

1 **UPPER CARBONIFEROUS MUDROCKS, MALTON, YORKSHIRE, ENGLAND**
2 **AND THEIR UNCONVENTIONAL HYDROCARBON POTENTIAL**

3
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12
13 In order to investigate the shale-gas potential of Upper Carboniferous (Namurian) black
14 shales in the upper Bowland-Hodder unit in the Cleveland Basin, Yorkshire (northern
15 England), a cored section from the Malton-4 well was selected for multidisciplinary
16 analysis complemented by geochemical (Rock-Eval pyrolysis and biomarkers) and
17 sedimentological data. The black shales are interbedded with bioturbated and bedded
18 sandstones ("Millstone Grit") and represent offshore-basinal to prodelta lithofacies. The
19 total organic carbon (TOC) content of the black shales ranges from 0.37 to 2.45 wt %.
20 Rock-Eval pyrolysis data indicate that the organic matter is mainly composed of Type II
21 and III kerogen. Tmax (436-454oC), and 20S/(20S+20R) and $\beta\beta/(\beta\beta+\alpha\alpha)$ C29 sterane
22 ratios indicate that organic matter is in the early- to mid-mature stage with respect to
23 hydrocarbon generation. Sedimentological and geochemical redox proxies indicate that
24 the black shales were deposited in periodic oxic-dysoxic and probably anoxic bottom
25 waters with at least episodic oxic conditions, explaining the relatively low TOC values.
26 Deposition of the shales took place in a moderately deep basinal - prodelta setting, and
27 bioturbated sandstones represent prograding delta-front facies. The Rock-Eval parameters
28 suggest that the mudrocks have a limited shale-gas potential and that a shale-oil resource
29 can be ruled out.

30

31 **Key words:** black shale, shale gas, biomarker characterization, organic matter, thermal
32 maturity, hydrocarbon potential, Cleveland basin, Carboniferous, Yorkshire, England.

33

34 **INTRODUCTION**

35

36 Organic-rich black shales are important source rocks and may also serve as seals for
37 conventional oil and gas reservoirs. Recent advances in drilling and completion
38 technology, specifically horizontal drilling and hydraulic fracturing (“fracking”), have
39 made the production of natural gas from shales economic. Shale gas is an unconventional
40 gas-system in which the shale is both the source of, and reservoir for, natural gas [Jarvie,
41 2012]. The gas is derived from the organic matter within the shale as a result of biogenic
42 and/or thermogenic processes.

43

44 In the USA, annual shale-gas production reached 7.85 tcf in 2011, approximately 34% of
45 dry gas production (www.eia.gov). Major gas-producing shales in the USA are organic-
46 rich (total organic carbon, TOC = 0.45 – 25 %), early mature to highly overmature
47 (vitrinite reflectance, $R_r = 0.4 - 3.4$ %) and buried to variable depths (150 - 3350 m)
48 (Jarvie, 2012). As shale is the most abundant sedimentary rock on Earth, shale gas
49 resources have also been investigated in other countries [e.g. Boyer et al., 2011; Jarvie,
50 2012]. In addition, liquid oil (“tight oil”) may also in theory be extracted from organic-
51 rich shales, whose poroperm properties prevent the oil from escaping.

52

53 Gas shales and tight-oil shales have a higher potential for commercial hydrocarbon
54 production if the shales contain significant proportions of brittle framework grains such
55 as quartz and feldspar (~>30%) and also carbonate, rather than being dominated by clay
56 minerals (Bunting and Breyer, 2012; Jarvie, 2012). The presence of brittle grains allows
57 the shales to be fractured more easily during reservoir development operations.

58

59 In the UK, organic-rich shales of Cambrian to Jurassic ages, deposited in marine,
60 transitional marine and lacustrine settings, are widely distributed. Smith et al. (2011)
61 described Lower Palaeozoic shale basins on the English Midland microcraton, Lower

62 Carboniferous (Mississippian) shales in the Central Pennine Basin, and Upper
63 Carboniferous (Pennsylvanian) shales in the Stainmore and Northumberland basins.
64 These authors concluded that the Mississippian Hodder Mudstone Formation and
65 Bowland Shale Formation (informally referred to as the Bowland –Hodder unit) may
66 constitute the most prospective shale-gas play. Andrews (2013) calculated that the
67 Bowland-Hodder shale-gas play__in north-central Britain may include gas resources
68 totalling 822 to 2281 tcf, although these estimates refer to the volume of gas contained in
69 the shale strata, not the volume of gas which can be recovered. These estimates of gas in-
70 place can be viewed as preliminary in view of the lack of reliable data on gas content and
71 recoverable gas reserves. In addition, incomplete or scarce information on kerogen type,
72 original hydrogen index (HI) values, mineralogy, gas content, porosity and pressure
73 values for the Bowland-Hodder shales make the calculation of recoverable gas reserves
74 uncertain.

75

76 In the present paper, we focus on geological and geochemical analyses of a cored section
77 of the Carboniferous (Namurian) Bowland-Hodder unit_from the Malton-4 well in the
78 Cleveland Basin, northern England (Fig. 1). Based on the results, the shale-gas potential
79 of the cored section is described and evaluated.

80

81 **GEOLOGICAL AND TECTONIC FRAMEWORK**

82

83 During the Carboniferous the UK was situated at low latitudes to the north of the Rheic
84 Ocean. Carbonates and coarse clastics were deposited in extensive shallow seas and
85 deeper-water areas were dominated by mudrocks (George et al. 1976; Waters et al. 2007).
86 The Early Carboniferous (Mississippian) was a time of north-south extension which
87 resulted in a series of positive blocks/platforms (mostly underlain by Caledonian granite)
88 and rapidly subsiding basins. This was followed in the Late Carboniferous
89 (Pennsylvanian) by more regional subsidence and then a phase of compression,
90 culminating with latest Carboniferous -- Early Permian deformation and inversion
91 (Gawthorpe et al., 1989; Fraser and Gawthorpe, 1990).

92

93 In northern England, Fraser and Gawthorpe (1990, 2003) identified a syn-rift
94 megasequence (Upper Devonian to upper Brigantian: EC in Fig. 2), followed by a post-
95 rift megasequence (LC) from the upper Brigantian to the upper Westphalian C. Within
96 these two megasequences, sequences were distinguished based on minor changes in
97 tectonic regime: EC1 through EC6 and LC1 (a/b/c) and LC2 (Figs 2, 3).

98

99 Platform areas in northern England are from north to south the Cheviot, Alston, Askrigg
100 and Market Weighton blocks; these are separated by the Northumberland, Stainmore-
101 Cleveland and Bowland-Craven-Pennine-Leeds basins (Gawthorpe et al., 1989; Dean et
102 al., 2011). In the latest Early Carboniferous (Asbian-Brigantian) to early Namurian
103 (sequences EC4 through LC1a/b), deltas gradually advanced and prograded southwards
104 from the Scottish Borders -- Southern Uplands region, depositing mudrock-sandstone
105 units across shallow-water carbonates (Johnson, 1984; Dean et al., 2011). As a result of
106 orbitally-forced sea-level fluctuations, numerous (~70) Yoredale “cycles” were generated
107 comprising shallow-marine limestone passing up into prodelta mudrock then delta-front
108 and delta-plain sandstones, locally with coals (Tucker et al., 2009). Thinner successions
109 were deposited on the platforms, and thicker, mudrock-dominated successions in the
110 basins.

111

112 In the Cleveland-Leeds basins in NE Yorkshire, shales of the Bowland-Hodder unit were
113 deposited in the Brigantian to early Namurian (EC6-LC1a/b) until the deposition of
114 coarser-grained clastics (“Millstone Grit”) derived from the prograding delta-plain
115 system from the north-NE (Fig. 4) (Johnson, 1984; Dean et al., 2011). The shales in the
116 Cleveland Basin are organic-rich, as shown by the presence of oil-shows and high gamma
117 responses (150-180 API) recorded in the Seal Sands borehole near Hartlepool [locate it
118 in Fig. 1] (Johnson et al., 2011).

119

120 The Malton-4 well was drilled during exploration for gas in the Permian Zechstein in
121 1985, and the Permian-Carboniferous boundary occurs at a depth of 5149 ft (1569.4 m;
122 Fig. 5. Some 17.5 metres of Carboniferous strata were cored and recovered, and the
123 facies are described below. In terms of stratigraphy, the core is probably located in the

124 upper part of the Bowland-Hodder unit (Arnsbergian) within the LC1b sequence of
125 Fraser and Gawthorpe (1990).

126

127 **SAMPLES AND METHODS**

128

129 Five shale core samples from the Upper Carboniferous succession of the Malton-4 well
130 were collected for sedimentological, petrographic and organic geochemical analyses. For
131 SEM, freshly broken surfaces were coated with silver to observe micro- and nano-sized
132 pores in the black shales and also their petrographic composition. A high vacuum and
133 partial vacuum (10Pa - 10⁻⁴Pa) JEOL JSM 5600 LV scanning electron microscope
134 (SEM) was used with a secondary electron detector based on the scintillator-
135 photomultiplier design of Everhardt & Thornley. The SEM was also fitted with a solid-
136 state backscattered electron detector used for compositional and topographical
137 information and energy-dispersive spectrometry (EDS) for elemental analysis.
138 Accelerating voltages between 1 - 30KV were used.

139

140 **Rock Eval pyrolysis/TOC analysis**

141

142 Samples were analysed using a Rock-Eval 6 analyser configured in standard mode
143 (pyrolysis and oxidation as a serial process). Powdered drill-core samples (60 mg /dry wt)
144 were heated from 300°C to 650°C at 25°C/min in an inert atmosphere of N₂ and the
145 residual carbon then oxidised at 300°C to 850°C at 20°C/min (hold 5 min). Hydrocarbons
146 released during the two-stage pyrolysis were measured using a flame ionization detector
147 and CO and CO₂ measured using an IR cell. The performance of the instrument was
148 checked every 10 samples against the accepted values of the Institut Français du Pétrole
149 (IFP) standard (IFP 160 000, S/N1 5-081840). Rock-Eval parameters were calculated by
150 integration of the amounts of HC (thermally-vaporized free hydrocarbons) expressed in
151 mg/HC/g rock (S1) and hydrocarbons released from cracking of bound OM expressed in
152 mg/HC/g rock (S2) (Engelhart et al., 2013). The Hydrogen Index (HI) was calculated
153 from S₂ x 100/TOC and the Oxygen Index (OI), S₃ x 100/TOC. However comparative
154 analyses of shales and extracted kerogens by Rock-Eval 6 versus an acid washed /

155 elemental analyzer (Leco SC-444) suggested that although there was a strong overall
156 correlation ($r^2 = 0.95$), the former method slightly underestimates whole rock TOC
157 (Behar et al., 2001).

158

159 **Biomarker Characterisation**

160 Gas chromatography (GC) and gas chromatography – mass spectrometry (GC-MS)
161 analyses were conducted on extracts obtained from the five samples. Powdered (20 g)
162 core samples were extracted using a Soxhlet apparatus with 200 ml
163 dichloromethane:methanol (9:1, v/v) for 24 h; copper was added to the round-bottomed
164 flask to remove elemental sulphur. Aliquots of total lipid extract were separated into
165 polar and apolar fractions using a column with activated silica gel (230-400 mesh, 4 cm,
166 bottom). Elution proceeded with 3 ml hexane (saturated fraction),
167 hexane:dichloromethane (3:1, v/v; aromatic fraction), and 5 ml methanol (polar fraction),
168 respectively.

169

170 1 μ l aliquots of each fraction were analysed by GC using a Hewlett Packard Series II
171 5890 instrument, fitted with an on-column injector and a capillary column with a CP
172 Sil5-CB stationary phase (60 m x 0.32 mm, $df = 0.10 \mu\text{m}$). Detection was achieved with
173 flame ionisation (FID) with helium as the carrier gas. The temperature programme
174 consisted of three stages: 70-130 °C at 20 °C per min rate; 130-300 °C at 4 °C per min;
175 and 300 °C at which the temperature was held for 10 min. GC-MS analyses were
176 performed using a ThermoQuest Finnigan Trace GC-MS fitted with an on-column
177 injector and using the same column and temperature programme as for GC analyses. The
178 detection was based on electron ionization (source at 70 eV and scanning range 50-580
179 Daltons), and compounds were identified by comparison of retention times and mass
180 spectra to the literature.

181

182 **RESULTS AND DISCUSSION**

183 **Sedimentology**

184

185 The 17.5 m core consists of shales and sandstones; apart from a 0.6 m section, the core is
186 virtually complete (Fig. 5). Four major lithofacies can be distinguished: (i) mudrock, (ii)
187 sandy mudrock, (iii) bioturbated sandstone and (iv) “massive” sandstone. These
188 lithofacies are arranged into several packages.

189

190 The *mudrock* lithofacies ranges from mudstone to siltstone, and from laminated and
191 fissile shale to blocky and massive mudstone. “Poker-chip” shale with a weak lamination
192 (the name refers to its fissility) also occurs. The colour is in general black although some
193 layers are dark grey. Lamination is at a mm-scale (Fig. 6a) and is defined by sub-mm
194 partings of clay, organic matter and muscovite. The laminae are composed of silt-sized
195 quartz grains, well-sorted with an average grain-size of 20 µm. Organic matter is present
196 as lamina-parallel and impersistent streaks and along stylolite seams. Pyrite crystals and
197 framboids are common. Burrows are mostly absent, although local ovoid and elongate
198 patches of clay-rich, silt-poor sediment are probably small burrow fills (Fig. 7). More
199 massive mudrocks are non-laminated. From thin-section the typical composition of the
200 shales is 60% clay matrix, altered feldspar and other grains, 30% quartz silt grains, 5%
201 mica (mostly muscovite) and 5% opaque grains and dark streaks (pyrite crystals and
202 framboids, and organic matter which can be distinguished in reflected light) (Fig. 8).
203 Pellets of clay, 10 microns in diameter and commonly flattened, were observed. In the
204 core, the mudrocks form units up to 5 m thick.

205

206 SEM examination together with EDS of the shale indicates the presence of quartz, clay
207 minerals, pyrite and organic matter (Fig. 9). Although some plucking of grains is likely to
208 have occurred, pores are clearly observed within and between clay flakes, within the
209 organic matter, and between silt grains (Figs 8a-c, 9). Micron-sized pyrite framboids are
210 common and some porosity is present between crystallites (Fig. 8d, 9a). XRD analysis of
211 the mudrocks indicated that quartz is dominant in some samples, and that chlorite and
212 illite are present in variable quantities. Muscovite is also present.

213

214 *Sandy mudrock* was present as a minor component and consists of planar- and cross-
215 laminated thin beds of quartz silt to fine sand within the dark mudrock. One 5 cm thick

216 unit of fine sand may be a storm bed or tempestite (Fig. 6b). Cm-size sand-filled
217 *Planolites*-type burrows are common within dark grey-black mudrock. The sandy
218 mudrock units are mostly less than 20 cm in thickness and are in general transitional
219 between black mudrock and lighter-coloured sandstone.

220

221 *Bioturbated sandstone* is fine to medium-grained, sometimes with a low mud content (up
222 to ~20%) present as streaks and wisps associated with burrow structures (Fig. 6c,d). The
223 sandstones are characterised by well-developed trace fossils as well as more vague
224 bioturbation structures. *Ophiomorpha* tubes 1-2 cm in diameter and filled with sand are
225 present and are lined by clay, 1-2 mm thick. *Thalassinoides* are larger nodular structures,
226 2-3 cm in diameter, with vague internal laminae (Fig. 6c). Both *Ophiomorpha* and
227 *Thalassinoides* are probably the result of burrowing by crustaceans. Some bioturbated
228 areas have curved, convex-up closely stacked clay laminae, up to 3 cm across, and are
229 interpreted as burrows due to the activity of bivalves such as *Pelecypodichnus* and
230 *Lockeia* (Fig. 6d). Simple *Planolites* burrows have a weak internal structure, cm-thick
231 curved and cross-cutting, and are oriented horizontally across the core (Fig. 6d).

232

233 “*Massive sandstones*” are cream to white in colour and in the cut, but unpolished core
234 appears structureless or has only faint lamination/bedding. Cross- and planar- bedding
235 and bioturbation may be present but these features are difficult to resolve. Some sharp
236 surfaces are present indicating erosion and scour. Units of this facies are up to 1 m thick.

237

238 **Facies stacking and interpretation**

239

240 Two coarsening-upward units can be recognised in the core studied (Fig. 5). In the lower
241 part of the core (1586-1579 m depth), ~5 m of mudrock with “poker chip” facies passes
242 up through sandy mudrock into bioturbated and “massive” sandstone. An overlying unit
243 (1579-1576 m depth) also shows a coarsening-up package into massive sandstone. The
244 upper part of the core mostly consists of bioturbated sandstone and interbedded mudrock.

245

246 The two coarsening-upward packages probably represent prograding delta-front facies,
247 from basinal-prodelta muds through to mouth-bar sands. The black, organic-rich nature
248 of the mudrocks could indicate suboxia-anoxia in a stratified basin as has been suggested
249 for contemporaneous basin facies elsewhere in UK (e.g. Fraser and Gawthorpe, 1990;
250 Andrews, 2013). The sandy mudrocks are shallower-water deposits and the presence of
251 discrete muddy sand beds with planar- and cross- lamination could indicate a storm
252 influence (tempestites) or distal hyperpycnal flows from rivers (Fig. 6b). The bioturbated
253 sand facies indicates intermittent sand supply, allowing sediment reworking by an
254 infauna in a distal to medial mouth-bar setting. The more massive sands are interpreted to
255 have been deposited in a more-proximal higher-energy mouth bar setting, where
256 subaqueous distributary/river-outflow currents and waves reworked the sand. At this time
257 (in the early Namurian), the delta front with distributary channels and bays, shoreline
258 sands and delta-top channels and coal-forming swamps-mires were located some way to
259 the north and NE in the Cleveland Basin, but the delta system was prograding to the
260 south.

261

262 The Upper Carboniferous mudrock facies observed in the studied core is similar to those
263 described from age-equivalent shale-gas formations, including the Barnett Shale
264 (Mississippian, Texas: Abouelresh and Slatt, 2012) and other mud-rich successions (e.g.
265 Plint, 2014, for a Cretaceous pro-delta system).

266

267 **Total organic matter**

268

269 The total organic matter content (TOC % wt/wt) within the Upper Carboniferous
270 mudrocks of Malton-4 ranged from 0.37 to 2.45 % with an arithmetic mean of 1.57 %
271 (Table 1). This mean is influenced by one outlier at 0.37 % obtained from the uppermost
272 part of the succession close to the boundary with the Rotliegend sandstones. In general,
273 TOC values at or greater than 2 % appear to indicate a potentially viable shale-gas
274 resource (Andrews, 2013 and references therein). In addition, the presence of clay
275 minerals may reduce S1 and S2 values in samples with TOC values less than 2.0 %.
276 Therefore, this suggests that the mudrocks from 1570.3-1579.5 m may have potential as

277 an unconventional shale-gas resource, whereas samples at 1569.4 and 1583.1 m fall
278 below the TOC threshold. Overall, the potential for shale gas is based upon just one
279 sample and that higher resolution sampling for Rock-Eval analysis is required before a
280 definitive conclusion can be drawn.

281

282 The low TOC values in the upper part of the latter thickness range may be due to the
283 post-depositional, early-diagenetic aerobic oxidation of sedimentary organic matter,
284 known as burn-down (Kodrans-Nsiah et al., 2009). Burn-downs have been postulated to
285 explain decreasing TOC and palynomorph concentrations in turbidite sediments off Cape
286 Verde and Mediterranean sapropels (Thomson et al., 1995; Robinson, 2001), the process
287 suggests a strong preservation control on organic matter accumulation as compared to
288 changes in productivity and is initiated by an influx of oxygenated bottom water and
289 sediment pore water which then drives aerobic oxidation of the organic matter that was
290 already deposited. In this current work, a similar burn-down event maybe plausible
291 particularly if the overlying Rotliegend sandstones were deposited in oxidising conditions
292 but not were rapidly buried.

293

294 The TOC values presented here for the Upper Carboniferous mudrocks from the Malton-
295 4 well fall within the range previously reported for the Bowland-Hodder unit (TOC = 1-3
296 %), but do not equal the high TOC values of up to 8 % reported in some Namurian shales
297 in the UK (Andrews, 2013).

298

299 **Maturity of the organic matter**

300 In sedimentary rocks thermal maturity can be measured by vitrinite reflectance (Rr) and
301 an equivalent can be estimated using Rock-Eval (Tmax) values. In this study (Table 1),
302 Tmax values ranged from 436 to 454oC which is approximately equivalent to Rr of 0.70
303 – 1.01 (Jarvie et al., 2001). Taking the arithmetic mean of % Rr (estimated) of 0.85 (±
304 0.13), the black shales analysed fall in the middle of the oil window (Rr 0.6-1.0). Wet-gas
305 generation, that is gas containing >12 % of non-methane gas, is generally taken to begin
306 at 450 °C or about 1.0% Rr. Thus the black shales appear to be of sufficient maturity to
307 have generated liquid oil and possibly some wet gas but are not sufficiently mature

308 enough to have generated significant amounts of dry gas (above about 470 °C \approx Rr 1.4
309 %).

310

311 Values of the production index $PI = S1/(S1 + S2)$ for the shale samples ranged from 0.05
312 to 0.15 (Table 1). The PI typically increases with depth and also increases prior to
313 expulsion; it is therefore correlated with maturity. Here, the PI indicates at least early oil
314 window maturity (Peters and Cassa, 1994).

315

316 The $20S/(20S+20R)$ and $\beta\beta/(\beta\beta + \alpha\alpha)$ sterane ratios increase with maturity and reach
317 equilibrium values of 0.55 and 0.70, respectively, and can be used for maturity
318 evaluations (Mackenzie et al., 1980). $20S/(20S+20R)$ and $\beta\beta/(\beta\beta + \alpha\alpha)$ sterane ratios for
319 shale samples are 0.42-0.56 and 0.40-0.55 respectively, which indicate that organic
320 matter is at the early- to mid-mature stage (Table 2). $20S/(20S+20R)$ sterane ratios (0.53-
321 0.56) in two samples show that epimerisation at the C20 position has been completed and
322 has reached equilibrium (Seifert and Moldowan, 1986).

323

324 The values of the $Ts/(Ts + Tm)$ and moretane/hopane (M/H) ratios obtained from the
325 shale samples are highly variable among the five samples (Table 2). The equilibrium
326 value for the $Ts/(Ts + Tm)$ ratio is 0.52 to 0.55 (Seifert and Moldowan, 1986), although it
327 is also governed by lithology and depositional environment (Peters et al., 2005). The M/H
328 ratio decreases with thermal maturity from approximately 0.8 in immature bitumens to
329 <0.15 in mature source rocks to a minimum of 0.05 (Mackenzie et al., 1980; Seifert and
330 Moldowan, 1980); the ratio also depends on the facies and depositional environment
331 (Peters et al., 2005). Thus, observed significant variations through the section in both the
332 $Ts/(Ts + Tm)$ and M/H ratios of the black shales studied suggest changes in organic
333 matter input.

334

335 Based on pyrolysis and biomarker data -- $20S/(20S+20R)$ and $\beta\beta/(\beta\beta + \alpha\alpha)$ sterane ratios
336 -- and assuming there are no subtle differences in the maturity of the organic matter from
337 the shales studied, the results indicate that the organic matter in the Namurian shales
338 analysed is at the early mature to mid-mature stage.

339

340 **Type of organic matter**

341

342 Total organic carbon (TOC) measurements and Rock-Eval S₂, HI and OI indices can be
343 used to investigate the kerogen type, which in this case consists in general of a mixed
344 assemblage of organic matter (Behar et al., 2001) (Table 1). Hydrogen indices range from
345 43 to 140 mg/kg, TOC varies from 0.37 to 2.45 (mean 1.57), and OI values range from 0
346 to 21 at T_{max} of 436 to 454°C. These values suggest type III kerogen (Fig. 10, Table 1).
347 A probable minor contribution of Type II kerogen which yields higher HI values of >300
348 can be inferred for at least one of the samples (1570.3 m) which plots in close proximity
349 to the Type II boundary (Fig. 10). In general, Type III kerogens are composed of woody,
350 bacterial and other sources of organic matter which have not undergone severe oxidative
351 alteration. This terrestrial to mixed terrestrial - marine input of organic matter is broadly
352 consistent with the basinal-prodelta depositional environment of the mudstones. Oxygen
353 indices are low and invariant (0 to 21) which suggest that the organic matter has not
354 undergone severe microbial decay or photochemical alteration. However, although
355 measurement and interpretation of HI and OI values are useful, these values are
356 influenced with increasing maturation and become less reliable as an interpretative tool as
357 values approach the origin (Fig. 10).

358

359 Gas chromatograms of saturated hydrocarbons show a similar n-alkane distribution in the
360 mudrock samples (Fig. 11), displaying a full suite of saturated hydrocarbons between
361 C₁₄-C₃₉ n-alkanes and the isoprenoids pristane (Pr) and phytane (Ph). The n-alkane
362 distributions exhibit a predominance of low to medium molecular weight compounds (n-
363 C₁₄ to n-C₂₀) with the presence of significant waxy alkanes (+n-C₂₇), suggesting a high
364 contribution of marine organic matter with moderate terrigenous organic matter
365 contribution (Eglinton et al., 1962).

366

367 Cross-plots of Pr/n-C₁₇ versus Ph/n-C₁₈ (Shanmugam, 1985) also suggest a mixed
368 (terrestrial-marine) or terrestrial source of organic matter (Fig. 12).

369

370 Terpenoids are abundant with C19-C29 tricyclic terpanes and C30-C35 hopanes in all
371 samples (Fig. 13). The most probable biological precursors of the hopanoid biomarkers
372 are bacteriohopanetetrol and 3-desoxyhopanes (Ourisson et al., 1979; Rohmer et al.,
373 1992). Hopanes have also been reported as products of hopanoic acids (Bennett and
374 Abbott, 1999).

375

376 Of all steranes the C27 sterane is generally predominant (Fig. 13, Table 2). All of the
377 samples are characterized by similar C27/C29 (0.7 to 1.53) and C28/C29 (0.73 to 1.33)
378 sterane ratios. In general, C29 steranes are the major steroids derived from higher plants,
379 but significant quantities of C29 steranes can also be derived from a marine algal source
380 (e.g. Volkman, 2005). C27 steranes are commonly associated with zooplankton, and C28
381 steranes with chlorophyll-c containing phytoplankton (Huang and Meinschein, 1979).
382 However, Peters et al. (2005) and Volkman (2005) suggested caution in such
383 interpretations because many algae synthesize C29 sterols and there are many sources of
384 C27 and C28 sterols. Here, the distribution of C27-C28-C29 regular steranes shows a
385 slight dominance of C27 steranes (29-45 %), with slightly lower C29 (26-41 %), and
386 intermediate C28 (26-35 %) (Fig. 14, Table 2). The relative distributions of C27-C28-
387 C29 regular steranes are similar, but considerable variability within the proportions is
388 present in particular samples. Moreover, such variation is typical of Phanerozoic marine
389 source rocks (Grantham and Wakefield, 1988; Schwark and Emt, 2006). Therefore these
390 organic matter sources suggest that Namurian black shales contain marine algal and
391 terrigenous organic matter, with significant amounts of bacterial (microbially reworked)
392 organic matter.

393

394 Regular sterane/hopane ratios in Namurian shales show that the sterane abundance is
395 much lower than that of hopanes (0.05-0.27) which suggests a significant contribution of
396 prokaryotic organisms to the total biomass but is also consistent with terrestrial (soil)
397 inputs. A strong bacterial contribution is further confirmed by the high 2-methylhopane
398 index (2-MHP) which varies from 11.7 to 19.4 % (Table 2). The methylhopane index is
399 determined from the abundance of 2 α -methyl-17 α ,21 β (H)-hopane normalized to
400 17 α ,21 β (H)-homohopane. The shale samples contain abundant 2 α -methylhopanes,

401 ranging in carbon number from C29 to C32. Hopanoids methylated at the C-2 position
402 can be derived from cyanobacteria (Summons et al., 1999), but a recent study has shown
403 that their phylogenetic occurrence is potentially much broader (Welandar et al., 2010).

404

405 Jarvie (2012) showed that marine-dominated shale gas resource systems (e.g. Barnett and
406 Fayetteville Shales, with moderate HI values of 30-40 mg hydrocarbon/g TOC) can be
407 excellent shale-gas targets. This is because at higher maturities the convertible carbon
408 fraction decreases when expulsion occurs. Therefore, determination of the original (post
409 burial) TOC and HI provides a more accurate means to assess organic matter quality and
410 generation potential. Comparison with immature shale rock equivalents showed original
411 HI of about >400 and original TOC of about 6%. However, in such settings, the organic
412 matter is mainly Type II (hydrogen rich) with high amounts of generative carbon.

413

414 In the present study, the black shales show considerable variability over a short depth
415 range but predominantly contain Type III kerogen and are not readily comparable to
416 organic matter deposited in deeper marine settings. Nevertheless, it is entirely reasonable
417 to assume that the low present-day TOC and HI values are an underestimate of original
418 values and that type III/II kerogen can yield significant amounts of oil and, to a lesser
419 extent, shale gas.

420

421 **REDOX NATURE OF THE DEPOSITIONAL ENVIRONMENT**

422

423 The Namurian shales in the Yorkshire area were deposited in a shallow-marine, pro-delta
424 environment as indicated by lithology and biomarker data. The Pr/Ph ratio varies from
425 0.3 to 3.04. This ratio has been used to infer depositional redox conditions (Maxwell et
426 al., 1972; Powell and McKirdy, 1973), but it is also influenced by factors such as thermal
427 maturity, variable biomolecule sources, lithology and diagenetic effects (e.g. Didyk et al.,
428 1978; ten Haven et al., 1987; Rowland, 1990; Kohnen et al., 1991; Hughes et al., 1995).
429 Therefore, the generally high Pr/Ph ratios in most samples indicate dysoxic to oxic
430 depositional conditions. Similarly, a cross-plot of Pr/n-C17 versus Ph/n-C18 ratios also
431 suggests deposition in dysoxic to oxic bottom waters (Fig. 12).

432

433 In these black shales, isorenieratane, which is derived from isorenieratene produced by
434 brown-coloured green sulphur bacteria (Chlorobiaceae, Liaan-Jensen, 1978) and is
435 therefore indicative of photic zone euxinia, is absent. Instead, low abundances of C18-
436 C22 2,3,6-trimethyl aryl isoprenoids (Summons and Powell, 1987) were detected. These
437 structures are diagenetic alteration products of isorenieratene, although they can also be
438 derived from other carotenoids. Their trace concentrations precluded measurement of
439 $\delta^{13}\text{C}$ values and confirmation of a green sulphur bacterial (Quandt et al., 1977; Sirevag et
440 al., 1977; Koopmans et al., 1996; Jaraula et al., 2013) or algal source (Koopmans et al.,
441 1996; Jaraula et al., 2013). However, as gammacerane and isorenieratane were not
442 detected and the pristane/phytane ratio is in general >1 , clear evidence for anoxia is
443 lacking in all samples. A lack of profound water column anoxia is corroborated by the
444 lack of high total organic carbon (TOC) content (0.3 – 2.4 wt%).

445

446 On the other hand, the presence of pyrite framboids, which are spherical aggregates of
447 pyrite microcrystals and are similar to those in modern/ancient marine sediments,
448 suggests deposition under oxygen-restricted conditions (Wilkin et al., 1996; 1997;
449 Wignall and Newton, 1998). Hence, it is suggested that the Namurian mudrocks may
450 have been deposited under conditions of periodic bottom water anoxia.

451

452 **HYDROCARBON POTENTIAL**

453

454 The hydrocarbon potential of the Malton-4 shales between 1568-1586 m depths can be
455 assessed as a shale-gas resource or can be viewed from the standpoint of generating and
456 retaining shale oil. The alternating shale-sandstone sequence suggests a hybrid system.
457 As a classic unconventional play (i.e. self-sourced reservoir), gas could be sorbed by the
458 mudstone-siltstone lithofacies; as a shale-oil system, oil could be generated and then
459 migrate for a short distance to adjacent sandy mudrocks and bioturbated sands (Table 1;
460 Fig. 5).

461

462 Setting aside these sedimentological considerations, prospective shale-gas plays, in
463 general have the following geochemical characteristics:

464

465 (i) good kerogen quality as determined from original hydrogen index values (HIo) of
466 250-800 mg/kg; (ii) high TOC >1.0 %; and (iii) thermal maturity of >1.4% VRo which is
467 equivalent to Tmax of about 500°C (e.g. $T_{max} \text{ } ^\circ\text{C} = (\text{VR } \% + 7.6) / (0.0180)$) (Andrews,
468 2013). Using Jarvie's (2007) HIo calculation and a not-unreasonable estimate of 50 %
469 Type II and 50 % Type III kerogen content, the Malton-4 black shales will have a HIo of
470 about 288 mg/g TOC. Combined with TOC values in the range of 0.37 to 2.46 %, These
471 values satisfy the basic organic geochemical characteristics of kerogen quality and
472 amount. However, the Tmax values (Table 2) suggest that the mudrocks analysed in this
473 study are too immature to be considered as a shale-gas resource. This does not
474 necessarily preclude limited gas generation, since small amounts of wet-gas are generated
475 in the early oil window.

476

477 The hydrocarbon potential of shale-oil systems can be assessed using the oil saturation
478 index (OSI: $S_1 \times 100 / \text{TOC}$); potential resources are identified using empirical OSI
479 values >100 mg/g TOC. The premise here is that organic matter sorbs oil generated at
480 values <100 mg /g TOC and that the sorption threshold is exceeded at OSI >100 (the "oil
481 cross-over"). OSI values for the Malton-4 succession ranged from 4 to 17 mg/g TOC
482 (arithmetic mean 9 mg/g TOC), which falls well below the 100 mg cut-off and indicates
483 that the Upper Carboniferous mudrocks between (1569-1586 m depth) do not contain
484 enough oil to be considered a viable shale-oil resource.

485

486 **CONCLUSIONS**

487

488 The Upper Carboniferous succession studied in the Malton-4 well consists of four major
489 lithofacies: mudrock, sandy mudrock, bioturbated sandstone and massive sandstone. The
490 sandy mudrocks are shallower-water deposits and the presence of discrete muddy sand
491 beds with planar- and cross- lamination could indicate a storm influence (tempestites) or
492 distal fluvial hyperpycnal flows. The bioturbated sand facies indicates a distal to medial

493 mouth-bar setting whereas the more massive sands are interpreted to have been deposited
494 in a more proximal higher-energy location on a mouth bar.

495

496 Values of the total organic carbon content, and Rock-Eval S2, HI and OI indicate that
497 kerogen in general consists of type III material with a probable minor contribution of
498 Type II kerogen. This mixed terrestrial – marine (algal) and microbially reworked input
499 of organic matter is broadly consistent with the basinal-prodelta depositional environment
500 of the mudstones. Organic matter is at the early to mid-mature stage with respect to
501 hydrocarbon generation and was likely deposited in a mixed oxic-dysoxic-anoxic marine
502 environment.

503

504 The alternating shale-sandstone sequence suggests a hybrid system which could sorb gas
505 in the mudstone-siltstone Lithofacies, and could also generate shale oil which would
506 migrate a short distance to the sandy mudrocks and bioturbated sands. However, the
507 Rock-Eval parameters suggest that the mudrocks are not sufficiently mature to be
508 considered as a shale-gas resource and rule out a shale-oil potential. However this does
509 not preclude limited gas generation since small amounts of wet gas can be generated in
510 the early oil window.

511

512 **ACKNOWLEDGEMENTS**

513 To be added

514

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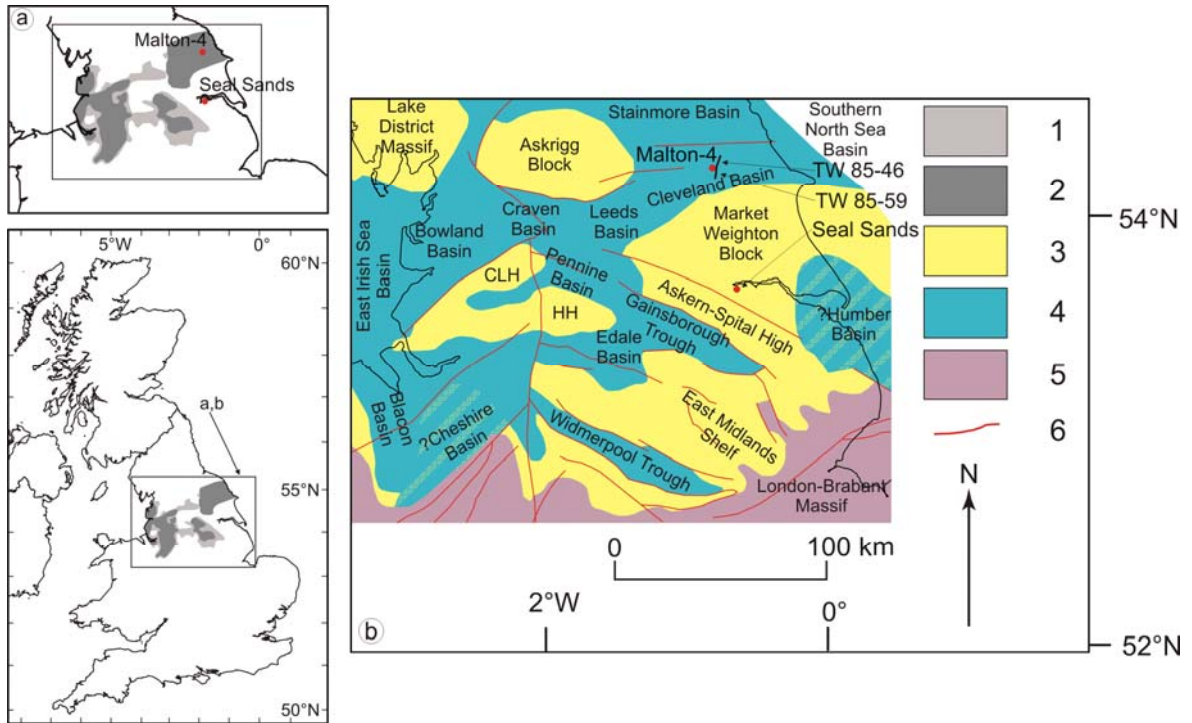
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680 Figure captions:

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685 Fig. 1A. Location of Malton-4 well [not located in this figure] and prospective areas for
686 shale gas in the Bowland-Hodder unit in the northern England (after Andrews, 2013).

687 Also shown are the locations of the seismic lines presented in Fig. 1b. Key: 1. prospective
688 area for gas in lower (Visean) Bowland-Hodder unit; 2. prospective area for gas in upper
689 (Namurian) Bowland-Hodder unit

690 B. Palaeogeography of northern England during the mid-Carboniferous showing the
691 location of blocks and basins (modified from Fraser and Gawthorpe, 2003).

692 Key: 3. platform; 4. basin; 5. basement high; 6. fault; CLH - Central Lancashire High;
693 HH - Holme High.

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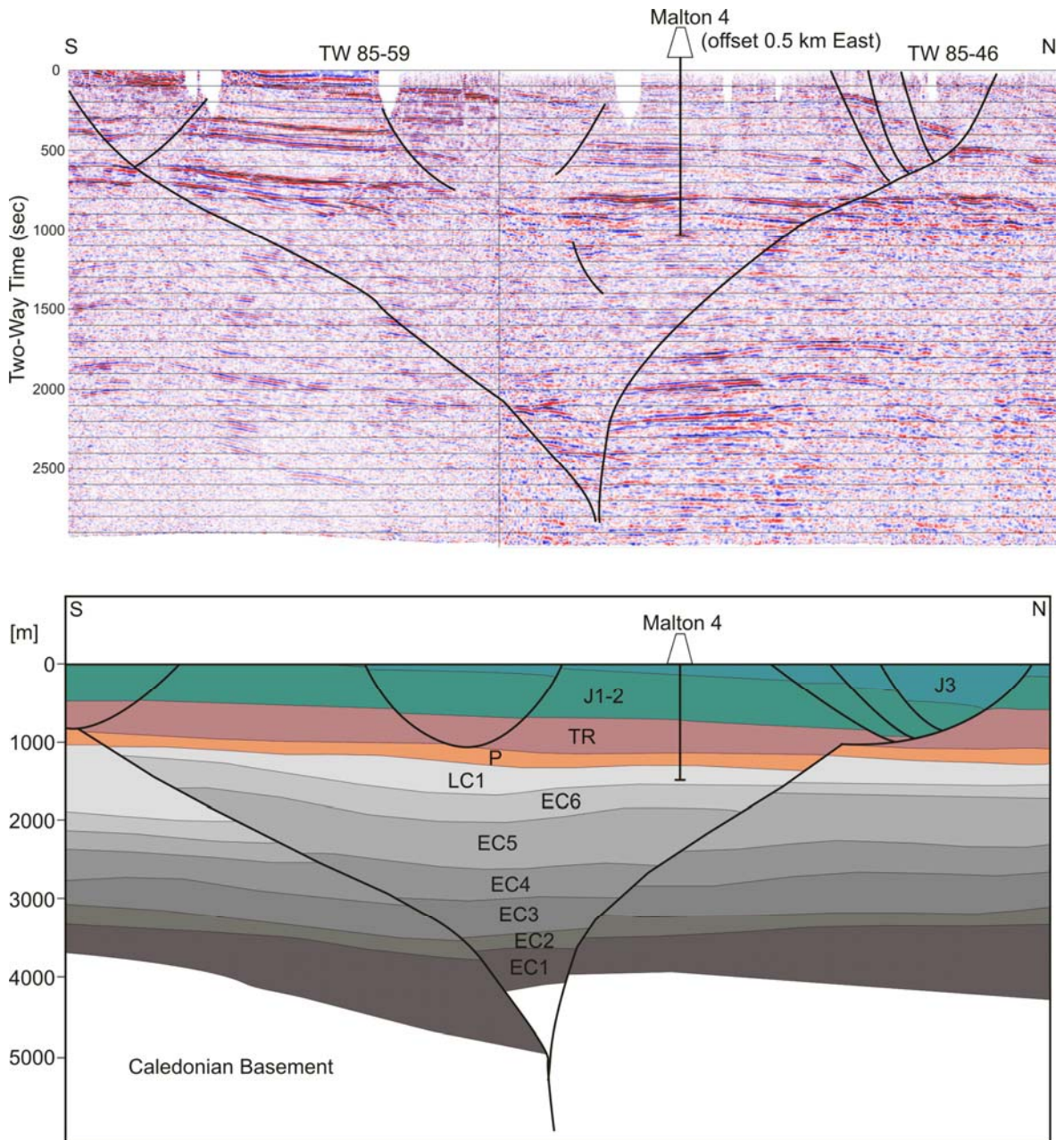
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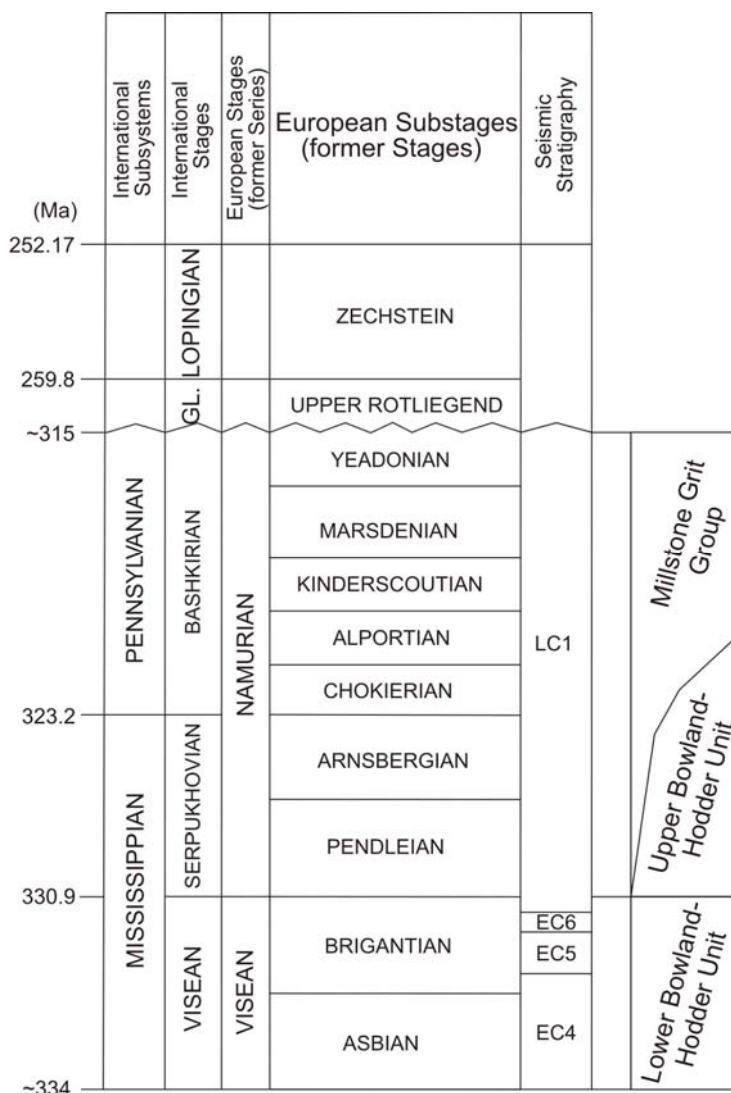
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705 Fig. 2. Geological cross-section interpreted from seismic lines TW 85-46 and TW 85-59
706 across the Cleveland Basin (simplified from Fraser and Gawthorpe, 2003). J1-2: Early-

707 Middle Jurassic; J3: Late Jurassic; TR: Triassic; P: Permian; LC1: Namurian seismic
 708 stratigraphic cycles; EC1 to EC6: Mississippian seismic stratigraphic cycles. See Fig. 3
 709 for the lithostratigraphy.

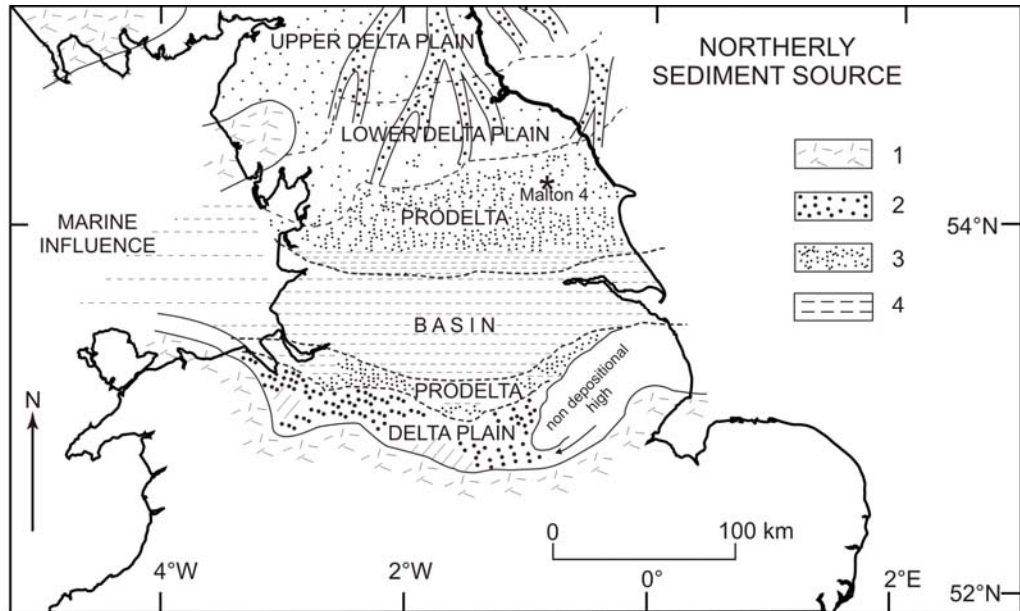
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715
 716 Fig. 3. Chronostratigraphic framework for the Carboniferous and Permian in the study
 717 area. Seismic sequences from Fraser et al. (1990). GL – Guadalupian. Numerical ages for
 718 all systems are after Gradstein et al. (2012).

719

720



721

722 Fig. 4. Palaeofacies map for the post-rift LC1a/b sequence (Arnsbergian-Kinderscoutian)

723 in northern England (modified after Fraser and Gawthorpe, 1990). 1, Lower

724 Palaeozoic/Precambrian basement; 2, coarse, mostly fluvial clastics; 3, finer sandstones

725 and mudrocks, local coals; 4, mudrocks, locally organic-rich shales.

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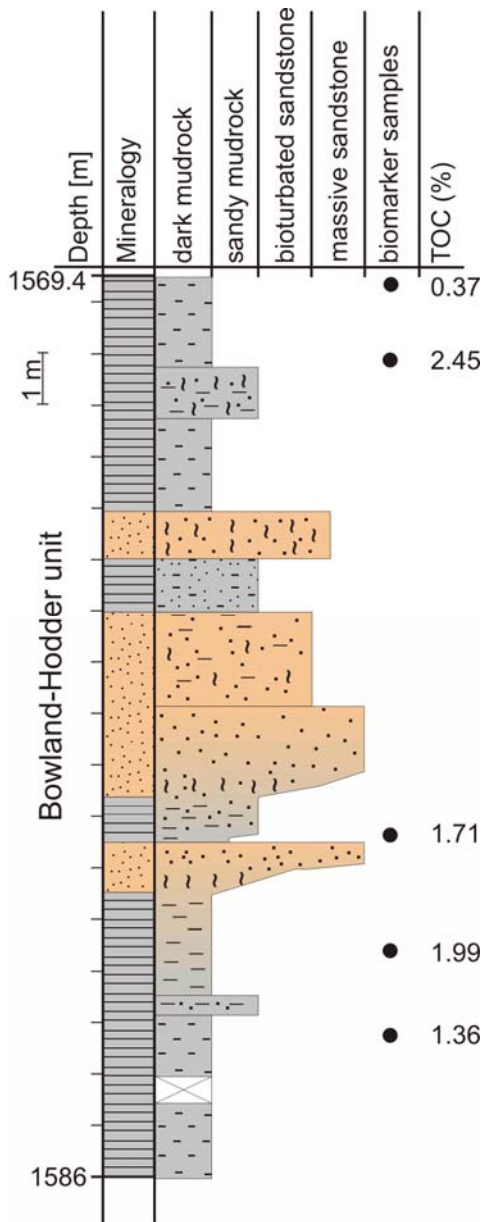
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737 Fig. 5. Sedimentary log of Upper Carboniferous mudrocks and sandstones from the
 738 Malton-4 well.

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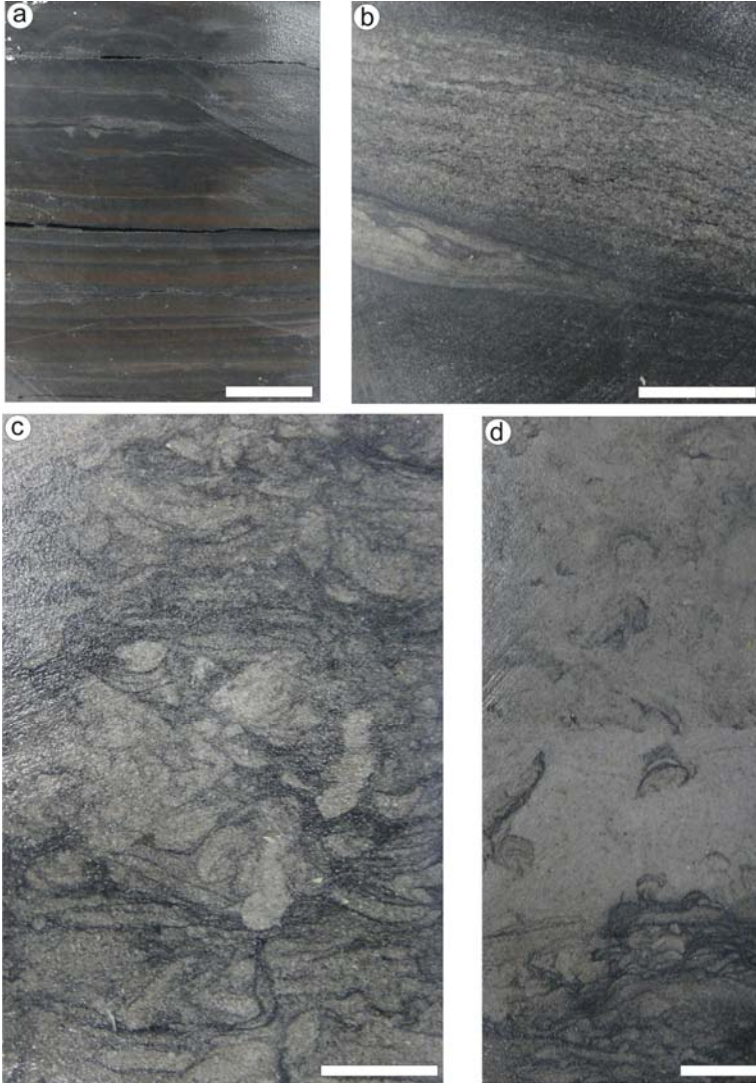
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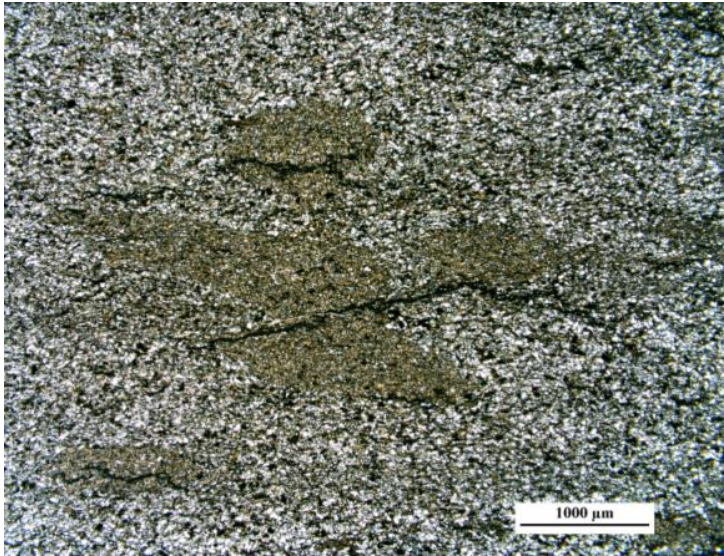
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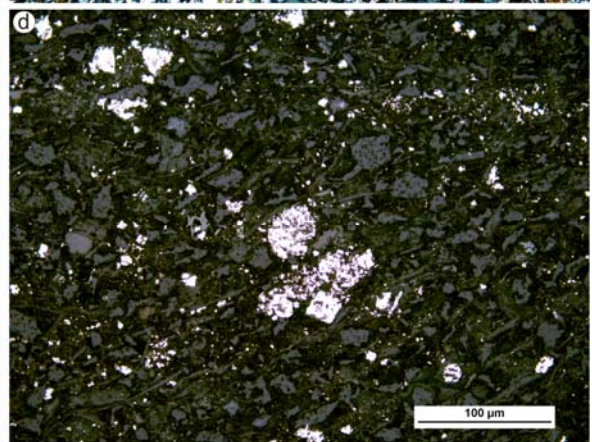
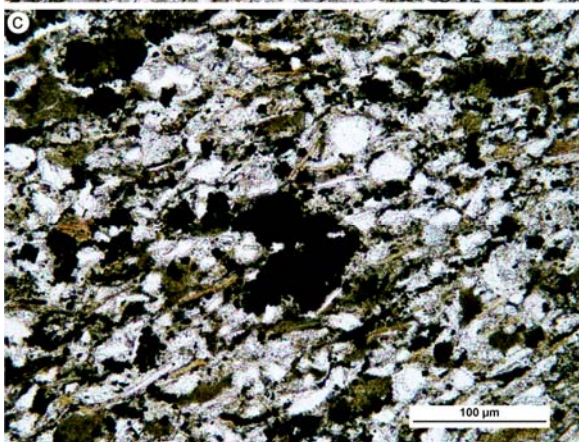
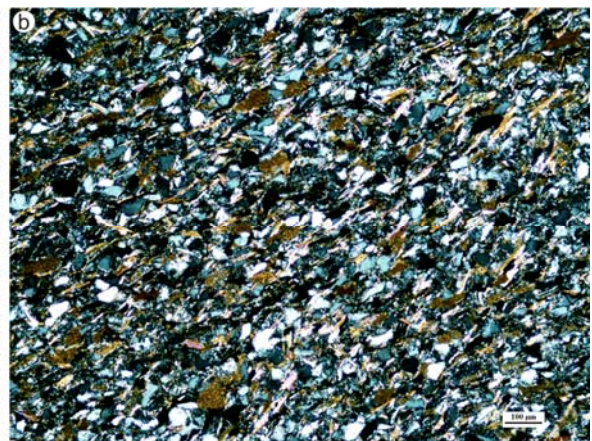
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746 Fig. 6. Sedimentary features in samples from the Malton-4 well. (a) Black shale with
747 mm-lamination and no bioturbation; (b) Mudrock with 5-cm thick tempestite /
748 hyperpycnite siltstone-fine sandstone from pro-delta facies; (c) Bioturbated, muddy fine
749 sandstone with Planolites, Chondrites and Thalassinoides burrows; (d) Bioturbated
750 muddy to clean sand with Chondrites, Pelecypodichnus and Planolites burrows. Scale
751 bars 2 cm.



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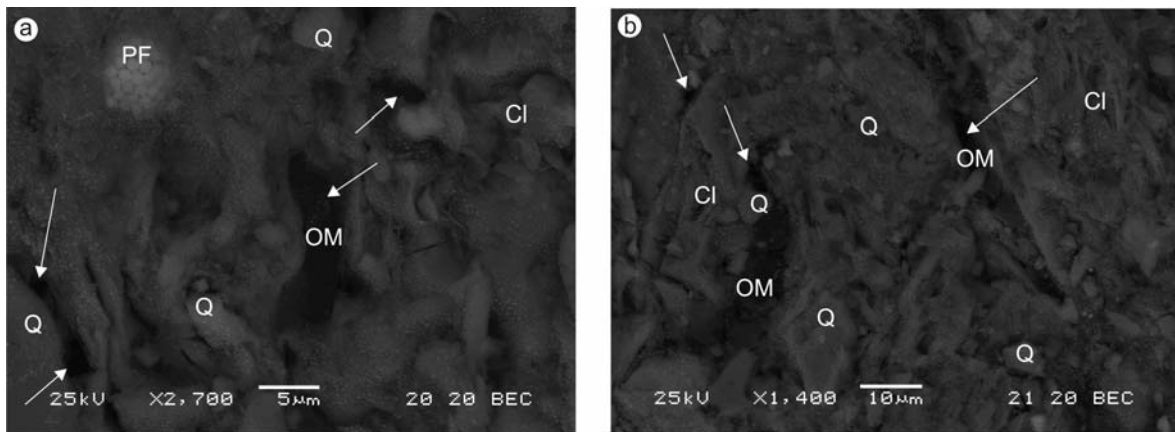
753 Fig. 7. Silty mudrock with silt-poor areas which are probably burrow fills. Discontinuous
754 irregular stylolitic seams show concentrations of organic matter.

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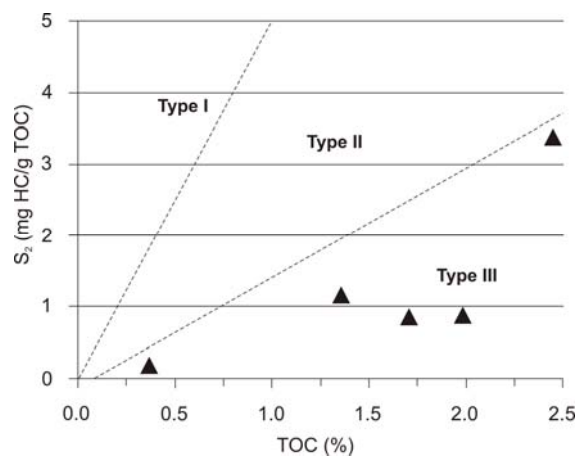
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757 Fig. 8. Mudrock in plane-polarized light (a) and crossed-polarized light (b) showing
 758 quartz silt grains (~30%), mica (~5%, mostly muscovite), opaque/black pyrite and
 759 organic matter (~5%), and clay matrix, altered feldspar and other grains (60%). Mudrock
 760 in plane-polarized light (c) and reflected light (d) showing that some of the opaque grains
 761 are pyrite (white in D); other black areas are organic matter. White arrows point
 762 microporosity. In the photomicrographs, lamination is oriented NE-SW.
 763



764
 765 Fig. 9. Back-scattered scanning electron microscopic images of Upper Carboniferous
 766 mudrock; lamination oriented north-south. (a) higher magnification showing organic
 767 material in centre, pyrite framboid (upper left), clay, fine-silt quartz grains and nano-
 768 pores; (b) shows two fragments of organic matter (dark elongate areas), fine, silt-sized
 769 quartz grains, and clay flakes. Nano-pores are present between some grains; OM -
 770 organic material, Q - quartz, Cl - clay, PF - pyrite framboid.

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776 Fig. 10. Kerogen type in Malton-4 succession defined by present-day S₂-TOC cross-plot.

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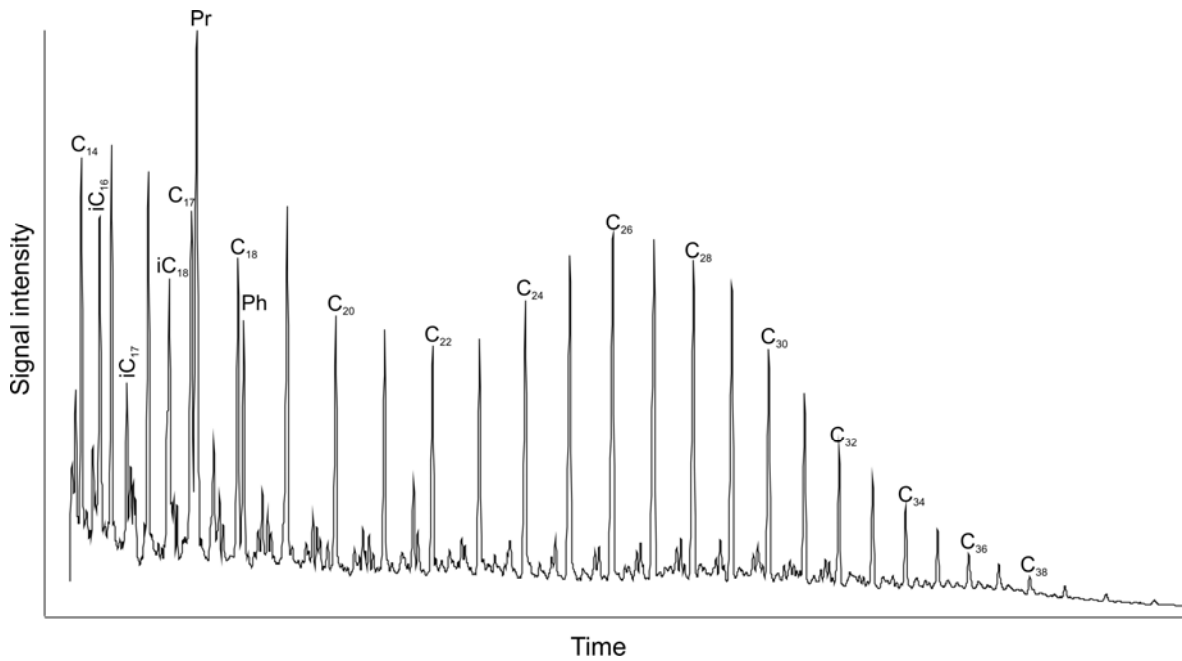
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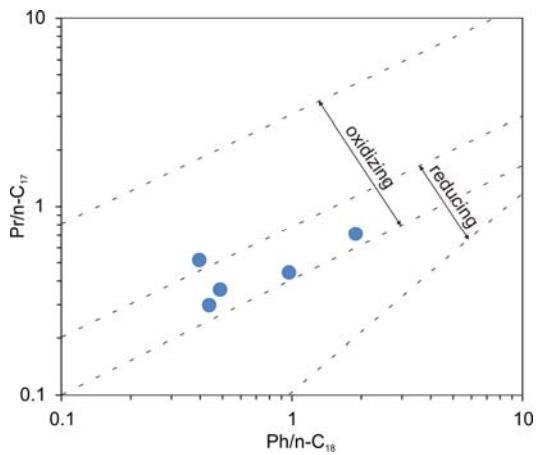
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788 Fig. 11. Gas chromatogram of saturated hydrocarbons of the studied Namurian shale
 789 extracts. iC16-18 – acyclic isoprenoids; Pr – pristane; Ph – phytane.

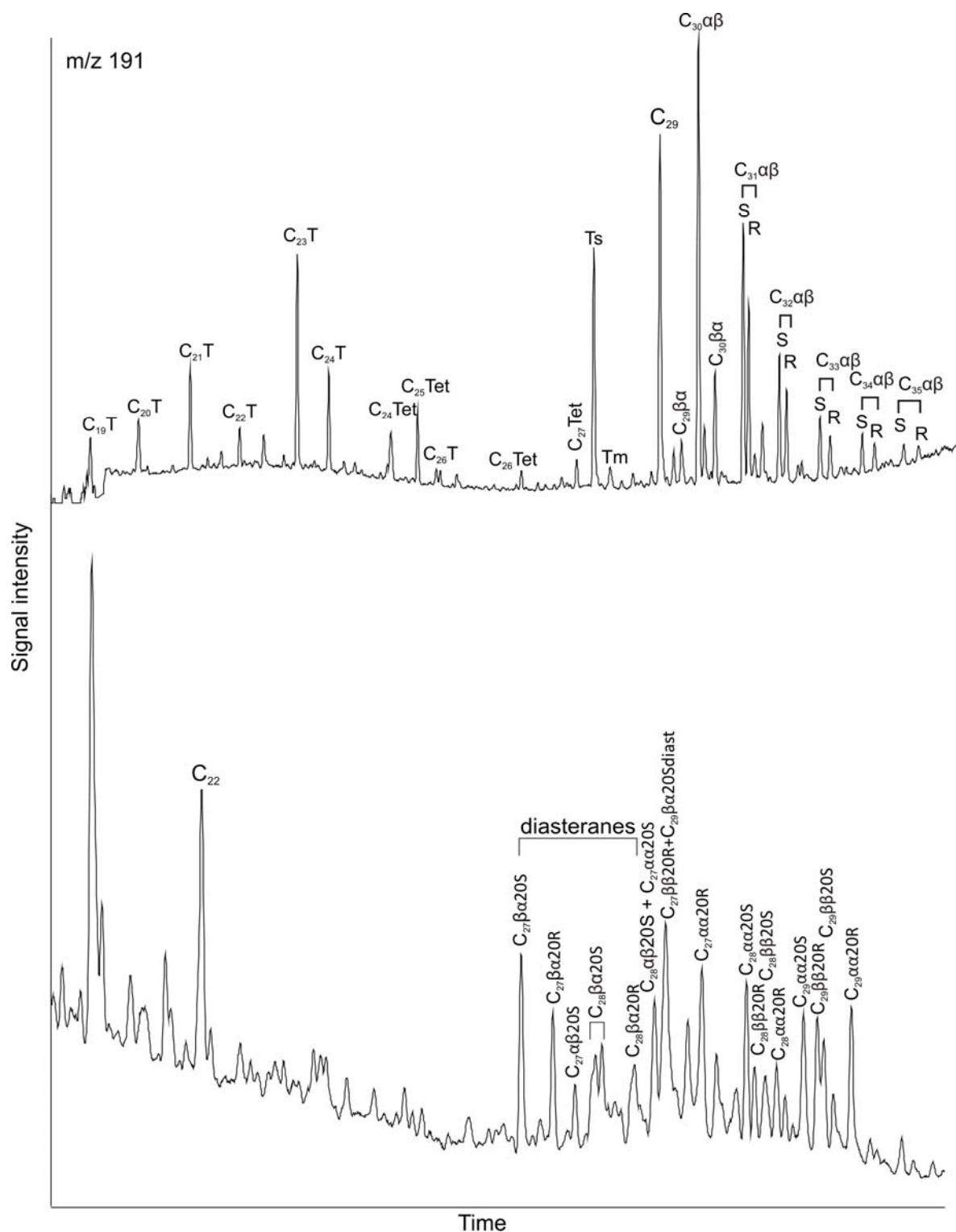
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792 Fig. 12. Pr/n-C17 vs. Ph/n-C18 plot for all samples indicating deposition under oxidizing
 793 to oxygen-depleted conditions.

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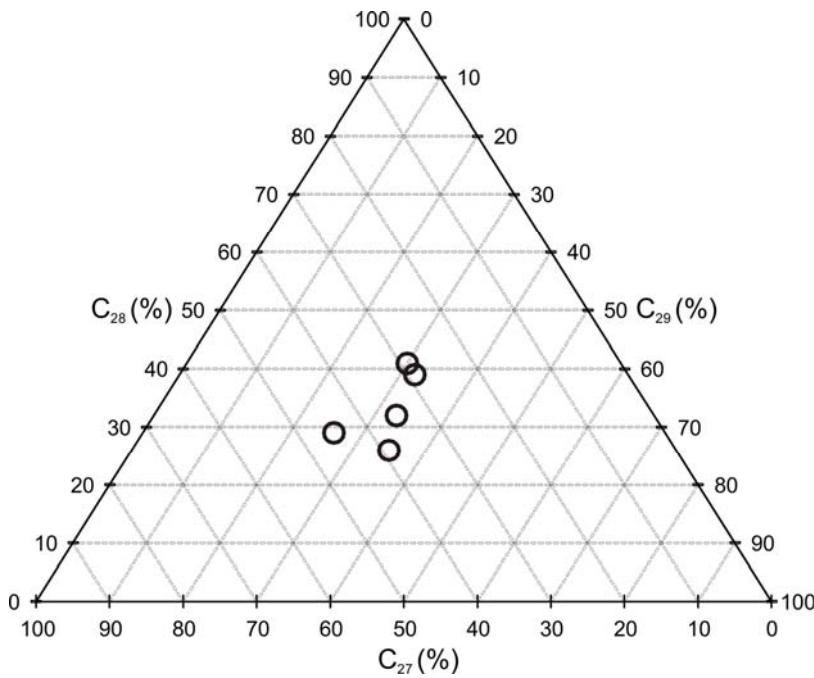
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Fig. 13. The m/z 191 and m/z 217 mass chromatograms of saturated hydrocarbon fractions of the analysed Namurian shale extracts. C19-26T – tricyclic terpenoids; C25-27Tet – tetracyclic terpenoids; Ts - C27 18 α -trisnorhopane; Tm - C27 17 α -trisnorhopane.

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801 Fig. 14. A ternary plot of C27 vs. C28 vs. C29 regular steranes (as normalised
802 percentages) for the Carboniferous mudrocks.

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Depth (m)	TOC ^a (%)	S ₁ ^b (mg HC/g rock)	S ₂ ^b (mg HC/g rock)	T _{max} ^d (°C)	HI ^e (mg HC/g rock)	OI ^f (mg g/g rock)	PI ^g (S ₁ /(S ₁ +S ₂))
1569.5	0.37	0.02	0.20	443	53	30	0.05
1570.3	2.45	0.43	3.38	436	138	4	0.11
1579.5	1.71	0.13	0.87	451	51	16	0.13
1581.3	1.99	0.15	0.89	454	45	12	0.15
1583.1	1.36	0.14	1.17	440	87	21	0.11

806

807 Table 1. Results of total organic carbon analyses (TOC) and Rock-Eval pyrolysis for the
808 shale samples from Malton 4.

809 aTOC, total organic carbon

810 bS₁, volatile hydrocarbon (HC) content, mg HC/g rock

811 cS₂, remaining HC generative potential, mg HC/g rock

812 dT_{max}, temperature at maximum of S₂ peak

813 eHI, hydrogen index
 814 fOI, oxygen index
 815 gPI, production index.
 816

Depth (m)	Pr/Ph ^a	Pr/n-C ₁₇	Ph/n-C ₁₈	Ts/Tm ^b	M/H ^c	HHI ^d	C ₂₉ αα S/(S+R) ^e	C ₂₉ ββ/(ββ +αα) ^f	C ₂₇ /C ₂₉ ^e	C ₂₈ /C ₂₉ ^f	C ₂₇ , 28, 29, steranes	Sterane/hopane	2-MHP ^g
1569.5	0.31	0.37	0.51	0.55	0.19	0.14	0.47	0.42	1.11	1.03	32, 33, 35	0.27	11.72
1570.3	3.04	1.89	0.71	0.28	0.19	0.04	0.56	0.48	1.53	0.88	29, 26, 45	0.19	11.81
1579.5	1.05	0.48	0.35	nd	0.24	0.06	0.47	0.46	0.76	0.83	39, 32, 29	0.09	13.02
1581.3	0.86	0.43	0.29	0.11	0.27	0.04	0.42	0.40	0.70	0.73	41, 30, 29	0.05	12.26
1583.1	2.07	0.97	0.44	0.66	0.16	0.06	0.53	0.55	1.50	1.33	26, 35, 39	0.11	19.46

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819 Table 2. Overview of geochemical parameters measured and discussed in this study. nd –
 820 not determined.

821 a Pr/Ph: pristane / phytane ratio

822 b Ts/Tm: C₂₇ 17α-trisnorhopane (Tm) / C₂₇ 18α-trisnorhopane ratio expressed as
 823 Ts/(Ts+Tm)

824 c M/H (moretane/hopane ratio): 17β(H),21α(H) – moretane/17α(H),21β(H) – hopane

825 d HHI (homohopane index): C₃₅αβ(22S+22R) / (ΣC₃₁-C₃₅ αβ 22S+22R)

826 e,f C₂₇/C₂₉ and C₂₈/C₂₉ are sterane ratios respectively

827 g 2-MHP: C₃₂ 2α-methylhopanes (22S + 22R) / C₃₁ (22R) homohopane

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