During the Serpukhovian (late Mississippian) Stage, the Pennine Basin, now underlying much of northern England, consisted of a series of interlinked sub-basins that developed in response to the crustal extension north of the Hercynic orogenic zone. For the current study, mudstone samples of the Morridge Formation from two sub-basins located in the south-eastern part of the Pennine Basin were collected from the Carsington Dam Reconstruction C3 borehole (Widmerpool Gulf sub-basin) and the Karenight 1 borehole (Edale Gulf sub-basin). Detailed palynological analyses indicate that aside from the dominant (often 90% or more) heterogeneous amorphous organic matter (AOM), variable abundances of homogeneous AOM and phytoclasts are present. To complement the palynological dataset, a suite of geochemical and mineralogical techniques were applied to evaluate the prospectivity of these potentially important source rocks. Changes in the carbon isotope composition of the bulk organic fraction (\(\Delta^{13}C_{OM}\)) suggest that the lower part (Biozone E2a) of Carsington DR C3 is markedly more influenced by terrigenous kerogen than the upper part of the core (Biozones E2a3–E2b1). The Karenight 1 core yielded more marine kerogen in the lower part (Marine Bands E1–E2b) than the upper part (Marine Band E2b). Present day Rock-Eval™ Total Organic Carbon (TOCpd) surpasses 2% in most samples from both cores, a proportion suggested by Jarvie (2012) that defines prospective shale gas reservoirs. However, when the pyrolysable component that reflects the generative kerogen fraction is considered, very few samples reach this threshold. The kerogen typing permits for the first time the calculation of an original hydrogen index (HIo) and original total organic carbon (TOCo) for Carboniferous mudstones of the Pennine Basin. The most prospective part of Carsington Dam Reconstruction C3 (marine bands E2b1–E2a3) has an average TOCo of 3.2% and an average HIo of 465 mg/g TOCo. The most prospective part of Karenight 1 (242.80–251.89 m) is characterized by an average TOCo of 9.3% and an average HIo of 504 mg/g TOCo. Lastly, X-ray diffraction (XRD) analysis confirms that the siliceous to argillaceous mudstones contain a highly variable carbonate content. The palynological, geochemical and mineralogical proxies combined indicate that marine sediments were continuously being deposited throughout the sampled intervals and were punctuated by episodic turbiditic events. The terrestrial material, originating from the Wales-Brabant High to the south of the Pennine Basin, was principally deposited in the Widmerpool Gulf, with much less terrigenous organic matter reaching the Edale Gulf. As a consequence, the prospective intervals are relatively thin, decimetre-to-meter-scale, and further high resolution characterization of these intervals is required to understand variability in prospectivity over these limited intervals.

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1. Introduction

Between 1872 and 1876 two boreholes drilled in Netherfield (East Sussex, UK) were found to not only contain thick gypsum deposits (Sub-Wealden Exploration Company, 1873) but also in flammable gases from 'petroleum bearing strata' (Willett, 1875 in...
These findings were the result of the Sub-Wealden Exploration, an academic effort to complete the knowledge of the range of Palaeozoic rocks underneath the Weald (Topley et al., 1872). For more than a century, very little research was directed towards further exploring the prospectivity of this energy resource. Then, following the start of shale gas exploration in the United States in 1982 (Steward, 2007), interest of the research community in the UK was reinvigorated with efforts focused on Carboniferous organic-rich shales (Selley, 1987; Smith et al., 2010). More recently, the Namurian (Visean–Serpukhovian) Bowland Shale Formation and its lateral equivalents including the Edale Shale and the Morridge formations (Waters et al., 2007), were identified as the most promising targets (Andrews, 2013; Selley, 2012; Smith et al., 2010). These British Namurian-aged shales

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**Fig. 1.** Mississippian palaeogeography of Southern Britain, showing major basin bounding faults and the location of the Carsington Dam Reconstruction C3 and Karenight 1 boreholes (based on Waters et al., 2009). BH – Bowland High; BT – Bowland Trough; CLH – Central Lancashire High; DH – Derbyshire High; EG – Edale Gulf; GT – Gainsborough Trough; LDH – Lake District High; Manx High; WG – Widmerpool Gulf. Contains Ordnance Survey data © Crown Copyright and database rights 2017.
were deposited in a mosaic of interlinked basins in a proximal position with emergent areas to the north (the Southern Uplands) and the south (Wales Brabant High) serving as the main sources of terrigenous material (Figs. 1 and 2) (Aitkenhead et al., 2002; Fraser and Gawthorpe, 1990; Waters et al., 2009). During the Mississippian (359–323.2 Ma), the Pennine Basin was located in an equatorial position, proximal to Laurussia with Gondwana stretching to the South Pole (McKerrow and Scotese, 1990), bordered by two emerging land masses. Because of its position, ice sheets were likely to persist on Gondwana (Isbell et al., 2003) which influenced the sedimentation history in the patchwork of sub-basins forming the Pennine Basin (e.g. Stephenson et al., 2010).

Here we present a high resolution, multiproxy dataset to characterize the potentially prospective intervals of the Mississippian successions in the southern part of the Pennine Basin. We present geochemical (Rock-Eval™, organic carbon isotopes), palynological and lithological-mineralogical (X-ray diffraction, XRD) results from two cored boreholes: Carsington Reconstruction Borehole C3 (British Geological Survey reference number SK25SW/113) and Karenight 1 (British Geological Survey reference number SK36NW/13). The former was drilled in the Widmerpool Gulf while the latter originates close to the Derbyshire High—Edale Gulf boundary (Figs. 1 and 2). In both boreholes we studied an interval containing the E2a marine band, which is part of the late Serpukhovian (late Mississippian). This interval was chosen because of the availability of pre-existing data (e.g. Konitzer et al., 2014) on this marine band in the Widmerpool Gulf. The Karenight 1 core is one of very few well-preserved cores to prove the same interval from the Edale Gulf, a neighbouring sub-basin of the Widmerpool Gulf in the Pennine Basin.

The aim of the study is to (1) describe the kerogen content of the Namurian mudstones in the Widmerpool–Edale Gulf area; (2) establish the amount of variability in the kerogen content of the mudstones within a single marine band (E2a); and (3) evaluate the

**Fig. 2.** A: Map of the U.K. with the study area highlighted in green; B: Location of the Carsington Dam Reconstruction C3 (yellow) and Karenight 1 (red) Boreholes in relation to bedrock geology. U. – Upper; M. – Middle; L. – Lower. Digital geological map data BGS © NERC; contains Ordnance Survey data © Crown Copyright and database rights 2017. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
2. Namurian stratigraphy of the deposits in the Pennine Basin

The Pennines in the central UK comprise a dissected plateau (up to 600m) composed of an asymmetrical anticline with Carboniferous strata gently dipping to the east and more steeply to the west (Aitkenhead et al., 2002). During the Chadian—early Arundian and late Asbian—Brigantian, a SSE—NNW crustal extension caused a fragmentation of Early Palaeozoic deposits giving rise to a rifted topography of fault-bounded blocks interspersed with developing grabens and half-grabens including the Widmerpool and Edale Gulf (Gawthorpe, 1987; Lee, 1988). By the end of the Visean, rift-associated extension in the area was replaced by a regime of thermal sag and an epicontinental sea transgressed the Pennine Basin leaving only the Southern Uplands and the Wales-Brabant High emergent (Fig. 1)(Leeder, 1982; Leeder and McMahon, 1988).

The Namurian was a period of prograding deltas in the Pennine Basin when the basin topography, created during the Visean, was gradually filled. The sediments deposited during this stage correspond broadly to the Millstone Grit Group (Fig. 3). Regular marine incursions punctuated the deltaic successions giving rise to a remarkable cyclicity: shale and/or dark-coloured limestone rich in marine fossils, typically goniatites (so-called ‘marine bands’), are overlain by shale and sandstone with fewer fossils (Gross et al., 2014; Holdsworth and Collinson, 1988; Martinsen et al., 1995). In the 13 million year span of the Namurian around 60 marine bands occur (Martinsen et al., 1995), 46 characterized by the occurrence of a key goniatite species (Bisat, 1923; Holdsworth and Collinson, 1988; Ramsbottom, 1977; Ramsbottom et al., 1962). The average duration of a marine band is estimated at 180 kyr, although considerable variation between the marine bands may occur (Maynard and Leeder, 1992).

For the Pendleian—Arnsbergian interval, marine band periodicities of 111 kyr have been estimated, and they are linked to an eccentricity forcing (Waters and Condon, 2012) of glacio-eustatic sea level fluctuations (Isbell et al., 2003; Stephenson et al., 2008; Veevers and Powell, 1987). Superimposed on these minor cycles, eleven longer duration, 1.1–1.35 myr, mesothems have been identified (Ramsbottom, 1977). These mesothems are interpreted as longer term marine transgressions, characterized by the appearance of new ammonoid genera and each one capped by an extensive ammonoid band (Ramsbottom, 1979). In a sequence stratigraphic context, the marine bands can be thought of as parasequences representing the maximum flooding surfaces, while the mesothems correspond to sequences (Posamentier et al., 1988).

2.1. Visean–Namurian deposits in the Widmerpool and Edale Gulf

The Visean—early Namurian Craven Group from the Widmerpool Gulf comprises the Long Eaton, Lockington Limestone and Widmerpool formations (Fig. 3). The overlying Bowland Shale Formation, formerly termed the Edale Shales (Waters et al., 2009), commences at the base of the Emstites leion (E1a1) (formerly Cravenoceras leion) Marine Band and has a highly diachronous upper boundary with the feldspathic sandstones typical of the Millstone Grit Group (Stevenson et al., 1971). The Bowland Shale Formation is
a dark grey calcareous mudstone with thin turbiditic sandstones which in the southern part of the Pennine Basin, close to the northern margin of the Wales-Brabant High, passes over in the shaly mudstones and pale grey protozoanitiz siclinites of the Morridge Formation (Waters et al., 2009). The Morridge Formation is an early Namurian equivalent of the Millstone Grit Series (Fig. 3) and was introduced by Waters et al. (2007) to reflect the predominantly southern provenance of the terrigeneous material making up the sandstone intervals: coarse quartz-feldspathic sediments derived from Greenland and Fennoscandia make up the terrigenous component of the Millstone Grit Series (Drewery et al., 1987) while quartz-rich sediments in the sandy intervals of the Morridge formation originate from the Wales-Brabant High (Trewin and Holdsworth, 1973).

The late Visean, Asbian and Brigantian, deposits in the Edale Gulf were described by Gutteridge (1991) and consist of the Ecton Limestone and Widmerpool Formations (Fig. 3). The Namurian successions of the Derbyshire High—Edale Gulf are poorly understood as they are only described from the Alport and Edale Boreholes that were drilled in the late 1930s. During the late Brigantian—early Pendleian, carbonate production waned over the Derbyshire High and up to 356 m of mudstone-dominated successions of the Bowland Shale Formation were deposited ranging in age from Pendleian to Kinderscoutian (Fig. 3) (Waters et al., 2009). The lower part of the Bowland Shale Formation in the Edale Gulf consists of a succession of grey mudstone with thin beds of calcareous quartzose siltstones which may represent the distal delta-slope equivalent of the Morridge Formation (Waters et al., 2009).

### 2.2. The Carsington Dam Reconstruction Borehole C3

The Carsington Dam Reconstruction Borehole C3 (1.63°W; 53.05°N; Fig. 2) was drilled in 1990 to assess fluid movements and pressures of the reconstructed Carsington Dam following its failure in 1984 (Skempton and Vaughan, 1993). In the palaeogeographic reconstruction of the Namurian, it is located close to the centre of the Widmerpool Gulf half graben (Fig. 1). In total, 38 m of mudstones, siltstones, sandstones and limestones belonging to the Morridge Formation were cored across the E2a Cravenoceratoides edalensis Marine Bands (Aitkenhead, 1991) (Fig. 3). The E2a2 and E2a3 bands are part of the N1 mesothem, while the E2a3—E2b1 boundary forms the transition between the N1 and N2 mesothems (Aitkenhead, 1991).

### 2.3. The Karenight 1 borehole

The Karenight 1 borehole (1.53°W; 53.18°N; Fig. 2) was drilled as a mineral exploration borehole by Drilling and Prospecting International in 1973. It was drilled near the northern boundary of the Derbyshire High towards the Edale Gulf (Fig. 1). The borehole was drilled to a terminal depth of 428.37 m and was cored below 59.59 m onwards (Wilson and Stevenson, 1973). In the current study we investigated the 234.70—251.89 m interval, consisting of mostly carbonate-cemented mudstone interspersed with limestone (250.93—244.5 m) and siltstone (244.5—234.70 m) (Fig. 6). This interval comprises the upper part of the Pendleian Substage (E1; 251.89—248.55 m) and the E2b Eumorphoceras zone with the E2b marine band tentatively recognized at 241.90m (Wilson and Stevenson, 1973).

### 3. Methodology

#### 3.1. Palynological analysis

In total, the palynofacies composition of 55 samples assessed: 22 from the Carsington Dam Reconstruction C3 Borehole (Carsington DR C3) (Appendix 1) and 33 from the Karenight 1 Borehole (Appendix 2). Approximately 5 g of each sample was processed at the British Geological Survey utilizing hydrochloric (36%) and hydrofluoric acid (40%) to eliminate carbonates and silicates. Samples were spiked with Lycopodium clavatum (Batch No. 3862) to enable concentration and flux calculations utilizing the marker grain method (Maher, 1981; Stockmarr, 1981). Subsequently, the kerogen fraction was sieved on a 10 μm nylon mesh and was straw-mounted on microslides using Elvacite™. Optical examination was performed using a Nikon Eclipse Ci-L microscope (400× for routine study, 1000× for studying morphological details) equipped with a Prior H101A Motorized Stage that was controlled by a Prior™ Proscan III unit connected to a PC with the open source microscopy software μManager (https://micro-manager.org/wiki/Micro-Manager) preinstalled. Per sample, 300 particles were identified following the palynofacies classification of Tyson (1995) and using randomly generated slide positions. All slides were scanned for the presence of spores which were recorded separately from the palynofacies analyses. Furthermore, we studied the slides using blue light excitation (near UV) on a Zeiss Universal microscope operating in incident-light excitation mode with a III RS filter set 09 (exciter filter: 450—490 nm; chromatic beam splitter: 510 nm; barrier filter: 515—565 nm). We followed the standard recommendations for epifluorescence observations on palynological slides (Tyson, 1995, Table 1).
Images of palynomorphs (Plates 1–2) in transmitted white light were taken with a Nikon DS-Fi3 camera mounted on the Nikon Eclipse Ci-L microscope and the NIS Elements™ microscope imaging software.

### 3.2. Rock-Eval™ pyrolysis

In total 169 samples were analysed from Carsington DR C3 (Appendix 3) and 72 samples from Karenight 1 (Appendix 4) using a Rock-Eval™ (6) analyser configured in standard mode. Freeze-dried, powdered samples (60 mg/dry wt) were heated at 300 °C for 3 min and then heated from 300 °C to 650 °C at 25 °C/min in N₂ atmosphere and the residual carbon oxidised at 300 °C–850 °C at 20 °C/min. Hydrocarbons released during the two-stage pyrolysis were measured using a flame ionization detector (FID) and CO and CO₂ measured using an infra-red (IR) cell. Rock-Eval parameters were calculated by integration of the amounts of hydrocarbon (HC), thermally-vaporized free hydrocarbons, expressed in mg HC/g rock (S₁) and hydrocarbons released from cracking of bound OM expressed in mg HC/g rock (S₂). The Hydrogen Index (HI) and Oxygen Index (OI) were calculated following Newell et al. (2016) and Słowiakiewicz et al. (2015) and expressed in mg/g TOC:

\[
HI_{pd} = \frac{S_2 * 100}{TOC_{pd}}
\]

\[
OI_{pd} = \frac{S_3 * 100}{TOC_{pd}}
\]

Thermal maxima values (T max) were determined from the highest yield of bound hydrocarbons (S₂). The performance of the instrument was checked every 8 samples against the accepted values of the Institut Français du Pétrole (IFP) standard (IFP 160 000, S/N 5–081840) and instrumental error (standard deviation) was S₁ ± 0.1 mg HC/g rock, S₂ ± 0.77 mg HC/g rock, TOC ± 0.04% weight, mineral C ± 0.04% weight, Tmax ± 1.4 °C.

### 3.3. X-ray diffraction analysis

The mineralogy of 17 samples from Carsington DR C3 (Appendix 5) and 10 samples from Karenight 1 (Appendix 6) was determined by quantitative X-ray diffraction (XRD) analysis. Samples were analysed using a PANalytical™ X’Pert Pro series diffractometer equipped with a cobalt-target tube, X’Celerator detector and operated at 45 kV and 40 mA. Whole-rock analysis was carried out on spray-dried, micronised powders which were scanned from 4.5 to 85°2θ at 2.06°2θ/minute. Mineral phases were identified using PANalytical™ X’Pert HighScore Plus version 4.5 software coupled to the latest version of the International Centre for Diffraction Data (ICDD) database. Quantification was achieved by using the Rietveld refinement technique (e.g. Snyder and Bish, 1989) with the same
HighScore™ Plus software and reference files from the Inorganic Crystal Structural Database (ICSD).

The clay mineralogy of the samples (Appendices 7, 8) was determined using a broadly similar approach to that detailed in Kemp et al. (2016). Where whole-rock XRD analysis indicated that the samples were composed of substantial amounts of carbonate species, these were removed using a buffered sodium acetate/acetic acid (pH 5.3). For this study, <2 μm fractions were isolated, oriented mounts prepared and scanned from 2 to 40°/2θ at 1.02°/2θ/minute after air-drying, ethylene glycol-solvation (16 h) and heating at 550°C (2 h). Clay mineral species were then identified from their characteristic peak positions and intensities and their reaction to the diagnostic testing program. Further clay mineral characterization and quantitative evaluation was carried out using Newmod II™ software (Reynolds and Reynolds, 2013) modelling of the glycol-solvated XRD profiles on all the samples.

3.4. Organic carbon isotope composition (δ¹³C₉M)

We determined the organic carbon isotope composition (δ¹³C₉M) from 30 Carsington DR C3 samples (Appendix 9) and from 57 Karenight 1 samples (Appendix 10). ¹³C/¹²C analyses were performed by combustion in a Costech Elemental Analyser (EA) on-line to a VG TripleTrap and Optima dual-inlet mass spectrometer, with δ¹³C₉M values calculated to the VPDB scale using a within-run laboratory standards calibrated against NBS-18, NBS-19 and NBS-22. Replicate analysis of well-mixed samples indicated a precision of ±<0.1‰ (1 SD).

4. Results

The palynofacies analysis, Rock-Eval™ and δ¹³C₉M and XRD results are presented below and are summarized in the Appendices 1–10. The palynofacies analysis was conducted on samples that were also used for geochemical (Rock-Eval™ and δ¹³C₉M) analyses. Additional samples were collected for XRD analyses.

4.1. Palynofacies analysis

The palynofacies assessment follows the palynological kerogen classification of Tyson (1995). Structureless (heterogeneous + homogeneous) amorphous organic matter (AOM) was distinguished from structured material (phytoclasts, sporomorphs, phytoplankton, fungal remains) and any residual mineral matter, mainly pyrite, which was not eliminated during sample preparation.

4.1.1. Carsington DR C3

The palynological analysis of the 22 Carsington DR C3 samples is summarized in Appendix 1 and Fig. 5. Structureless organic
constituents dominate the kerogen fractions making up on average 86% of the counts with a minimum of 74% (SSK45636; 31.61 m) and a maximum of 95% (SSK45607; 26.18 m). Within this structureless category, heterogeneous AOM (Plate I, Figs. 1–4) with grumose AOM (Plate I, Fig. 1) as the most important constituent is the dominant organic category averaging 62% of the counts, with a minimum of 19% (SSK46355; 53.57 m) and a maximum of 86% (SSK46331; 46.08 m). Homogeneous AOM, with gelified organic matter as the dominant constituent (Plate I, Fig. 5), forms on average 25% of the kerogen fraction, with a minimum of 4% (SSK45621; 42.89 m) and a maximum of 60% (MPA65588; 53.57 m). The abundance of homogeneous AOM surpasses the abundance of heterogeneous AOM in four samples: SSK46355 (53.57 m), SSK46311 (42.58 m), SSK45634 (31.11 m) and SSK45616 (28.22 m).

Within the structured organic material, phytoclasts are the most abundant organic constituent averaging about 8% of the counts with a minimum of 2% (SSK45607; 26.18 m) and a maximum of 22% (SSK46301; 40.83 m). Phytoclasts (Plate I, Fig. 5, black arrow) are especially abundant below the E2a3 Marine Band. Palynomorphs are very sparse in the section averaging 1.95% (with a minimum of 0.21% at 45.28 m and a maximum of 5.16% at 48.60%, while PC averages 0.33 with a minimum of 0.02% at 31.11 m and a maximum of 1.02% at 43.33 m. The TOCpd (and PC) are higher in the E2a3 and E2b1 marine bands with TOCpd reaching an average of 3.52% with a maximum of 5.52% at 24.23 m and a minimum of 0.5% while PC averages 0.77% with a minimum of 0.06% at 20.10 m and a maximum of 1.66% at 25.68 m.

The HIpd of the section from E2a to the E2b3 boundary averages 162 mg/g TOCpd, with a minimum of 28 mg/g TOCpd at 34.28 m and a maximum of 428 mg/g TOCpd at 38.77 m. For the upper part of the studied section HIpd averages 228 mg/g TOCpd with a minimum of 81 mg/g TOCpd at 27.08 m and a maximum of 366 mg/g TOCpd at 26.78 m.

The E2a–E2b3 boundary is also coeval with an upheal rise in S1; the S1 diagram with an average of 0.19 mg/g for the lower part (minimum of 0.01 mg/g at 34.28 m; maximum of 1.28 mg/g at 33.72 m) and an average of 0.54 mg/g (minimum of 0.04 mg/g at 20.10 m; maximum of 1.01 at 25.68 m).

The HIpd remains relatively constant throughout the entire interval averaging 435 °C. Only in the sandstone and siltstone interval around 34 m a drop in T_max to a minimum of 366 °C has been recorded.

The δ13COM data follow the trend of TOCpd and S1 with higher values in the lower part of the section (55.46–25.40 m) averaging –26.2% (with a minimum of –28.7% and a maximum of –24.0%). In the upper part of the section (25.40–18.44 m), δ13COM average –28.0% (with a minimum of –30.0% and a maximum of –25.0%).

4.1.2. Karenight 1

The palynological analysis of the 33 samples of Karenight 1 is summarized in Appendix 2 and Fig. 6. Structureless organic constituents dominate all Karenight 1 samples (as with the Carsington DR C3 results), averaging a relative abundance of 88% with a minimum of 72% (SSK53146; 251.89 m) and a maximum of 97% (SSK51212; 245.50 m). Heterogeneous AOM is the dominant category of structureless material with on average a relative abundance of 77% (minimum 58% in SSK53146 at 251.89 m; maximum 94% in SSK51212 at 245.50 m). Heterogeneous AOM is the dominant category of structureless material with on average a relative abundance of 77% (minimum 58% in SSK53146 at 251.89 m; maximum 94% in SSK51212 at 245.50 m). Heterogeneous AOM is the dominant category of structureless material with on average a relative abundance of 77% (minimum 58% in SSK53146 at 251.89 m; maximum 94% in SSK51212 at 245.50 m).

Phytoclasts comprise the most abundant structured organic constituent with a relative abundance of 7% (maximum of 22% in SSK53146 at 251.89 m; minimum of <1% in SSK46369 at 235.98 m and SSK51182 at 238.46 m). The highest phytoclast abundances are reached during the Pendleian (E1). Palynomorphs are very sparse in the Karenight 1 section averaging only 1% (maximum of 5% in SSK51192 at 240.93 m and SSK53146 at 251.89 m) including five samples where no palynomorphs were recorded in 300 fields of view (SSK53135, SSK52580, SSK51208, SSK51204, SSK51182). Spores are the most common discrete palynomorphs, with poor preservation causing most to remain unidentified. Lycospora pusilla is again the most common identified spore with minor occurrences of Granulatisporites granulatus, Florinites spp. and Cingulizonates biulatus.

4.2. Geochemical analyses: Rock-Eval™ pyrolysis and δ13COM

4.2.1. Carsington DR C3

Nine Rock-Eval™ parameters (S₁, S₂, S₃, HIpd, Oil, T_max, TOCpd) and PC are summarized in Appendix 2 and δ13COM in Appendix 10. In Fig. 6 we show the TOCpd, PC, S₁, T_max, HIpd and δ13COM data alongside the sedimentological log. For the E2a2 zone up to E2a3, TOCpd and PC are relatively low, with TOCpd values averaging 1.95% (with a minimum of 0.21% at 45.28 m and a maximum of 5.16% at 48.60%, while PC averages 0.33 with a minimum of 0.02% at 31.11 m and a maximum of 1.02% at 43.33 m. The TOCpd (and PC) are higher in the E2a3 and E2b1 marine bands with TOCpd reaching an average of 3.52% with a maximum of 5.52% at 24.23 m and a minimum of 0.5% while PC averages 0.77% with a minimum of 0.06% at 20.10 m and a maximum of 1.66% at 25.68 m.

The HIpd of the section from E2a to the E2b3 boundary averages 162 mg/g TOCpd, with a minimum of 28 mg/g TOCpd at 34.28 m and a maximum of 428 mg/g TOCpd at 38.77 m. For the upper part of the studied section HIpd averages 228 mg/g TOCpd with a minimum of 81 mg/g TOCpd at 27.08 m and a maximum of 366 mg/g TOCpd at 26.78 m.

The E2a–E2b3 boundary is also coeval with an upheal rise in S1; the S1 diagram with an average of 0.19 mg/g for the lower part (minimum of 0.01 mg/g at 34.28 m; maximum of 1.28 mg/g at 33.72 m) and an average of 0.54 mg/g (minimum of 0.04 mg/g at 20.10 m; maximum of 1.01 at 25.68 m).

The HIpd remains relatively constant throughout the entire interval averaging 435 °C. Only in the sandstone and siltstone interval around 34 m a drop in T_max to a minimum of 366 °C has been recorded.

The δ13COM data follow the trend of TOCpd and S1 with higher values in the lower part of the section (55.46–25.40 m) averaging –26.2% (with a minimum of –28.7% and a maximum of –24.0%). In the upper part of the section (25.40–18.44 m), δ13COM average –28.0% (with a minimum of –30.0% and a maximum of –25.0%).
242.80 m: low and relatively consistent HIpd values, 108 mg/g TOC (217 mg/g TOC) 260 mg/g TOC and lower Tmax, 424 °C (431 °C) 442 °C. From 242.80 to 234.80 m: low values for HIpd, 82 mg/g TOC (183 mg/g TOC) 293 mg/g TOC, and Tmax, 425 °C (433 °C) 440 °C.

4.3. Mineralogical analysis

The whole-rock and <2 µm clay mineral XRD analyses for 17 samples from Carsington DR C3 are summarized in Appendices 5 and 7. The XRD analyses for 10 samples from Karenight 1 are summarized in Appendices 6 and 8. Results from both boreholes are summarized in the ternary mudstone classification diagram of Fig. 8.

4.3.1. Carsington DR C3

Thirteen samples originate from the bottom part of the section (E2a below E2a3; 53.57–28.22 m) which all plot in the siliceous and argillaceous mudstone fields. These samples are generally carbonate-free with only a single sample containing minor amounts of rhodocrosite (1.6% at 40.83 m). Silicates (quartz with rare plagioclase feldspar) dominate the composition with on average 41%, with a maximum of 33.63% and a minimum of 23.6% (43.26 m). Pyrite forms up to 7.6% of these samples and the oxidation products jarosite and gypsum were also detected. The phyllosilicate/clay mineral assemblages of the E2a samples are dominated by undifferentiated ‘mica’ species (including muscovite, biotite, illite and illite/smectite (I/S)) with minor amounts of kaolinite and chlorite. Less than 2 µm analyses and Newmod II-modelling confirm this assemblage and subdivided the ‘mica’ into discrete illite and an R1-ordered I/S containing 80% illite interlayers.

The remaining four samples (E2a3 and E2b1; 18.44–26.18 m) all plot in the siliceous mudstone field. These samples are characterized by a higher carbonate (calcite, dolomite, Fe dolomite/ankerite) content (on average 7.63%) and a maximum of 24.2% in the lowermost sample (26.18 m). These samples are also pyritic but are less phyllosilicate/clay mineral-rich than the underlying samples. Although the detected clay minerals in the <2 µm fractions are similar to the shales below E2a3, they noticeably contain a lower proportion of kaolinite and chlorite and higher proportions of I/S and illite.

4.3.2. Karenight 1

The lowermost six samples 251.84–242.98 m interval (E1–E2b?) plot in the argillaceous mudstone and siliceous mudstone fields. While low, the carbonate content of this interval is higher than in the bottom part of Carsington DR C3 averaging 4.7% with a maximum of 10.7% at 251.84 m. The four samples from the top part of the section (E2b?; 236.07–242.32 m) are generally richer in carbonates (calcite and dolomite, averaging 28.5%) with a maximum of 49.4% at 238.33 m. This sample plots in the mudstone field of Fig. 8.

Less than 2 µm XRD analyses suggest R1 (80% illite) I/S- and illite-dominated clay mineral assemblages with only traces of kaolinite and chlorite, similar to those identified in the upper interval of the Carsington DR C3 borehole.

5. Discussion

To assess the shale gas prospectivity of the Widmerpool Gulf and Edale Gulf we apply the criteria detailed in Table 2 of Andrews (2013). With the data generated in the current study we can expand
the UK data set and discuss four criteria in more detail (Table 1): organic matter content (and original TOC, TOCo), kerogen type, original hydrogen index (HIo), mineralogy and clay content.

5.1. Organic matter content (TOC)

The TOCpd or organic richness of a potential source rock was assessed using TOCpd values. Table 1 summarizes the evaluation of widely accepted criteria to assess the prospectivity of shale gas plays.

### Table 1

| Criterion                  | Definitions                                                                 | Carsington DRC3 (Widmerpool Gulf) | Karenight 1 (Edale Gulf) |
|----------------------------|-----------------------------------------------------------------------------|---------------------------------|--------------------------|
| Organic matter content (TOCpd) | >2% (TNO, 2009; Gilman and Robinson, 2011; Andrews, 2013)                  | E2b1–E2a3: highest TOCpd averaging 3.52%. | 71 of 72 samples have a TOCpd >1; 68 have TOCpd >2. When PC is considered, 38 samples surpass 1%; 3 samples exceed 2%. |
| Kerogen Type               | Type I, II, IIS (Charpentier and Cook, 2011)                                 | With fluorescence weighting of heterogeneous AOM:E2b1–E2a3 (18.02–27.32 m): Type I: 34.3%; Type II: 40.3%; Type III: 22.2%; Type IV: 0.8%. E2a below E2a3: 46.9%; Type III: 30.3%; Type IV: 1.3%. E2a below E2a3: HIo averages 448 mg/g TOCo; TOCo averages 4.4%. E2a–E1: (242.80–251.89 m): HIo averages 504 mg/g; TOC0 averages 9.3%. |
| Original Hydrogen index (HIo) and original TOC (TOCo) | >250 mg/g (TNO, 2009; Charpentier and Cook, 2011)                           | E2b1–E2a3: (18.02–27.32 m): HIo averages 465 mg/g TOCo; TOCo averages 3.2%. E2a below E2a3: (27.32–55.46 m): HIo averages 396 mg/g TOCo; TOCo averages 1.0%. E2a–E1 (242.80–251.89 m): HIo averages 448 mg/g TOCo; TOCo averages 4.4%. E2a–E1 (242.80–251.89 m): HIo averages 504 mg/g; TOC0 averages 9.3%. |
| Mineralogy and clay content | Low clay content (<35%) (Andrews, 2013). Significant silica content (>30%) with some carbonate and presence of non-swelling clays (Jarvie, 2012). Ductile brittle transition zone 40–60% clay content. | E2b1–E2a3: (18.02–27.32 m): dominantly siliceous mudstones with a variable carbonate content (maximum 24%); clay content: 10–54%. E2a below E2a3: (27.32–55.46 m): dominantly argillaceous mudstones with a very low carbonate content (maximum 2%); clay content: 11–78%. E2a–E1 (242.80–251.89 m): siliceous–argillaceous mudstones with a low carbonate content (maximum 10%); clay content: 34–62%. |

Fig. 8. Ternary carbonates-clay-silicates summarizing the XRD results from the Carsington Dam Reconstruction C3 (black) and Karenight 1 (red) cores compared to Palaeozoic shale plays in the US (yellow; Anderson, 2014). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
measured using Rock-Eval™ pyrolysis and is reported in dry weight percent. Because organic matter generates hydrocarbons during maturation, TOCpd is generally viewed as an important variable that has a strong influence on the amount of potential hydrocarbons that can be generated. Even though there is consensus that a potential source rock should be rich in organic matter and TOCpd can serve as a proxy for that, reported cut-off values vary from basin to basin and from author to author: e.g., in the Pennine Basin, Andrews (2013) utilizes a TOCpd cut-off of 2% to 2011; TNO, 2009), screen potentially viable shale horizons. However, it is important to acknowledge that measured values relate to TOCpd composed of the pyrolysable fraction of the organic carbon (PC) and the remaining carbon after pyrolysis (RC) (Fig. 9). The RC represents the present day generative part (GOCpd) while the RC represents the present day non-generative part of the organic carbon (NGOCpd) of the sample that was subjected to Rock-Eval pyrolysis. From the moment of sampling to the acquisition of the pyrolysis results, losses of organic carbon occur due to storage, handling and sample processing. Losses also occur due to natural processes associated with basin evolution, including diagенesis and maturation of the sediments and due to migration of formed hydrocarbons (Fig. 9). As a result, the original TOC (TOCo) is composed of the original GOC (GOCo) and the original NGOC (NGOCo). Jarvie (2012) provides a methodology to calculate TOCo (see paragraph 5.2) and uses a cut-off value of 1% TOCo as a criterion for prospective shale plays. Thus, the interpretation of TOC values relies on the assumption that the loss of carbon from deposition to analysis is not biased towards GOC or its components, and quantitatively similar for all compared samples. While this may be a reasonable assumption for a set of samples from the same bed, TOCpd can vary by as much as 10% within the same shale system (Fig. 7 in Jarvie, 2012) which draws into doubt the validity of inter-basinal comparisons of TOC values. Indeed, some techniques that rely on indirect estimates of the OM component to estimate shale gas resource, such as the Passey Method (Passey et al., 1990) applied to down-hole geophysical logs, may give unrealistically high estimates of gas generative potential.

In the Carsington DR C3 core 142 of a total of 169 samples have TOCpd values above 1% and 97 samples have TOCpd higher than 2% (Appendix 3). Biozones E2b1 and E2a3 (18.02–27.32 m) have the highest TOCpd with only the thin limestone bed at 20.10 m containing less than 1% organic carbon. However when PC is considered, values are much lower and only 7 samples, 6 of which originating from the E2b1–E2a3 interval, show higher than 1% PC and no samples exceed 2% PC. In conclusion, the majority of the Carsington DR C3 samples meet the >2% criterion of Andrews (2013) for TOC values of a prospective shale interval, especially in the E2b1 and E2a3 and only in restricted intervals in the rest of the studied interval. When PC is considered, no samples exceed the 2% threshold.

In the Karenight 1 core, 71 of a total of 72 samples have TOCpd higher than 1% and 68 have TOCpd higher than 2% (Appendix 4). The only samples that do not meet the 2% requirement are limestone that are present throughout the interval. When PC is considered, only 38 samples surpass 1%, concentrated in the lower part of the core, and only 3 samples exceed 2%.

5.2. Kerogen type, original HI (HIo) and original TOC (TOCo)

The palynofacies analyses are based on the classification of Tyson (1995) and are summarized in Appendix 1 (Carsington DR C3) and Appendix 2 (Karenight 1) and on a AOM—Phyto-clast—Palynomorph (APP) plot (Fig. 7). Kerogen typing follows the summary given in Table 2 following Tyson (1995). The kerogen types encountered in the two boreholes studied here correspond broadly with the tentative kerogen typing for the Widmerpool and Edale Gulf by Ewbank et al. (1993). Mudstone contains higher percentages of Type II kerogen while coarser-grained intervals are richer in Type III. There is very little evidence of algal material (even though Botryococcus specimens were recorded in the upper part of Carsington DRC3; Plate I, Fig. 6) and phytolipids in the samples, a common observation in the Late Palaeozoic, dubbed as the Late Palaeozoic palynolipid blackout (Riegel, 2008). Heterogeneous amorphous organic matter seems a likely candidate to represent these cryptic fossil groups. This has potentially important consequences for the typing of kerogen materials and the subsequent assessment of the prospectivity of source rocks. It is possible that a proportion of the heterogeneous AOM can be considered as Type I. In addition to transmitted white light, all samples were scanned using near-UV blue light and scored following Tyson’s qualitative fluorescence scale (FSI) (Fig. 7). Figure 7 shows that samples rich in heterogeneous AOM generally exhibit stronger fluorescence. The fluorescent compounds, fluorophors, are carotenoids of sporinite, isoprenoids of alginite and the phenols of cutinite and suberinite (Lin and Davis, 1988). Hydrocarbon potential and fluorescence are closely related (Van Gijzel, 1982) as fluorescence is enhanced when these compounds are distributed in an aliphatic environment (Robert, 1988). Using the relative abundances of AOM and phytoclasts, the qualitative fluorescence scale, a fluorescence scale index (FSI) can be calculated (Tyson, 2006):

$$ FSI = \frac{AOM}{AOM + Phyto} $$

Where FSI is the fluorescence scale, AOM is the relative abundance of amorphous organic matter and Phyto represents the relative abundance of phytoclasts. The maximum value for FSI is 6, when the maximum of FSI = 6 is reached in a sample where the palynological counts reach 100% AOM. Therefore, to have an estimate of how much of the heterogeneous AOM consists of the highly fluorescent algal material, and therefore Type I kerogen, we divided the acquired FSI by 6 and multiplied it with relative abundance of

| Kerogen type | Organic constituent |
|--------------|---------------------|
| Type I       | Algal material      |
| Type II      | Spores and pollen, phytoplankton, cuticles |
| Type III     | Homogeneous AOM, phytofossil detritus |
| Type IV      | Coiled material     |

![Fig. 9. Total organic carbon (TOC) model from deposition to analysis. Subscripts 'o' and 'pd' indicate original and present day estimates respectively. The parameters generative organic carbon (GOC) and non-generative organic carbon (NGOC) are defined following Jarvie (2012, 2015).](image)
heterogeneous AOM. This provides an estimate of the abundance of highly fluorescent AOM. The remainder of the fraction of hetero-
genous AOM was regarded as Type II kerogen. It is possible that this fraction of low fluorescing, heterogeneous AOM was formed through bacterial modification of plant material, a class which other authors (Horsfield, 1984; Cooper and Barnard, 1984; Tyson, 1995) also tabulated under Type II kerogen. The HIo equation of Jarvie et al. (2007):

\[
HIo = \left( \frac{\% \text{ Type I}}{100} \times 750 \right) + \left( \frac{\% \text{ Type II}}{100} \times 450 \right) + \left( \frac{\% \text{ Type III}}{100} \times 27.6 \right)
\]

The HIo results from the Carsington DR C3 Borehole are summarized in Table 3.

Using the HIo, the original TOC (TOCo) can be calculated following Jarvie (2012):

\[
TOCo = \frac{TOC_{pd} - \left( 0.085 \times \left( S1_{pd} + S2_{pd} \right) \right) - (HIo \times 0.0008)}{(1 - HIo/1177)}
\]

Overall, the samples of Carsington DR C3 have an average HIo of 409 mg/g TOCo and an average TOCo of 2.28% (Table 3). The geochemical trends observed from HIpd and TOCpd measurements are maintained. Downhole, the E2b1–E2a interval shows higher HIo and TOCo values (465 mg/g TOC and 3.20% respectively) compared to the remainder of the E2a interval (396 mg/g TOC and 1.04% respectively).

The HIo and TOCo results from the Karenight 1 Borehole are shown in Table 4. Both HIo and TOCo show a similar pattern as the present day values obtained by analysis and shown in Fig. 6. The average HIo value in the Karenight 1 Borehole is relatively stable throughout: 352 mg/g TOCo (479 mg/g TOCo) 607 mg/g TOCo. The upper part of the studied section (242.48–243.77 m) shows lower HIo and TOCo values averaging 448 mg/g TOCo and 4.43% respectively. The lower part of the section (251.89–242.48 m) shows an average HIo of 504 mg/g TOCo with an average TOCo of 9.34%. The interval from 243.67 to 245.50 m is notable in that it is characterized by a relatively high average TOCo of 12.11%.

5.3. Mineralogy, clay content and maturity

The XRD results are plotted as a ternary diagram with carbonates, clay and silicates as end members with the results of similar analyses from producing North American shale reservoirs (Fig. 8) and the ductile-brittle transition zone from Anderson (2014). Jarvie (2012) suggests a clay content <35%, a silicate content exceeding 30% with some carbonates and the presence of non-swelling clays is required to enable hydraulic fracturing. This is again based on observations from the Barnett Shale and there are examples of productive shales with higher clay contents (e.g. Sone and Zoback, 2013). Indeed, even plastic clays will hydrofracture if the pressurization rate is high enough (Cuss et al., 2015).

The upper part of the Carsington DR C3 borehole (18.44–27.60 m) is dominantly a siliceous mudstone with a variable carbonate content (up to 24%). On average, these samples contain
28% clay minerals. In contrast, the lower part of Carsington DR C3 (27.60–55.46 m) is generally carbonate-free and higher clay content (57% on average). Hence, this interval is considered an argillaceous mudstone.

The upper part of the Karenight 1 borehole (236.07–241.39 m) consists of argillaceous and siliceous mudstones with a considerable carbonate content (maximum 49%) and a relatively high clay content (25–55%). Calcite is most commonly developed with the exception of SSK59376 (236.07 m) which has a dolomitic content of 85.8%. The lower part of Carsington 1 (246.11–250.80 m) consists of siliceous and argillaceous mudstone with a low carbonate content (maximum 10%) and a clay content 32–58%.

These results indicate the high variability of the mudstone mineralogy in both the Widmerpool and Edale gulfs. The same subdivisions that became apparent in the geochemical parameters (Figs. 5 and 6) are reflected in the XRD analyses. A knowledge of the clay mineralogy of these mudstones is important in determining their potential engineering behaviour (Jarvie, 2012). No discrete smectite, the most common high shrink-swell clay mineral, was identified in either of the borehole intervals examined. However, the ubiquitous presence of R1-ordered I/S (80% illite, 20% smectite) should be noted and influence the design of any hydraulic fracture programmes.

In addition, clay minerals can also provide a geothermometer for comparison with more traditional organic maturation indices, as illustrated by the Basin Maturity Chart of Merriman & Kemp (1996). The consistent presence of R1-ordered I/S (80% illite, 20% smectite) in borehole intervals suggests burial temperatures of ~100 °C and places the formation in the late (or deep) diagenetic metapelitic zone, equivalent to burial of perhaps 4 km at normal geothermal gradients (~25 °C/km). In terms of hydrocarbon zones, the clay data suggest light oil maturity. This is consistent with the acquired Rock-Eval™ parameters for both studied intervals. The Tmax values in the Carsington DR C3 interval remains constant around 430–440 °C (Fig. 5), showing a uniform maturity near the bottom of the oil window (435–470 °C). Only the sandstone interval between 33.50 and 34.75 m shows a drop in Tmax to 366 °C. The bulk organic matter in this interval is from a distinctively different origin than the rest of the interval: sample SSK45647 at 33.63 m has the lowest recorded HI and a low FS of 2.

### Table 4

| BGS Sample | Depth (m) | Hl (mg/g) | HFO (mg/g) | TOC (%) | TOC cr (mg/g) | FSI | Type I | Type II | Type III | Type IV |
|------------|----------|-----------|------------|---------|--------------|-----|-------|--------|----------|--------|
| SSK46364   | 234.80   | 3.01      | 2.41       | 3.84    | 1.43         | 1.75| 22.46 | 56.88  | 11.00    | 0.33   |
| SSK46366   | 235.38   | 4.00      | 2.83       | 4.74    | 1.90         | 2.16| 29.46 | 52.54  | 12.67    | 0.00   |
| SSK46369   | 235.98   | 4.46      | 3.53       | 6.02    | 2.49         | 1.44| 21.96 | 70.37  | 4.00     | 0.00   |
| SSK51175   | 236.70   | 3.83      | 3.13       | 4.76    | 1.62         | 1.42| 15.61 | 56.05  | 27.00    | 0.33   |
| SSK51178   | 237.59   | 3.07      | 2.25       | 3.83    | 1.59         | 2.85| 36.29 | 43.05  | 17.33    | 0.00   |
| SSK51180   | 237.90   | 3.84      | 2.49       | 2.91    | 0.95         | 1.77| 11.95 | 49.41  | 24.67    | 0.33   |
| SSK51182   | 238.46   | 4.48      | 3.23       | 5.29    | 2.06         | 2.16| 28.61 | 50.73  | 12.33    | 0.00   |
| SSK51184   | 238.86   | 4.48      | 3.11       | 5.44    | 2.33         | 2.58| 36.12 | 48.21  | 13.67    | 0.00   |
| SSK51186   | 239.40   | 2.10      | 1.44       | 2.36    | 0.92         | 2.48| 31.52 | 45.48  | 15.67    | 0.33   |
| SSK51388   | 239.80   | 5.70      | 4.00       | 7.28    | 3.28         | 3.34| 45.53 | 37.81  | 16.00    | 0.00   |
| SSK51390   | 240.39   | 4.88      | 3.23       | 3.90    | 1.58         | 3.14| 37.49 | 38.51  | 19.67    | 0.00   |
| SSK51392   | 240.93   | 3.30      | 2.41       | 3.57    | 1.16         | 1.34| 18.88 | 54.85  | 19.33    | 1.00   |
| SSK51194   | 241.39   | 4.70      | 3.43       | 5.37    | 1.94         | 1.51| 18.77 | 56.56  | 24.33    | 0.00   |
| SSK51197   | 242.15   | 1.65      | 1.13       | 1.74    | 0.61         | 1.58| 18.81 | 54.85  | 19.33    | 1.00   |
| SSK51200   | 242.80   | 4.74      | 3.54       | 5.40    | 1.86         | 1.46| 16.91 | 55.09  | 26.00    | 0.00   |
T$_{\text{max}}$ variations in this instance can be attributed to the origin of the organic matter rather than a change in maturity. In the Karenight 1 core, T$_{\text{max}}$ averages 435 °C and remains in the narrow interval 424–445 °C over the entire studied interval, averaging 435 °C. There is an increase of about 10 °C in T$_{\text{max}}$ occurring around 245.70 m below the lowest occurrence of visible plant material in the core. The lithological composition, the fossil content and the occurrence of some of the most negative δ$^{13}$C$_{\text{OM}}$ values (see Section 5.4) all point to a more marine depositional environment. Therefore we attribute the minor change in T$_{\text{max}}$ at 245.70 m to the nature of the organic matter rather than to a change in maturity.

5.4. Organic matter δ$^{13}$C$_{\text{OM}}$

Peters-Kottig et al. (2006) investigated long and short term variations in δ$^{13}$C$_{\text{OM}}$ that occur in land plant organic matter in the late Palaeozoic. The rise of land plants during the Carboniferous and the Permian has been related to the drawdown of atmospheric CO$_2$ and the initiation of glacial episodes (Kump et al., 2000). This is linked to the rise in importance of lycophytes during the Serpukhovian (Cleal and Thomas, 2005); these plants were very efficient carbon sinks, large in size and they possessed photosynthetic leaf cushion covered stems and leaves (Phillips and diMichele, 1990; Thomas, 1978). Carbon burial during the late Mississippian was exacerbated by the widespread lignin production since the late Devonian (Robinson, 1990), leading to increased burial of organic matter resulting in a further CO$_2$ drawdown and a large pO$_2$ peak around 300 Ma and thus a lower δ$^{13}$C$_{\text{OM}}$ signature of the plant material as the Mississippian advanced (Berner et al., 2000) to values of around −25‰ (Peters-Kottig et al., 2006). Even though extant marine plants are generally characterized by higher δ$^{13}$C$_{\text{OM}}$ values than land plants (Craig, 1953; Silverman and Epstein, 1958), δ$^{13}$C$_{\text{OM}}$ measurements of marine kerogen are generally lower than terrestrial kerogen (e.g. Newman et al., 1973). This was confirmed for Mississippian shales of the Appalachian Basin where terrigenous organic matter has δ$^{13}$C$_{\text{OM}}$ of −26 to −25‰ while the δ$^{13}$C$_{\text{OM}}$ of the marine organic matter is around −30‰ (Maynard, 1981). Lewan (1986) evaluated δ$^{13}$C$_{\text{OM}}$ values of amorphous kerogens in Phanerozoic sediments and distinguished ‘h’ amorphous kerogens (−24 to −26‰) from ‘t’ amorphous kerogens (−35 to −26‰). Phytoplankton residing in environments with well-circulated water masses dominated by atmospheric-derived CO$_2$ will yield ‘h’ amorphous kerogen while ‘t’ amorphous kerogens were more likely formed in more restricted basins overlain by relatively shallow, well-stratified water masses where carbon in the photic zone is sourced from recycled organic material (Lewan, 1986).

These principles can be applied to the Mississippian deposits of the Pennine Basin, where the kerogen fraction is dominated by AOM (Figs. 5–7, Appendix 1–2). The contrasting δ$^{13}$C$_{\text{OM}}$ values between terrestrial and marine kerogen can be used to delimit marine and non-marine intervals. Stephenson et al. (2008, 2010) showed that the bulk δ$^{13}$C values of the mixed marine-terrestrial sequence in the Throckley and Rowland Gill boreholes is a function of the ratio marine:terrestrial δ$^{13}$C$_{\text{OM}}$. Similarly, Könitzer et al. (2014), demonstrated the influences of microfacies, organic matter source and biological activity in a cross plot of δ$^{13}$C$_{\text{OM}}$ and TOC for deposits of the Carsington DR C4 Borehole, which covers the same stratigraphic interval considered in the current study. In Fig. 10 the Karenight 1 and Carsington DR C3 δ$^{13}$C$_{\text{OM}}$ and TOC values are shown. The lower part of the Carsington DR C3 core, corresponding to the E$_{2a}$ biozone contains the lowest TOC and variable δ$^{13}$C$_{\text{OM}}$ values. The highest δ$^{13}$C$_{\text{OM}}$ values correspond with intervals where sandstone and siltstone, most likely deposited as turbiditic flows in the Widmerpool Gulf (Könitzer et al., 2014), carried more terrestrial sourced organic matter in the basin: around 54 m, 41–44 m, 34 m and 31 m. The isotope signature of the interpersed mudstones is lower and more marine-derived organic matter is incorporated in these sediments. The upper part of the Carsington DR C3 (biozones E$_{2a3}$ and E$_{2b1}$) shows the influence of increased marine

Fig. 10. Organic matter δ$^{13}$C versus TOC$_{\text{org}}$ values for Carsington DRC3 (black) and Karenight 1 (red) samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
There are two outliers: at 20.10 m a limestone (SSK45591) has the lowest recorded $\delta^{13}$C$_{\text{OM}}$ value ($-30\%$) combined with the lowest TOC value (0.32%). Limestone is characterized by a very low kerogen content and due to the depositional environment, what little kerogen there is, consists almost entirely of marine sourced organic matter. The other outlier is sample SSK45602 which has a relatively high $\delta^{13}$C$_{\text{OM}}$ value of $-25\%$. Despite the marine character of the lithology (silty mudstone), some plant fossils were recovered (Fig. 5) from the interval which could explain the terrestrial nature of the $\delta^{13}$C$_{\text{OM}}$ signal. The lower part of the Karenight core (242.80–251.89 m) displays the lowest $\delta^{13}$C$_{\text{OM}}$ combined with the highest TOC values, reflecting the marine influence in this part of the section. The upper part contains a mix of marine derived kerogen, around 237–238 m and 240 m, interspersed with intervals containing more terrestrial-derived kerogen, 236–237 m. Relatively, the Karenight 1 samples contain a higher abundance of marine kerogen compared to the Carsington DR C3 samples.
5.5. The prospectivity of the Arnsbergian (late Mississippian) shales of the Widmerpool and Edale Gulf

During the Mississippian (359–323.2 Ma) the Pennine Basin was located close to the equator, proximal to Laurussia with Gondwana stretching to the South Pole (Mckerrow and Scotese, 1990) and it was bordered by two emerging land masses; the Southern Uplands to the north and the Wales-Brabant High to the south (Fig. 1). Because of its position, ice sheets were likely to persist on Gondwana (Isbell et al., 2003) which influenced the sedimentation history in the patchwork of sub-basins forming the Pennine Basin (e.g. Stephenson et al., 2010). These sea level fluctuations most likely exerted less of an impact on the contemporaneous Upper Barnett Shales (Fig. 3), deposited in the much more distally located Fort Worth Basin and one of the world’s most prolific shale gas plays with an estimated resource of 43 tcf (U.S. Energy Information Administration, 2011), than the mudstones considered in the current study.

The Fort Worth Basin was formed as a foreland basin in response to the collision of North and South America during the formation of Pangea (Walper, 1982) and its more distal position means the five lithofacies that are generally recognized in the Barnett Shale — i.e. black shale, lime grainstone, calcareous black shale, dolomitic black shale and phosphatic black shale (Loucks and Ruppel, 2007; Montgomery et al., 2005; Pollastro, 2003) — lack the turbidites that were encountered in the Carsington DR C3 core and the siltstones in the Karenight 1 core of the current study and indeed in most of the Namurian cycles in the Pennine Basin (Aitkenhead et al., 2002; Andrews, 2013). The more continuous nature of marine deposits of the Fort Worth Basin compared to the mudstone and turbidite successions of the Pennine Basin, reflects the respective position of both basins: the glacio-eustatic sea level fluctuations most likely exerted less of an impact on the contemporaneous Upper Barnett Shales deposited in the much more distally located Fort Worth Basin, than the mudstones considered in the current study. Most of the prospectivity criteria that were used to evaluate the Namurian shales from the UK, summarized in Table 1, are based on observations from the Barnett Shale (see also Andrews, 2013; Jarvie, 2012).

5.6. Carsington DR C3

The Carsington DR C3 samples cover the E2a, E2a3 and E2b1 marine bands (Fig. 5). The lower part of the studied interval corresponds to the E2a marine band below E2a3. The TOCpd of the mudstones of this interval is comparatively low (2% on average). There is variation in the TOCpd with some intervals (32.50–34.50 m and 40.5–44 m) characterized by a low TOCpd while some intervals (for example, around 37 m and 47–50 m) have a TOCpd that surpasses 2.5%. However, the pyrolysable content of none of these samples surpasses the 2% constraint that is required for an unconventional gas reservoir (Andrews, 2013; Gilman and Robinson, 2011; TNO, 2009). The kerogen fraction contains a high calculated average of 70% Type II (Table 3), with an important contribution (7.8%) of Type III organic matter. The HI reaches an average of 174 mg/g TOC while the HI reaches an average of 468 mg/g TOC falling in the prospective window of 250–800 mg/g TOC defined by Jarvie (2012) with an associated TOC of 2.28% on average. It should be noted that there is a considerable amount of variability in the TOC values throughout, with a minimum of 0.46% (SSK45632 at 30.89 m) and a maximum of 4.79% (SSK46019 at 37.10 m). The XRD analyses show there is a very low amount of carbonate contained in the lower part of Carsington DR C3 and a highly variable amount of silicates. Most samples are considered as argillaceous mudstones while three samples contain enough silicates to be classified as siliceous mudstones (Fig. 8).

The upper part of Carsington DR C3 (18.44–27.60 m) covers the E2a3 and E2b1 bands which together correspond to an important transgression (Trewin and Holdsworth, 1973; Waters and Condon, 2012). The TOCpd averages 3.5% (n = 27) and TOC exceeds 3.44% (n = 4). In both instances these values surpass the 2% limit set as a criterion for organic matter content that defines an unconventional play (Andrews, 2013; Gilman and Robinson, 2011; TNO, 2009). However, when the reactive, pyrolysable carbon content representing the generative part of the kerogen fraction is considered, no samples surpass the 2% boundary. Assigning AOM to a kerogen Type I is tentatively done by utilizing the autofluorescence properties of the kerogen fraction (Section 5.2). Kerogen Types II and III are better constrained by transmitted white light observations and average 62% and 1.8% respectively. This shows marine organic matter dominates over terrestrial organic matter which is significantly lower than the lower part of the section. The HI index averages 532 mg/g TOC and is well above the 250 mg/g TOC constraint (Charpentier and Cook, 2011; TNO, 2009) and falls in the 250–800 mg/g TOC interval suggested by Jarvie (2012). The siliceous mudstones contain variable amounts of carbonate (up to 24%) and one sample (SSK44595 at 22.99 m) has a low silica and carbonate content plotting in the ductile to brittle transition zone (Fig. 8). No discrete smectite was identified in the sampled Carsington DR C3 interval, as required by Jarvie (2012) (Appendix 8). Both mineralogy and T_max values indicate however that the studied material is immature for gas generation (Section 5.3).

5.7. Karenight 1

The studied section of the Karenight 1 core covers the E1 (Pendleian) to E2 biozone transition (Fig. 6). The lower part of the section (242.80–251.89 m) is dominated by mudstone with subordinate and interspersed limestone intervals. All samples of the lower part of Karenight 1 surpass 4% TOC with an average of 6.9%. When the pyrolysable carbon of TOCpd is considered however, the average TOCpd is 1.5% and only three samples pass the 2% threshold (Appendix 3). The organic matter mostly consists of heterogeneous AOM (80.5% on average) with an average calculated 17.4% of Type II (Table 4) and 1.3% Type III reflecting the very limited influx of terrestrial sourced AOM, also reflected in the low δ13C_Om values. The HI reaches an average of 554 mg/g TOC with TOC exceeding 9.92%. These values fall in the prospectivity window described by Jarvie (2012). XRD analysis of the bottom part of Karenight 1 shows that the lithology varies from argillaceous to siliceous mudstones, but all samples have a silica content over 30% (Appendices 6 and 8).

The upper part of the Karenight 1 core (234.77–242.80 m) covers the E2b1 biozone, possibly containing evidence of the E2b1 Marine Band around 241.50 m. The TOCpd values are less than in the lower part of the core (3.68%) and the kerogen fraction is composed of 78.6% heterogeneous AOM, a calculated average of 67% Type II kerogen (Table 4) and 2.7% Type III kerogen. Again, these values combined with the relatively light carbon isotopic signature show the dominance of marine conditions. The somewhat higher average values of Type III kerogen show the influence of terrestrial matter which is associated with the presence of siltstone intervals (Fig. 6). The average calculated H_I is somewhat lower than the bottom part of the section (500 mg/g TOC) while TOC is significantly lower (4.89%). These values are still within the constraints of the prospectivity criteria (Table 1). The upper part of the section contains a highly variable amount of carbonates but all samples have a silicate content that surpasses the 30% threshold (Fig. 8). No discrete smectite was identified in the sampled Karenight 1 interval (Appendix 8) as for Carsington DR C3, the mineralogy and T_max values indicate that the Karenight 1 material is immature for gas generation.
5.8. Implications for the prospectivity of Arnsbergian shales in the southern part of the Pennine Basin

The Arnsbergian mudstones from the Morridge Formation in the Widmerpool and Edale Gulf proved by the Carsington DRC 3 and Karenight 1 boreholes were deposited coeval with active unconventional exploration targets in the Craven and Bowland Basins and the Upper Barnett Shales from the Fort Worth Basin (USA) (Fig. 3). Karenight 1 contains more marine organic material and is characterized by higher FSI (Fig. 5), TOCpd, TOC0 and HI0 values than Carsington DR C3 (Tables 4 and 5), which exhibits frequent sandstone intervals and a higher fraction of kerogen Type III. The terrestrial material in the Morridge Formation originates from the Wales-Brabant High to the south of the Pennine Basin (Trewin and Holdsworth, 1973; Waters et al., 2009). Therefore, we hypothesise that when turbiditic flows entered the Pennine Basin sourced from the Wales-Brabant High to the south (Fig. 1), most of the terrestrial material was deposited in the Widmerpool Gulf. The remnant of the south-eastern part of the Derbyshire High, located between Carsington DR C3 and Karenight 1 during the Arnsbergian represents a barrier to sediment input from the north into the Edale Gulf, resulting in the deposition of only a relatively small fraction of these sediments with a terrigenous character at Karenight 1. However, even in the intervals of Carsington DR C3 that are characterized by a terrestrial signature (e.g. 33.63 ± 3.35 m and 40.50 ± 4.44 m), marine influences are noticeable: Type II kerogen remains important in the palynofacies counts and δ13C_Om exceeds −24‰. This suggests a continuous sedimentation of marine-derived material, punctuated by influxes of terrestrial material from the Wales-Brabant High diluting the marine deposits. This means that prospective intervals in both the Widmerpool and Edale Gulf are relatively thin (decimetre to metre scale) and consequently high resolution characterization of these intervals is required in future research to quantify reservoir fairways. Given the high diversity of spores recovered from both cores (Appendices 1 and 2), a comprehensive, quantitative re-evaluation of the spore biozonation from these intervals on a metre-to decimetre-scale (i.e., at a higher resolution than typical goniatite marine band cyclicity), may aid in the identification of the prospective intervals.

The work flow employed in the current study (Rock-Eval, stable isotope, XRD, epifluorescence, palynofacies analysis) gives a complete assessment of the organic matter of potentially prospective shale gas plays. This approach allows for a calculation of HL0 and TOC0 which give a more meaningful evaluation of prospectivity estimates. In this way, we show that the most prospective part of the Carsington DRC3 borehole is the E2b1–E2a3 with a HL0 of 465 mg/g TOC0 and TOC0 of 3.2% while for the Karenight 1 borehole the most prospective part is the E1(?)–E2a3 interval with an average HL0 of 504 mg/g TOC0 and TOC0 of 9.3%. In Table 5, these values are compared with the top 10 shale gas systems as reported by Jarvie (2012). The most prospective intervals of both the Carsington DRC3 and the Karenight 1 boreholes have HL0 and TOC0 values that are comparable to the contemporaneous US shales. The least prospective intervals from the Carsington DRC3 core have values that are well below the contemporaneous US shales, most likely reflecting the higher amount of terrestrial material with on average 30.3% Type III kerogen. For the Barnett Shale, kerogen Type II with a minor admixture of Type III (Bruner and Smosná, 2011) has been reported. Though no actual palynofacies counts were cited, Jarvie et al. (2007) use a 95% Type II and 5% Type III for their calculation of HL0 for the Barnett Shale.

6. Conclusions

We investigated Namurian (late Mississippian) mudstones from two boreholes drilled in the southern part of the Pennine Basin (UK): the Carsington Dam Reconstruction C3 borehole from the Widmerpool Gulf and the Karenight 1 borehole from the Edale Gulf. Both prove mudstone-dominated intervals of Arnsbergian (Serpukhovian) age, with the Carsington DR C3 borehole comprising the E2b1–E2a3 marine bands, while the Karenight 1 borehole the E2b and E1 marine bands. We describe a fully integrated, multi-proxy approach to describe the geochemical, palynological and sedimentological properties:

Heterogeneous AOM dominates the E2b1–E2a3 samples in the Carsington core with important contributions of Type II kerogen and only minor amounts of Type III kerogen. The E2a3 interval below E2a3 averages respectively 465 mg/g TOC0 and 3.2%. For E2a3 below E2a3, HL0 averages 396 mg/g TOC0 and TOC0 1.0%. Carsington DR C3 contains mainly siliceous mudstones with a variable carbonate content, while the Karenight 1 borehole the E2b1 and E1 marine bands. We describe a fully integrated, multi-proxy approach to describe the geochemical, palynological and sedimentological properties.

Table 5

| US Shales (Jarvie, 2012) | (Sub)System | HL0 (mg/g TOC0) | TOC0 (%) |
|-------------------------|-------------|----------------|----------|
| Barnett                 | Mississippi | 434            | 6.27     |
| Fayetteville            | Mississippi | 404            | 6.32     |
| Woodford                | Devonian    | 503            | 8.95     |
| Bossier                 | Upper Jurassic | 419     | 2.75     |
| Haynesville             | Upper Jurassic | 722     | 5.05     |
| Marcellus               | Devonian    | 507            | 7.83     |
| Muscovia                | Devonian    | 532            | 3.62     |
| Montney                 | Triassic    | 354            | 3.27     |
| Utica                   | Ordovician  | 379            | 2.23     |
| Eagle Ford              | Upper Cretaceous | 411     | 4.63     |

| United Kingdom (this study) | (Sub)System | HL0 (mg/g TOC0) | TOC0 (%) |
|-----------------------------|-------------|----------------|----------|
| Widmerpool Gulf (E2a3–E2a1) | Mississippi | 465            | 3.2      |
| Widmerpool Gulf (E2a below E2a3) | Mississippi | 396 | 1.0      |
| Edale Gulf (E2a–E1)         | Mississippi | 448            | 4.4      |
| Edale Gulf (E1)             | Mississippi | 504            | 9.3      |
H₄ and TOC₃ are within the limits of known producing plays (Tables 1 and 5). However, the XRD results and Tₘₐₓ values suggest the Namurian deposits of the Widmerpool Gulf are too immature for gas generation.

The Karenight 1 core samples are dominated by heterogeneous AOM throughout while Kerogen Type II is also important and Type III kerogen is of minor importance. TOC₃ surpasses 2% in 68 of 72 considered samples, however when the pyrolysable carbon content is considered, only 3 samples surpass 2%. In the bottom part of Karenight 1 (242.80–251.89 m) H₄ averages 504 mg/g TOC₃ with a TOC₃ of 9.3% while in the top part (234.77–242.80 m) H₄ averages 448 mg/g TOC₃ with a TOC₃ of 4.4%. In the Karenight 1 core we find carbonate poor siliceous and argillaceous mudstones in the bottom part and mudstones with a markedly higher carbonate content in the top part. The clearest marine intervals (lowest δ¹³C) are high with high TOCPd occur in the lower part of Karenight 1 yielding some of the most organic rich Namurian deposits in the Pennine Basin. As for the Namurian deposits in the Widmerpool Gulf, the Namurian strata in the Edale Gulf have organic contents combined with hydrogen indices that fall well within the limits of known shale gas plays, but Tₘₐₓ suggests the deposits are immature for gas.

The terrestrial material that enters the southern Pennine Basin likely originates from the Wales Brabant High and therefore we conclude that most of the terrestrial material was deposited in the Widmerpool Gulf as turbidite flows and only a relatively small fraction reached the Edale Gulf, resulting in a more marine character in the Karenight 1 core. However, there is still a considerable amount of kerogen Type II in Carsington DR C3, even in intervals with a terrigenous sedimentary signature. This points to continuous marine conditions across the southern part of the Pennine Basin, at times diluted by turbidite deposits, most likely related to. Because of this, the intervals prospective for hydrocarbon generation in especially the Widmerpool Gulf and to a lesser extent in the Edale Gulf, are relatively thin (decimetre to meter scale). Consequently, high resolution characterization, at sub-marine band resolution, of these intervals should be the focus of future research. Quantitative spore analysis and fluorescence microscopy may be of considerable help to achieve this goal given the high diversity of well-preserved spores recovered in the current study.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.marpetgeo.2017.06.033.

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