in the Devonian sample, should be noted. Durness Group composition does not match either of the younger source rocks.

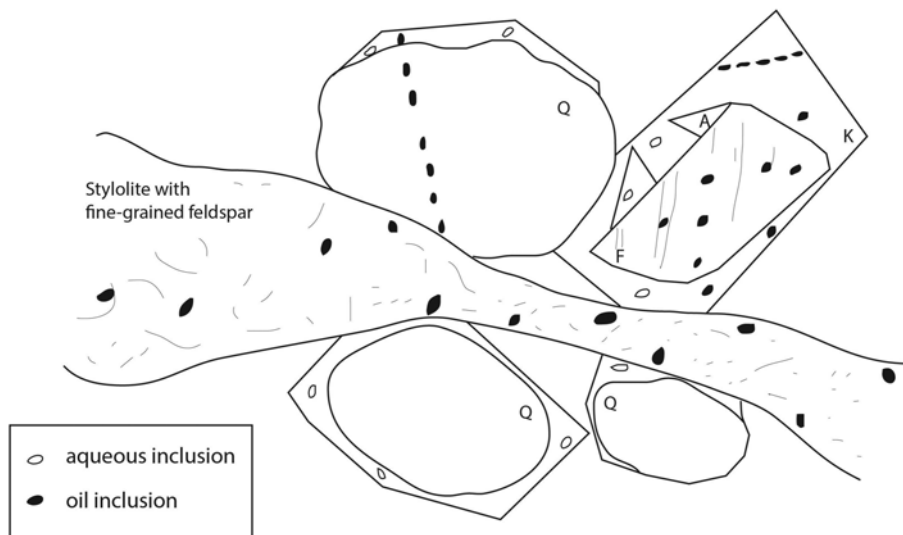


Fig. 8. Schematic petrography of stylolite cutting Eriboll Formation sandstone, Ullapool and Dundonell Forest. Fluid inclusions were measured in each of quartz (Q), albite (A) and K-feldspar (K). F, detrital feldspar grain.

Timing of hydrocarbon generation

In terms of regional thermal history, we require to know when the heat, which caused hydrocarbon generation, was applied.

The surviving thickness of rocks in the Durness Group is inadequate to cause hydrocarbon generation by burial prior to metamorphism: at a geothermal gradient of $30^{\circ}\text{C km}^{-1}$, a minimum of 2–3 km burial would be required, and a maximum of 1.5 km for the entire Cambro-Ordovician is preserved (Swett 1969; Smith & Rasmussen 2008). However, in more complete Laurentian sequences, extending up into the Silurian and Devonian, up to several kilometres extra thickness of rock is present, and in north Greenland, Quebec and the Canadian Arctic, hydrocarbon generation from the Ordovician section is predicted to have occurred owing to burial heating in Siluro-Devonian times (Fig. 2; Christiansen 1989; Parnell *et al.* 2007; Grundman *et al.* 2012). Elsewhere on the Laurentian continent, the additional section was a continuation of platform sedimentation, but Soper *et al.* (1999) suggested that in Scotland synorogenic deposits related to easterly Grampian deformation (Arenig–Llanvirn) succeeded the Durness carbonates not far above their present upper limit. Either additional platform sediments or synorogenic deposits could have caused oil generation in Scotland before Caledonian thrusting, or contributed to maturation that continued post-thrusting.

Structural burial owing to thrust-stacking in the orogenic belt could cause hydrocarbon generation, if the source rocks had not been depleted prior to the orogeny. Examples of thrust-enhanced hydrocarbon generation have been discussed by Morley (1992) and Parnell *et al.* (2003).

Hydrocarbon generation since the orogeny is unlikely. The Ordovician rocks currently at outcrop along the Moine Thrust Zone have not been buried deeply since denudation of the Scottish Highlands occurred to about their present level in Devonian times (Watson 1984; Hall & Bishop 2002). Thus they were not buried more deeply at the post-orogenic stage than in the pre-orogenic stage.

The fluid inclusion data can be related to burial history and used to constrain the timing of oil generation. The stylolites that cut the quartz cement represent pressure dissolution, which is associated with thrust-related deformation of the Eriboll Formation (Knipe 1990). However, the data obtained from the quartz cement indicate temperatures much higher than could be explained by the pre-thrust burial alone. The subsequent feldspar cements yield lower temperatures, so may have been precipitated during uplift following thrusting. Uplift was rapid (Laubach & Diaz-Tushman 2009; Hooker *et al.* 2011). This sequence of events is consistent

with thrusting over 435–425 Ma, and feldspar precipitation at $415 \pm 5.5/5.8$ Ma. Thus the feldspar, and its included oil, was introduced by an episode of fluid flow soon after thrusting. A broadly similar paragenesis of quartz followed by feldspar is recorded in the Moine Thrust Zone from fracture systems through the Eriboll Formation (Laubach & Diaz-Tushman 2009). The

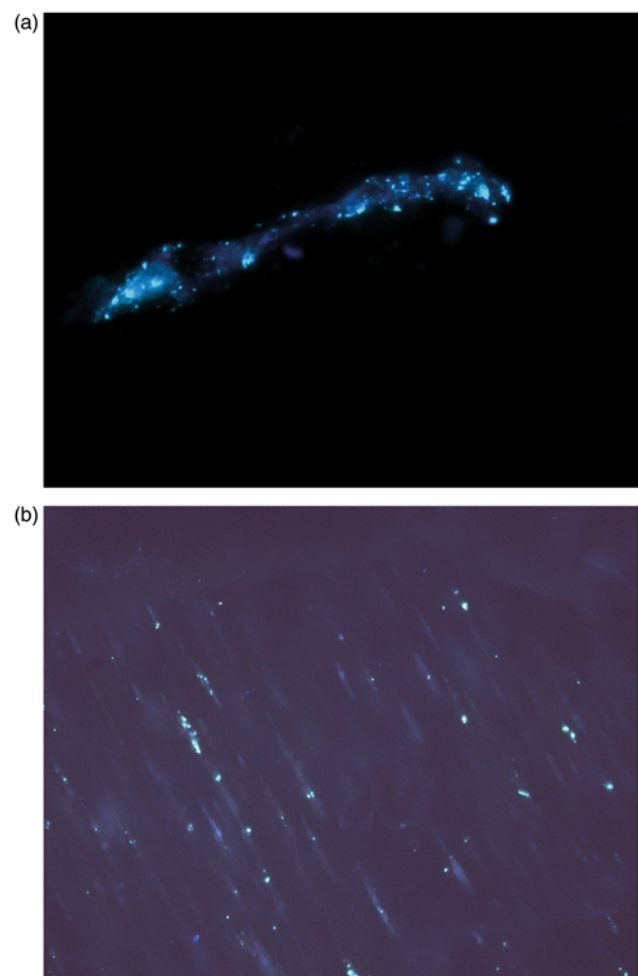


Fig. 9. Oil inclusions fluorescing under ultraviolet light, in stylolite zone. (a) Oil inclusions in trail through quartz grain; (b) oil inclusions in altered K-feldspar. Polished wafer, Eriboll Formation, Ullapool. Field widths 200 μm . Microthermometric data are reported in Table 3.

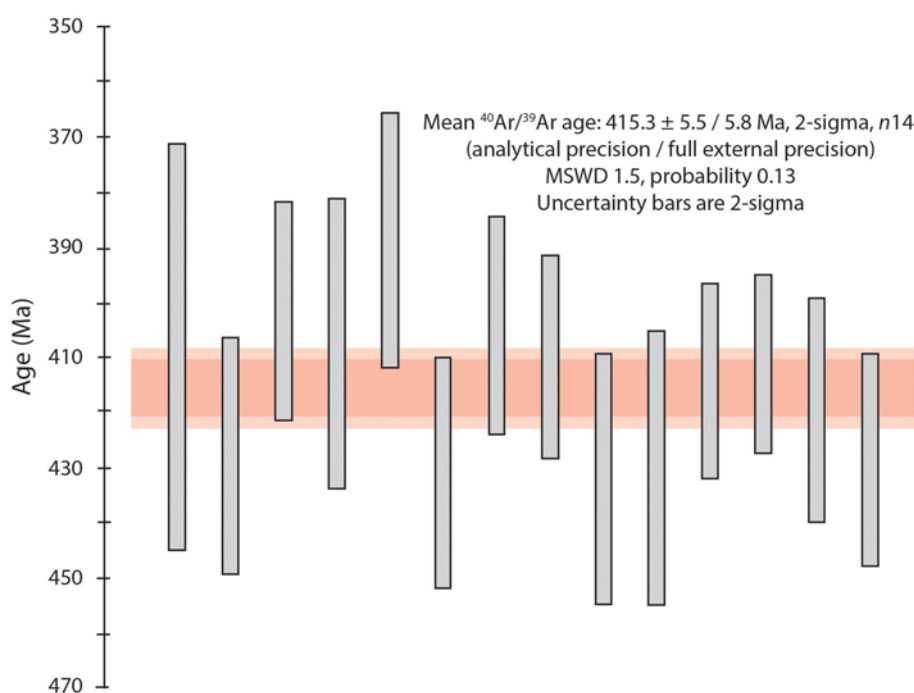


Fig. 10. $^{40}\text{Ar}/^{39}\text{Ar}$ data for 14 samples (shown at 2σ uncertainty), plotted against the geological timescale. The data give a mean age of $415 \pm 5.5/5.8$ Ma (2σ , analytical precision/full external precision).

earliest quartz yields fluid inclusion temperatures up to 170°C , but is pre-stylolite and so is interpreted to be pre-thrusting. The latest quartz yields temperatures $<80^\circ\text{C}$, and is demonstrably post-thrusting, although it could be as young as Cenozoic (Laubach & Diaz-Tushman 2009).

Primary fluid inclusions in quartz cements in a larger set of Eriboll Formation sandstones along the Moine Thrust Zone also yield temperatures up to 200°C , interpreted to represent pre-orogenic fluids (Baron *et al.* 2003). Temperature trend data also exist for K-feldspar cements in the An-t-Sron Formation (Mark *et al.* 2007). Two stages of cementation are evident: a moderate-temperature (up to 115°C) stage dated at *c.* 470 Ma (mid-Ordovician), followed by a hotter (up to 145°C) stage synchronous with stylolite formation dated at *c.* 432 Ma (Silurian). These two stages are consistent with an elevation of temperature at the time of compressional deformation (Mark *et al.* 2007), but even the first stage is hotter than could be explained by burial alone.

In summary, four studies (Baron *et al.* 2003; Mark *et al.* 2007; Laubach & Diaz-Tushman 2009; this study) all indicate temperatures $>100^\circ\text{C}$ in advance of the stylolitization event, which is assumed to relate to thrusting. Thrusting would have caused burial to temperatures at which quartz dissolution and reprecipitation could occur, so it is likely that some quartz observed was deposited as thrusting commenced or very soon afterwards (Laubach & Diaz-Tushman 2009). However, the consistent evidence of quartz precipitation pre-stylolites suggests an earlier source of anomalous heat. The source of this heat may be a regional episode of magmatism. Major and minor intrusions in the Assynt district were emplaced before thrusting (Halliday *et al.* 1987; Goodenough *et al.* 2004). This magmatic activity indicates high heat flow, and

provides an explanation for the circulation of high-temperature fluids to precipitate quartz cement.

Additional evidence from calcite vein mineralization in the Durness region is consistent with the deduced timing of oil formation. Where outcrops of black dolomite are cut by mineral veins (usually calcite), or fracture surfaces, there is no macroscopic evidence for hydrocarbon residues in the structures, or hydrocarbon fluid inclusions in the calcite. This includes localities where thrusting is accompanied by brittle deformation and mineral veining in the footwall. The evidence suggests that the veins were not conduits for charging the dolomites with oil or for draining oil from them. In the Durness region, fragments of black dolomite rock occur within calcite veining. These observations indicate that oil charge occurred before the brittle deformation.

Conclusions

Geochemical data support a model in which the Laurentian margin rocks of Scotland were charged with oil at about the time of orogenic deformation. This implies a thermal history adequate to generate hydrocarbons from Early Palaeozoic source rocks. The current thickness of Early Palaeozoic sediments is inadequate for hydrocarbon generation. However, several factors could have contributed to generation: (1) the pre-thrusting succession included a greater thickness of rocks now excised by thrusting; (2) as the source rocks probably lay to the east in deeper water facies where the section was thicker, generation could have occurred earlier than in the outcropping section; (3) enhanced heat flow pre-thrusting, indicated by magmatic activity and implicit in regional tectonic models, could have enhanced maturation; (4) additional heating could have occurred owing to structural burial during thrusting. These factors may have combined, so that flexural loading and greater burial in a source rock kitchen to the east, during Grampian and Scandian deformation (Dewey 2005), produced hydrocarbon-bearing fluids that migrated westwards up-dip, especially when thrusting provided new migration pathways.

The orogenic deformation that dominates the Laurentian succession in NW Scotland caused thermal maturation beyond the stage of oil preservation, except in fluid inclusions, but paradoxically has left us with a fluid inclusion record in stylolites to provide

Table 3. Summary of fluid inclusion data for Eriboll Formation sample, Ullapool

Mineral	Aqueous T_h range ($^\circ\text{C}$)	Wt% NaCl	Primary oil inclusions	Secondary oil inclusions
Quartz	113–128	6–8	No	Yes
Albite	104–111	6–8	No	Yes
K-feldspar	70–93	3–4	Yes	Yes

evidence of oil generation. The evidence for oil generation in the Scottish succession adds to existing records that record a huge hydrocarbon province in the carbonate platform rocks of Laurentia.

Acknowledgements We are grateful to B. Fulton, J. Johnston and C. Taylor for skilled technical help. A. G. Leslie and H. Volk provided critical comments that helped to improve the paper.

Funding NERC is thanked for continued funding of the Argon Isotope Facility, which is housed at SUERC. D.M. was in receipt of a NERC PhD studentship.

Scientific editing by Veerle Vandeginste

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