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Carbonaceous residues in the Southern Uplands accretionary prism of Ireland and Scotland

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Abstract

Carbonaceous residues occur in mudstones and turbidites of the Lower Palaeozoic accretionary prism in Ireland and Scotland (Longford-Down, Southern Uplands). The accretionary prism was host to fluid migration during both the Lower Palaeozoic and Carboniferous-Triassic, so the age of the carbonaceous fluids is uncertain. Raman spectroscopy data for the carbonaceous residues in the Lower Palaeozoic rocks indicate palaeotemperatures similar to those measured in their host rocks, and much higher than those in the Carboniferous cover rocks or in residues in the cover rocks. These data show that residues in the prism rocks are of Lower Palaeozoic age, and were not contributed by younger mineralizing fluids. The residues represent hydrocarbons generated from source rocks in the prism that were part of the Ordovician-Silurian deposits of the Iapetus Ocean.

Introduction

Fluid flow in accretionary prisms may be long-lived and complex. From their initial construction, when thrust stacking can cause fluid overpressure, to hydrothermal mineralization related to plate margin magmatism, a wide range of fluid types under a wide range of conditions can be expected (e.g. Carson & Screaton, 1998; Bierlein et al., 2009; Chen et al., 2020; Watson et al., 2020). The sediments scraped off the subducting sea floor ('accreted') are commonly rich in organic matter, so that the prism can become hydrocarbon-prospective if other factors (e.g., thermal history, seals, traps, reservoir properties, migration pathways) are suitable such as in the Mesozoic Franciscan Complex (Larue, 1991) or the Cenozoic Sacramento, Talara, Barbados and Nankai accretionary prisms (Parnell et al., 1994; Hessler & Sharman, 2018; Shiraishi et al., 2019). Here hydrocarbon fluids are expressed as seeps at the Earth surface and as carbonaceous veins in exhumed prism rocks (Larue, 1991; Stevenson, 1993; Parnell et al., 1994; Hessler & Sharman, 2018; Shiraishi et al., 2019).

The Lower Palaeozoic (Ordovician-Silurian) rocks of the Southern Uplands accretionary prism of Scotland and Ireland (Fig. 1) contain numerous black shale horizons, among which the Moffat Shale Group at the base of the succession acted as the major detachment horizon during prism formation (Needham, 2004). The black shales have organic carbon contents up to percentage level (higher than 1%) (Thickpenny & Leggett, 1987; Needham, 2004), which gave them a hydrocarbon source rock potential when they were at a lower thermal maturity than their current low-grade metamorphic facies (Kemp et al., 1985;
Pearce et al., 1991; Pearce & Clayton, 1995; Merriman & Roberts, 2000). The prism rocks are cut by minor veinlets of carbonaceous/graphitic matter (Fig. 2; bitumen *sensu lato*), which may reflect such hydrocarbon generation. However, the prism rocks are also cut by numerous mineralized veins, some of which contain base metal deposits and are dated as Carboniferous-Triassic (Samson & Banks, 1988; Baron & Parnell, 2005; Stone et al., 2012), i.e. formed after the prism was exhumed during Silurian-Devonian times (Mendum, 2012). Carboniferous rocks deposited on the exhumed prism also have source rock potential (Parnell, 1995), and represent an alternative source of hydrocarbons into the veins. Elsewhere in Britain, hydrocarbons entered fracture systems in basement rocks by downward migration from the Carboniferous (Parnell et al., 2017; Baba et al., 2019), so a source in the Carboniferous for prism-hosted bitumen is quite feasible. There is, therefore, ambiguity about the origin of fracture-bound bitumen in Silurian rocks at the southern margin of the prism, where it was recorded by the celebrated engineer Thomas Stevenson in the course of erecting a lighthouse (Stevenson, 1843). This study assesses the origin and history of the carbonaceous matter, using Raman spectroscopy.

The objectives of the work are:

(i) Assessment of the homogeneity of data along the accretionary prism. Are the data uniform, or have they been modified by, for example, the Variscan Orogeny in Ireland, or younger hydrothermal mineralization?

(ii) Comparison of the data with values from the host rocks, i.e., Ordovician-Silurian organic matter.

(iii) Test if there is a clear distinction between the data and values in the unconformably overlying Carboniferous rocks, so that an origin from younger deposits can be excluded.

**Geological Setting**

The British and Irish Caledonides include an imbricate thrust belt of Ordovician-Silurian strata deposited along the Laurentian margin of the Iapetus Ocean, referred to as the Southern Uplands—Down—Longford terrane (Fig. 1). The terrane is bounded to the northwest by the Southern Upland Fault and occupies the hanging wall of the Iapetus Suture located in its southern margin (Fig. 1). The belt is largely composed of turbidites (as wacke-type sandstones and siltstones) with interbedded mudstones. Detachment occurred, within the mudstones, to define at least 20 fault-bounded tracts trending NE–SW parallel to strike (Floyd, 2001). A major basal detachment, where the sedimentary successions were stripped from the basement, is recognized in the Landeilo to Llandovery Moffat Shales (Leggett et al., 1979). Three main thrust sheets, the Northern, Central and Southern Belts, young toward the SE whereas internally they show an opposite younging trend. This structural pattern is
characteristic of accretionary prisms (Leggett et al., 1979; Stone 2014). After deformation, the terrane was intruded by granites of Silurian-Devonian age. The emplacement of such intrusions was commonly associated with sinistral transpression such as in the Moniaive Shear Zone area (Phillips et al., 1995).

Both the northwestern terrane boundary, the Southern Upland Fault, and the southeastern boundary, the Iapetus Suture, are overstepped by Carboniferous and younger strata. In addition, extensional basins, oriented NNW-SSE, are down-faulted into the Ordovician-Silurian accretionary prism rocks near-normal to the structural strike of the prism (Anderson et al., 1995). These have fills of Lower Carboniferous marine sediments, Upper Carboniferous coal-bearing sediments and Permian continental sediments.

Methods

Materials

The project is based on Raman spectroscopy of carbonaceous veins (Fig. 2), and prospective carbon-bearing source rocks of Lower Palaeozoic (prism rocks) and Carboniferous (cover rocks) ages.

Sampling was from 9 carbonaceous veins in the Lower Palaeozoic rocks, in Scotland (Ettrickbridge, Glangar Hill, Palnire, Coulter Quarry and Tweedsmuir), Northern Ireland (Coalpit Bay, Helen’s Bay) and the Republic of Ireland (Clontibret, Kilnaleck Co.Cavan). The veins crosscut the bedding of the host rocks, except at Kilnaleck Co. Cavan, where carbon is concentrated parallel to the rock fabric, and was formerly exploited as a ‘coal’ bed. For comparison, carbonaceous vein matter was sampled from Carboniferous cover rocks in southern Scotland at Glencartholm, (locality described by Cater et al., 1989), Kershope Burn (Lumsden et al., 1967) and Portling Bay (Miller & Taylor, 1966).

The source of the veins was assessed by comparison with carbonaceous shales of Lower Palaeozoic and Carboniferous ages. The Lower Palaeozoic shales are an integral part of the accretionary prism and were sampled in Scotland in Dob’s Lin, Whitshiels, Duff Kinnel, Knockville and Och Tree and in Northern Ireland in Yates Corner, Acton and Newton Hamilton localities (Tab. 1 and Fig. 1). The Carboniferous rocks are from the overstepping margins of the prism (at Cultra, Portling Bay, and Barnsness) and from down-faulted basins (aqt Altmush and Kello Water). Carboniferous rocks from the extreme western end of the region were avoided, as they were heated, during Hercynian deformation, to temperatures much higher than in the rest of the region (Clayton et al., 1989).

Raman spectroscopy on carbonaceous material (RSCM)
Raman spectroscopy is a widely used technique that provides information on the molecular structure of both organic and inorganic compounds, based on the inelastic scattering properties of visible light. The position of Raman bands on a spectrum reflects the wave numbers of the vibrational frequencies of molecular bonds and their assemblage can thus be used as a fingerprint for different materials. The Raman spectrum (Fig. 3) of carbonaceous material consists of two main bands at ~1585 cm\(^{-1}\) (the graphite peak, G) and ~1350 cm\(^{-1}\) (the disorder peak, D; Tuinstra & Koening, 1970) with minor bands where numbers vary with thermal maturity (see Henry et al., 2019 for a complete review). Their mutual relationships change with thermal maturity (Tuinstra & Koening, 1970) up to the graphite stage (Beyssac et al., 2002), allowing determination of the degree of order of the organic matter and thus palaeotemperatures experienced by the rocks during prograde metamorphism (Beyssac et al., 2002; Lahfid et al., 2010; Lünsdorf et al., 2017) or in diagenesis (Schito et al., 2017; Henry et al., 2019).

Measurements were taken on fresh cut surfaces. Prism and cover rocks samples were cut perpendicular to the main foliation while bitumen samples were cut perpendicular to veins. A Renishaw inVia reflex Raman spectrometer was used for micro-Raman analyses, with a backscattering geometry in the range of 700 – 3200 cm\(^{-1}\) (first and second order Raman spectra), with a 2400 l/mm spectrometer grating and CCD detector under a maximum of x100 optical power (numerical aperture (NA) of the lens of 0.90). The slit opening was 65 μm with CCD area of approximately 10 pixels (80% of the total signal height hitting the CCD chip) and a confocal hole of 200 μm. A 514.5 nm diode laser was used for excitation with an output of 50 mW. Optical filters (1%) were used to adjust the power of the laser to less than 0.5 mW. Raman backscattering was recorded after an integration time of 20 s for three repetitions for each measurement. The Raman system was calibrated against the 520.7 cm\(^{-1}\) band of silica.

Maximum palaeotemperatures were derived by two approaches. The first was that proposed by Lünsdorf & Lünsdorf (2016) for low to high metamorphic grades, while the method of Schito & Corrado (2020) was used to convert Raman parameters into vitrinite reflectance equivalent in the diagenetic realm. The automatic method proposed by Lünsdorf & Lünsdorf (2016) is designed to offer a comparability of Raman results at different stages of “organic metamorphism” from about 150 to 700°C. It is based on the IFORS software that curve-fits Raman spectra of carbonaceous material, modelling simultaneously the background with a fifth-order polynomial curve and the Raman signal with pseudo-Voight bands. The optimization of the curve is an iterative process that adds pseudo-Voight functions until the best fit of the baseline-subtracted spectrum is achieved (Lünsdorf & Lünsdorf, 2016; Lünsdorf et al., 2017). Among Raman parameters measured by this process, the normalized intensities of the D and G bands (STA-D, STA-G) are used to calculate palaeotemperature by means of the third-degree polynomial equation proposed in Lünsdorf et al. (2017), based on samples collected across the central and western Alps from low to high metamorphic degree.
The method, proposed by Schito & Corrado (2020), is suitable for diagenetic samples in a temperature range between about 50 to 150°C. It involves a linear baseline subtraction and then separately analyses the D and G bands by measuring the intensity, position, width and integrated area by means of two asymmetric Gaussian functions (Schito & Corrado, 2020). Raman parameters carried out by deconvolution (including the Raman bands separation (RBS), the area and width of the two bands and intensity, width and area ratios) were converted into vitrinite reflectance equivalents using a multiparametric equation (see Schito & Corrado, 2020 for more details). Data in Lower Palaeozoic shales used graptolite fragments where possible. Peak temperatures were calculated converting vitrinite reflectance equivalent using the equation of Barker & Pawlewicz (1986).

**Results**

Raman spectroscopy data for all samples are reported in Table 1. Raman spectra of carbonaceous materials highlight a temperature gap between lower and upper Palaeozoic (i.e., prism and cover rocks; Fig. 4). Both dispersed organic matter and bitumen in lower Palaeozoic rocks show Raman spectra characterized by broad D bands and narrow G bands (Fig. 3). The change of relative intensities of the two bands shown in Fig. 3 indicates a progressive evolution towards formation at higher temperatures. In the Southern Uplands, Raman temperatures range between 170 and 330°C and are similar in dispersed organic matter and bitumen samples (Figs. 1, 4). The lowest temperatures are found in Silurian rocks to the east whereas the highest were reached in the Cairnsmore locality near a granite pluton (Fig. 1). Samples from the lower Palaeozoic rocks in the north of Ireland show similar Raman temperatures, generally between 230 and 320°C (Table 1; Figs. 1, 4).

Raman analyses on Carboniferous samples were mainly measured in dispersed organic matter because bitumen is only present in three samples collected in southern Scotland (Fig. 1). Raman spectra are characterized by the presence of two weak D and G bands rising from a high fluorescence background (Fig. 3). Raman-derived temperatures are comparatively low, mainly ranging between 50 and 100°C (Table 1) and indicating thermal maturity extending from the immature stages of hydrocarbon generation to the onset of the oil window.

**Discussion**

**Approach to data assessment**

The RSCM geothermometer has become one of the most widely used methods of assessing peak temperatures during prograde metamorphism (see Henry et al., 2019 for a complete review). Different correlations between Raman parameters and temperatures have been proposed, based on more or less complex curve-fitting approaches (Beyssac et al., 2002;
Aoya et al., 2010; Lahfid et al., 2010; Kouketsu et al., 2014; Lünsdorf et al., 2014; 2017). However, increasing the complexity of curve-fitting means that multiple solutions are present at the same time and thus user interpretation can affect the final results. On the other hand, the automated approach, using IFORS software (Lünsdorf et al., 2014), has been shown to minimize the influence of operator error on Raman temperature calculations in metamorphic rocks. Round-robin tests (Lünsdorf et al., 2014) and recent work by Schito et al. (2022), demonstrated a correlation between palaeo-temperatures calculated through IFORS software and classical methods (i.e., converted from R2 and/or RA2 ratios, see Beyssac et al., 2002; Aoya et al., 2010; Lahfid et al., 2010).

In studies of diagenesis, Raman parameters are generally correlated with thermal maturity levels expressed as vitrinite reflectance (Ro%, see Henry et al., 2019). The Ro% equivalent, calculated from Raman spectra (Schito & Corrado, 2020), is converted into palaeo-temperatures by means of the Barker & Pawlewicz equation (1986). Such conversions are known to be imprecise, because thermal maturity is a function of temperature and heating rates and should be modelled taking into account both the thermal and burial histories of the basin (Sweeney & Burnham, 1990). However, for the purposes of this work the approximation of Barker & Pawlewicz’s equation is adequate. Nevertheless, temperature conversions for bitumen are slightly underestimated because the approaches of both Schito & Corrado (2020) and Barker & Pawlewicz (1986) are calibrated for kerogen.

Interpretation of data

The Raman spectroscopy data show clear patterns differentiating samples. The prism rocks are consistently more mature than the cover rocks and are characterised by temperature equivalents of 214-318°C, whereas the temperature equivalents of the cover rocks are 46-83°C (Fig. 4 and Table 1).

Abrupt changes in maturity across tract-bounding faults (Merriman & Roberts, 2000) show that the Ordovician-Silurian prism rocks reached their maximum maturity before burial beneath the unconformable cover of Upper Palaeozoic rocks. As the cover rocks never reached the high temperatures of the prism rocks, there was no post-Silurian overprinting. The bitumen samples of the prism are characterised by temperature equivalents of 173-328°C. These values compare to those of the prism rocks, but are unlike those of the cover rocks. This implies that the bitumens were derived from the prism rocks. They would originally have been mobile at lower temperatures (the oil generation window), and would then have been further heated along with the host rocks. The bitumen in the cover rocks is characterised by relatively low temperature equivalents of 67-98 °C. The highest temperature from cover rock bitumen is from Kershope Burn, where bitumen is accompanied by vein pyrite and could be a product of hydrothermal fluids. The conclusion that the prism-hosted bitumens have a prism origin is consistent with independent
evidence at Clontibret for deposition of the bitumen during Caledonides-age deformation (Morris et al., 1986).

Some bitumen samples show more evidence of heating than others. The most heated is a single sample at Cairnsmore, but samples from Clontibret and Kilnaleck were also heated to a greater degree than others. At Cairnsmore, mineralization is related to a diorite intrusion, which was in turn metamorphosed by a large Caledonian granite pluton (Power et al., 2004). There were therefore two episodes of magmatic heating in addition to regional heating by tectonic burial. The country rocks include black shales, which were a ready source of bitumen. At both Clontibret and Kilnaleck, the bitumen is believed to be associated with Caledonian deformation (Morris et al., 1986; Bishopp, 1943). The lowest-temperature sample, with an equivalent value of 173 °C, is from Ordovician rocks in Coulter Quarry at the northern margin of the prism. The same formation also yields the least crystalline illite in a large data set across the prism (Merriman & Roberts, 2000). The mutually consistent data indicate the locality is still in the zone of diagenesis rather than of metamorphism, albeit much hotter than the Carboniferous samples.

One sample (from Duff Kinnell) has greater maturity that could be attributed to shearing (Muirhead et al., 2021), as it is located in the Moniaive Shear Zone. Merriman & Roberts (2000) using Illite crystallinity values, also indicate anchizonal thermal maturity levels (i.e., temperatures between 200-300°C according to Frey, 1987) with local increases toward the epizone (i.e., temperatures higher than 300°C) around plutons and in shear zones.

Previous data suggest that the maturity of the Ordovician-Silurian shales varies greatly and reaches a maximum of 8 % non-vitrinite reflectance in both Scotland (Kemp et al., 1985) and Northern Ireland (Illing & Griffith, 1986). However, Merriman & Roberts (2000) found that most palaeotemperatures were in the 200-300 °C range, as is inferred from the Raman spectroscopy data.

Lower Palaeozoic source rocks

The black shales in the prism are predominantly of Late Ordovician to Llandovery age. The Ordovician oceans are considered to have been rich in algal matter with high hydrocarbon potential (Reed et al., 1986; Makled et al., 2021). The prism rocks are also rich in graptolite debris, which also had high hydrocarbon potential (Agapitov, 2014; Luo et al., 2020). Combined, these organic components would have generated oil that pooled along bedding planes in impermeable shale-rich sections, and eventually solidified to bitumen. Comparable generation of solid bitumen from Ordovician shales has been described from Oklahoma (Cardott, 1991) and New York (O’Reilly & Parnell, 1999). Lower Palaeozoic hydrocarbon source rocks analysed in this work were part of the widespread deposition of Ordovician-Silurian richly carbonaceous sediments in the Iapetus Ocean as far east as Russia (Zhang, 2008; Schulz et al., 2021).
Conclusions

The carbonaceous residues sampled from the Lower Palaeozoic accretionary prism were generated from rocks within the prism. The data show that the inferred palaeotemperatures:

(i) Overlap with values from the host rocks, as expected if the host rocks were the source.
(ii) Are distinctly higher than values in the overlying Carboniferous rocks, so that an origin from the younger deposits can be excluded.
(iii) Are consistent across the region, but show mildly anomalous high values due to Caledonian granite intrusion and deformation.

In summary, despite the evidence of an ingress of mineralizing fluids into the prism rocks during the Carboniferous-Triassic, there is no evidence that this resulted in a corresponding influx of carbonaceous matter into the prism within those fluids.

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References


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Figures

Fig. 1. Sample localities and inferred palaeotemperatures in Southern Uplands accretionary prism in Ireland and Scotland. A, Simplified geological map; B, Simplified cross-section (redrawn and modified after Rice et al., 2018).

Fig. 2. Vein rocks in Lower Palaeozoic containing carbonaceous residues. A, bitumen in quartz vein, Clontibret, Ireland; B, bitumen in calcite vein, Coulter Quarry, Scotland.

Fig. 3. Representative Raman spectra for samples indicating different palaeotemperature. EB, Ettrickbridge; MQ, Molly Quarry; CIM, Palnure, Cairnsmore; CU, Cultra; KB, Kershope Burn.

Fig. 4. Schematic SW-NE section showing palaeotemperature-equivalents determined from Raman spectroscopy data. Inferred palaeotemperatures for bitumen and host rock in Lower Palaeozoic rocks are consistently higher than in Carboniferous rocks.
Table 1. Characterization of maximum temperatures experienced by dispersed carbonaceous material and bitumen in the Southern Uplands. Raman temperatures were calculated according to the approach of Lunsdorf et al. (2017). See method section for further information. Sample localities abbreviation and corresponding Raman temperatures are plotted in Fig. 1a. Acronyms: R_0 % eq.: Vitrite reflectance equivalent calculated by means of Raman parameters according to Schito and Corrado (2020); std: standard deviation; Raman Temperatures are calculated using the IFORS software according to Lunsdorf et al. (2017) or by conversion of R_0 % eq. using Barker and Pawlewicz (1986) equation.

<table>
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<th>Sample type</th>
<th>Sample names</th>
<th>Locality</th>
<th>Grid Reference</th>
<th>Host rock</th>
<th>R_0 % eq.</th>
<th>Raman Temperature (°C)</th>
<th>std</th>
</tr>
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<td>18.3</td>
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<td>Clontibret</td>
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<td>NY 408773</td>
<td>Carboniferous</td>
<td>0.53 ± 0.08</td>
<td>83.0</td>
<td>12.8</td>
</tr>
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<td>CU</td>
<td>Cultra</td>
<td>J 407804</td>
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<td>0.48 ± 0.11</td>
<td>73.6</td>
<td>18.2</td>
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<td>AB</td>
<td>Altmush</td>
<td>N792873</td>
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<td>75.0</td>
<td>22.8</td>
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<tr>
<td>------------</td>
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<td>---------</td>
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</tr>
<tr>
<td>Cover rock</td>
<td>BN</td>
<td>Barns Ness</td>
<td>NT 722772</td>
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<td>0.38 ± 0.08</td>
<td>55.3</td>
<td>18.1</td>
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<td>Portling Bay</td>
<td>NX 884541</td>
<td>Carboniferous</td>
<td>0.34 ± 0.08</td>
<td>46.3</td>
<td>21.2</td>
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</tbody>
</table>
Figure 3

Lower Palaeozoic  Carboniferous

220°C  EB  G
280°C  MQ
320°C  CIM

70°C  CU  D  G
100°C  KB

Raman shift (cm⁻¹)

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