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# The role of organic carbon in the Southern Uplands-Down-Longford Terrane accretionary prism, Scotland and Ireland

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## Abstract

Carbonaceous shales in the Southern Uplands-Down-Longford Terrane accretionary prism had extremely high potential for hydrocarbon generation in the Lower Palaeozoic. Structural thickening in the prism enhanced the rapid generation of oil. Shale horizons are separated by thick turbidites composed of low-permeability greywackes, so oil under high fluid pressure either pooled along shale bedding surfaces or migrated into fractured greywackes. Pooled oil became solidified to bitumen, which locally formed deposits on a scale of tonnes, mined as coal. The carbon-rich shale also sequestered large amounts of sulphur from seawater, which precipitated as pyrite firstly during early diagenesis, then further during fluid flow through the shale beds. The oil was also sulphur-bearing. Deformation focussed on the shale beds during the evolution of the accretionary prism would have been closely related to the fluid flow which precipitated bitumen and sulphides. The palaeo-fluids were also anomalously rich in methane and hydrogen, similar to fluids venting from modern accretionary prisms.

## Geological Setting

The Ordovician-Silurian sedimentary package that constitutes the Southern Uplands-Down-Longford Terrane (SUDLT) was deposited and deformed on the northern margin of the Iapetus Ocean. The package is dominated by marine turbidites, with subordinate pelagic mudrocks and basalts. The mudrocks include a prominent unit of graptolitic black shales. The succession is structurally repeated by strike-parallel faults, which are the basis of an accretionary prism model for the package (Leggett

1980, Floyd 2001, Stone & Merriman 2004, Beamish et al. 2010). The black shales in the prism are of Llanvirn (Upper Ordovician) to Llandovery (Silurian) age, collectively termed the Moffat Shale (Floyd 1996). The imbricate structure of the SUDLT prism was facilitated by detachment on the Moffat Shale (Webb 1983, McCurry & Anderson 1989, Needham 2004). The black shale deposits of the Ordovician oceans had high hydrocarbon potential due to flourishing oil-rich algae (Reed et al. 1986, Makled et al. 2021), and abundant graptolite debris, with similar high hydrocarbon potential (Agapitov 2014, Luo et al. 2020). This study reports the evidence for hydrocarbon generation in the Southern Uplands-Down-Longford Terrane (Fig. 1).

The context for this assessment is a history of mining the Lower Palaeozoic for so-called 'coal'. This was a carbonaceous substance in the shales which must have been emplaced post-deposition, as it cross-cuts the bedding (Whitty 1854). Some records may be exaggerated, but accounts of mining and selling fuel are indisputable, and as recently as the twentieth century the Commission of Inquiry into the Resources and Industries of Ireland (1921) suggested the possibility of including the fuel in briquettes.

The objectives of the study are:

- (i) Measurement of the carbon content of selected localities in the Moffat Shale, and determination of a mean value for the richer beds.
- (ii) Reconstruction of the original carbon content before hydrocarbon generation and low-grade metamorphism.
- (iii) Assessment of burial history and likely hydrocarbon generation history within the context of accretionary prism construction.
- (iv) Petrographic study of the distribution of hydrocarbon residues.
- (v) Collation of supporting information on attempts to mine 'coal' in the Ordovician-Silurian rocks of the prism.
- (vi) Measurement of sulphur isotope data in pyrite in the Moffat Shale as an indicator of fluid sources.

## Methodology

Petrographic studies were performed at the University of Aberdeen ACEMAC Facility using a Zeiss Gemini field emission gun scanning electron microscope (FEG-SEM) on polished blocks of the marble. Samples were carbon coated and analysed at 20 Kv, with a working distance of 10.5 mm. Samples were analysed using Oxford Instruments EDS X-ray analysis. The standards used were a

mixture of natural minerals, metal oxides and pure metals, as calibrated by the factory. Oxygen contents were determined by stoichiometry.

Organic carbon and sulphur contents were measured in black shales of the Moffat Shale Group using a LECO CS225 elemental analyser, after decarbonatization with hydrochloric acid, to a precision of  $\pm 0.05\%$ .

There are several assessments of how to reconstruct the original carbon content before hydrocarbon generation (e.g., Raiswell & Berner 1987, Pang et al. 2014, Allan et al. 2016, Daly & Edman 2019). The carbon loss is related to kerogen type, increasing from the relatively recalcitrant kerogen type III to the oil-prone type I. Lower Palaeozoic graptolitic shales are considered to have a composition approximating to kerogen type II (Gupta et al. 2006, Luo et al. 2020). The carbon content of kerogen type II is reduced to about a third to a half of the original content by the time it is through the gas window. We adopt a conservative value of 50% carbon loss. The hydrocarbon source rock potential is evaluated using a plot of TOC and Hydrogen Index (after Çiftçi et al. 2010).

#### Sulphur isotopes

For sulphur isotope analysis, pyrite samples from the Moffat Shale were combusted with excess  $\text{Cu}_2\text{O}$  at  $1075^\circ\text{C}$  in order to liberate the  $\text{SO}_2$  gas under vacuum conditions. Liberated  $\text{SO}_2$  gases were analysed on a VG Isotech SIRA II mass spectrometer, with standard corrections applied to raw  $\delta^{66}\text{SO}_2$  values to produce true  $\delta^{34}\text{S}$  values. The standards employed were the international standard NBS-123, IAEA-S-3, and SUERC standard CP-1.

#### Fluid inclusions

Fluid inclusions were measured in samples from Elvanfoot and Coalpit Bay, where bedding-parallel quartz veining is well developed in black shale, and contains bitumen in the latter case. Fluid inclusion studies were performed on doubly polished wafers using a Linkam THMS-600 heating–freezing stage mounted on a Nikon Labophot transmission light microscope. The instrument equipped with a range of objective lenses including a  $100\times$  lens, was calibrated against synthetic  $\text{H}_2\text{O}$  ( $374.1$  and  $0.0^\circ\text{C}$ ) and  $\text{CO}_2$  ( $-56.6^\circ\text{C}$ ) standards (Synthetic Fluid Inclusion Reference Set, Bubble s Inc., USA). Approximate pressure corrections were made following the approach of Goldstein & Reynolds (1994).

#### Gas analysis

A test of methane generation, which could have been evolved during maturation, was made using quantitative fluid inclusion gas analysis (Blamey 2012). Fluid inclusion volatile analysis was done in

vacuum using the CFS (crush-fast scan) method at University of Western Ontario's Fluid Inclusion Gas laboratory. Samples were first cleaned with NaOH to reduce surface organic contamination, and then were rinsed with deionized water. Approximately 0.1 gram of sample was incrementally crushed under a vacuum of  $\sim 10^{-8}$  Torr yielding two to ten crushes per sample. The analyses were performed by means of two Pfeiffer Prisma quadrupole mass spectrometers operating in fast-scan, peak-hopping mode. The system routinely analyzed for a range of gases including methane and carbon dioxide. The instrument was calibrated using commercial gas mixtures, synthetic inclusions, and in-house fluid inclusion gas standards. Samples were analysed from five localities; at Helen's Bay, Coalpit Bay and Coalheugh Burn where veins record the chemistry of fluids through black shales during their Lower Palaeozoic maturation, and Conlig and Wanlockhead, where veins record post-prism, Upper Palaeozoic mineralization history. Data are recorded on a reference cross-plot of carbon dioxide/methane and nitrogen/argon ratios, used to distinguish fluids originating in different environments (Blamey 2012).

## Results

### Petrography

Migrated bitumen (hydrocarbon residues that clearly post-date deposition) occurs in the SUDLT prism rock as:

- (i) Small (usually <1 cm) lenses along bedding surfaces in the Moffat Shale (Fig. 2). The surfaces may anastomose, following bedding-parallel deformation.
- (ii) Masses larger than above which cross-cut the shales where they are heavily deformed, including near fault structures.
- (iii) Traces along fractures through greywackes, usually mineralized by calcite/quartz (Fig. 2, 3). Many dark veins cut the greywackes, but they consist of phyllosilicates such as illite and/or chlorite (Needham 2004).

Measurement of 59 Moffat Shale samples from 14 localities in Scotland and Ireland yield organic carbon contents (Table 1) mostly in the range 2 to 5 % TOC with a mean value of 2.45 % TOC. Previous data for the Moffat Shales are similarly in the range 2-4 % TOC (Thickpenny & Leggett 1987). Much other published TOC data for shales, especially for the Dob's Linn section, is at the 1-2 % level (Hammarlund et al. 2012, Koehler et al. 2019, Bond & Grasby 2020). Adopting the value of 50% carbon loss for shales with type II kerogen indicates an original mean content of up to 10 %.

Measurements of the hydrogen index for graptolitic carbon give values in the range up to 500 mg/g TOC (Bustin et al. 1989, Luo et al. 2020).

The carbon content range of 2 to 5 % TOC, even before reconstruction of the original content of double this value, and an assumed hydrogen index in the range 300 to 500 mg/g TOC for type II kerogen rich in graptolites place the rocks in the excellent/excellent category of an evaluation diagram for hydrocarbon source rocks (Fig. 4).

The post-prism fluids are over 99 % water, while the syn-prism fluids contain up to 30 % non-aqueous gas (Table 2). The evaluation of methane in syn-prism and post-prism fluids is made by their carbon dioxide/methane ratios, which avoids complexity due to variations in the abundance of fluid inclusions and contributions of other gases. The data from the syn-prism and post-prism samples mostly plot separately, with some minor overlap (Fig. 5). The syn-prism gas data plot particularly in the region of organic-derived fluids, while the post-prism gas data plot in the fields of shallow meteoric and evolved crustal fluids.

The carbon dioxide/methane ratio varies from 0.03 to 1.34 (mean 0.17, n=22) in the syn-prism veinrock at Helen's Bay, Coalpit Bay and Coalheugh Burn and from 0.14 to 26.32 (mean 7.23, n=30) in the post-prism veinrock at Conlig and Wanlockhead. In summary, the syn-prism rocks contain a higher proportion of methane. Few measurements of modern gas seepages are available in the SUDLT, but a single borehole in Ordovician rocks contains a high (150 µg/L) methane level (Bell et al. 2016). In addition, the syn-prism veinrock samples contain hydrogen, which is completely absent from the post-prism veinrock. Examples of fluid composition are given in Table 2.

A collation of localities in Ireland and Scotland where attempts to mine 'coal' were made in the Ordovician-Silurian rocks of the SUDLT prism (Fig. 6) includes some places where fuel was actually produced and used. Most of the productive localities were in Ireland, especially the Kilnaleck coal mine (Moore 1872a,b, McEvoy 1885). The full archive of localities is given in Supplementary Information (Table S1).

Bitumen in the Moffat Shale from several localities has a mean sulphur content which varies from 0.17 to 0.96 % (Table 3).

The mean sulphur content in the Moffat Shale is about 1.4 % (Table 1), reflecting an abundance of pyrite. Pyrite is mostly finely disseminated, but it also forms megascopic seams (Armstrong & Coe 1997), and there is additionally pyrite in cross-cutting fractures. Pyrite yielded sulphur isotope compositions from 21 samples (Table 4; Fig. 7). The compositions are bimodal, comprising a light range (-17 to -45 ‰) and a heavier range (+3 to -10 ‰). Most samples of pyrite in a detailed profile

through the Moffat Shale section at Dob's Linn are also lighter than -20 ‰ (Hammarlund et al. 2012).

Bedding-parallel quartz in the Moffat Shale at Coalpit Bay yields a range of primary fluid inclusion homogenization temperatures from 132 to 155 °C (n=10) and a salinity of 11-12 wt.% equiv. NaCl (n=4). Accounting for a pressure correction at several kilometres depth, the temperature was probably at least 200 °C. Bedding-parallel quartz from Elvanfoot yields two populations of primary fluid inclusions. These yield homogenization temperatures of 150-170 °C (n=27) and 220-240 °C (n=21).

## Discussion

### Structural context

The pattern of late diagenesis/low-grade metamorphism was acquired during the development of the accretionary architecture, when the strata were already steeply dipping, i.e., stacking of thrust slices commenced at lower than final temperatures (Merriman & Roberts 2000). Structural evolution particularly involved movement on the Moffat Shale horizons, repeated by the stacking process. The shale-turbidite boundaries exhibit progressive deformation from soft-sediment movement to anastomosing shear zones containing multiple generations of calcite and quartz veins, with subsidiary phyllosilicates and sulphides (Needham 2004). Fractures in the turbidites similarly show progression from partly lithified faults to mineralized brittle fractures. The veining focussed in the shale horizons likely reflects dilatant fracturing following a build-up of high fluid pressure due to low permeability (Needham 2004). The turbidites are composed of greywackes, which have low permeability due to an abundance of matrix clay (MacDonald et al. 2007). The extensive quartz and carbonate veining is typical of accretionary prisms, in which precipitation implies large volumes of fluid flow through limited fracture space (Fisher & Byrne, 1990, Moore & Vrolijk 1992).

### Hydrocarbon generation

The TOC contents measured in the Moffat Shale are much higher than those reported in a worldwide review of subduction zone sediments (Japan, Alaska, Costa Rica, Barbados, Mariana), which are almost all less than 1 wt. % TOC (Raimbourg et al. 2017). Hydrocarbon generation in an environment of high TOC, and temperature increase faster than normal burial, would be abnormal. A hydrocarbon source rock with exceptional generating capacity (excellent carbon content and hydrogen index) can produce huge volumes of oil once it enters the oil window. This may be

achieved by structural repetition in thrust belts including accretionary prisms (Edman & Surdam 1984, Gusterhuber et al. 2013, Lyu et al. 2020). If the oil window is entered rapidly because of rapid tectonic loading, the result may be a catastrophic addition of fluid that has little space to enter. The sequence of shales and turbiditic greywackes with very low porosity provided negligible opportunities for the migration of hydrocarbons, which would then be under high fluid pressure. The result was the retention of hydrocarbons in rock matrix and pooling of hydrocarbons along bedding surfaces within the source rock, so-called in-source reservoirs with in-source bitumen (Masterlerz et al. 2018, Yao et al. 2021). The early-formed bitumen could be a significant component of the total hydrocarbons.

As liquid hydrocarbons, and the first-formed bitumen, are progressively buried, including within in-source reservoirs, they are heated to the point where they undergo cracking to yield methane-rich gases and a solid residue (Xiong et al. 2016, Zhao et al. 2017, Raimbourg et al. 2017). Typically, the cracking commences at about 135 to 150 °C (Zhao et al. 2017, Sanei 2020), or even lower if the hydrocarbons are sulphur-bearing (Kelemen et al. 2010, Mastalerz et al. 2018), which was reached and exceeded in the SUDLT. The entrained gas in syn-prism veinrock is methane-rich, while the gas in post-prism veinrock is carbon dioxide-rich. The carbon dioxide/methane ratio is over an order of magnitude lower in the syn-prism veinrock. This distinction supports a model of cracking of hydrocarbons to produce the solid bitumen, and the cessation of organic maturation by the time of Upper Palaeozoic mineralization.

Cracking of the organic matter to liberate methane would further increase the fluid pressure (Raimbourg et al. 2017), while leaving a solid bitumen residue. The generation of hydrocarbons would make detachment on the bedding surface much easier (Cobbald et al. 2004, Zanella et al. 2014, Pereira et al. 2018). This would add to the phyllosilicate growth (Merriman et al. 1995) and water-rich bentonites in the Moffat Shale (McCurry & Anderson 1989) which both accommodated bedding-parallel movement.

The occurrence of hydrogen with methane in the syn-prism veinrock is probably also a product of thermal maturation. The two gases are released together during pyrolysis of carbonaceous shales, which simulates thermal maturation (Li et al. 2015). Thermally mature organic matter can be made to release hydrogen in an industrial process using catalysts and it is speculated that this would occur naturally on a geological timescale (Huang et al. 2021). The most thermally altered coals also yield hydrogen (Zgonnik 2020). Suzuki et al. (2017) showed that carbonaceous shales in the temperature range up to 200 °C would yield methane, then progressively start generating hydrogen instead.



The composition of typical fluids from recent and ancient accretionary prisms is evident from cold seeps. The fluids in cold seeps and hydrothermal vents on the sea floor are dominated by methane and hydrogen sulphide, but also include molecular hydrogen (Newell et al. 2007, Dong et al. 2020). The fluids trapped within the SUDLT are thus consistent with the fluids that emerge as seeps.

The high nitrogen/argon ratios in the syn-prism fluids reflect liberation of nitrogen from organic matter during thermal maturation (Gai et al. 2020). Lower Palaeozoic black shales, including Ordovician shales at Dob's Linn in the SUDLT, are nitrogen-bearing (Kiipli & Kiipli 2013, Gai et al. 2020), and as nitrogen content increases with the content of organic matter (Kiipli & Kiipli 2013), highly carbonaceous shales can yield more nitrogen.

The temperature range inferred from fluid inclusions in bedding-parallel veins at Coalpit Bay and Elvanfoot (cooler population) is comparable to the temperatures of 150-320 °C inferred from chlorite compositions (Merriman et al. 1995) and 170-300 °C from Raman spectroscopy of organic carbon (Schito et al. 2022) in the SUDLT prism (Fig. 8). This is also the temperature range of maximum release of hydrous fluids in accretionary prisms (Massonne & Willner 2008, Willner et al. 2009), and the cracking of organic matter within prisms (Raimbourg et al. 2017). Bedding plane slip and decollement are typically initiated at temperatures of 100-200 °C (Raimbourg et al. 2017), which is consistent with thrust stacking at lower than final temperature in the SUDLT.

Elsewhere in the SUDLT in two base metal-bearing deposits in County Down, two populations of fluid inclusions have been identified in quartz veins (Baron & Parnell 2005). A population with temperatures 220 to 360 °C is followed by a set with temperatures 70 to 240 °C, attributed to heating by Caledonian intrusions and Carboniferous-younger base metal mineralization, respectively. Both populations are probably younger than the inclusions in black shales, although the higher set of temperatures at Elvanfoot may represent the Caledonian heating. Caledonian plutons in the Southern Uplands are Devonian age, so post-dated the deformation during accretion, and may have been emplaced using the existing shear fabric of the prism (Brown et al. 2008).

The cracking process leaves a high proportion, up to 50%, of the original oil as a solid (Xiong et al. 2016, Zhao et al. 2017). Thus, in the SUDLT where very rich source rocks yielded substantial amounts of oil that could not migrate, large deposits of solid bitumen could be formed. This history of hydrocarbon generation explains the formation of the bitumen mined as 'coal' in several parts of the SUDLT (Fig. 6).

In addition to cracking of kerogen to produce bitumen, it is possible that bitumen was cracked to produce more thermally altered bitumen (pyrobitumen) and gas. This is a process which contributes to the formation of gas, including shale gas, at temperatures above 150 °C (Uguna et al. 2016,

Meredith et al. 2019). Large amounts of pyrobitumen occur in some gas reservoirs (e.g., Wang et al. 2021, Li et al. 2022). Where bitumen is cut by calcite or quartz in the SUDLT (Fig. 2), we have not observed a second phase of bitumen formation in the veins. However, additional maturation may not have produced a new solid, but just altered the existing solid and generated gas.

The temperatures indicated by Raman Spectroscopy, from 200 to 300 °C (Schito et al. 2022), indicate the maximum temperature reached, which were probably higher than the temperature of bitumen formation in many cases. However, bitumen at Clontibret, Ireland (Schito et al. 2022), which is associated with antimony mineralization (Fig. 9) at about 300 °C (Steed & Morris 1986) implies that at least some bitumen was deposited at a temperature high enough to suggest that cracking of a previous solid was possible.

### Sulphur isotopes

Further insight stems from the sulphur isotope composition of pyrite in the black shale. The pyrite can be divided into precipitates from two stages:

- (i) Finely disseminated pyrite, which forms framboids visible using electron microscopy (Fig. 10); together with pyrite which replaces graptolite fossils. These occurrences are attributed to (early) diagenesis, before any deformation.
- (ii) Pyrite crystals up to 2 mm size, which occur along brittle fractures, either parallel to bedding planes or oblique to them. The fractures also carry bitumen and quartz. The fractures are post-compaction, and they must be related to deformation.

The two stages of pyrite are matched by the bimodal distribution of sulphur isotope compositions. The diagenetic pyrite has a light isotope composition (mean -24.2 ‰), while the vein-filling pyrite has a heavier composition (mean -1.1 ‰). The light values are typical of pyrite precipitated by microbial sulphate reduction (MSR) at low temperatures (Machel 2001). The heavier composition is sufficiently different that it is very unlikely to be simply derived from the light pyrite, which implies that a new supply of sulphur was introduced. Three explanations that may have contributed to this heavier composition are closed system modification of existing sulphur (e.g., Bonnetti et al. 2020), introduction of magmatic sulphur from igneous rocks, and thermochemical sulphate reduction (TSR). Limited evidence from pyrite in Ordovician basalts in the region (excepting vesicular pyrite derived by microbial sulphate reduction of sea water) indicates it has a zero to positive signature (Parnell et al. 2015), so this composition would have been available for possible release at elevated temperature. Thermochemical sulphate reduction is commonly associated with bituminous residues, especially bitumen enriched in sulphur (Machel 2001, Keleman et al. 2010, Walters et al. 2015). The measured sulphur content in the prism bitumen could be an indicator of TSR, but the contents are

not high. The bitumen and quartz within the same fractures imply a temperature range  $>100\text{ }^{\circ}\text{C}$ , when TSR and associated cracking of oil to solid bitumen could occur (Kelemen et al. 2010, Mastalerz et al. 2018). However, TSR would not yield such light isotopic compositions from seawater with a composition of almost 30 ‰ (Machel 2001, Hu et al. 2021). Closed system behaviour would be consistent with the overpressure typical of an accretionary prism. The heavier  $\delta^{34}\text{S}$  signature of the second stage pyrite would reflect more complete sulphate reduction associated with a strong enrichment of residual  $^{34}\text{S}$ , during the transition from an open to a closed system. Data from a modern accretionary setting indicate that this is a feasible explanation. Bottrell et al. (2000) reported pyrite compositions from the Cascadia Margin accretionary wedge which transition from shallow light values due to MSR to deeper much heavier values when oxidation of the shallow pyrite had liberated new sulphate for further reduction.

The SUDLT is cross-cut by base metal sulphide mineralization, formerly mined, including at Leadhills-Wanlockhead, Scotland and Conlig, Ireland (Rice et al. 2018), and at the western end is overlain by the giant zinc deposit in Carboniferous rocks at Navan. These ore deposits were formed in the Upper Palaeozoic, after prism evolution was complete, but it is likely that some of the sulphur in the deposits was derived from the sulphur-rich prism rocks which they cross-cut (Rice et al. 2018). The SUDLT contains stratabound metal anomalies located in carbonaceous shales, including a copper-rich black shale belt near Moffat (British Geological Survey 1993). The black shales have also been implicated as a host to gold mineralization during Caledonian deformation, and the carbon suggested as a ligand to promote gold transport (Naden & Caulfield 1989, Rice et al. 2018). Thus, both Caledonian and post-Caledonian mineralization may be a legacy of the organic-rich oceanic sediments which sequestered abundant diagenetic pyrite.

#### The Lower Palaeozoic

The high hydrocarbon yield and association with sulphides ultimately reflects the nature of Ordovician oceanic sedimentation, which was characterized by anoxia, especially during the late Ordovician-early Silurian (Berry 2010, Landing 2011, Bartlett et al. 2018, Edwards et al. 2018, Stockey et al. 2020). The anoxic environment allowed both high burial of organic matter, and associated sulphide precipitation during early diagenesis. The sulphidic nature of the anoxia, which is implicated in the Late Ordovician mass extinction, is documented specifically in the SUDLT (Hammarlund et al. 2012, Dahl et al. 2021).

The abundance of sulphides precipitated due to the high organic carbon content in the seafloor sediments potentially also sequestered a large quantity of trace elements including base metals

(Gregory et al. 2015). Other metals like vanadium and uranium may be concentrated directly by the reductive properties of the organic matter (Parnell 2022). Consequently, the carbonaceous nature of the Lower Palaeozoic sediments resulted in metal concentrations at the mineable scale elsewhere (e.g., Goodfellow 1987, Bian et al. 2021, Parnell 2022). In the SUDLT, syn-prism mineralization was limited to the copper-rich black shales noted above. Cross-cutting gold-antimony mineralization was more likely related to late Caledonian (Devonian) shear zones, which may nevertheless be focussed within the black shales (Rice et al. 2018).

Several other reports of cracking to yield methane and solid residues are based on Lower Palaeozoic successions elsewhere (e.g., Huc et al. 2000, Zhao et al. 2017, Schwangler et al. 2020). This may partly reflect the lower likelihood of younger successions reaching the burial depths and hence temperatures required for cracking to occur. However, the high incidence of cracking in the Lower Palaeozoic can be related to the abundance of successions with rich hydrocarbon source rocks due to the anoxia noted above.

The Ordovician-Silurian of northwest Europe has been considered a potential resource of shale gas (Schovsbo et al. 2012, 2014), especially in the region from Denmark to the Baltic countries. The rocks in Scotland do not contribute to this resource, because of relatively high thermal maturity, and the lack of evidence for any surviving gas volumes.

## Conclusions

The Southern Uplands-Down-Longford Terrane accretionary prism is exceptional in including deposits of solid bitumen, which historically have been mined. The bitumen was formed by a singular combination of factors:

- (i) The Ordovician oceans were anoxic and buried sediment with carbon contents much higher than in modern subduction zones.
- (ii) Rapid maturation due to structural repetition caused generation of large volumes of hydrocarbons.
- (iii) The low permeability of shale and intervening turbidite greywackes resulted in high fluid pressure and dilatant fracturing.
- (iv) Cracking of the hydrocarbons left solid bitumen within the source rock shales. Additionally, early solid bitumen retained within the rock could have cracked to yield gas and thermally more mature bitumen (pyrobitumen).

- (v) Further thermal maturation led to fluids that were anomalously rich in methane, nitrogen and hydrogen.

In addition, the carbonaceous sediment contains abundant pyrite sulphur precipitated by MSR, which contributed sulphur to the hydrocarbons and fracture-hosted sulphides.

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Figures

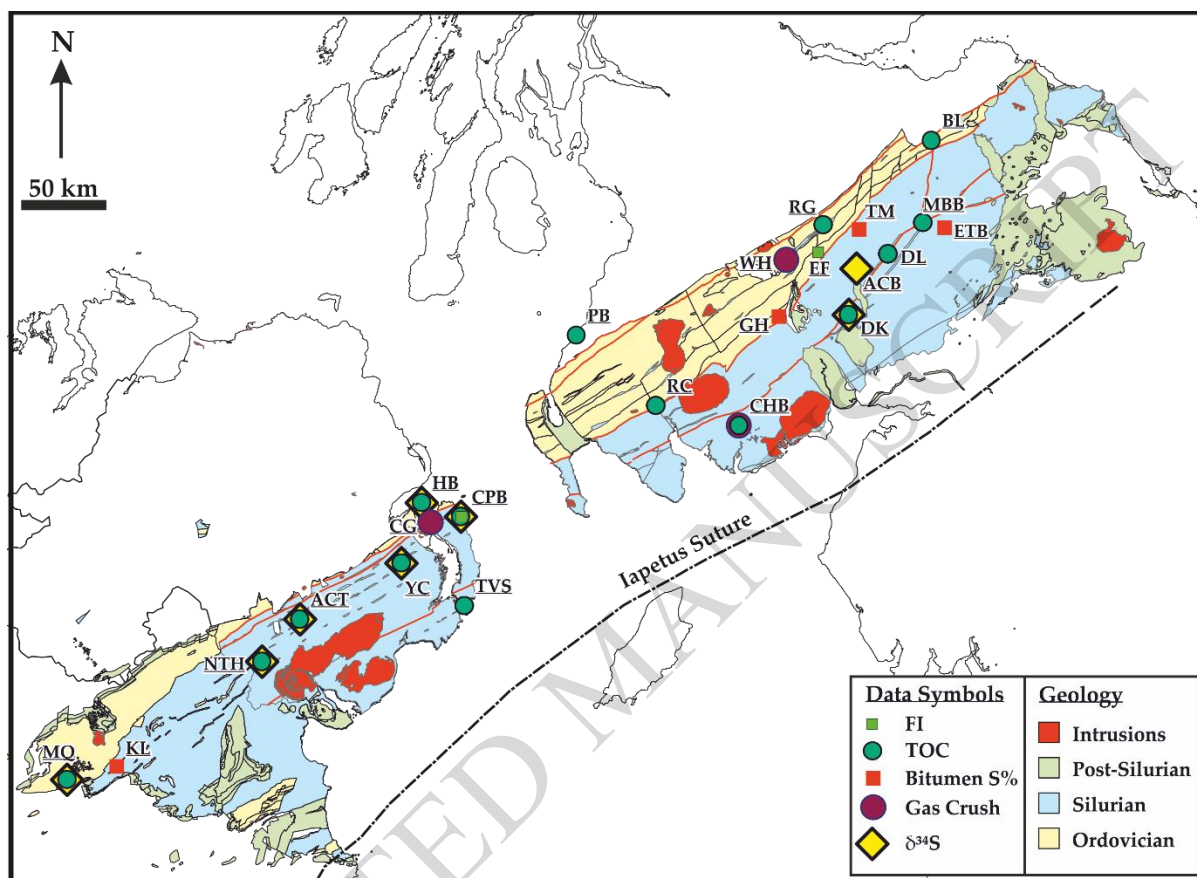


Fig. 1. Map of Southern Uplands-Down-Longford Terrane, showing sample localities for petrographic study and geochemical analysis.

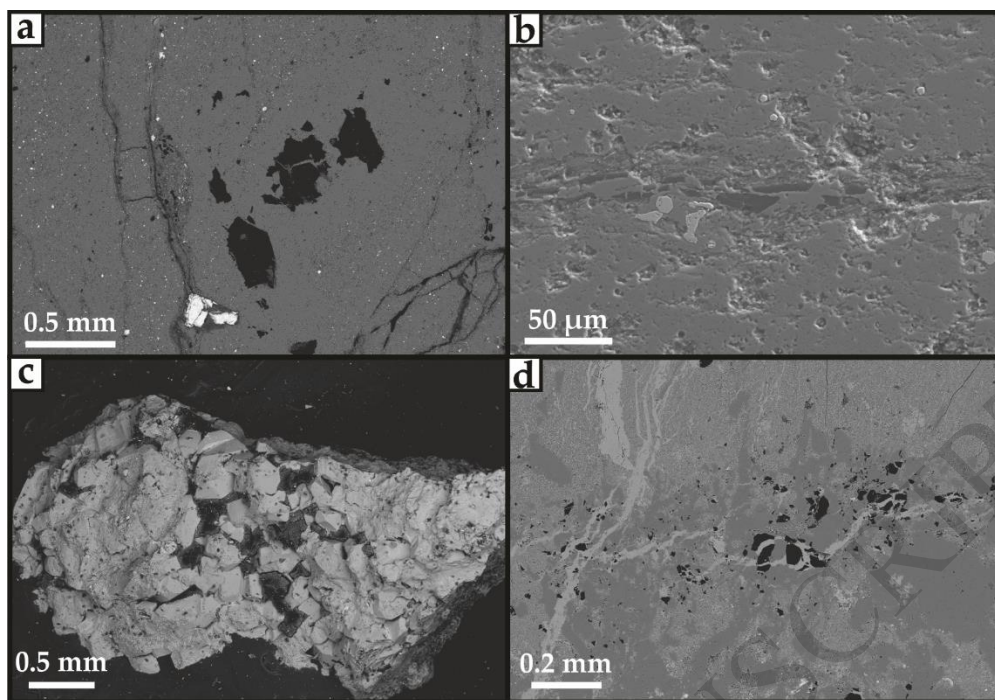


Fig. 2. Electron micrographs of migrated bitumen. A, Bitumen (black) in quartz vein, Molly Quarry; B, Bitumen (dark) in quartz vein (horizontal in image), Newtonhamilton; C, Bitumen (black) in quartz vein, Glengar Hill; D, Bitumen (black) in calcite veinlets cutting through shale, Tweedsmuir.

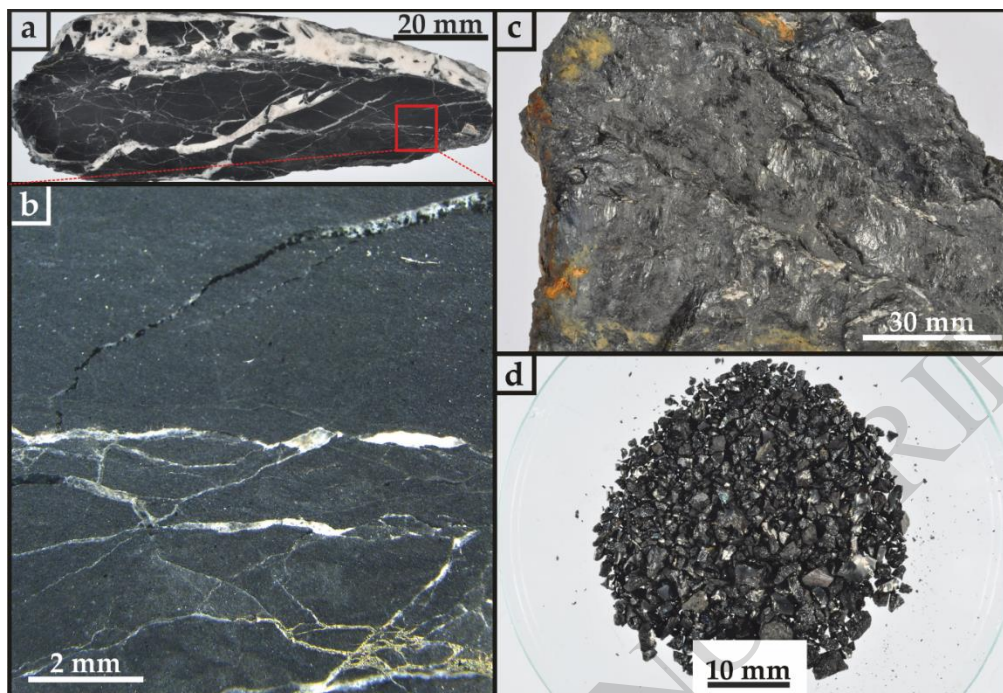


Fig. 3. Specimens from Moffat Shale localities. A, Extensive bedding-parallel veining, Coalpit Bay; B, Close-up of A, showing bitumen (black) and pyrite (golden) within calcite veins; C, Coal-like rock with polished movement surfaces, Lindean; D, Bitumen fragments, Kill Mine, Kilnaleck.



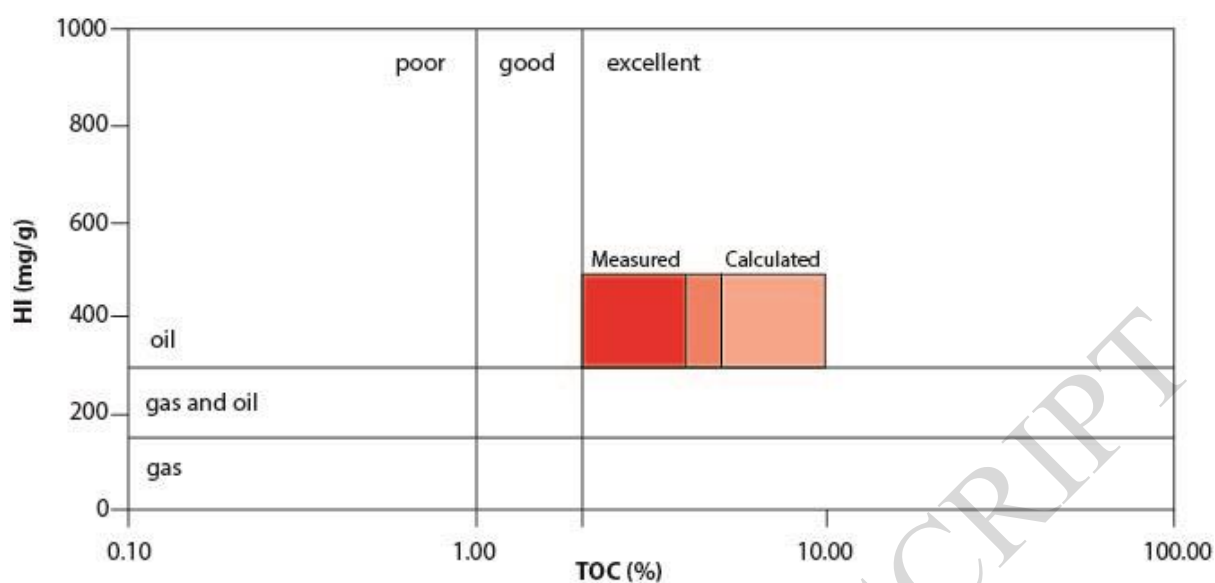


Fig. 4. Cross-plot of ranges of total organic carbon (TOC) content versus inferred Hydrogen Index (HI), indicating that the carbonaceous shales have an excellent capacity to generate oil (template after Çiftçi et al. 2010). Original TOC content assumes 50 % loss from kerogen type II during maturation. Data sources in text.

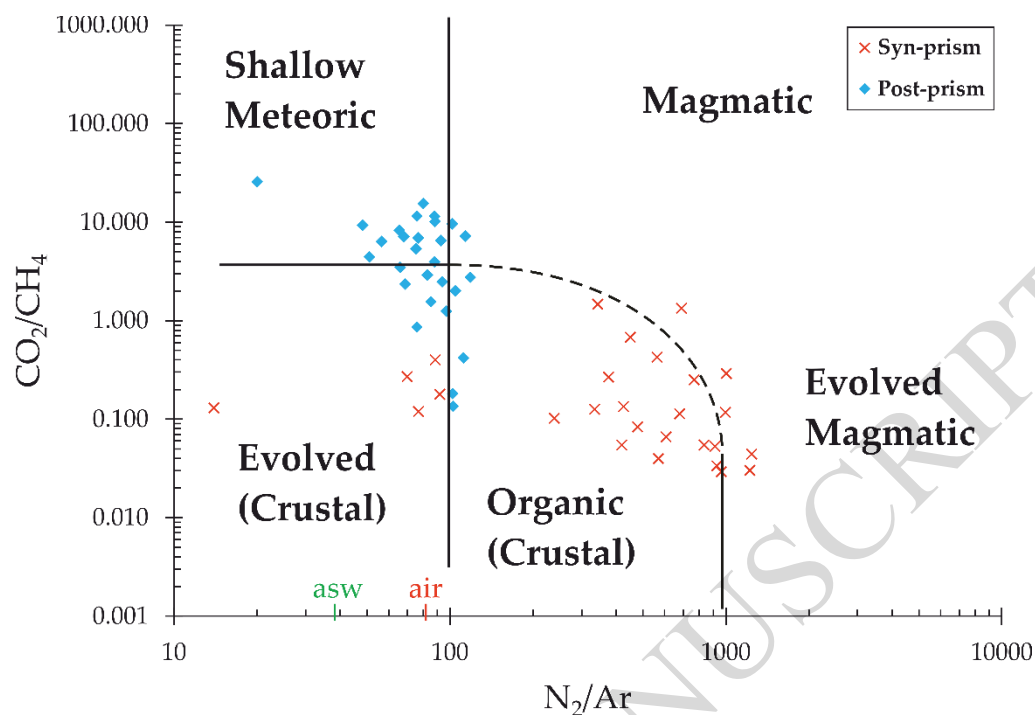


Fig. 5. Cross-plot of carbon dioxide/methane and nitrogen/argon ratios from crush-gas analyses of quartz veins through SUDLT prism rocks and cross-cutting post-prism mineralization (reference template modified from Blamey 2012). Carbon dioxide/methane ratios are much lower, and nitrogen/argon ratios much higher, in syn-prism mineralization.



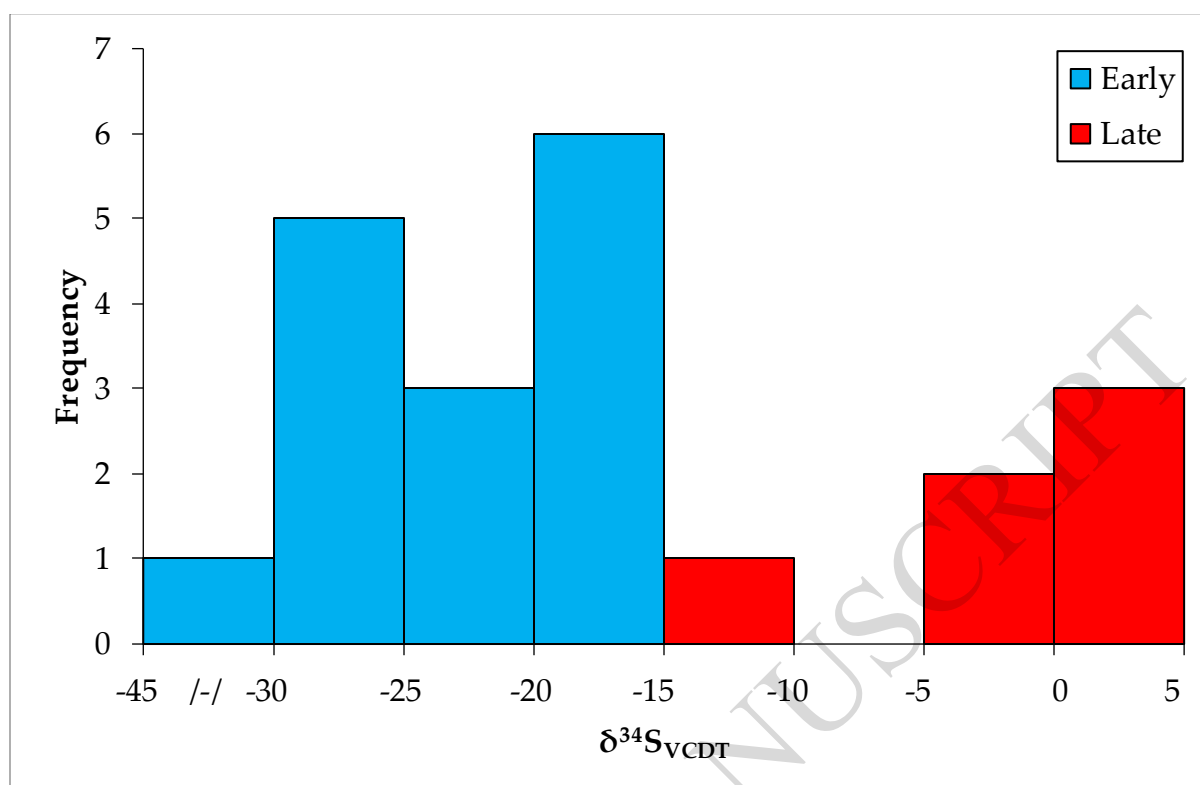


Fig. 7. Sulphur isotope data (‰ CDT) for pyrite in Moffat Shale, Scotland, Northern Ireland and Republic of Ireland. Values for early pyrite are lighter than -15 ‰, which reflects microbial sulphate reduction during diagenesis. A smaller population of near-zero values were obtained from late, vein-hosted pyrite.



Fig. 8. Temperatures inferred from measurements of SUDLT rocks (fluid inclusion homogenization temperatures, chlorite compositions, Raman spectroscopy of carbon), and processes in accretionary prism shales (decollement, cracking of kerogen, hydrogen generation). Data sources in text.

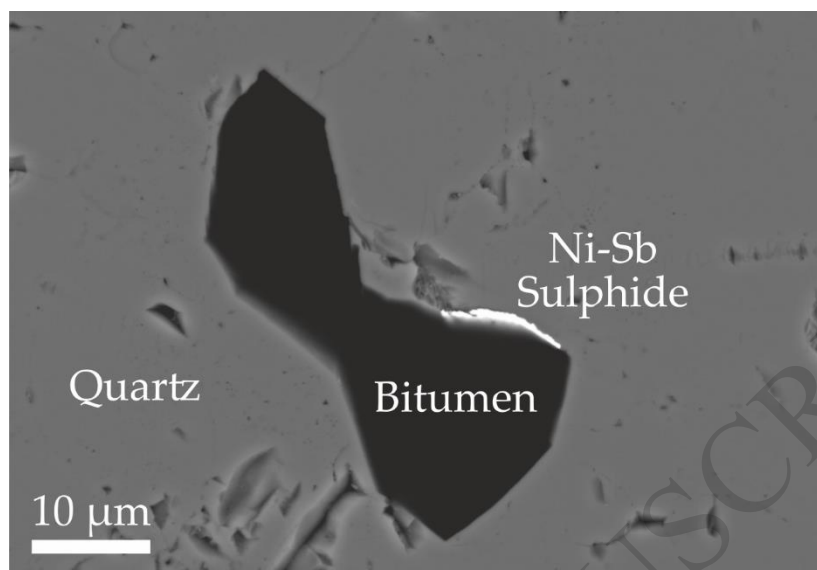


Fig. 9. Bitumen in quartz vein, Clontibret, SUDLT (close to BL on Fig. 6), with associated antimony (Sb) mineralization (bright) formed at about 300 °C.

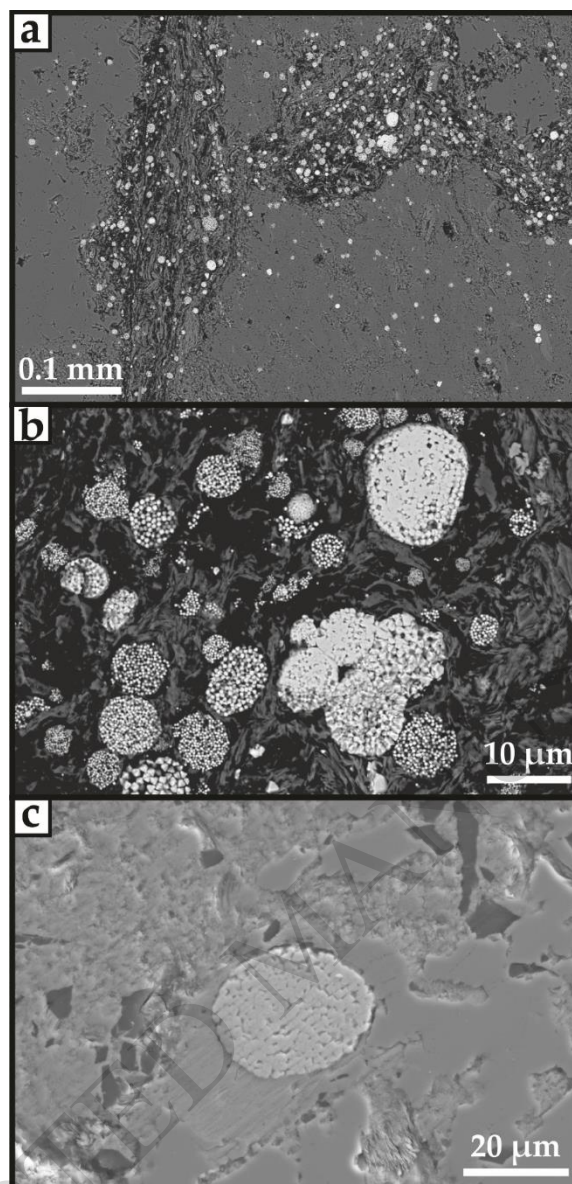


Fig. 10. Electron micrographs of pyrite framboids, Southern Uplands. A, Framboids in bitumen-rich shale, Coalheugh Burn; B, Close-up of A, showing framboids in matrix of bitumen (black), Coalheugh Burn; C, Framboid and bitumen (black), calcite veining, Tweedsmuir.

Table 1. Total Organic Carbon (TOC) and Total Sulphur (TS) contents (%) for black shale samples, Southern Uplands-Down-Longford Terrane.

Locality	Map code	Grid Reference	No. anal. (n)	Mean TOC (%)	Mean TS (%)
<i>Scotland</i>					
Coalheugh Burn	CHB	NX 680593	5	3.12	0.78
Broad Law	BL	NT 347532	1	1.39	0.22
Dob's Linn	DL	NT 196158	10	2.09	2.21
Duffkinnel	DK	NY 060957	3	1.46	0.03
Mount Benger Burn	MBB	NT 314259	3	3.74	2.41
Pinbain Burn	PB	NX 142916	1	2.81	0.91
Rein Gill	RG	NS 981259	2	2.38	1.21
River Cree	RC	NX 401669	3	0.90	0.16
<i>Ireland</i>					
Coalpit Bay	CPB	J 595788	6	1.26	1.75
Helen's Bay	HB	J 459831	1	1.43	4.60
Yates Corner	YC	J 396623	7	2.87	0.71
Acton	ACT	J 053421	5	1.50	0.83
Newtownhamilton	NTH	H 926273	11	3.87	1.47
Molly Quarry	MQ	N 255855	1	1.63	2.52
<b>Weighted mean</b>			59	2.45	1.36



Table 2. Representative cold-crush gas analyses for samples of syn-prism veinrock, and post-prism veinrock.

Locality	Coalpit Bay (syn-prism)	Coalheugh Burn (syn-prism)	Conlig (post-prism)	Wanlockhead (post-prism)
Water (wt.%)	89.68	73.90	99.49	99.70
CH <sub>4</sub>	9.38	24.25	0.01	0.04
CO <sub>2</sub>	0.78	1.33	0.16	0.20
H <sub>2</sub>	0.04	0.05	0.00	0.00
He	0.0002	0.0003	0.0002	0.0003
N <sub>2</sub>	0.12	0.47	0.34	0.04
Ar	0.0003	0.0006	0.0042	0.0008
H <sub>2</sub> S	0.0000	0.0003	-	0.01
CO <sub>2</sub> /CH <sub>4</sub>	0.08	0.06	15.56	4.47
N <sub>2</sub> /Ar	479	834	80	51
Mols gas (non-aqueous)	1.59E-10	1.58E-09	1.02E-10	1.03E-10

Table 3. Sulphur contents of migrated bitumen, Southern Uplands-Down-Longford Terrane

Locality	Grid Reference	Host rock	No. measurements	Mean sulphur content (%)
Molly Quarry, Co. Longford	N 255855	Quartz in black shale	22	0.72
Newtownhamilton, Co. Armagh	H 925274	Quartz in black shale	7	0.96
Kilnaleck, Co. Cavan	N 430905	'Coal' vein in black shale	10	0.50
Helen's Bay, Co. Down	J 459831	Vein in greywacke	18	0.36
Coalheugh Burn, Dumfries & Galloway	NX 679593	Quartz in black shale	20	0.68
Glengar Hill, Dumfries & Galloway	NX 825957	Vein in greywacke	8	0.17
Ettrickbridge, Scottish Borders	NT 386242	Vein in greywacke	10	0.44
Tweedsmuir, Scottish Borders	NT 101241	Vein in greywacke	11	0.54

Table 4. Sulphur isotope compositions for pyrite in Southern Uplands-Down-Longford Terrane.

Sample ID	Locality	Grid Reference	$\delta^{34}\text{S}_{\text{VCDT}}$ (‰)	Notes
ACT1	Acton	J 053421	-23.6	Replaced graptolite
ACT2	Acton	J 053421	-22.7	Replaced graptolite
ACT3	Acton	J 053421	-23.7	Replaced graptolite
CAT28-dS1	Auchencat Burn	NT 090110	-19.8	Cu-Bearing
CAT28-dS2	Auchencat Burn	NT 090110	-19.2	Cu-Bearing
CPB1	Coalpit Bay	J 595788	-25.8	
CPB2	Coalpit Bay	J 595788	-25.8	
CAT18-dS3	Coalpit Bay	J 595788	-44.5	
CAT23-dS1	Duff Kinnel	NY 060957	-29.7	
MQ1	Molly Quarry	N 255855	-19.8	
MQ2	Molly Quarry	N 255855	-18.0	
MQ3	Molly Quarry	N 255855	-18.7	
ST315-dS4	Molly Quarry	N 255855	-16.8	
YC1	Yates Corner	J 396623	-27.2	
YC2	Yates Corner	J 396623	-28.3	
JGA 355	Newtonhamilton	H 926273	-2.0	Bedding Parallel; Euhedral
ST355-dS2	Newtonhamilton	H 926273	-1.0	Bedding Parallel; Euhedral
ST355-dS4	Newtonhamilton	H 926273	-10.3	Oblique Vein
HB1	Helen's Bay	J 459831	2.2	Euhedral
HB2	Helen's Bay	J 459831	2.4	Euhedral
HB3	Helen's Bay	J 459831	2.2	Euhedral