

# Accepted Manuscript

Evolution of porosity and pore types in organic-rich, calcareous, Lower Toarcian Posidonia Shale

Eliza J. Mathia, Leon Bowen, K. Mark Thomas, Andrew C. Aplin



PII: S0264-8172(16)30104-0

DOI: [10.1016/j.marpetgeo.2016.04.009](https://doi.org/10.1016/j.marpetgeo.2016.04.009)

Reference: JMPG 2527

To appear in: *Marine and Petroleum Geology*

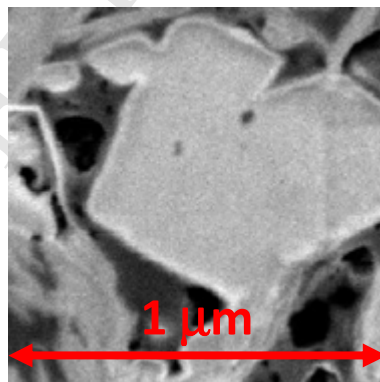
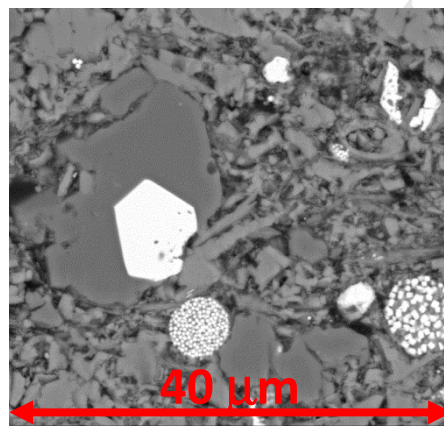
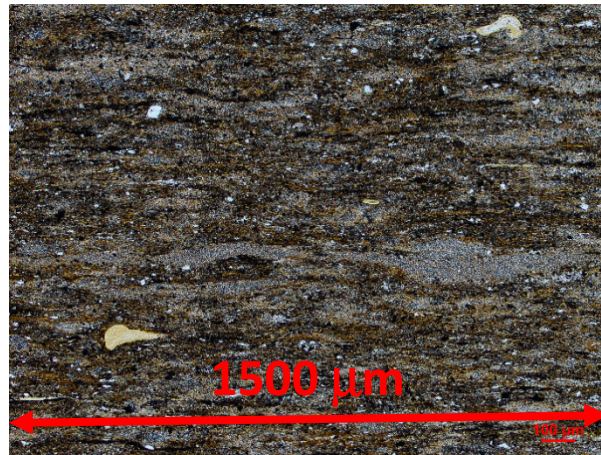
Received Date: 3 February 2016

Revised Date: 10 April 2016

Accepted Date: 11 April 2016

Please cite this article as: Mathia, E.J., Bowen, L., Thomas, K.M., Aplin, A.C., Evolution of porosity and pore types in organic-rich, calcareous, Lower Toarcian Posidonia Shale, *Marine and Petroleum Geology* (2016), doi: 10.1016/j.marpetgeo.2016.04.009.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



1 **Evolution of Porosity and Pore Types in Organic-rich, Calcareous, Lower**  
2 **Toarcian Posidonia Shale**

3  
4  
5 **Eliza J. Mathia<sup>1,5,\*</sup>, Leon Bowen<sup>2</sup>, K. Mark Thomas<sup>3</sup>, Andrew C. Aplin<sup>4,\*</sup>**

6  
7 <sup>1</sup>School of Civil Engineering and Geosciences, Newcastle University, Newcastle upon Tyne,  
8 NE1 7RU, United Kingdom

9  
10 <sup>2</sup>Department of Physics, Durham University, Science Laboratories, South Road, Durham,  
11 DH1 3LE, United Kingdom

12  
13 <sup>3</sup>School of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle  
14 upon Tyne, NE1 7RU, United Kingdom

15  
16 <sup>4</sup>Department of Earth Sciences, Durham University, Science Laboratories, South Road,  
17 Durham, DH1 3LE, United Kingdom

18  
19 <sup>5</sup>Present address: Chemostrat Ltd., 2 Ravenscroft Court, Buttington Cross Enterprise Park,  
20 Welshpool, Powys, SY21 8SL, United Kingdom

21  
22 \*Corresponding Authors: [elizamathia@chemostrat.com](mailto:elizamathia@chemostrat.com); [a.c.aplin@durham.ac.uk](mailto:a.c.aplin@durham.ac.uk)

23

**Abstract**

24  
25  
26 Low and high resolution petrographic studies have been combined with mineralogical, TOC,  
27 RockEval and porosity data to investigate controls on the evolution of porosity in  
28 stratigraphically equivalent immature, oil-window and gas-window samples from the Lower  
29 Toarcian Posidonia Shale formation. A series of 26 samples from three boreholes (Wickensen  
30 Harderode and Haddessen) in the Hils syncline was investigated. The main primary  
31 components of the shales are microfossiferous calcite (30-50%), clay minerals (20-30%) and  
32 Type II organic matter (TOC = 7-15%, HI = 630-720 mg/gC in immature samples).  
33 Characteristic sub-centimetric light and dark lamination reflects rapid changes in the relative  
34 supply of these components. Total porosities decrease from 10-14% at  $R_o = 0.5\%$  to 3-5% at  
35  $R_o = 0.9\%$  and then increase to 9-12% at  $R_o = 1.45\%$ . These maturity-related porosity  
36 changes can be explained by (a) the primary composition of the shales, (b) carbonate  
37 diagenesis, (c) compaction and (d) the maturation, micro-migration, local trapping and  
38 gasification of heterogeneous organic phases. Calcite undergoes dissolution and  
39 reprecipitation reactions throughout the maturation sequence. Pores quantifiable in SEM ( $>$   
40 ca. 50 nm) account for 14-25% of total porosity. At  $R_o = 0.5\%$ , SEM-visible macropores<sup>1</sup> are  
41 associated mainly with biogenic calcite. At this maturity, clays and organic matter are not  
42 visibly porous but nevertheless hold most of the shale porosity. Porosity loss into the oil  
43 window reflects (a) compaction, (b) carbonate cementation and (c) perhaps the swelling of  
44 kerogen by retained oil. In addition, porosity is occluded by a range of bituminous phases,  
45 especially in microfossil macropores and microfractures. In the gas window, mineral-hosted  
46 porosity is still the primary form of macroporosity, most commonly observed at the organic-  
47 inorganic interface. Increasing porosity into the gas window also coincides with the  
48 formation of isolated, spongy and complex meso- and macropores within organic particles,

<sup>1</sup> Classification of pores by the International Union of Applied and Pure Chemistry (IUAPC): micropores (< 2 nm in diameter), mesopores (2-50 nm), macropores (> 50 nm).

49 related to thermal cracking and gas generation. This intraorganic porosity is highly  
50 heterogeneous: point-counted macroporosity of individual organic particles ranges from 0 -  
51 40%, with 65% of organic particles containing no macropores. We suggest that this reflects  
52 the physicochemical heterogeneity of the organic phases plus the variable mechanical  
53 protection afforded by the mineral matrix to allow macroporosity to be retained. The  
54 development of organic macroporosity cannot alone account for the porosity increase  
55 observed from oil to gas window; major contributions also come from the increased volume  
56 of organic micro- and meso-porosity, and perhaps by kerogen shrinkage.

57

58 **Keywords**

59 Posidonia Shale, Porosity, Mineralogy, Petrography, Geochemistry

60

## 61 1. Introduction

62 The quality of a shale petroleum reservoir - its ability to store and then to yield oil and  
63 gas - is an integrated reflection of the way in which sedimentology, mineralogy, diagenesis  
64 and organic matter maturation combine to influence shale pore systems and mechanical  
65 properties. Whilst each one of these four subjects has been studied for decades in the context  
66 of palaeoenvironment, petroleum source rocks and basinal fluid flow (see e.g. Tissot and  
67 Welte 1984; Tyson 1995; Welte *et al.*, 1997; Potter *et al.*, 2005; Aplin and Macquaker, 2010),  
68 the focus on shales as reservoirs is more recent, requiring a more detailed approach and an  
69 integration of disciplines (e.g. Passey *et al.*, 2010).

70 In recent years, conventional organic geochemical approaches to source rock  
71 characterisation (e.g. Jarvie *et al.*, 2007) have been combined with high resolution electron  
72 microscope and synchrotron techniques (Bernard *et al.*, 2010; 2011) to gain a deeper  
73 understanding of petroleum retention and the diversity of organic phases in shales. Improved  
74 electron microscope technologies have also generated substantial new insights into the nature  
75 of shale pore systems, especially when combined with other techniques such as low pressure  
76 gas sorption and small angle scattering (Loucks *et al.*, 2009; 2012; Ross and Bustin, 2009;  
77 Desbois *et al.*, 2009; Slatt and O'Brien, 2011; Heath *et al.*, 2011; Bernard *et al.*, 2012;  
78 Fishman *et al.*, 2012; Klaver *et al.*, 2012; Clarkson *et al.*, 2013; Houben *et al.*, 2013; Milliken  
79 *et al.*, 2013; Rexer *et al.*, 2014; Liang *et al.*, 2014; Tang *et al.*, 2014). Other studies have  
80 focussed on mineral diagenesis in organic-rich mudstones (Milliken *et al.*, 2012; Macquaker  
81 *et al.*, 2014; Pommer and Milliken, 2015).

82 Many previous studies have focussed on shales of a specific maturity and/or to  
83 demonstrate the use of a specific technique as a tool to evaluate shale properties. The aim of  
84 this paper is to combine mineralogical, microscopic, petrophysical and organic geochemical  
85 data to shed light on the controls of what are very substantial, maturity-related changes in the

86 porosity of marine, organic-rich, calcareous mudstones from the Posidonia shale (*ca.* 100 to  
87 180°C; 0.53% to 1.45% Ro). The samples are particularly useful because previous studies  
88 have shown that the organic matter type and mineralogy of samples from the three wells are  
89 similar, albeit in the presence of sub-centimetric heterogeneities (e.g. Rullkötter *et al.*, 1988;  
90 Littke *et al.*, 1991; Vandenbroucke *et al.*, 1993). We were thus able to track the evolution of  
91 the inorganic framework, organic matter and porosity as a result of increasing thermal stress,  
92 in addition to the role that small-scale heterogeneity plays in the development of porosity.  
93 Also, whilst the Posidonia Shale is not currently a major shale reservoir target, our results  
94 show that it shares common mineralogical, sedimentological and geochemical characteristics  
95 with the organic-rich facies of both the Haynesville (Hammes and Frébourg, 2012; Klaver *et*  
96 *al.*, 2015) and Vaca Muerta (Kietzmann *et al.*, 2011) shales, both of which are important  
97 shale gas resource plays.

98

## 99 **2. Samples and Methodologies**

100 The Posidonia Shale of the Lower Saxony Basin, North Germany is a fine-grained,  
101 calcareous sediment deposited in an epicontinental sea during the Lower Toarcian, second-  
102 order sea level rise (e.g. Littke *et al.*, 1991; Röhl and Schmid-Röhl, 2005). The Lower  
103 Toarcian transgression was a global event that induced worldwide shelf anoxia and produced  
104 excellent petroleum source rocks (Bachmann *et al.*, 2008). Temporal changes within the  
105 Posidonia Formation are suggested to reflect higher order sea level changes, coupled with  
106 subtle climatic fluctuations (Röhl *et al.*, 2001). Based on macro- and microscopic  
107 observations, the formation is sub-divided into three units: lower marlstone (I), middle  
108 calcareous clay-shale (II) and upper calcareous clay-shale (III) (Figure 1b). While the  
109 marlstone differs from the overlying shales in having higher carbonate contents (55-61 wt.%),

110 units II and III are lithologically similar (35-38 wt.%) and are distinguished by the common  
111 occurrence of bivalves in the middle (II) shale (Littke *et al.*, 1991, Rullkötter *et al.*, 1988). All  
112 three units contain well-preserved, Type II marine organic matter with minor contributions of  
113 terrestrial macerals (Bour *et al.*, 2007; Littke *et al.*, 1991; Röhl *et al.*, 2001).

114 For this study, samples were taken from the stratigraphically equivalent sections of three  
115 boreholes in the Hils syncline: Wickensen (0.53%  $R_o$ ), Harderode (0.89%  $R_o$ ) and Haddessen  
116 (1.45%  $R_o$ ) (Figure 1a). The Hils half-graben forms part of a series of horst and graben  
117 structures that evolved during the Late Jurassic and Cretaceous (Bruns *et al.*, 2014; Radke *et*  
118 *al.*, 2001). Partly due to the complex tectonic and thermal history of the area, the origin of  
119 maturity variations in the Hils area is still debated. Some proposed that local variations in  
120 maturity relate to a Cretaceous intrusive body, the Vlotho Massif (Schaefer and Littke, 1988),  
121 whilst others suggest that the maturity gradient is a function of differential burial (Mackenzie  
122 *et al.*, 1988; Munoz *et al.*, 2007). Recent 3D modelling studies suggest that the region  
123 experienced a complex burial and thermal history, with differential heat flow associated with  
124 the Mesozoic rifting episodes (Bruns *et al.*, 2014).

125 26 samples representing different stratigraphic units and maturities were selected for  
126 bulk analyses including Rock-Eval, TOC, grain density and total porosity (Figure 1b). The  
127 majority of samples were taken the lowest and highest maturity wells, mainly because of  
128 sample availability. Total Organic Carbon was measured with a LECO carbon analyzer  
129 equipped with a HF-100 Induction Furnace on a carbonate-free aliquot. Standard Rock-Eval  
130 was performed according to Espitalié *et al.* (1977) using a Delsi Rock Eval OSA. To correct  
131 for an oil-in-kerogen peak, 4 shale samples were solvent extracted with a mixture of  
132 dichloromethane (93%) and methanol (7%) and subsequently analysed for its remaining  
133 hydrocarbon potential.



134 The X-ray diffraction was performed by Macaulay Scientific Consulting Ltd. Bulk  
 135 samples were wet ground (in ethanol) in a McCrone mill and spray dried to produce random  
 136 powders with the optimum distribution of grains. X-ray powder diffraction (XRPD) patterns  
 137 were recorded from 2-75°2 $\theta$  using Cobalt K $\alpha$  radiation. Quantitative analysis was done by a  
 138 normalised, full pattern reference intensity ratio (RIR) method. Expanded uncertainty using a  
 139 coverage factor of 2, i.e. 95% confidence, is given by  $\pm X^{0.35}$ , where X = concentration in  
 140 wt.%, e.g. 30 wt.%  $\pm 3.3$ .

141 Grain density was measured on samples dried at 105°C using the “Small Pycnometer  
 142 Method” with an error  $\pm 0.02$  g/cm<sup>3</sup>. In this method (Rexer *et al.*, 2013), 3 g of dry powdered  
 143 shale sample was added to a pre-weighed pycnometer of a nominal value 50 mL, immersed in  
 144 the 10 mL of surfactant (5% Teepol) and gently shaken. The slurry was outgassed in a  
 145 dessicator overnight, filled with the outgassed deionized water up to the total volume of the  
 146 pycnometer and weighed at temperature 25°C. The grain density was calculated from  
 147 Equation 1:

$$148 \quad \rho_g = \frac{\rho_w (m_2 - m_1)}{(m_4 - m_1) - (m_3 - m_2)} \quad (1)$$

149 where  $\rho_g$  (g/cm<sup>3</sup>) is the shale grain density,  $\rho_w$  (g/cm<sup>3</sup>) is the density of water at 25°C, m1  
 150 (g) is the pycnometer mass, m2 (g) is the mass of the pycnometer plus dry sample, m3 (g) is  
 151 the mass of the pycnometer plus dry sample plus water, and m4 (g) is the mass of the  
 152 pycnometer plus water.

153 Total shale porosity was determined from the measured grain density and bulk density  
 154 when immersed in mercury at the pressure 25 psia using Equation 2:

$$155 \quad \emptyset = 1 - \frac{\rho_b}{\rho_g} \quad (2)$$

156 where  $\emptyset$  (%) is the calculated total shale porosity,  $\rho_b$  (g/cm<sup>3</sup>) is the measured bulk density at  
157 25 psia, obtained using a Micromeritics Autopore IV Mercury Injection Porosimeter, and  $\rho_g$   
158 (g/cm<sup>3</sup>) is the predetermined grain density (Rexer *et al.*, 2014).

159 For microscopic studies, 20 highly-polished thin sections and 3 resin covered blocks, cut  
160 perpendicular to bedding, were prepared. Thin sections were first scanned using an Epson  
161 Perfection V500 scanner with 9600 dpi resolution. Subsequently, each thin section was  
162 examined with a Nikon Eclipse LV100 POL transmitted light petrographic microscope with  
163 an attached Nikon Digital Sight DS-U3 camera. Polished blocks were examined in reflected  
164 and UV light using an Oil Zeiss Immersol 518N oil immersion microscope. The fluorescence  
165 of organic matter was determined qualitatively using UV light with an HXP 120C accessory.

166 Carbon-coated polished thin sections were examined using a Hitachi SU-70 High  
167 Resolution Analytical SEM, equipped with an Oxford Instrument Energy Dispersive X-ray  
168 microanalysis system (INCA Energy 700). Samples were viewed in Back Scattered Electron  
169 (BSE) mode using the YAG detector with the following conditions: 15-8 mm WD, 15keV  
170 accelerating voltage, 2-4 nA filament current. To reduce the shale topography, prior to the  
171 SEM imaging, selected samples were polished with an argon broad ion beam (BIB) in a  
172 GATAN 691 Precision Ion Polishing System (PIPS<sup>TM</sup>). In order to fit into the system's  
173 chamber, the sample size was reduced to a 3 mm diameter disc with a GATAN 601  
174 Ultrasound Disc Cutter using a water emulsion of boron nitrate powder as a saw. Discs were  
175 inserted into the PIPS<sup>TM</sup> chamber and bombarded with Ar ions in a vacuum (10<sup>-2</sup> Pa) for 6  
176 hours (angle 3°, 5kV, 1-20  $\mu$ A). Images used to quantify porosity were captured in Secondary  
177 Electron (SE) mode using a through-the-lens detector (TLD) at magnification 6,000x (pixel  
178 size 15 nm). The total image porosity (practically, macroporosity due to the magnification  
179 used) was quantified on image mosaics covering a total area 6000  $\mu$ m<sup>2</sup> with the point

180 counting method (10,000 counts) in the image analysis software JMicroVision 1.2.7. (Roduit,  
181 2008).

182 For selected areas, element maps were generated using Energy Dispersive X-rays (EDX).  
183 Settings for the EDX collection were 300  $\mu\text{m}$  dwell time for 35 frame acquisition, 15kV  
184 accelerating voltage and 2.5 nA filament current.

185 For high resolution imaging, three samples were milled, polished and imaged with a  
186 gallium (Ga) focused ion beam (FIB) in the FEI Helios Nanolab 600, using a FEG source. 15  
187  $\mu\text{m}$  x 5  $\mu\text{m}$  trenches were cut using 8-16kV accelerating ion beam voltage and 0.93-5.5 nA  
188 beam current. Samples were viewed in BSE Immersion or secondary electron mode with the  
189 following conditions: 4.1 mm WD, 1.5-3.0 kV accelerating voltage, 0.17-1.4 nA beam  
190 current, using a through-the-lens detector for better spatial resolution. The images were  
191 captured at magnifications between 10,000-200,000x, corresponding to pixel sizes 25-1.2 nm.  
192 These images were not used for quantitative porosity estimates due to the limited and thus  
193 non-representative areas covered by the image.

194

### 195 **3. Results**

196

#### 197 **3.1 Composition and Texture**

198 Low maturity Posidonia shale from the Wickensen (WIC) borehole ( $R_o = 0.53\%$ ) is a  
199 medium grey, calcareous nannoplankton-bearing to calcareous nannoplankton-rich mudstone  
200 (with the majority of mineral grains  $< 62.5 \mu\text{m}$  in diameter), showing mineralogical  
201 differences on scales ranging from millimetres to metres (Figures 1, 2). Bulk mineralogy  
202 (Table 1) indicates similar proportions (30-40 wt.%) of both calcite and clays in the upper  
203 shale units, with higher amounts of calcite compared to clays in the lower marlstone unit

204 (~50% and ~25% respectively). As the main minerals, calcite and phyllosilicate abundances  
205 are inversely correlated. The visible calcareous fraction is much coarser in the lowest  
206 marlstone unit (up to 0.6 mm; Figures 2, 3f) in comparison to both clay-rich units (typically  
207 <0.1-0.3 mm; Figures 3a, 3b, 3c). Macrofossils were rarely observed in this study except for  
208 rare occurrences of foraminifera (Figures 4e, 7a), bivalves (Figure 4c), fish-bone fragments  
209 and other, unrecognized calcareous skeletal fragments.

210 Although the finest particles and cements constituting the shale matrix cannot be  
211 resolved with standard petrographic methods, the microcrystalline nature of the  
212 microscopically distinguishable carbonate aggregates suggest that they are compacted faecal  
213 pellets (Bour *et al.*, 2007; Littke *et al.*, 1987; Röhl *et al.*, 2001; Röhl and Schmid-Röhl, 2005;  
214 Schieber, 1999). Their distribution varies from (a) sparse and in some cases aligned into  
215 discontinuous layers in the calcareous shales, to (b) densely packed in the marlstone unit.

216 All three units of the Posidonia contain more-or-less apparent, sub-centimetric light and  
217 dark laminae, reflecting differences in the proportion of carbonate and clay components  
218 (Figure 2). This lamination is most pronounced in the upper shale unit (Figures 3a, 3b), with  
219 individual laminae typically up to 3 mm thick (Figure 2a). In both the lower calcareous shale  
220 (Figure 3c) and marlstone horizons (Figures 3d, 3e, 3f) the sub-centimetric lamination is  
221 typically less pronounced. In the marlstone unit, horizontal lamination is partly imparted by  
222 variations in the abundance of faecal pellets (Figures 2b, 3d, 3e, 3f). Here, due to the large  
223 size of individual pellets (often exceeding 0.5 mm), lenticular lamination is common (Figures  
224 2b, 3e, 3f) and convoluted lamination also occurs. In all units, contacts between laminae are  
225 parallel and vary from sharp to gradual (Figures 2a, 2b, 3b). The regular character of the  
226 lamination suggests that it is primary, reflecting changes in the relative supply of the clastic  
227 and biogenic components. Rarely, boundaries between laminae are marked by an erosional  
228 contact or the presence of a thin layer of silt-grade carbonate or quartz (Figure 3c).

229 Modest changes in composition and fabric occur at maturities of  $R_o > 0.9\%$  and  $1.45\%$ .  
230 While the total clay and carbonate contents do not differ from those encountered in the  
231 immature section, there is a relative increase in the proportion of dolomite to calcite,  
232 irrespective of the unit (Table 1). Although there is no conclusive petrographic evidence for  
233 the timing of dolomite formation, its absence in low maturity shale, plus the higher content of  
234 Na-rich plagioclase in rocks of higher maturity (Table 1), suggests that both minerals formed  
235 at oil window maturities. The textural effect of these processes can be seen at the thin section  
236 scale. In both Harderode and Haddessen, the primary sub-centimetre lamination is either still  
237 preserved (Figures 4b, 5d), modified (Figures 2c, 4a) or obliterated (Figure 2d) due to  
238 diagenetic changes affecting the matrix calcite and generation/expulsion/redistribution of  
239 organic matter (Figures 4, 5). Authigenic carbonate is common, with crystals reaching  $> 100$   
240  $\mu\text{m}$ , and up to  $0.05\text{-}0.1\text{ mm}$  (Figures 4d, 5b, 5c, 5e), commonly cementing algal bodies  
241 (Figure 4c), fossil cavities (Figure 4e) or fractures (Figure 4f). Some layers are more affected  
242 by diagenetic changes (Figure 4a) and may reflect differences in the original composition,  
243 e.g. higher calcite or quartz contents. Consistent with the observations from the low maturity  
244 borehole, faecal pellets are more abundant in the marlstone unit (Figure 5f) than in the  
245 calcareous clay-shale (Figures 5a, 5e).

246

### 247 **3.2 Microstructure**

248 High-resolution BSEM micrographs show that most of the carbonate fraction in the early  
249 mature Wickensen samples is of biogenic origin, deposited as faecal pellets (Figures 6a, 6c).  
250 Nannofossils, mostly coccoliths and schizospheres, form debris dispersed in the shale matrix  
251 or concentrated in microlayers or ellipsoidal aggregates (Figure 6c). Although individual  
252 particles are often mechanically broken (Figure 6b), some samples still contain a high

253 proportion of less disarticulated material. The size of nannofossil aggregates varies from <5  
254  $\mu\text{m}$  (Figure 6b) in the calcareous shale units to over 500  $\mu\text{m}$  in the marlstone samples. In all  
255 units, microlamination is typical, but its pattern is different in the sub-centimetre light and  
256 dark laminae. In lighter laminae, nannofossil material tends to form continuous, <50  $\mu\text{m}$  thick  
257 layers (Figure 6a), whilst in the dark laminae, isolated islands of faecal pellets are commonly  
258 surrounded by the clay-rich matrix (Figure 6b). The biogenic fraction shows signs of  
259 diagenetic alterations, but its intensity is different in the marlstone and calcareous shale units.  
260 Calcite diagenesis is more prominent in the marlstone unit (Figure 6c) and involves  
261 precipitation of calcite cement in the intrafossil and intergranular porosity of coccoliths and  
262 schizosphere debris. Cement precipitation, and possibly local dissolution and reprecipitation  
263 of fossiliferous grains, is documented by the appearance of faceted calcite crystals coexisting  
264 with still unaffected fossil structures. In the two more clay-rich Posidonia units, carbonate  
265 cement is also present, but the intensity of calcite diagenesis is lower. Nevertheless, we  
266 observed subtle authigenic overgrowths on biogenic fragments (Figure 6b), authigenic  
267 cement within biogenic aggregates, and the presence of small microcarbs of unknown origin,  
268 infilling porosity. Overall, authigenic calcite precipitation is more prevalent in the sub-  
269 centimetre, light laminae, which contain greater concentrations of nannofossil material, and is  
270 weaker in the clay-rich zones where biogenic fragments are more dispersed.

271 Loss of nannofossil structures and precipitation of new authigenic phases is more  
272 advanced in samples of maturity 0.9% Ro (HAR) and 1.45% Ro (HAD). In both HAR and  
273 HAD, the infilling of coccolith canals and foraminifera cavities with calcite cement is  
274 ubiquitous (Figures 7a, 7b). The biogenic structures, although still present, are less  
275 discernible, and fusing features within faecal pellets are common (Figure 7e). The loss of  
276 individual nannofossil structures suggests calcite dissolution and reprecipitation, but little  
277 specific textural evidence is observed, apart from the presence of faceted calcite crystals in

278 place of coccoliths (Figure 7d). Individual subhedral and euhedral crystals of authigenic  
279 calcite vary in size from  $< 1 \mu\text{m}$  up to tens of microns (Figure 7e). In some cases, calcite  
280 cement fills algal cysts (Figure 6e), preventing them from compacting mechanically. Some  
281 zones are fully cemented, and their size can reach up to  $1000 \mu\text{m}$  in length (Figure 7f).  
282 Alternatively, these large calcite masses may represent modified and unrecognizable, large  
283 fossil fragments. Authigenic dolomite is common, and can be observed either as small ( $< 20$   
284  $\mu\text{m}$ ), discrete crystals (Figure 7b), or as large, cemented zones up to  $100 \mu\text{m}$  in length.

285 The composition of the clay fraction is similar at all maturities. Detrital clays are  
286 potassium-rich; authigenic kaolinite is present and is usually observed filling algal cysts and  
287 cavities in fossil canals, or alternatively as framework replacive/displacive cement (Figure  
288 7f). The detrital silt fraction is dominated by quartz, forming anhedral, rounded to subangular  
289 grains varying in size from under  $1 \mu\text{m}$  up to  $20 \mu\text{m}$  (Figures 6a, 7a). In samples at higher  
290 maturities, authigenic quartz often cements detrital quartz grains (Figure 7a). In some cases,  
291 recrystallized quartz forms part of diagenetically modified microlayers (Figure 6f). Finally,  
292 authigenic pyrite is present at all maturities, forming small euhedra (Figures 6f, 7c), oval  
293 framboids (Figures 6c, 7b, 7d), nodules, or directly replacing biogenic calcite and quartz  
294 (Figure 7c).

295 Physical compaction can be seen as horizontal flattening of algal cysts, clay aggregates,  
296 and faecal pellets (Figures 3a, 6d, 8). The collapse of the shale structure can also be seen  
297 adjacent to rigid shale components associated with compaction shadows. The shortening of  
298 the matrix in the vertical direction is clear at maturities between 0.5-0.9%  $R_o$ , often related to  
299 the collapse of algal cysts (Figure 6d).

300

### 301 **3.3 Organic matter**

302 In the least mature shale at 0.53%  $R_o$  (WIC), TOC varies between ~ 7-15 wt.% (mean 10  
303 wt.%), decreasing to an average of ~ 7% in the peak oil window (HAR 0.89%  $R_o$ ) and down  
304 to ~ 6% in the gas window (HAD 1.45%  $R_o$ ; Table 2). RockEval data confirm the maturation  
305 pathway typical for the Type II marine kerogen. We also observed a consistent drop in both  
306 S1 and S2 yields, resulting in a decrease in HI from ~650 to ~60 mg/gTOC. A significant  
307 drop in yield, from 10 to 1 mg/g, was observed for the amount of organic matter pyrolyzable  
308 under standard RockEval conditions, but on samples pre-extracted with organic solvents  
309 ( $S2_a$ ). For all samples,  $S2_a$ , which is that part of the S2 peak which can be solvent-extracted  
310 and can thus be considered as a form of bitumen, is consistently higher than RockEval-  
311 measured S1 (Table 3). Oil saturation indices, calculated as the ratio of ( $S1 + S2_a$ ) to TOC,  
312 vary from 105 mg/gTOC for the early oil window sample, 66 and 102 for the two peak oil  
313 window samples and 27 mg/gTOC for the gas window sample.

314 Most of the organic matter is unresolved in the standard petrographic sections. Resolved  
315 organic matter occurs as flat, up to 0.3 mm long, organo-clay aggregates (Figures 3d, 3f) and  
316 as highly compacted, discrete cysts (Figure 3a). Large terrestrial organic particles (up to 500  
317  $\mu\text{m}$ ) are scarce, but relatively more common in the marlstone unit (Figures 2b, 3e, 3f).

318 Organic macerals show a gradual change in type, volume and colour as a function of  
319 maturity. At  $R_o = 0.53\%$ , structured algal liptinite (e.g. Tasmanales, Leiosphaeriales) is  
320 common, forming well-preserved laminae or thick bodies (Figures 9a, b), and co-existing  
321 with less pronounced lamellar bituminite. The shale matrix is strongly fluorescing,  
322 comprising a bituminous-mineral groundmass, with its organic component, the so-called  
323 matrix bituminite, representing a non-structured degradation product of marine phytoplankton  
324 and zooplankton (Tao *et al.*, 2012); this forms the most abundant organic component in the  
325 shale. In low maturity Posidonia, the bituminous groundmass is primarily associated with  
326 clays (Figure 6a), but may also fill the interstices within fossils. Terrestrial macerals,



327 including vitrinite and inertinite, are dispersed and are present in low abundance. Both  
328 structured liptinite and terrestrial macerals contain sulphur, typically incorporated into  
329 organic matter as a by-product of bacterial sulfate reduction processes taking place in anoxic  
330 sediment (Macquaker *et al.*, 2014, and references therein).

331 At the peak oil window maturity, structured algal liptinite is volumetrically less abundant  
332 and has a weak, brownish fluorescence (Figure 9c). The bodies of Tasmanales are collapsed  
333 (Figure 6d), or locally filled with diagenetic carbonates (Figure 6e). The bituminous  
334 groundmass is much less fluorescent and instead, a dense network of non-solvent extractable,  
335 solid bitumen fills intergranular space (Figures 9d, 10a). The increased concentration of solid  
336 bitumen within faecal pellets provides a strong contrast to the typical organo-clay  
337 associations observed at lower maturity. Solid bitumen can also be found within  
338 microfractures, often in association with diagenetic carbonates (Figure 9d).

339 At the gas window maturity, the bituminous groundmass exhibits a very weak  
340 fluorescence, and no structured algal liptinite is present (Figure 9e). A tight network of  
341 irregularly-shaped, non-extractable, solid bitumen is a dominant feature (Figures 9f, 10b).  
342 The bitumen phase pervasively fills the tight, clay-carbonate matrix and microfractures.

343

### 344 **3.4 Porosity**

#### 345 **3.4.1 Total Porosity**

346 Average grain densities increase as a function of maturity from  $\sim 2.3 \text{ g/cm}^3$  at 0.53%  $R_o$ ,  
347 to  $\sim 2.5$  at 0.89%  $R_o$  and  $\sim 2.6$  at 1.45%  $R_o$ , reflecting the reduction in organic matter volume  
348 and the increase in kerogen density (Okiongbo *et al.*, 2005; Rexer *et al.*, 2014; Table 2). At  
349 0.53%  $R_o$ , porosities vary between 10-14% and, despite the decrease in TOC and expulsion  
350 of petroleum, decline to 2.5-4.5% in the peak oil window (0.89%  $R_o$ ) (Table 2). In contrast, at  
351 gas window maturities, with further reduction of the organic carbon content, total porosity

352 increases to 9-14%, similar to those at 0.53%  $R_o$ . Porosity does not correlate with mineralogy  
353 or TOC at any maturity, although any potential patterns would be difficult to discern given  
354 the relatively narrow range of both mineralogy and TOC content.

355 Grain densities and total porosities change when soluble bitumen is extracted (Table 3).  
356 The most significant increase in grain density was measured in the peak oil window sample,  
357 with an insignificant increase in the gas window shale and a very slight decrease in the early  
358 mature shale (Table 3). On the basis of the change in the grain density of bulk shale “pre-”  
359 and “post-extraction”, we estimated the amount of the extractable bitumen and thus the  
360 “minus-soluble bitumen” total porosity for three samples of medium (HAR 7060, 7070) and  
361 high maturity (HAD 7110). We assumed that the extractable bitumen occludes porosity, and  
362 therefore its amount is equivalent to the fraction of porosity filled with soluble bitumen. The  
363 results show that the amount of the extractable bitumen present in samples decreases from 2.8  
364 volume % in the marlstone and 3.4 volume % in the calcareous shale at the peak oil window  
365 maturity to 0.68% (calcareous shale) in the gas window (Table 3); this corresponds to oil  
366 saturations (i.e. % of porosity filled with soluble bitumen) of *ca.* 44%, 44% and 7%  
367 correspondingly. Some of this bitumen is likely to be physically associated with kerogen and  
368 so the oil saturations should be taken as maxima. Hypothetical, bitumen-free total porosities  
369 after solvent extraction are higher than those measured in the as-received shale (Table 2),  
370 amounting to 6.3-7.8% and 10.1% in the peak oil window and gas window samples  
371 respectively (Table 3).

372

### 373 **3.4.2 SEM Observation of Meso- and Macroporosity**

374 Porosity point-counted from BIB-SEM images is not significantly different in samples of  
375 different maturity, amounting to 1.3% in the Wickensen sample, and 1.1% and 1.5% in the  
376 Harderode and Haddessen samples respectively (Figure 11a). Due to the limited image

377 resolution (pixel size 15 nm), almost all point-counted pores lie within the macropore size  
378 range ( $> 50$  nm). Mesoporosity (2-50 nm) is thus greatly underestimated or, along with the  
379 microporosity ( $< 2$  nm), unresolved. Consequently, the point-counted image porosity is only  
380 14-25% of the experimentally measured total porosity, with the highest fraction of resolved  
381 porosity found in the oil window shale (Figure 11b).

382 Pores were classified into interparticle, intraparticle and organic matter-hosted using the  
383 general classification of Loucks *et al.* (2009). Our division is based on the spatial relation of  
384 pores with respect to mineral phases and organic matter, and not on the origin of pores. The  
385 following definitions of different pore types were adopted here:

386

- 387 • Interparticle: 1) pores between detrital grains, authigenic minerals, nanofossils and clay  
388 flakes; 2) pores (in 2 or 3D space) associated with the interface of organic matter and  
389 mineral matrix that do not visibly extend into an organic particle, and that are either  
390 irregularly shaped or mirror the shape of the adjacent mineral phase;
- 391 • Intraparticle: 1) pores within single mineral grains or fossil bodies; 2) pores within well-  
392 defined faecal pellets and pyrite framboids; 3) moldic pores formed due to dissolution of  
393 mineral phases; 4) pores at the interface of inorganic matrix and organic macerals that do  
394 not visibly extend into an organic particle, contained within a fossil body, faecal pellet or  
395 pyrite framboid;
- 396 • Organic matter-hosted: 1) discrete, round, bubble-like pores in the organic matter; 2)  
397 sponge-like pores within the organic matter, often interconnected and grouped; 3) pores  
398 typically at the interface of organic matter and mineral matrix, irregular in shape, but  
399 visibly extending in 3D into the organic particle; 4) visible cracks within OM particles,  
400 often with jagged edges and extending into the particle.

401

402 Pore types estimated by point-counting change through the maturity sequence from  
403 exclusively inter- and intraparticle in the low maturity sample, to inter- and intraparticle-  
404 dominated in the peak oil window and finally, to inter- and intraparticle-rich with a moderate  
405 proportion of organic matter-hosted pores in the sample from the gas window maturity  
406 (Figure 12). Visual observations of different pore types using high-resolution SEM  
407 micrographs show a varied assemblage of pores with sizes as small as 5 nanometers  
408 (200,000x magnification), up to a few  $\mu\text{m}$ .

409 In the least mature sample (Figure 13), visible pores are associated mainly with biogenic  
410 calcite, with no significant porosity within the clay matrix. The typical intraparticle pores  
411 associated with calcite are found within fully-open coccolith canals, coccolith canals partly  
412 cemented with authigenic calcite, within fragments of *Schizosphaerella*, as well as between  
413 fragmented or crushed nanofossils and authigenic calcite phases within well-defined faecal  
414 pellets (Figures 13a-e). Intraparticle pores are also found within zones cemented with  
415 authigenic calcite, between cement crystals, and within discrete calcite crystals as a result of  
416 carbonate dissolution (Figure 13h). In some cases, those pores are lined with organics,  
417 imparting a smooth, pendular shape to pore edges (Figure 13e).

418 In contrast to the intraparticle pores, interparticle, carbonate-associated pores are found  
419 mostly between carbonate phases and the organo-clay matrix (Figures 13i, j). The size and  
420 shape of inter- and intraparticle pores is strongly related to the extent of precipitation of  
421 diagenetic carbonates (Figure 13i). The size of visible, calcite-associated pores ranges from  
422 tens of nanometres to  $\sim 3 \mu\text{m}$ . Pores found in the fossil bodies of *Schizosphaerelles* are usually  
423 equant and straight edged, up to 500 nm in diameter. Large inter- and intraparticle pores  
424 associated with altered nanofossils and carbonate cements can be straight edged or  
425 spheroidal, reaching up to  $3 \mu\text{m}$ .

426 Non-calcite-associated porosity is relatively minor but small amounts of interparticle  
427 pores occur between detrital clays, or adjacent to quartz, or pyrite, often at the interface with  
428 organic matter. These pores can reach 2-5  $\mu\text{m}$  in diameter but also may form narrow, < 100  
429 nm rims around or adjacent to mineral phases or organic matter (Figure 13k). Elongated  
430 intraparticle pores occur within clay group minerals, more pronounced where pyrite has  
431 precipitated between clay platelets (Figure 13f). Large intraparticle pores, often lined with  
432 organic matter, can also be sporadically found within pyrite framboids (Figure 13g).

433 At the maturity of 0.5%  $R_o$ , the majority of organic matter is not internally macroporous.  
434 Occurrences of intraparticle organic matter-hosted pores are very rare but include remnant  
435 porosity within walls of semi-compacted Tasmanales bodies (Figure 13l) and well-defined,  
436 round or angular, < 1  $\mu\text{m}$  pores found within arcuate, likely terrestrial organic particles.

437 In the shale at oil window maturity, most of the pore types observed at lower maturities  
438 are absent, lost due to compaction (mechanical and chemical) or occluded by solid bitumen  
439 (Figure 10a). Several new types of intra- and interparticle pores occur (Figure 14).  
440 Commonly, pores are associated with organic matter and/or authigenic phases. Elongated  
441 pores with jagged edges cross-cut organic particles and resemble microfractures (Figures 14a,  
442 b). Many pores are found at organo-mineral interfaces and exhibit complex shapes which  
443 match those of the surrounding mineral phases (Figure 14e). Most of these interface pores are  
444 associated with diagenetic calcite and are occasionally filled with authigenic phases (Figure  
445 14f). In 3D, pores found directly within organics can always be traced to particle edges  
446 (Figures 14c, d).

447 Pores in oil window shales are also hosted within inorganic domains (Figure 14g).  
448 Fracture or cleavage-related porosity is associated with clay-mineral platelets (Figure 14h),  
449 sometimes partially filled with authigenic phases such as pyrite (Figure 14i). Crack-like pores  
450 are also observed at clay-carbonate interfaces. In 3D Slice and View reconstructions, crack-

451 shaped pores often follow the shape of underlying organic phases. Within carbonate minerals,  
452 intraparticle dissolution pores can be found (Figure 14k), ranging in size from < 100 nm up to  
453 2  $\mu\text{m}$ . Rare intraparticle porosity, not clogged by bitumen, is also encountered within  
454 domains of authigenic calcite (Figure 14l) and pyrite framboids (Figure 14j).

455 Gas window shale, in contrast to samples of lower maturities, contains porosity *within*  
456 organic particles (Figure 15). This porosity is highly heterogeneous, such that the point-  
457 counted porosity of individual organic particles ranges from 0-40%; 65% of organic particles  
458 contain no SEM-visible porosity, i.e. no pores larger than around 50 nm.

459 Although the shape and size of organic matter-hosted pores form a continuum, we  
460 distinguished several end-members:

461

462 1. Isolated, bubble-like pores, generally < 100 nm in diameter. Their spatial  
463 distribution within organic components is varied, sometimes uniformly  
464 distributed within an organic 'particle' (Figure 15a), or occupying only a fraction  
465 of a 'particle' (Figure 15c), or concentrated at 'particle' margins (Figure 15f).

466 2. Similar to 'bubble' pores, but usually clustered in groups, are sponge-like pores  
467 (Figure 15b). They are very often visibly interconnected in 2D and in 3D Slice  
468 and View images, with elongated shapes of sizes exceeding 100 nm. The  
469 direction of elongation is often along the margin of two adjacent phases, for  
470 example at the interface of porous and non-porous organic phases, or near an  
471 organic-inorganic interface. Similarly to discrete pores, sponge-like pores may be  
472 evenly distributed or occupy only a fraction of an organic 'particle'.

473 3. With the increase in size and connectivity of individual pores, sponge-like pores  
474 may be replaced by irregularly shaped or spheroidal organic matter-hosted pores.  
475 Although often present directly within organic matter (Figure 15d), in 3D they

476 are usually associated with organic-inorganic interfaces (Figures 15e, 15h). In 3D  
477 Slice and View images, the interiors of complex pores branch out into numerous  
478 spongy-pores, penetrating the organic mass (Figure 15e). Depending on the size  
479 of a host organic 'particle', the diameter of a single complex pore may reach 500  
480 nm.

481 4. Similar in shape to sponge-like pores, but usually associated with 'particle'  
482 margins and less likely to agglomerate into complex pores, are oval, 'pendular'  
483 pores (Figure 15c). Ranging in diameter from a few tens to a few hundreds of  
484 nanometers, a single 'pendular' pore can occupy a large fraction of a 'particle' or  
485 alternatively, may be located only at the 'particle' interface. Within a single  
486 organic 'particle', 'pendular' pores can co-exist with other organic matter-hosted  
487 pore types.

488 5. The last type of intraparticle organic matter-hosted pore is found within terrestrial  
489 macerals (Figure 15g). The shape of these pores varies from angular to oval, and  
490 their size may reach up to 1  $\mu\text{m}$  in diameter.

491  
492 Although intraorganic pores are a very characteristic feature of the gas window  
493 Posidonia shale, mineral-associated porosity is still the primary form of SEM-visible porosity  
494 (Figure 12). As for the irregular and complex organic matter-hosted pores, mineral-associated  
495 pores are commonly present at the organic-inorganic interface, but do not visibly penetrate  
496 adjacent organic matter (Figures 15h, 16a, 16d-f). These interface pores have jagged edges,  
497 with an irregularly-shaped organic face (Figure 15h), or smooth outlines (Figure 16b, c),  
498 resembling the smooth interface pores already present in the oil window (Figure 14e).  
499 Depending on their relation to the surrounding inorganic phases, the mineral-associated pores  
500 can be classified either as intraparticle or interparticle. The locations of the highest density of

501 the interface pores include faecal pellet domains and pyrite framboids (Figures 15i, 16e), but  
502 the jagged-shaped pores can also be found in the vicinity of detrital grains and clay packages  
503 (Figure 16f). The interface pores are the largest pores present in the gas window Posidonia,  
504 and their size can exceed 2  $\mu\text{m}$  in diameter.

505 Other types of mineral-hosted pores in the gas mature sample are relatively uncommon  
506 but include: intraparticle pores within mica group minerals (Figure 16g), intracrystal  
507 carbonate dissolution pores with characteristic rhomboidal outlines (Figure 16h) and possibly  
508 blind pores between carbonate cement crystals (Figure 16i).

509

## 510 **4. Discussion**

### 511 **4.1 Mineralogy and Texture**

512 The laminated texture of the immature Posidonia shale, observed mainly at the sub-  
513 centimetre scale in this study, primarily reflects variations in the relative rates of supply of  
514 biogenic calcite and detrital, clay-rich material. The predominantly concordant contacts  
515 between laminae confirm the primary nature of the lamination and the lack of bioturbation  
516 supports the probability that bottom waters were depleted in oxygen, as required for the  
517 preservation of significant organic matter. In contrast to Trabucho-Alexandre *et al.* (2012)  
518 who investigated Posidonia Shale from the Dutch Central Graben characterized by a higher  
519 clastic input, we did not encounter evidence of wave or current activity, apart from rare layers  
520 of silt-sized material of unknown origin and very rare scours (Figure 4a).

521 Littke *et al.* (1991) ascribed variations in the amount of carbonate and clay minerals to  
522 relative changes in the rate of nutrient-dependent primary production in surface waters as  
523 compared to the supply of terrigenous clays. Similar vertical laminations have also been  
524 observed in the Posidonia Shale deposited in the Southwest German Basin (Röhl *et al.*,



2001). In this study, the importance of variations in carbonate and clay is less its palaeoenvironmental significance but rather the way it influences diagenesis, the migration and trapping of petroleum and the related way in which the pore system evolved. This is explored in the next section.

529

#### 530 **4.2 Porosity and MacroPores**

531 A key observation of this study is the way in which porosity changes as a function of  
532 maturity. Porosities of as-received samples, at the start of oil generation ( $R_o = 0.5\%$ , *ca.*  
533  $100^\circ\text{C}$ ), are 10-14%, declining to 3-5% at  $R_o = 0.9\%$  (*ca.*  $150^\circ\text{C}$ ) and then increasing to 9-  
534 12% at  $R_o = 1.45\%$  (*ca.*  $180^\circ\text{C}$ ). In rationalizing these results, we must recall that the  
535 petrographic data we present in this paper, whilst quantitative in terms of point-counted  
536 porosity, only accounts for around 15-25% of total porosity. Since the effective resolution in  
537 this study is around 50 nm, we can only quantify macroporosity, which in these samples is  
538 mainly associated with carbonate-rich areas of the sediment and, in the gas window samples,  
539 organic matter. As discussed by Rexer *et al.* (2014) in a study of WIC 7145, WIC 7155, HAR  
540 7038, HAR 7060, HAD 7090 and HAD 7119, which are also part of this study, the majority  
541 of porosity in these shales is micro- and mesoporous, associated mainly with clay minerals  
542 and organic matter, and cannot be considered here. Nevertheless, the division of resolved and  
543 unresolved porosity and their occurrence in specific mineral and organic domains points to  
544 the importance of original rock fabric as a starting point to model porosity retention, loss and  
545 development.

546 We argue here that maturity-related porosity changes reflect the complex interplay of (a)  
547 the primary clay/carbonate fabric, (b) carbonate diagenesis, (c) organic matter maturation,  
548 migration and trapping, (d) gas generation and (e) chemically-enhanced mechanical

549 compaction. Some of these processes occur simultaneously and cause positive or negative  
550 feedback to others.

551

#### 552 ***4.2.1 Carbonate Diagenesis***

553 Resulting from redox reactions during shallow burial, early diagenetic carbonate is  
554 common in many organic-rich mudstones (e.g. Hesse, 1990; Macquaker *et al.*, 2007;  
555 Macquaker *et al.*, 2014) and is observed here as uncompacted, calcite-filled coccolith canals.  
556 Nevertheless, early diagenetic pore-filling carbonate is relatively rare so that much of the  
557 SEM-visible porosity in the lowest maturity samples is associated with fragments of biogenic  
558 carbonate, often concentrated within faecal pellets (Figures 3, 6, 13).

559 Whilst there is some evidence for authigenic calcite in the low maturity samples (Figures  
560 6b, 6c), it is not pervasive. Disappearance of nannofossils, recrystallization of carbonate and  
561 precipitation of cement continues from the lowest to highest maturity samples, i.e. at  
562 temperatures between 100 and 180°C, concomitant with oil and gas generation. The  
563 diagenesis of calcite in organic- and clay-rich shales has not been studied in detail, but our  
564 observations suggest that it may proceed at a different rate to that observed in purer fine-  
565 grained carbonate rocks such as chalk. Pressure solution in chalk starts at temperatures as low  
566 as 20°C, with dissolution seams and stylolites common at 30-40°C (e.g. Mallon and  
567 Swarbrick, 2002). Carbonate recrystallization in chalk is very advanced by 100-120°C,  
568 similar to the temperature experienced by our lowest maturity sample. In contrast, calcite  
569 cementation and recrystallization in the Posidonia are limited at  $R_o = 0.53\%$ , becoming  
570 increasingly evident at 0.9% and 1.45%. Whilst we do not have sufficient information to be  
571 conclusive about the apparently retarded carbonate diagenesis in the Posidonia compared to  
572 chalk, experimental data suggest that argillaceous chinks, due to the inhibition of carbonate  
573 precipitation, are less prone to chemical compaction than pure chalk (Baker *et al.*, 1980). This

574 is consistent with our observations that calcite diagenesis is more advanced in the more  
575 carbonate-rich Posidonia marlstone compared with the more clay-rich middle and upper  
576 Posidonia units. It has also been observed that diagenesis and cementation can be retarded in  
577 oil-filled carbonate and quartzose reservoirs as a result of alterations in the wetting state of  
578 the reservoir from water-wet to oil-wet, and a concomitant reduction of the amount of water  
579 available for solution transfer (e.g. Scholle, 1977; Worden *et al.*, 1998; Heasley *et al.*, 2000).  
580 It is certainly plausible that in an organic-rich shale like the Posidonia, carbonate surfaces  
581 become oil-wet even prior to oil generation, as a result of sorption of polar organic molecules  
582 (van Duin and Larter, 2001; Aplin and Larter, 2005). Nevertheless, it is also plausible that,  
583 similar to oil-saturated chalks, minor recrystallization of calcite continued even under oil-wet  
584 conditions (Fabricius, 2003).

585 Petrographic data are inconclusive about the diagenetic processes which result in the  
586 precipitation of carbonate cements and loss of nanofossil structures. Recrystallization  
587 features, such as euhedral calcite in place of biogenic structures, and contact-cement  
588 structures occur in the lowest maturity samples and are significantly better developed in the  
589 more calcite-rich laminae. Recrystallization and redistribution (for example calcite in  
590 bitumen-bearing microfractures) has clearly occurred, but the relevance of pressure solution  
591 to that process cannot be quantified. We also note that diagenetic dolomite occurs in samples  
592 at 150 and 180°C, which requires a source of magnesium. Whilst the Mg could in principle  
593 be released as a result of the smectite to illite transformation reaction (McHargue and Price,  
594 2006), dolomite in these samples formed at temperatures higher than the main illitisation  
595 window; an alternative source of magnesium has been suggested to be high salinity brines  
596 (Munoz *et al.*, 2007; Bernard *et al.*, 2013).

597 The implications of carbonate diagenesis for porosity evolution are difficult to quantify.  
598 Whilst pore-filling calcite is observed, the loss of biogenic structures suggests that most

599 diagenetic calcite is recrystallized from a biogenic precursor, implying a change from a less  
600 to a more stable calcite type (Fabricius, 2003). Recrystallization of calcite without porosity  
601 modification has been described in chalk (Fabricius *et al.*, 2008) and may inhibit compaction  
602 by forming a stiffer framework due to the development of contact cements. Finally, whilst  
603 stylolitisation is a well-known porosity reduction mechanism in carbonates, resulting in  
604 calcite cement precipitation in pores away from the stress point (Fabricius *et al.*, 2008;  
605 Scholle and Halley, 1985), it is not commonly observed in our samples, at least on a  
606 microscopic scale.

607

#### 608 **4.2.2 Organic matter maturation, migration and trapping**

609 Whilst the way in which different kerogen types decompose to bitumen, oil and gas has  
610 been extensively studied, both generally and specifically within the Posidonia (e.g. Behar *et al.*  
611 *et al.*, 2008a; 2008b; 2010; Bernard *et al.*, 2011; Dieckmann *et al.*, 1988; Horsfield *et al.*, 1992;  
612 Leythaeuser *et al.*, 1988; Lewan, 1997; Rullkötter *et al.*, 1988), the mechanisms of primary  
613 migration, phase behaviour, bitumen entrapment and evolution of organic matter-hosted  
614 porosity are still debated. Behar *et al.* (2008b) proposed a kinetic scheme where kerogen  
615 initially decomposes into a very viscous, NSO-rich liquid which is further decomposed into  
616 more soluble non-hydrocarbon compounds and finally, cracked into hydrocarbons. The  
617 occurrence of a heavy, intermediate bitumen phase was also proposed by Michelis *et al.*  
618 (1996) and Lewan (1997). In this study, RockEval data for unextracted and extracted samples  
619 confirm the presence of a substantial amount of a non-volatile bitumen phase within the low  
620 maturity Posidonia shale (*cf.* Clementz, 1978; Wilhelms *et al.*, 1990). This early-formed  
621 bitumen has a similar density to kerogen (Figure 12) and, based on the lack of petrographic  
622 evidence for porosity-filling bitumen at this maturity, we suggest that it has limited mobility  
623 and is, in the main, physically associated with the precursor kerogen.

624 Continued cracking of the viscous phase into the heart of the oil window results not only  
625 in a less viscous petroleum (Dieckmann *et al.*, 1988; Rullkötter *et al.*, 1988; Schenk *et al.*,  
626 1997) but also a poorly soluble, high molecular weight residue, often described as solid  
627 bitumen, residual petroleum or prechar. Whilst terms such as “petroleum” and “prechar”  
628 simplify what is a complex chemical process which may involve more than two end-member  
629 phases, we can imagine that different phases generated at different temperatures will have  
630 radically different viscosities and mobility. Whilst much of the generated petroleum is of  
631 course expelled from the shale, some remains physically associated with microporous  
632 kerogen (Sandvik *et al.*, 1992; Jarvie *et al.*, 2007); another part, of particular interest here, is  
633 trapped within the pore and microfracture system of the shale (Figures 9; 10). In our study,  
634 micromigration and local trapping is corroborated by microscopic observations which show  
635 the highly dispersed nature of the solid bitumen, forming a semi-continuous network (Landis  
636 and Castaño, 1995; Loucks and Reed, 2014; Milliken *et al.*, 2014). The dispersed nature of  
637 the retained bitumen phase partly reflects that of precursor amorphous organic matter filling  
638 spaces between mineral grains in the immature shale (Figures 6b, 9a). However, in contrast to  
639 the immature kerogen, which is mainly associated with the clays (see also Littke *et al.*, 1991),  
640 it is very common in the peak oil window and gas window to see organic matter infilling  
641 porosity within microfossiliferous domains, indicating micromigration and trapping. It is  
642 plausible that bitumen within the source rock followed the path of least capillary resistance,  
643 entering large pores within microfossils which then acted as micro-capillary traps. At gas  
644 window maturities, the observation of solid bitumen associated with what are now areas of  
645 cement and recrystallized calcite suggests that migration of the bitumen phase was inhibited  
646 once it became trapped in porous, rigid, microfossiliferous zones. Similar solid bitumen,  
647 although of different genesis, is well known in oil and gas reservoirs (Hwang *et al.*, 1998;

648 Lomando, 1992) and also as a product of solidification of heavy oil in coals (Mastalerz and  
649 Glikson, 2000).

650 On average, approximately 3 weight % TOC is lost from our samples between  $R_o =$   
651 0.53% and  $R_o = 0.89\%$  (Table 2). Converting this to a volume % organic matter by assuming  
652 a density for organic matter approximately half that of the mineral matrix (Okiongbo *et al.*,  
653 2005), this would lead to an *increase* in porosity of around 7.5%, assuming a completely rigid  
654 mineral framework and thus zero compaction. There is petrographic evidence for minor  
655 porosity generation. For instance, the appearance of pores at the interface of organic and  
656 inorganic phases (Figures 14d-f) suggests a volume loss of organic matter due to petroleum  
657 generation, although similar observations in the Marcellus shale have also been interpreted as  
658 desiccation, depressurization or post-coring, phase alteration features (Milliken *et al.*, 2013).  
659 Fracture-like pores with jagged edges are also seen (Figures 14a, 14b), but they are relatively  
660 scarce and subordinate to microscale calcite- or bitumen-filled fractures which probably  
661 result from pore pressure increases related to petroleum generation (*cf.* Curtis *et al.*, 2013).

662 Overall, however, there is an average porosity *loss* of 7.9% between maturities of 0.53  
663 and 0.89%  $R_o$  (11.8% to 3.9%; Table 2). Although hard to quantify, petrographic  
664 observations suggest that some of the porosity loss is due to what we term here chemically-  
665 enhanced mechanical compaction, seen for example in the collapse of algal bodies as a result  
666 of petroleum generation (Figure 6d). Bitumen phases may also fill porosity (Figures 9, 10).  
667 Since early mature samples have higher porosities and have the largest amounts of the  
668 extractable bitumen, we suggest that this early bitumen did not migrate but remained  
669 associated with kerogen (Sandvik *et al.*, 1992). In the peak oil window, continued generation  
670 resulted in micromigration, trapping and occlusion of both fracture and matrix porosity  
671 (Figures 9, 10); this can account for up to 3% porosity in the peak oil window (Table 3).

672 The average loss of TOC between 0.89 and 1.45% Ro is 1.0% (Table 2), corresponding  
673 to a potential porosity increase of approximately 2.4%, assuming a constant organic matter  
674 density and no mechanical compaction. This would result in an average gas window porosity  
675 of 6.3%, or 9.3% if we include the fraction of porosity potentially occluded by soluble  
676 bitumen in the oil window, compared to the measured average of 11.3% (which is remarkably  
677 similar to the average porosity of samples directly prior to petroleum generation; 11.8%;  
678 Table 2). The increased porosity coincides with the formation of isolated, spongy and  
679 complex organic matter-hosted meso- and macropores (Figures 15; 16), similar to those  
680 reported in several other gas-mature shales (Milliken *et al.*, 2012; 2013; 2015; Chalmers *et*  
681 *al.*, 2012; Loucks *et al.*, 2012; Bernard *et al.*, 2012; 2013). The lack of similar intraorganic  
682 porosity in immature and oil window samples suggests that it is the gasification process  
683 which generates the pores. However, the heterogeneity of the intraorganic porosity, even on a  
684 scale of a few microns (Figure 16) indicates that the processes which generate porosity in  
685 organic matter are quite complex. In our gas window sample, 65% of organic particles were  
686 not visibly porous in the SEM (although they are microporous; Rexer *et al.*, 2014). Equally,  
687 at the scale observed in the BIB-SEM images, only 25% of total visible porosity is contained  
688 directly within organics, with the majority associated with minerals. Bernard *et al.*'s (2010;  
689 2012) synchrotron-based studies suggested that macropores were specifically associated with  
690 pyrobitumen, rather than kerogen, asphaltene or NSO-rich bitumen, in both the Barnett and  
691 Posidonia Shale. Milliken *et al.*'s (2013) careful petrographic studies of gas-mature  
692 Marcellus shale came to a similar conclusion. Although it is difficult to be sure about the  
693 composition and origin of organic matter in SEM studies, the close association of porous and  
694 non-porous organic phases in gas-mature Posidonia shale, often directly adjacent to one  
695 another on a micron-scale, suggests that pyrobitumen-like, porous phases may have directly  
696 evolved from the neighbouring non-porous particles, were unable to migrate as a result of

697 capillary trapping and/or their high viscosity, and underwent further thermal cracking at  
698 higher temperatures. In this case, the visible pore structure likely marks a boundary between  
699 two different organic phases. This scenario may also apply to non-porous, arcuate terrestrial  
700 macerals, which are often rimmed with a porous organic phase.

701 Although we cannot be certain about the exact role of bitumen heterogeneity on the  
702 distribution of organic porosity, many authors point to the importance of hydrogen donor  
703 compounds such as asphaltenes or hydroaromatics as preventing cross-linking during  
704 cracking reactions (Behar and Pelet, 1988; Michelis, 1996; Schenk *et al.*, 1997) and therefore  
705 delaying the conversion and aromatization of the organic polymers (Lewan, 1997). On the  
706 other hand, Tiem *et al.* (2008) believed that although the absence of hydrogen donors may  
707 enhance cross-linking and reduce oil potential of an organic molecule, it will increase its gas  
708 potential at higher temperatures. It seems probable that the highly variable porosity  
709 development in organic phases relates to different chemophysical properties of the organic  
710 matter at the time of cracking, their association with unexpelled oil and their potential to  
711 release different hydrocarbon fractions, including wet gas and methane. Pyrolysis  
712 experiments on various coals have revealed different potential for porosity development  
713 depending on the maceral composition, their plastic properties as well as coal rank, with the  
714 viscosity and the advance in cross-linking shown to control the extent of the coal  
715 devolatilization (Alvarez *et al.*, 1997). The “bubble-like” nature of some pores may then  
716 represent the last step in gas exsolution from already polycondensed aromatic molecules  
717 (Tiem *et al.*, 2008), which were not able to release the pressure build up during gas  
718 generation but were viscous enough to prevent pore closure.

719 Although methane can be generated from high maturity kerogens in the laboratory (Guo  
720 *et al.*, 2009; Mahlstedt and Horsfield, 2012), it is still debatable whether residual kerogen  
721 itself can participate in development of organic porosity at gas window maturities. Bernard *et*



722 *al.* (2011) did not find any porosity in overmature kerogen, whereas Loucks *et al.* (2009) and  
723 Reed *et al.* (2014) suggest that porosity is developed within kerogen, including within the oil  
724 window. Our SEM micrographs show that in the HAD sample, approximately 65% of  
725 organic phases are not visibly porous. Sorption experiments by Rexer *et al.* (2014) showed  
726 that insoluble, bulk organic matter extracted from the overmature Posidonia shale is  
727 microporous – as is coal - but they did not separate kerogen from residual bitumen. It is  
728 plausible that the presence of internal microporosity within kerogen facilitates diffusive  
729 release of gas from kerogen and does not favour development of pores (Vanderbroucke and  
730 Largeau, 2007). Such microporosity may not occur in bitumen.

731 Recalling that 65% of organic matter particles in our gas window sample do not contain  
732 macropores, the macroporosity that we do observe in organic matter using SEM techniques  
733 cannot alone account for the substantial porosity increase observed from oil to gas window.  
734 Two other porosity sources seem plausible. Firstly, low pressure CO<sub>2</sub> and N<sub>2</sub> sorption  
735 experiments show that the volume of micro- and meso-porosity, unseen in our SEM studies,  
736 doubles or even triples in Posidonia kerogen between 0.89 and 1.45% Ro (Rexer *et al.*,  
737 2014). Secondly, it is possible that kerogen shrinks as it matures from oil to gas window as a  
738 result of the loss of that fraction of oil which is generated within the kerogen and which is  
739 retained as sorbed oil (Sandvik *et al.*, 1992). Swelling ratios of 1.1 to 1.7 were measured by  
740 Larsen and Li (1994) on Type II Albany kerogen using a set of solvents of different polarity,  
741 so that shrinkage upon loss of the oil is plausible and may be reflected as irregular pores both  
742 within organic matter and, more commonly, at the interface of organic and mineral matter.

743

## 744 **5. Summary and Conclusions**

745 1. Within our limited sample set, the porosity of Posidonia shales halves in the oil  
746 window compared to the immature shale and doubles in the gas window compared to

- 747 the oil mature shale. These changes can be explained by reference to (a) the primary  
748 composition of the shales, (b) carbonate diagenesis, (c) compaction and (d) the  
749 maturation, micro-migration, local trapping and gasification of heterogeneous organic  
750 phases.
- 751 2. Biogenic calcite undergoes recrystallization, dissolution and reprecipitation reactions  
752 throughout the maturity sequence; we suggest that the apparent retardation of  
753 carbonate diagenesis, compared to chalk, is due to the higher clay contents of the  
754 Posidonia shales, and also their likely oil-wet state.
- 755 3. Pores quantifiable by SEM ( $>$  ca. 50 nm) only account for 14-25% of total porosity.  
756 At  $R_o = 0.5\%$ , SEM-visible pores are associated mainly with biogenic calcite, with  
757 essentially no macroporosity within the clay matrix or organic matter. At this  
758 maturity, clays and organic matter are not visibly porous but nevertheless hold most  
759 of the shale porosity.
- 760 4. Porosity loss in the oil window is due to (a) compaction, (b) carbonate cementation  
761 and (c) perhaps the swelling of kerogen by retained oil. Porosity, especially in  
762 macropores within microfossils, is also occluded by a range of bituminous phases,  
763 some but not all of which can be extracted with organic solvents. Bitumen is also  
764 observed in microfractures, probably related to increasing pressure in pores resulting  
765 from petroleum generation. Some new pores are formed in the oil window, commonly  
766 at organo-mineral interfaces and often associated with diagenetic calcite.
- 767 5. Increasing porosity into the gas window coincides with the formation of isolated,  
768 spongy and complex meso- and macropores within organic matter, related to thermal  
769 cracking and gas generation. Intraorganic porosity is highly heterogeneous; the  
770 macroporosity of individual organic particles ranges from 0 - 40%, with 65% of  
771 organic particles containing no macropores. The large variation in organic

772 macroporosity is considered to reflect both the differing chemophysical properties of  
773 individual particles and the protection against compaction which a rigid mineral  
774 matrix may afford softer organic phases. Microfossils thus play an important role in  
775 the generation and retention of organic porosity since they are (a) bitumen traps and  
776 (b) rigid.

777 6. The development of organic macroporosity cannot alone account for the porosity  
778 increase observed from oil to gas window; an additional contribution must come from  
779 the increased volume of micro- and meso-porosity. Furthermore, whilst intraorganic  
780 pores are a very characteristic feature of gas window Posidonia shale, mineral-hosted  
781 porosity is still the primary form of macroporosity, most commonly observed at the  
782 organic-inorganic interface.

783

784

## 785 **7. References**

786 ALVAREZ, D., BORREGO, A.G., MENENDEZ, R. 1997. Unbiased methods for the  
787 morphological description of char structures. *Fuel*, **76**, 1241-1248.

788 APLIN, A.C., LARTER, S.R. 2005. Fluid Flow, Pore Pressure, Wettability, and Leakage  
789 in Mudstone Cap Rocks. AAPG Special Bulletin: *AAPG Hedberg Series*, **2**, 1-12.

790 APLIN, A.C., MACQUAKER, H.S. 2010, Getting started in shales: American  
791 Association of Petroleum Geologists/Datapages, Getting Started Series GS20.

792 BACHMANN, G.H., VOIGT, T., BAYER, U., VON EYNATTEN, H., LEGLER, B.,  
793 LITTKE, R. (2008): Depositional history and sedimentary cycles in the Central European  
794 Basin System. In: Littke,R., Bayer, U., Gajewski, D., Nelskamp, S. (Eds), Dynamics of

795 Complex Intracontinental Basins - The Central European Basin System, Springer-Verlag,  
796 Berlin-Heidelberg, pp. 155-169.

797 BAKER, P.A., KASTNER, M., BYERLEE, J.D., LOCKNER, D.A., 1980. Pressure  
798 solution and hydrothermal recrystallization of carbonate sediments—an experimental study.  
799 *Marine Geology*, **38**, 185–203.

800 BEHAR, F., PELET, R. 1988. Hydrogen-Transfer Reactions in the Thermal Cracking of  
801 Asphaltenes. *Energy & Fuels*, **2**, 259-264.

802 BEHAR, F., LORANT, F., LEWAN, M. 2008a. Role of NSO compounds during  
803 primary cracking of a Type II kerogen and a Type III lignite. *Organic Geochemistry*, **39**, 1–  
804 22.

805 BEHAR, F., LORANT, F., MAZEAS, L. 2008b. Elaboration of a new compositional  
806 kinetic schema for oil cracking. *Organic Geochemistry*, **39**, 764–782.

807 BEHAR, F., ROY, S., JARVIE, D. 2010. Artificial maturation of a Type I kerogen in  
808 closed system: Mass balance and kinetic modelling. *Organic Geochemistry*, **41**, 1235–1247.

809 BERNARD, S., HORSFIELD, B., SCHULTZ, H.M., SCHREIBER, A., WIRTH, R.,  
810 TIEM, T.A.V., PERSSON, F., KÖNITZER, S, VOLK, H., SHERWOOD, N., FUENTES, D.  
811 2010. Multi-scale detection of organic and inorganic signatures provides insights into gas  
812 shale properties and evolution. *Chemie der Erde*, **70**, 119-133.

813 BERNARD, S., HORSFIELD, B., SCHULTZ, H.M., WIRTH, R., SCHREIBER, A.,  
814 SHERWOOD, N. 2011. Geochemical evolution of organic-rich shales with increasing  
815 maturity: A STXM and TEM study of the Posidonia Shale (Lower Toarcian, northern  
816 Germany). *Marine and Petroleum Geology*, **31**, 70-89.

817 BERNARD, S., WIRTH, R., SCHREIBER, A., SCHULZ, H.-M., HORSFIELD, B.  
818 2012. Formation of nanoporous pyrobitumen residues during maturation of the Barnett Shale  
819 (Fort Worth Basin). *International Journal of Coal Geology*, **103**, 3–11.

820 BERNARD, S., WIRTH, R., SCHREIBER, A., BOWEN, L., APLIN, A.C., MATHIA,  
821 E.J., SCHULZ, H.-M., HORSFIELD, B. 2013. FIB-SEM and TEM investigations of an  
822 organic-rich shale maturation series from the lower Toarcian Posidonia Shale, Germany:  
823 Nanoscale pore system and fluid-rock interactions. In: Camp, W., Diaz, E., Wawak, B.  
824 (Eds.), *Electron microscopy of shale hydrocarbon reservoirs*, *AAPG memoir*, **102**, 53-66.

825 BOUR, I. MATTIOLI, E., PITTET, B. 2007. Nannofacies analysis as a tool to  
826 reconstruct paleoenvironmental changes during the Early Toarcian anoxic event.  
827 *Palaeogeography, Palaeoclimatology, Palaeoecology*, **249**, 58–79.

828 BRUNS, B., LITTKE, R., GASPARIK, M., van WEES, J.-D., NELSKAMP, S. 2014.  
829 Thermal evolution and shale gas potential estimation of the Wealden and  
830 Posidonia Shale in NW-Germany and the Netherlands: a 3D basin modeling  
831 study. *Basin Research*, doi: 10.1111/bre.12096.

832 CHALMERS, G.R., BUSTIN, R.M., POWER, I.M. 2012. Characterization of gas shale  
833 pore systems by porosimetry, pycnometry, surface area, and field emission scanning electron  
834 microscopy/transmission electron microscopy image analyses: Examples from the Barnett,  
835 Woodford, Haynesville, Marcellus, and Doig units. *American Association of Petroleum*  
836 *Geologists Bulletin*, **96**, 1099-1119.

837 CLARKSON, C.R., SOLANO, N., BUSIN, R.M, BUSTIN, A.M.M., CHALMERS,  
838 G.R.L., HE, L., MELNICHENKO, Y.B., RADLINSKI, A.P., BLACH, T.P. 2013. Pore

839 structure characterization of North American shale gas reservoirs using USANS/SANS, gas  
840 adsorption, and mercury intrusion. *Fuel*, **103**, 606–616.

841 CLEMENTZ, D.M. 1978. Effect of oil and bitumen saturation on source-rock pyrolysis.  
842 *American Association of Petroleum Geologists Bulletin*, **63**, 2227-2232.

843 CURTIS, M.E., SONDERGELD, C.H., RAI, C.S. 2013. Relationship between organic  
844 shale microstructure and hydrocarbon generation. SPE Unconventional Resources  
845 Conference-USA, 10-12 April 2013, The Woodlands, Texas, USA.

846 DESBOIS, G., URAI, J.L., KUKLA, P.A. 2009. Morphology of the pore space in  
847 claystones – evidence from BIB/FIB ion beam sectioning and cryo-SEM observations.  
848 *eEarth*, **4**, 15–22.

849 DIECKMANN, V., SCHENK, H.J., HORSFIELD, B., WELTE, D.H. 1988. Kinetics of  
850 petroleum generation and cracking by programmed-temperature closed-system pyrolysis of  
851 Toarcian Shales. *Fuel*, **77**, 23-31.

852 ESPITALIE, J., LAPORTE, J.L., MADEC, M., MARQUIS, F., LEPLAT, P., PAULET  
853 J., BOUTEFEU, A. 1977. Methode rapide de caracterisation des roches meres, de leur  
854 potential petrolier et de leur degre d'evolution, *Rev. Inst. Franc. Pétrole.*, **32**, 23-42

855 FABRICIUS, I.L. 2003. How burial diagenesis of chalk sediments controls sonic  
856 velocity and porosity. *American Association of Petroleum Geologists Bulletin*, **87**, 1755 –  
857 1778.

858 FABRICIUS, I.L., GOMMESEN, L., KROGSBØLL, A., OLSEN, D. 2008. Chalk  
859 porosity and sonic velocity versus burial depth: Influence of fluid pressure, hydrocarbons,  
860 and mineralogy. *American Association of Petroleum Geologists Bulletin*, **92**, 201-223.

- 861 FISHMAN, N.S., HACKLEY, P.C., LOWERS, H.A., HILL, R.J., EGENHOFF, S.O.,  
862 EBERL, D.D., BLUM, A.E. 2012. The nature of porosity in organic-rich mudstones of the  
863 Upper Jurassic Kimmeridge Clay Formation, North Sea, offshore United Kingdom.  
864 *International Journal of Coal Geology*, **103**, 32–50.
- 865 GUO, L., XIANMING, X, HUI, T., ZHIGUANG, S. 2009. Distinguishing gases derived  
866 from oil cracking and kerogen maturation: Insights from laboratory pyrolysis experiments.  
867 *Organic Geochemistry*, **40**, 1074–1084.
- 868 HEASLEY, E.C., WORDEN, R.H., HENDRY, J.P. 2000. Cement distribution in a  
869 carbonate reservoir: Recognition of a paleo-oil–water contact and its relationship to reservoir  
870 quality in the Humbly Grove field, onshore, United Kingdom. *Marine and Petroleum*  
871 *Geology*, **17**, 639–654.
- 872 HAMMES, U., FRÉBOURG, G. 2012. Haynesville and Bossier mudrocks: A facies and  
873 sequence stratigraphic investigation, East Texas and Louisiana, USA. *Marine and Petroleum*  
874 *Geology*, **31**, 8-26.
- 875 HEATH, J.E., DEWERS, T.A., McPHERSON, B.J.O.L., PETRUSAK, R., CHIDSEY,  
876 Jr. T.C., RINEHART, A.J., MOZLEY, P.S. 2011. Pore networks in continental and marine  
877 mudstones: Characteristics and controls on sealing behaviour. *Geosphere*, **7**, 429–454.
- 878 HESSE, R. 1990. Origin of chert: diagenesis of biogenic siliceous sediments. In:  
879 McIlreath, I.A., Morrow, D.W. (Eds.), *Diagenesis Geoscience*, Geological Association of  
880 Canada, St. John's, Newfoundland, Canada, Reprint Ser., **4**, 227-251.
- 881 HORSFIELD, B., SCHENK, H.J., MILLS, N., WELTE, D.H. 1992. An investigation of  
882 the in-reservoir conversion of oil to gas: compositional and kinetic findings from closed-  
883 system programmed-temperature pyrolysis. *Organic Geochemistry*, **19**, 191-204.

884 HORSFIELD, B., LITTKE, R., MANN, U., BERNARD, S., TIEM, A.T.V., Di PRIMIO,  
885 R., SCHULZ, H.-M. 2010. Shale Gas in the Posidonia Shale, Hils Area, Germany. American  
886 Association of Petroleum Geologists Annual Convention, April 11-14, 2010, New Orleans,  
887 LA, USA.

888 HOUBEN, M.E., DESBOIS, G., URAI, J.L. 2013. Pore morphology and distribution in  
889 the Shaly facies of Opalinus Clay (Mont Terri, Switzerland): Insights from representative 2D  
890 BIB-SEM investigations on mm to nm scale. *Applied Clay Science*, **71**, 82-97.

891 HWANG, R.J., TEERMAN, S.C., CARLSON, R.M. 1998. Geochemical comparison of  
892 reservoir solid bitumens with diverse origins. *Organic Geochemistry*, **29**, 505-517.

893 JARVIE, D.M., HILL, R.J., RUBLE, T.E., POLLASTRO, R.M., 2007. Unconventional  
894 shale-gas systems: the Mississippian Barnett Shale of north-central Texas as one model for  
895 thermogenic shale gas assessment. *American Association of Petroleum Geologists Bulletin*,  
896 **91**, 475-499.

897 KIETZMANN, D.A., MARTÍN-CHIVALET, J., PALMA, R.M., LÓPEZ-GÓMEZ, J.,  
898 LESCANO, M. 2011. Evidence of precessional and eccentricity orbital cycles in a Tithonian  
899 source rock: The mid-outer carbonate ramp of the Vaca Muerta Formation, northern Neuquén  
900 Basin, Argentina. *American Association of Petroleum Geologists Bulletin*, **95**, 1459-1474.

901 KLAVER, J., DESBOIS, G., URAI, J.L., LITTKE, R. 2012. BIB-SEM study of the pore  
902 space morphology in early mature Posidonia Shale from the Hils area, Germany.  
903 *International Journal of Coal Geology*, **103**, 12-25.

904 KLAVER, J., DESBOIS, G., LITTKE, R., URAI, J.L. 2015. BIB-SEM characterization  
905 of pore space morphology and distribution in postmature to overmature samples from the  
906 Haynesville and Bossier Shales. *Marine and Petroleum Geology*, **59**, 451-466.



- 907 LANDIS, C.R., CASTAÑO, J.R. 1995. Maturation and bulk chemical properties of a  
908 suite of solid hydrocarbons. *Organic Geochemistry*, **22**, 137-149.
- 909 LARSEN, J.W., LI, S. 1994. Solvent swelling studies of Green River kerogen. *Energy &*  
910 *Fuels*, **8**, 932-936.
- 911 LEWAN, M.D., 1997. Experiments on the role of water in petroleum formation.  
912 *Geochimica et Cosmochirica Acta*, **61**, 3691-3723.
- 913 LEYTHAEUSER, D., LITTKE, R., RADKE, M., SCHAEFER, R.G. 1988. Geochemical  
914 effects of petroleum migration and expulsion from Toarcian source rocks in the Hils syncline  
915 area, NW-Germany. *Organic Geochemistry*, **13**, 489-502.
- 916 LIANG, C., JIANG, Z., ZHANG, C., GUO, L., YANG, Y., LI, J. 2014. The shale  
917 characteristics and shale gas exploration prospects of the Lower Silurian Longmaxi shale,  
918 Sichuan Basin, South China. *Journal of Natural Gas Science and Engineering*, **21**, 636-648.
- 919 LITTKE, R., BAKER, D.R., RULLKÖTTER, J. 1987 Deposition of petroleum source  
920 rocks. In: Welte, D.H., Horsfield, B., Baker, D.R. (Eds.). *Petroleum and Basin Evolution:*  
921 *Insights from petroleum geochemistry, geology and basin modelling.* Springer-Verlag,  
922 Heidelberg, pp. 271-333.
- 923 LITTKE, R., BAKER, D.R., LEYTHAEUSER, D., RULLKÖTTER, J. 1991. Keys to the  
924 depositional history of the Posidonia Shale (Toarcian) in the Hils Syncline, northern  
925 Germany. In: Tyson, R.V., Pearson, T.H. (Eds.) *Modern and ancient continental shelf anoxia.*  
926 *Geological Society Special Publication*, **58**, 311-333.
- 927 LOMANDO, A.J. 1992. The influence of solid reservoir bitumen on reservoir quality.  
928 *American Association of Petroleum Geologists Bulletin*, **76**, 1137-1152.

929 LOUCKS, R.G., REED, R.M., RUPPEL, S.C., JARVIE, D.M. 2009. Morphology,  
930 genesis and distribution of nanometer-scale pores in siliceous mudstones of the Mississippian  
931 Barnett Shale. *Journal of Sedimentary Research*, **79**, 848–861.

932 LOUCKS, R.G., REED, R.M., RUPPEL, S.C., HAMMES, U. 2012. Spectrum of pore  
933 types and networks in mudrocks and a descriptive classification for matrix-related mudrock  
934 pores. *American Association of Petroleum Geologists Bulletin*, **96**, 1071-1098.

935 LOUCKS, R.G., REED, R.M. 2014. Scanning-Electron-Microscope petrographic  
936 evidence for distinguishing organic-matter pores associated with depositional organic matter  
937 versus migrated organic matter in mudrocks. *GCAGS Journal*, **3**, 51-60.

938 MACKENZIE, A.S., LEYTHAEUSER, D., ALTEBÄUMER, F.-J., DISKO, U.,  
939 RULLKÖTTER, J. 1988. Molecular measurements of maturity for Lias 6 shales in N.W.  
940 Germany. *Geochimica et Cosmochimica Acta*, **52**, 1145-1154.

941 MACQUAKER, J.H.S., TAYLOR, K.G., GAWTHORPE, R.L. 2007. High-resolution  
942 facies analyses of mudstones: implications for paleoenvironmental and sequence stratigraphic  
943 interpretations of offshore ancient mud-dominated successions. *Journal of Sedimentary  
944 Research*, **77**, 324–339.

945 MACQUAKER, J.H.S., TAYLOR, K.G., KELLER, M., POLYA, D. 2014.  
946 Compositional controls on early diagenetic pathways in fine-grained sedimentary rocks:  
947 Implications for predicting unconventional reservoir attributes of mudstones. *American  
948 Association of Petroleum Geologists Bulletin*, **98**, 587–603.

949 MAHLSTEDT, N., HORSFIELD, B. 2012 Metagenetic methane generation in gas shales  
950 I. Screening protocols using immature samples. *Marine and Petroleum Geology*, **31**, 27-42.

- 951 MALLON, A.J., SWARBRICK, R.E. 2002. A compaction trend for non-reservoir North  
952 Sea Chalk. *Marine and Petroleum Geology*, **19**, 527-539.
- 953 MANN, U., MÜLLER, P.J. 1988. Source rock evaluation by well log analysis (Lower  
954 Toarcian, Hils syncline). *Organic Geochemistry*, **13**, 109-119.
- 955 MASTALERZ, M., GLIKSON, M. 2000. In-situ analysis of solid bitumen in coal:  
956 examples from the Bowen Basin and the Illinois Basin. *International Journal of Coal*  
957 *Geology*, **42**, 207–220.
- 958 McHARGUE, T.R., PRICE, R.C. 2006. Dolomite from clay in argillaceous or shale-  
959 associated marine carbonates. *Journal of Sedimentary Research*, **52**, 873-886.
- 960 MICHELIS, R., LANGLOIS, E., RUAU, O., MANSUY, L., ELIE, M., LANDAIS, P.  
961 1996. Evolution of asphaltenes during artificial maturation: A record of the chemical  
962 processes. *Energy & Fuels*, **10**, 39-48.
- 963 MILLIKEN, K.L., ESCH, W. L., REED, R. M., ZHANG, T. 2012. Grain assemblages  
964 and strong diagenetic overprinting in siliceous mudrocks, Barnett Shale (Mississippian), Fort  
965 Worth Basin, Texas. *American Association of Petroleum Geologists Bulletin*, **96**, 1553-1578.
- 966 MILLIKEN, K.L., RUDNICKI, M., AWWILER, D.N., ZHANG, T. 2013. Organic  
967 matter-hosted pore system, Marcellus Formation (Devonian), Pennsylvania. *American*  
968 *Association of Petroleum Geologists Bulletin*, **97**, 177-200.
- 969 MUÑOZ, Y.A., LITTTKE, R., BRIX, M.R. 2007. Fluid systems and basin evolution of  
970 the western Lower Saxony Basin, Germany. *Geofluids*, **7**, 335–355.

971 OKIONGBO, K.S., APLIN, A.C., LARTER, S.R. 2005. Changes in Type II kerogen  
972 density as a function of maturity: Evidence from the Kimmeridge Clay Formation. *Energy &*  
973 *Fuels*, **19**, 2495-2499.

974 PASSEY, Q. R., BOHACS, K. M., ESCH, W. L., KLIMENTIDISS, R., SINHA, S.  
975 2010. From Oil-Prone Source Rock to Gas-Producing Shale Reservoir – Geologic and  
976 petrophysical characterization of unconventional shale-gas reservoirs. *Proceedings of the*  
977 *North American Unconventional Gas Conference and Exhibition. Society of Petroleum*  
978 *Engineers*, Paper 131350, 29p.

979 POMMER, M., MILLIKEN, K. 2015. Pore types and pore-size distributions across  
980 thermal maturity, Eagle Ford Formation, southern Texas. *American Association of Petroleum*  
981 *Geologists Bulletin*, **99**, 1713-1744.

982 POTTER, P.E., MAYNARD, J.B., DEPETRIS, P.J. 2005. Mud and Mudstones:  
983 Introduction and overview. Springer-Verlag, Berlin, pp. 297.

984 RADKE, M., VRIEND, S.P., SCHAEFER, R.G. 2001. Geochemical characterization of  
985 Lower Toarcian source rocks from NW Germany: interpretation of aromatic and saturated  
986 hydrocarbons in relation to depositional environment and maturation effects. *Journal of*  
987 *Petroleum Geology*, **24**, 287-307.

988 REED, R.M., LOUCKS, R.G., RUPPEL, S.C. 2014. Comment on “Formation of  
989 nanoporous pyrobitumen residues during maturation of the Barnett Shale (Fort Worth  
990 Basin)”. *International Journal of Coal Geology*, **127**, 114-115.

991 REXER, T.F.T., BENHAM, M.J., APLIN, A.C., THOMAS, K.M. 2013. Methane  
992 adsorption on shale under simulated geological temperature and pressure conditions. *Energy*  
993 *& Fuels*, **27**, 3099-3109.

994 REXER, T.F.T, MATHIA, E.J., APLIN, A.C., THOMAS, K.M. 2014. High-Pressure  
995 Methane Adsorption and Characterization of Pores in Posidonia Shales and Isolated  
996 Kerogens. *Energy & Fuels*, **28**, 2886-2901.

997 RODUIT. 2008. JMicroVision: Image analysis toolbox for measuring and quantifying  
998 components of high-definition images. Version 1.2.7. Software available for free download at  
999 <http://www.jmicrovision.com/> accessed August, 2011.

1000 ROSS, D.J.K, BUSTIN. 2009. The importance of shale composition and pore structure  
1001 upon gas storage potential of shale gas reservoirs. *Marine and Petroleum Geology*, **26**, 916–  
1002 927.

1003 RÖHL, H.J., SCHMID- RÖHL, A., OSCHMANN, W., FRIMMEL, A., SCHWARK, L.  
1004 2001. The Posidonia Shale (Lower Toarcian) of SW-Germany: an oxygen-depleted  
1005 ecosystem controlled by sea level and palaeoclimate. *Palaeogeography, Palaeoclimatology,*  
1006 *Palaeoecology*, **165**, 27–52.

1007 RÖHL, H.J., SCHMID- RÖHL, A. 2005. Lower Toarcian (Upper Liassic) black shales  
1008 of the Central European epicontinental basin: a sequence stratigraphic case study from the  
1009 SW German Posidonia Shale. In: HARRIS, N. B. (Ed.), The deposition of organic carbon-  
1010 rich sediments: Models, mechanisms, and consequences: Society for Sedimentary Geology  
1011 Special Publication, **82**, 165-189.

1012 RULLKÖTTER, J., LEYTHAEUSER, D., HORSFIELD, B., LITTKE, R., MANN, U.,  
1013 MÜLLER, P.J., RADKE, M., SCHAEFER, H.-J., SCHWOCHAU, K., WITTE, E.G.,  
1014 WELTE, D.H. 1988. Organic matter maturation under the influence of a deep intrusive heat  
1015 source: A natural experiment for quantitation of hydrocarbon generation and expulsion from

1016 a petroleum source rock (Toarcian shale, northern Germany). *Organic Geochemistry*, **13**,  
1017 847-856.

1018 SANDVIK, E.I., YOUNG, W.A., CURRY, D.J. 1992. Expulsion from hydrocarbon  
1019 sources: the role of organic absorption. *Organic Geochemistry*, **19**, 77-87.

1020 SCHAEFER, R.G., LITTKE, R. 1988. Maturity-related compositional changes in the  
1021 low-molecular-weight hydrocarbon fraction of Toarcian shales. *Organic Geochemistry*, **13**,  
1022 887-892.

1023 SCHENK, H.J., DI PRIMIO, R., HORSFIELD, B. 1997. The conversion of oil into gas  
1024 in petroleum reservoirs. Part 1: Comparative kinetic investigation of gas generation from  
1025 crude oils of lacustrine, marine and fluviodeltaic origin by programmed-temperature closed-  
1026 system pyrolysis. *Organic Geochemistry*, **26**, 467-481.

1027 SCHIEBER, J. 1999. Distribution and deposition of mudstone facies in the Upper  
1028 Devonian Sonyea Group of New York. *Journal of Sedimentary Research*, **69**, 909-925.

1029 SCHOLLE, P. A. 1977. Chalk diagenesis and its relation to petroleum exploration: oil  
1030 from chalks, a modern miracle? *American Association of Petroleum Geologists Bulletin*, **61**,  
1031 982-1009.

1032 SCHOLLE, P. A., HALLEY, R. B. 1985. Burial diagenesis: out of sight, out of mind!  
1033 In: Schneidermann, N., Harris, P.M. (Eds.), Carbonate Cements: Tulsa, OK, *SEPM Special*  
1034 *Publication*, **36**, 309-334.

1035 SLATT, R.M., O'BRIEN, N.R. 2011. Pore types in the Barnett and Woodford gas  
1036 shales: Contribution to understanding gas storage and migration pathways in fine-grained  
1037 rocks. *AAPG Bulletin*, **95**, 2017–2030.

- 1038 TANG, X., ZHANG, J., WANG, X., YU, B., DING, W., XIONG, J., YANG, Y.,  
1039 WANG, L., YANG, C. 2014. Shale characteristics in the Southeastern Ordos Basin, China:  
1040 Implications for hydrocarbon accumulation conditions and the potential of continental shales.  
1041 *International Journal of Coal Geology*, **128-129**, 32-46.
- 1042 TAO, S., WANG, Y., TANG, D., WU, D., XU, H., HE, W. 2012. Organic petrology of  
1043 Fukang Permian Lucaogou Formation oil shales at the northern foot of Bogda Mountain,  
1044 Junggar Basin, China. *International Journal of Coal Geology*, **99**, 27–34.
- 1045 TIEM, V.T., HORSFIELD, B., SYKES, R. 2008. Influence of in-situ bitumen on the  
1046 generation of gas and oil in New Zealand coals. *Organic Geochemistry*, **39**, 1606–1619.
- 1047 TISSOT, B.P., WELTE, D.H. 1984. Petroleum formation and occurrence. Springer-  
1048 Verlag, New York, pp. 699.
- 1049 TRABUCHO-ALEXANDRE, J., DIRKX, R., VELD, H., KLAVER, G., De BOER, P.L.  
1050 2012. Toarcian black shales in the Dutch Central Graben: record of energetic, variable  
1051 depositional conditions during an Oceanic Anoxic Event. *Journal of Sedimentary Research*,  
1052 **82**, 104–120.
- 1053 TYSON, R.V. 1995. Sedimentary Organic Matter: Organic facies and palynofacies.  
1054 Chapman & Hall, London, pp.615.
- 1055 VANDENBROUCKE, M., BEHAR, F., SAN TORCUATO, A., RULLKÖTER, J.  
1056 1993. Kerogen maturation in a reference kerogen Type II series: the Toarcian shales of the  
1057 Hils syncline, NW Germany. *Organic Geochemistry*, **20**, 961-972.
- 1058 VANDENBROUCKE, M., LARGEAU, C. 2007. Kerogen origin, evolution and  
1059 structure. *Organic Geochemistry*, **38**, 719–833.

1060 VAN DUIN, A.C.T., LARTER, S.R. 2001. A computational chemical study of  
1061 penetration and displacement of water films near mineral surfaces, *Geochemical Transactions*  
1062 6.

1063 WELTE, D.H., HORSFIELD, B., BAKER, D.R. (Eds.). 1997. *Petroleum and Basin*  
1064 *Evolution: Insights from petroleum geochemistry, geology and basin modelling*. Springer-  
1065 Verlag, Berlin, Heidelberg, New York, London, Paris, Tokyo, Hong Kong, pp.535.

1066 WILHELMS, A., LARTER, S.R., LEYTHAEUSER, D., DYPVIK, H. 1990.  
1067 Recognition and quantification of the effects of primary migration in a Jurassic clastic  
1068 source-rock from the Norwegian. *Organic Geochemistry*, **16**, 103-113.

1069 WORDEN, R.H., OXTOBY, N.H., SMALLEY, P.C. 1998. Can oil emplacement prevent  
1070 quartz cementation in sandstones? *Petroleum Geoscience*, **4**, 129–137.

1071

## 1072 **8. Acknowledgements**

1073 This work was supported by the Gas Shales in Europe project funded by Bayerngas,  
1074 ExxonMobil, GdFSuez, Marathon, Repsol, Schlumberger, Statoil, Total, Vermilion and  
1075 Wintershall. Bruce Hart and Kitty Milliken are thanked for their highly constructive reviews.

1076



1077 **List of Figures**

1078 **Figure 1.** Location of Hils syncline, Northern Germany and three boreholes: Wickensen  
1079 (WIC;  $R_o$  0.53%), Harderode (HAR; 0.89%) and Haddessen (HAD, 1.45%) (after Mann and  
1080 Müller (1988) and Horsfield *et al.* (2010)). b) Lithological profile of the Posidonia Shale  
1081 from the three boreholes with a marlstone unit (I) and two calcareous shale units (II and III);  
1082 red dots represent sample locations (after Littke *et al.* (1991)).

1083  
1084 **Figure 2.** Scans of polished thin sections. The bedding plane is horizontal. Vertical arrows  
1085 denote thickness of distinguishable laminae. a) (WIC 7129): Horizontal lamination marked  
1086 by the alternation of more calcite- and clay-rich horizons. The thickness of individual laminae  
1087 reaches up to 3 mm. b) (WIC 7153): Lenticular lamination with large faecal pellets up to 0.6  
1088 mm. Faecal-pellet diluted horizons alternate with horizons with higher proportions of clay  
1089 (darker lamina). c) (HAD 7101): Alternating dark and light laminae, reflecting different  
1090 amounts of carbonate and clay are still visible in this higher maturity shale. d) (HAD 7119):  
1091 Any original lamination has been lost in this high maturity marlstone sample. D – dark, clay-  
1092 rich lamina, L – light, carbonate-rich lamina, FP – faecal pellet, T – terrestrial organic matter.

1093  
1094 **Figure 3.** Plane-polarized-light optical micrographs, Wickensen. a) (WIC 7129): Flattened,  
1095 compacted algal bodies (green arrow) and faecal pellets (red arrow) constitute well-oriented  
1096 components in the fabric of the calcareous clay-shale. b) (WIC 7139): Microlamination  
1097 marked by different amounts of matrix calcite. Lighter units (centre and bottom) are relatively  
1098 enriched in calcite and impoverished in clay as compared to darker units (top). Large faecal  
1099 pellets ( $> 500 \mu\text{m}$ ), visible at the top, are scarce in the upper, clay-rich Posidonia unit. c)  
1100 (WIC 7145): A layer of silt-sized carbonate grains separates two laminae. Shale below the silt  
1101 layer has larger faecal pellets (red arrow) and is lighter in plane-polarized light. d) (WIC

1102 7151): An example of lenticular microlamination in a sample from the marlstone unit. The  
1103 bright horizontal lenses (red arrow) are composed of well-defined faecal pellets. Flattened,  
1104 organic-rich clay aggregates are marked with a green arrow. e) (WIC 7153): Well-developed,  
1105 lenticular lamination due to the presence of ubiquitous faecal pellets (red arrow). Small  
1106 particles of woody organic matter are disseminated in the shale matrix (orange arrow). f)  
1107 (WIC 7153): Details of the lenticular lamination. Large faecal pellets, up to 500  $\mu\text{m}$  in length  
1108 (red arrow), alternate with brown organo-clay aggregates (green arrow). A woody organic  
1109 particle is marked with an orange arrow.

1110

1111 **Figure 4.** Plane-polarized-light optical micrographs, Harderode. a) (HAR 7038): Lamination  
1112 in this calcareous clay-shale is due to presence of layers containing differing amounts of  
1113 quartz and authigenic pyrite. An uneven surface below the bottom silt layer may be erosive  
1114 in origin. b) (HAR 7046): Preserved original lamination is picked out by a layer of silt-size  
1115 quartz grains in the middle of the image. c) (HAR 7060): Carbonate cement, most likely  
1116 precipitated within an algal cyst (red arrow). Green arrow denotes authigenic pyrite filling a  
1117 small bivalve. d) (HAR 7060): Carbonates often show rhombohedral shapes (red arrow),  
1118 suggesting in-situ precipitation. e) Large foraminifer test with intraparticle carbonate cement.  
1119 f) (HAR 7070): Sub- and euhedral carbonate crystals lining a small fracture (red arrow).

1120

1121 **Figure 5.** Plane-polarized-light optical micrographs, Haddessen. a) (HAD 7083): Small-scale  
1122 heterogeneity of the calcareous clay-shale is imparted by the presence of flattened and oval  
1123 faecal pellets (red arrows). The unit at the top has also more silty material (carbonates and  
1124 quartz), and more pyrite (green arrow). b) (HAD 7101): Diagenetic carbonates are  
1125 concentrated in specific layers. c) (HAD 7101): Micrograph of an area within (b). Flattened  
1126 carbonate aggregates are composed of sparry calcite cement (green arrow) or show

1127 microcrystalline texture in faecal pellets (red arrow). Matrix carbonates alternate with  
1128 aggregates enriched in clays and organic matter on a  $< 100 \mu\text{m}$  scale. d) (HAD 7101):  
1129 Microlamination marked by different concentrations of faecal pellets. A lamina in the centre  
1130 is more enriched in faecal pellets (red arrows) than the unit at the top of the image. e) (HAD  
1131 7110): Diagenetically altered matrix of the calcareous clay-shale, with large faecal pellets  
1132 (red arrow) and discrete carbonate cements (green arrow). Carbonate phases are disseminated  
1133 in the more clay-rich shale. f) (HAD 7119): In this carbonate-rich mudstone, the shale matrix  
1134 is dominated by a network of compacted faecal pellets (red arrows).

1135

1136 **Figure 6.** Backscattered electron micrographs, Wickensen and Harderode. The bedding plane  
1137 in all images is horizontal. a) (WIC 7129): Microlaminated calcareous clay-shale (light  
1138 lamina) with alternating faecal pellet-rich (red arrow) and clay-rich layers (green arrows).  
1139 Visible organic matter is mostly associated with the clay-rich areas. Silt-sized quartz and  
1140 pyrite are common, widely disseminated in the matrix. b) (WIC 7129): Details of the  
1141 nannofossil enrichment in a dark lamina of the calcareous shale. Biogenic calcite is  
1142 surrounded by clays. Coccoliths are mostly broken and authigenic overgrowths, if present,  
1143 are very subtle, resulting in more equant edges of coccoliths (red arrows). Organic matter  
1144 (green arrow) forms elongated laminae. c) (WIC 7155): Nannofossil-rich pellets in a  
1145 marlstone sample with ubiquitous inter- and intragranular cement and partially recrystallized  
1146 nannofossil structures. Recrystallized biogenic calcite fragments are suggested by the  
1147 presence of faceted calcite crystals (red arrows) coexisting with unmodified fossil structures.  
1148 Clay laminae (green arrow) are volumetrically less abundant than in the calcareous shale. d)  
1149 (HAR 7046): Calcareous clay-shale at peak oil window maturity, at low magnification.  
1150 Organic structures, ubiquitous at lower maturities, have collapsed (green arrows). e) (HAR

1151 7046): Calcite cement precipitated in an algal cyst, locally preventing compaction. f) (HAR  
1152 7046): A lamina of detrital quartz with intergranular quartz, pyrite and kaolinite cement.

1153

1154 **Figure 7.** Backscattered electron micrographs, Harderode and Haddessen. The bedding plane  
1155 in all images is horizontal except for image (f). a) (HAR 7060): A foraminifer with  
1156 intraparticle calcite and pyrite cement (red arrow) filling original intrafossil pores. Above, a  
1157 quartz-rich lamina with authigenic quartz cementing detrital grains (green arrow). The  
1158 biogenic material in faecal pellets (orange arrow) shows signs of local cement precipitation,  
1159 interlocking biogenic grains. b) (HAR 7070): Diagenetically-altered faecal pellet (centre)  
1160 showing inter- and intragranular authigenic calcite textures. Authigenic, rhombohedral  
1161 dolomite cement marked with a green arrow. c) (HAD 7083): Gas window shale. Authigenic  
1162 pyrite forms small euhedra, oval framboids or directly replaces biogenic calcite (red arrow)  
1163 and quartz (green arrow). Small authigenic calcite (microcarbs) grains are ubiquitous in the  
1164 matrix. d) (HAD 7083): Calcareous shale showing evidence of recrystallized calcite, with  
1165 faceted calcite crystals replacing coccoliths (red arrows) and intraparticle cement filling  
1166 intrafossil canals (green arrow). e) (HAD 7083): Interlocking calcite texture within a  
1167 fossiliferous aggregate, dominated by faceted authigenic calcite. Unaltered coccoliths are  
1168 very rare (red arrow). f) (HAD 7115): Large zone of calcite cement with authigenic kaolinite  
1169 in the centre. This large calcite zone may also be a now-unrecognizable fossil fragment.  
1170 Bedding plane is marked with a dashed line.

1171

1172 **Figure 8.** SEM-EDX-ray maps displaying microlamination at all maturities (a) WIC 7129, b)  
1173 HAR 7060, c) HAD 7110). The microlamination is marked by the alternating pattern of  
1174 carbonate-rich (blue) and clay-rich (green) laminae, and in the lower maturity samples, also  
1175 organic wisps (pink). The bedding plane in all images is horizontal.

1176

1177 **Figure 9.** Paired oil immersion (left) and reflected light (right) micrographs. Horizontal scale  
1178 bar denotes 50  $\mu\text{m}$ . Dashed line indicates direction of bedding plane. a, b) (WIC 7129):  
1179 Wisps and oval bodies of algal cysts ( $A_T$  Tasmanales,  $A_L$  Leiosphaeridales) constitute the  
1180 most prominent organic components. Other macerals include: unidentified alginates (A),  
1181 bituminite (B), vitrinite (V), inertinite (I). Strong fluorescence of the matrix is due to the  
1182 presence of the matrix bituminite. The contrast in this micrograph has been subdued due to  
1183 strong yellow fluorescence. c, d) (HAR 7060): Algal bodies are mostly collapsed ( $A_L$ ).  
1184 Matrix bituminite shows much weaker fluorescence. Solid bitumen ( $B_S$ ) is present in the  
1185 matrix, concentrated in fossiliferous zones. An inset in d) shows a fragment of a fracture  
1186 filled with solid bitumen and authigenic carbonates (C). e, f) (HAD 7110): No alginate is  
1187 present and the matrix is only marginally fluorescent. Solid bitumen ( $B_S$ ) forms a dense  
1188 network in the shale matrix and within fossiliferous units.

1189

1190 **Figure 10.** Secondary Electron micrographs of BIB-polished samples after solvent extraction.  
1191 a) (HAR 7060): Non-extractable solid bitumen (dark) in this oil window sample fills pore  
1192 space between faceted calcite crystals (black arrows) in a fossiliferous domain. b) (HAD  
1193 7110): In this gas window sample, non-extractable and porous solid bitumen (with pores <  
1194 100 nm) fills the pore space between pyrite crystallites in a framboid.

1195

1196 **Figure 11.** Point counted image porosity in % (a) and as a fraction of total porosity (b).

1197

1198 **Figure 12.** Ternary diagram showing distribution of visible SEM porosity (pixel size 15 nm)  
1199 in WIC 7129 (0.53% Ro) (black circle), HAR 7060 (0.89% Ro) (red circle) and HAD 7110  
1200 (1.45% Ro) (green circle).

1201

1202 **Figure 13.** FIB-SEM and BIB-SEM micrographs, Wickensen. Bedding is perpendicular to  
1203 the plane of view. a) Intraparticle pores within a coccolith canal; b) Intraparticle pores in a  
1204 fragment of Schizophærella; c) Intraparticle pores in a compacted, crushed faecal pellet; d)  
1205 Intraparticle pores in a faecal pellet with ubiquitous calcite cement; e) Intraparticle pores  
1206 lined with the organic material in a fragment of Schizophærella; f) Intraparticle pore in clay,  
1207 with authigenic pyrite precipitated between clay platelets; g) Intraparticle pore within a  
1208 calcite-cemented pyrite framboid; h) Intraparticle calcite dissolution pore; i) Interparticle pore  
1209 associated with faceted authigenic calcite and recrystallized biogenic debris; j) Interparticle  
1210 pore associated with biogenic calcite; k) Organic matter-associated pores at the interface with  
1211 the mineral matrix; l) Organic matter-hosted pore within an algal body. Cal – calcite, Dol –  
1212 dolomite, Py – pyrite, Qtz – quartz, OM – organic matter.

1213

1214 **Figure 14.** FIB-SEM and BIB-SEM micrographs, Harderode. Bedding is perpendicular to the  
1215 view plane. a) Fracture within organic matter (OM) extending into the organic-mineral  
1216 interface; b) Fracture at the interface of OM and calcite; c) Interparticle pore at the interface  
1217 of OM and calcite; d) Interparticle pores from the OM interface; e) Interparticle pores at the  
1218 interface of OM and authigenic calcite crystals; f) Interparticle, crack-like pore from the  
1219 interface of OM and diagenetic calcite; g) Interparticle pore associated with matrix dolomite  
1220 and calcite; h) Open fracture-like pore within clay; i) Intraparticle, cleavage-associated pore  
1221 in mica; j) Intraparticle pores within a pyrite framboid; k) Intraparticle pore formed due to  
1222 dissolution of dolomite ; l) Intraparticle pore associated with authigenic calcite. Cal – calcite,  
1223 Dol – dolomite, M – mica, Py – pyrite, Qtz – quartz, OM – organic matter.

1224

1225 **Figure 15.** FIB-SEM and BIB-SEM micrographs, Haddessen. Bedding is perpendicular to  
1226 the view plane. a) Discrete, bubble-like pores within an organic matter; b) Spongy organic  
1227 matter-hosted pores, visibly interconnected and grouped; c) Pendular, rounded organic  
1228 matter-associated pores; discrete pores are also present; d) Complex organic matter-hosted  
1229 pore from the interface with the mineral matrix; e) Complex organic matter-hosted pore  
1230 extending into the organic particle, occupying the interface with the mineral matrix in the 3D  
1231 space; f) Organic matter-hosted pores bordering a terrestrial organic maceral; g) Partly  
1232 compacted pores within a terrestrial organic maceral; h) Interparticle pore at the interface of  
1233 organic matter with diagenetic calcite and clays; i) Interparticle pores between clusters of  
1234 pyrite framboids and quartz. Cal – calcite, Py – pyrite, Qtz – quartz, OM – organic matter.

1235  
1236 **Figure 16.** FIB-SEM and BIB-SEM micrographs, Haddessen. Bedding is perpendicular to  
1237 the view plane. a) Interparticle pore between clay aggregates; b) Interparticle pore between  
1238 faceted calcite crystals. The pore is lined with organics and thus resembles organic matter-  
1239 hosted porosity; c) Interparticle pores at the interface of OM and diagenetic calcite. Note  
1240 discrete and spongy pores within the organic phase; d) Intraparticle pores in a fossil fragment;  
1241 e) Intraparticle pores in a pyrite framboid. Pyrite-associated pores coexist with complex and  
1242 spongy organic matter-hosted pores; f) Intra-clay pores, partly filled with OM and pyrite; g)  
1243 Intraparticle pores within clays evolved due to precipitation of diagenetic pyrite; h)  
1244 Intraparticle dolomite-dissolution pore; i) Intraparticle pores within calcite cement. Cal –  
1245 calcite, Dol – dolomite, Py – pyrite, OM – organic matter.

1246

1247 **Table 1.** TOC-normalized mineralogical composition (wt.%) for WIC (Ro 0.53%), HAR (Ro 0.89%)

1248 and HAD (Ro 1.45%). n.d. = not detected

	7129	WIC 7125	WIC 7145	WIC 7147	WIC 7155	HAR 7020	7046	7060	HAR 7070	HAD 7080	HAD 7090	7110	HAD 7110
Quartz	12.4	15.1	11.8	14.0	7.8	14.6	16.4	12.2	10.8	11.0	14.8	14.1	7.6
Plagioclase	1.0	0.2	0.9	0.6	1.3	1.9	2.0	2.6	3.7	2.4	2.8	3.2	4.5
K-Feldspar	0.7	0.0	0.0	0.0	0.0	0.5	0.4	0.4	0.5	0.5	0.1	0.7	0.6
Calcite	32.4	35.8	41.5	38.1	50.0	40.1	39.5	28.7	42.2	49.0	36.8	28.5	46.3
Dolomite	0.3	0.0	0.3	0.2	0.5	0.6	1.0	6.0	2.0	0.6	1.7	3.7	2.5
Siderite/ Ankerite	0.4	0.0	0.8	1.8	0.5	0.2	0.3	0.3	0.3	0.1	0.8	0.4	0.6
Aragonite	n.d.	n.d.	1.2	n.d.	1.2	n.d.	n.d.	n.d.	n.d.	n.d.	0.6	n.d.	1.4
Pyrite	4.8	4.5	3.5	3.7	4.9	5.2	4.8	8.6	5.2	6.9	4.6	6.6	4.2
Marcasite	0.7	n.d.	n.d.	n.d.	n.d.	0.6	0.2	0.9	1.2	n.d.	n.d.	0.2	n.d.
Anatase	0.3	0.1	n.d.	0.1	n.d.	0.3	0.2	0.2	0.3	0.2	n.d.	0.4	n.d.
Muscovite	2.3	2.2	0.0	1.2	0.1	2.9	2.8	3.5	3.0	2.4	1.2	4.4	0.0
Illite + I/S	21.7	22.0	20.0	25.4	17.5	17.0	18.9	24.7	18.3	13.2	22.1	23.5	18.1
Kaolinite	10.4	6.0	4.5	7.1	2.0	8.2	6.8	6.2	4.0	6.0	3.6	8.1	1.0
Dickite	n.d.	n.d.	1.1	n.d.	0.9	n.d.	n.d.	n.d.	n.d.	n.d.	1.2	n.d.	0.0
Chlorite	n.d.	0.4	1.8	0.2	1.6	n.d.	n.d.	n.d.	n.d.	0.0	0.6	n.d.	2.5
Gypsum	n.d.	0.3	2.0	0.4	2.2	n.d.	n.d.	n.d.	n.d.	0.4	1.7	n.d.	3.5
Halite	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	n.d.
TOC	12.6	13.3	10.9	7.3	9.7	7.9	6.8	5.8	8.7	6.4	7.4	6.4	7.2
Total	100	100	100	100	100	100	100	100	100	100	100	100	100

1249

1250



1251 **Table 2.** Leco, Rock-Eval, grain density and total porosity results for selected Posidonia samples from  
 1252 wells WIC (Ro 0.53%), HAR (Ro 0.89%) and HAD (Ro 1.45%).

Sample	TOC (%)	S1 (mgHC/g)	S2 (mgHC/g)	HI (mgHC/gC)	T <sub>max</sub> (°C)	Grain Density (g/cm <sup>3</sup> )	Total Porosity
WIC 7129	12.59	3.02	90.25	717	427	2.254	0.098
WIC 7133	8.71	2.57	54.90	630	434	2.392	0.128
WIC 7135	13.27	4.62	84.63	638	427	2.249	0.101
WIC 7137	10.25	3.18	68.10	665	427	2.343	0.106
WIC 7139	9.36	2.81	64.95	694	428	2.375	0.135
WIC 7142	10.43	3.52	72.37	694	426	2.346	0.122
WIC 7145	10.92	4.18	72.03	660	425	2.331	0.129
WIC 7147	7.28	2.26	47.76	656	434	2.458	0.114
WIC 7151	14.75	5.85	89.61	608	429	2.236	0.105
WIC 7153	7.34	2.45	48.37	659	431	2.489	0.139
WIC 7155	9.67	3.87	69.41	718	429	2.361	0.126
HAR 7038	7.91	3.29	30.17	382	449	2.493	0.031
HAR 7046	6.75	2.93	26.03	386	450	2.526	0.046
HAR 7060	5.78	1.47	19.72	341	447	2.592	0.045
HAR 7070	8.71	2.26	31.27	359	449	2.463	0.035
HAD 7083	7.35	0.75	4.10	56	465	2.589	0.137
HAD 7090	7.41	0.94	4.16	56	464	2.572	0.114
HAD 7094	5.21	0.845	3.52	68	459	2.608	0.121
HAD 7097	5.40	0.75	3.15	58	458	2.609	0.119
HAD 7099	6.51	0.98	3.86	59	463	2.576	0.106
HAD 7101	5.88	0.92	3.1	53	457	2.624	0.118
HAD 7104	5.04	0.72	3.385	67	459	2.620	0.116
HAD 7105	5.85	0.77	3.28	56	461	2.621	0.112

HAD 7110	6.36	1.07	3.79	60	462	2.600	0.094
HAD 7115	6.49	1.12	3.80	59	460	2.614	0.093
HAD 7119	7.15	1.23	3.16	44	459	2.607	0.115

1253

1254

ACCEPTED MANUSCRIPT

1255 **Table 3.** Rock-Eval evaluation after solvent extraction for four Posidonia samples, wells WIC (0.53%  
 1256 R<sub>o</sub>), HAR (0.89% R<sub>o</sub>) and HAD (1.45% R<sub>o</sub>).

Sample	S2a (mg/g)	S1 + S2a		S2b (mg/g)	Oil saturation index (mg/gTOC)	Grain density (g/cm <sup>3</sup> )	Total porosity (%)	Estimated bitumen content (%)
		(mg/g)	% TOC					
WIC 7129	10.4	13.20	10.5	79.89	104.8	2.236	n.d.	n.d.
HAR 7060	4.5	5.89	10.2	15.25	101.9	2.682	7.8	3.4
HAR 7070	3.5	5.71	6.6	27.79	65.6	2.533	6.3	2.8
HAD 7110	0.7	1.74	2.7	3.05	27.4	2.618	10.1	0.7

1257

1258

1259

1260

Figure 1. Two column

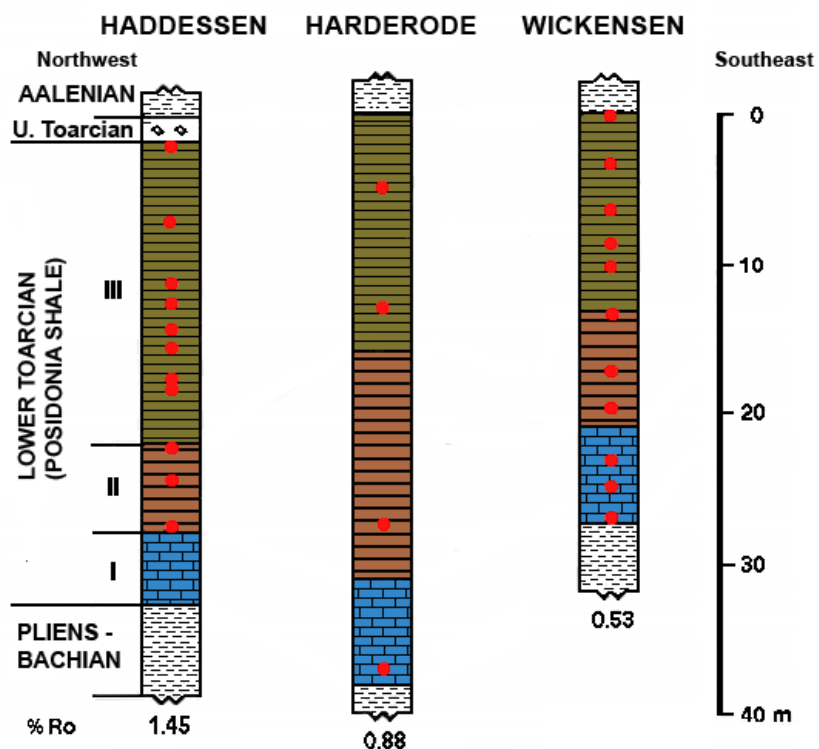
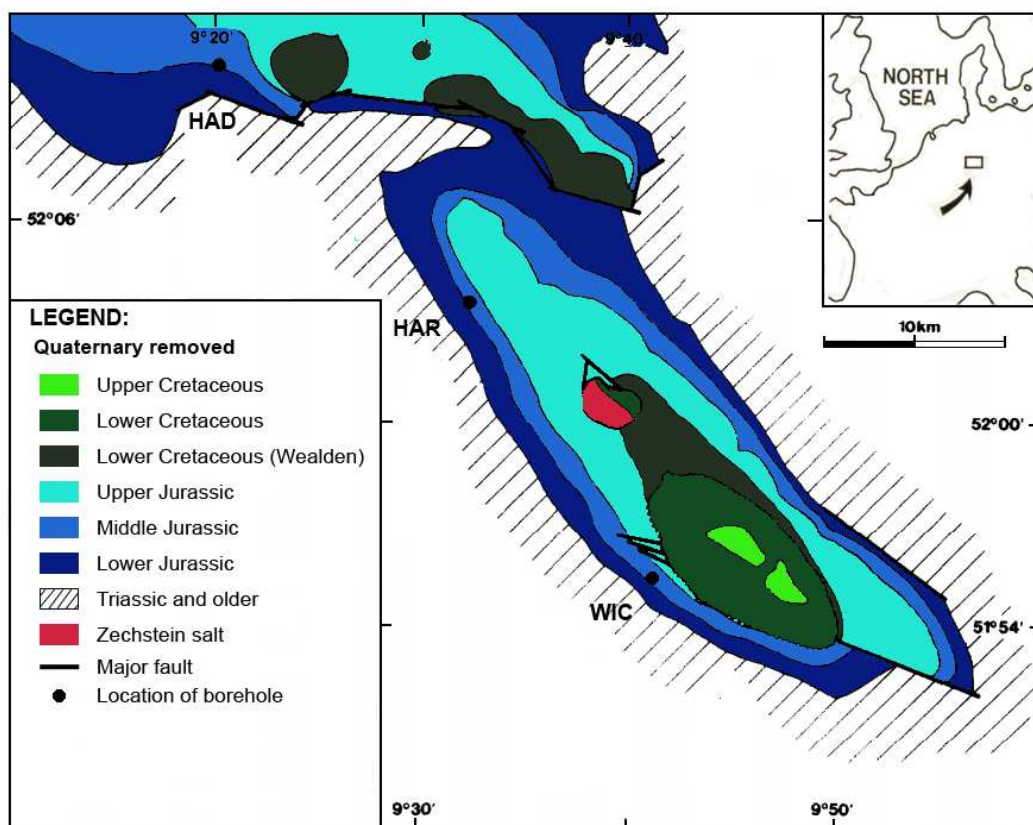


Figure 2 Two column

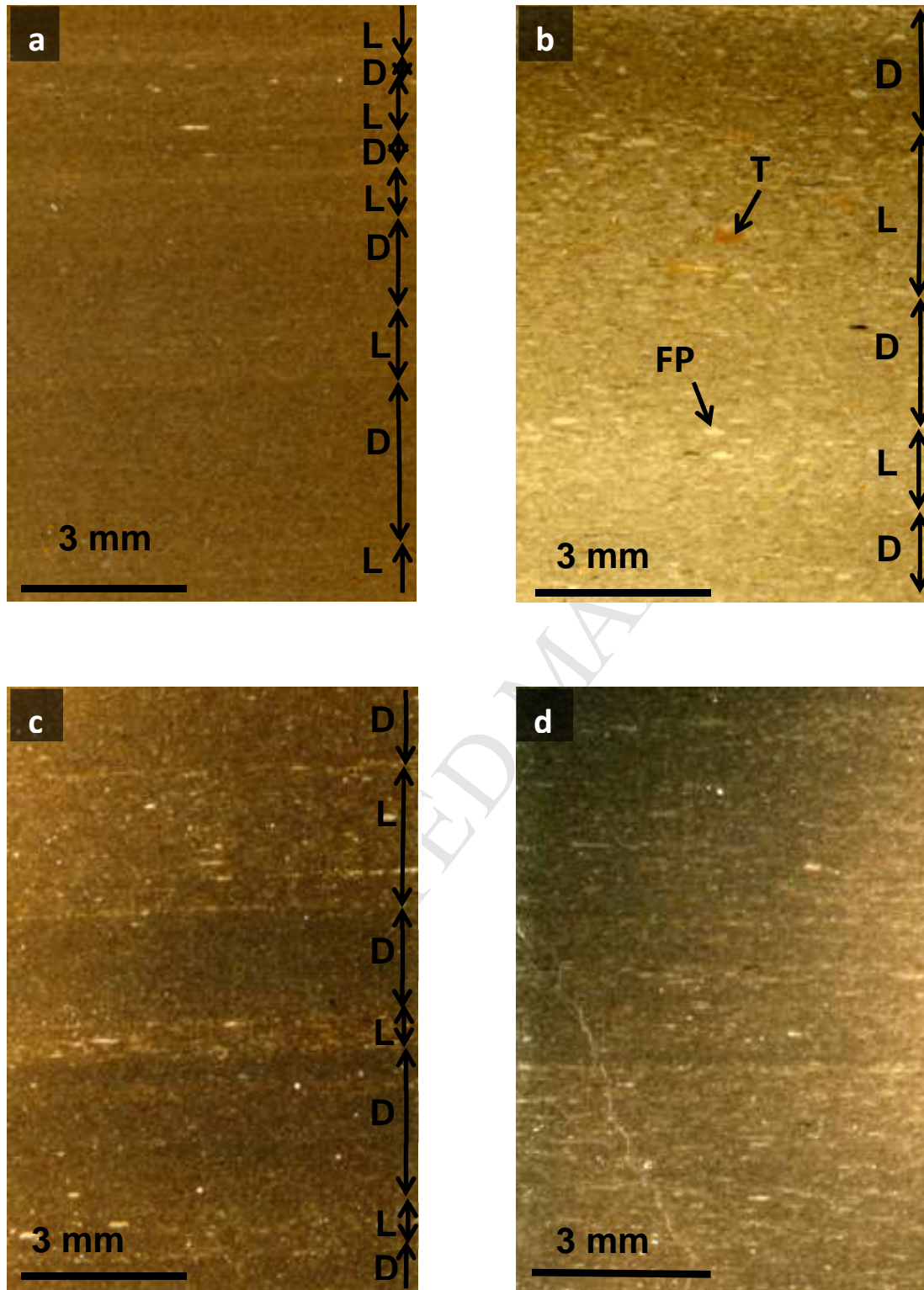


Figure 3 Two column

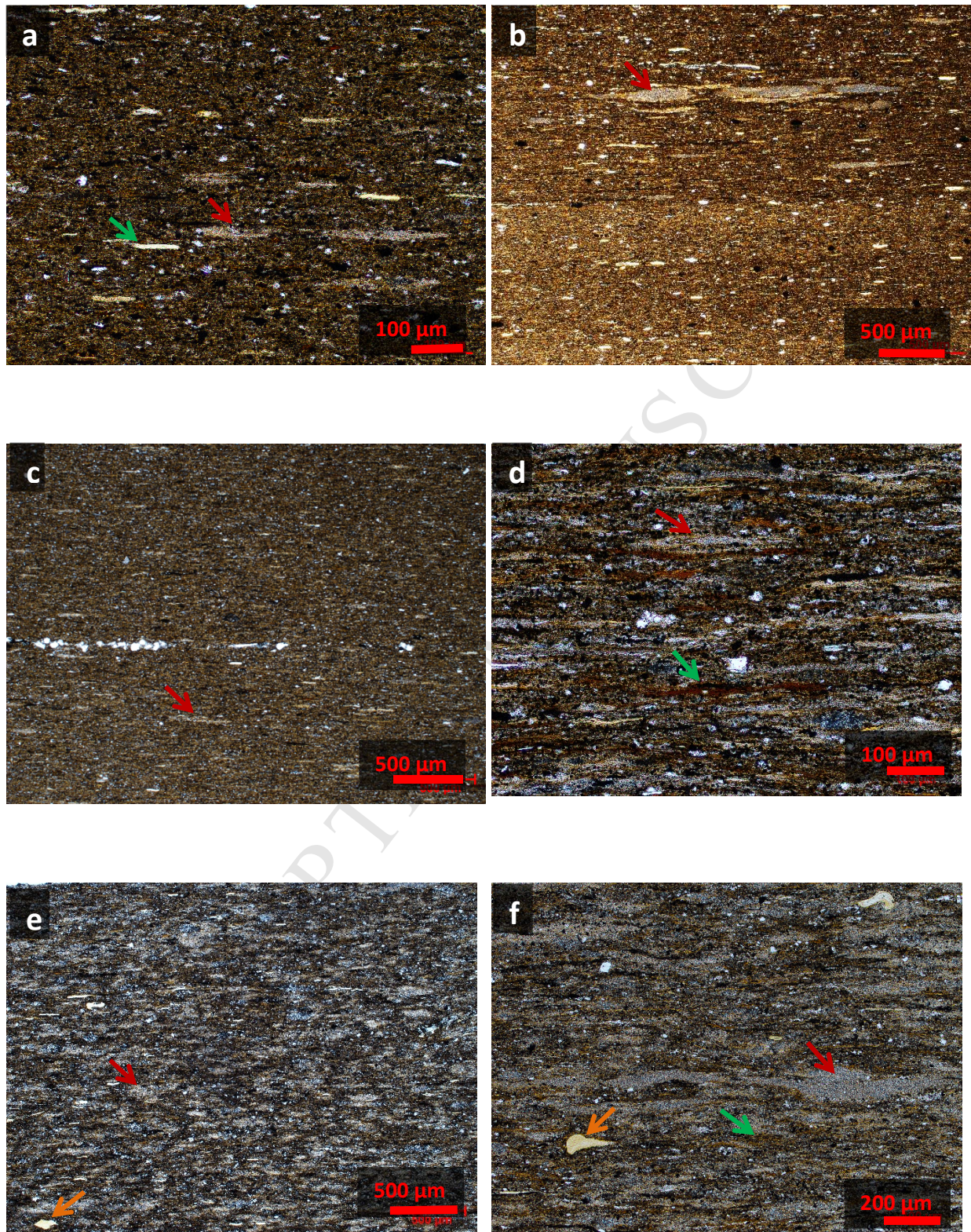


Figure 4 Two column

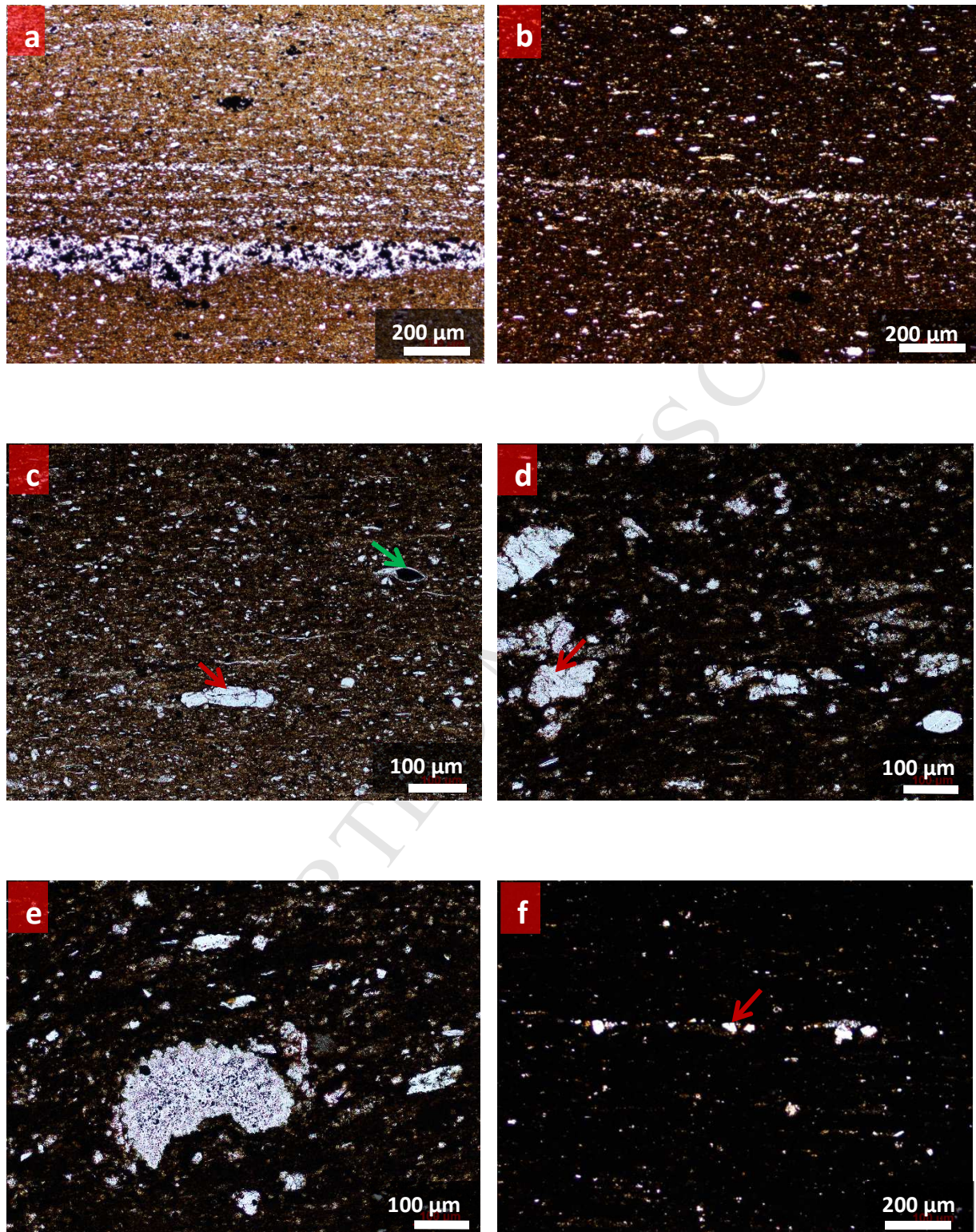


Figure 5 Two column

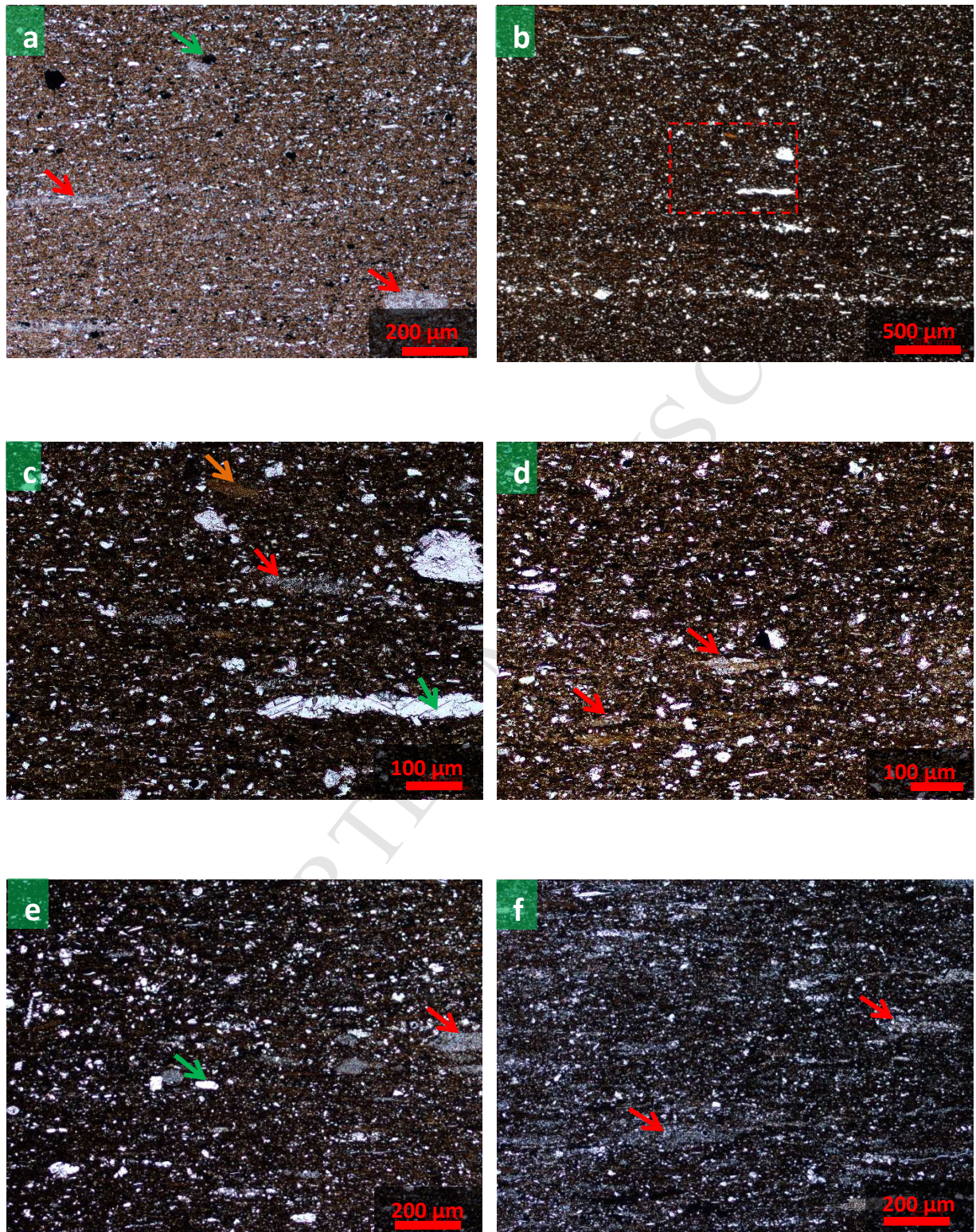




Figure 6 Two column

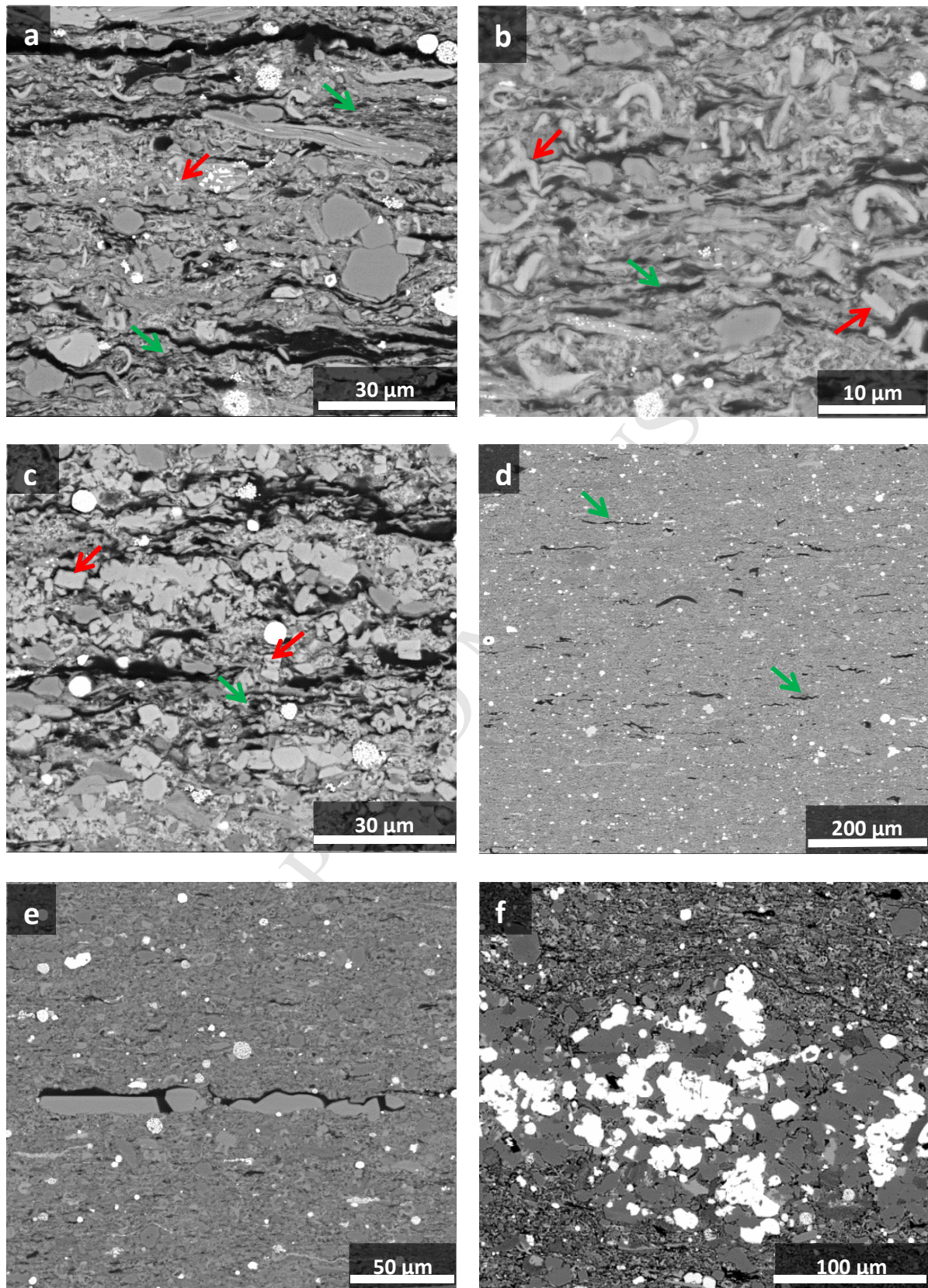


Figure 7 Two column

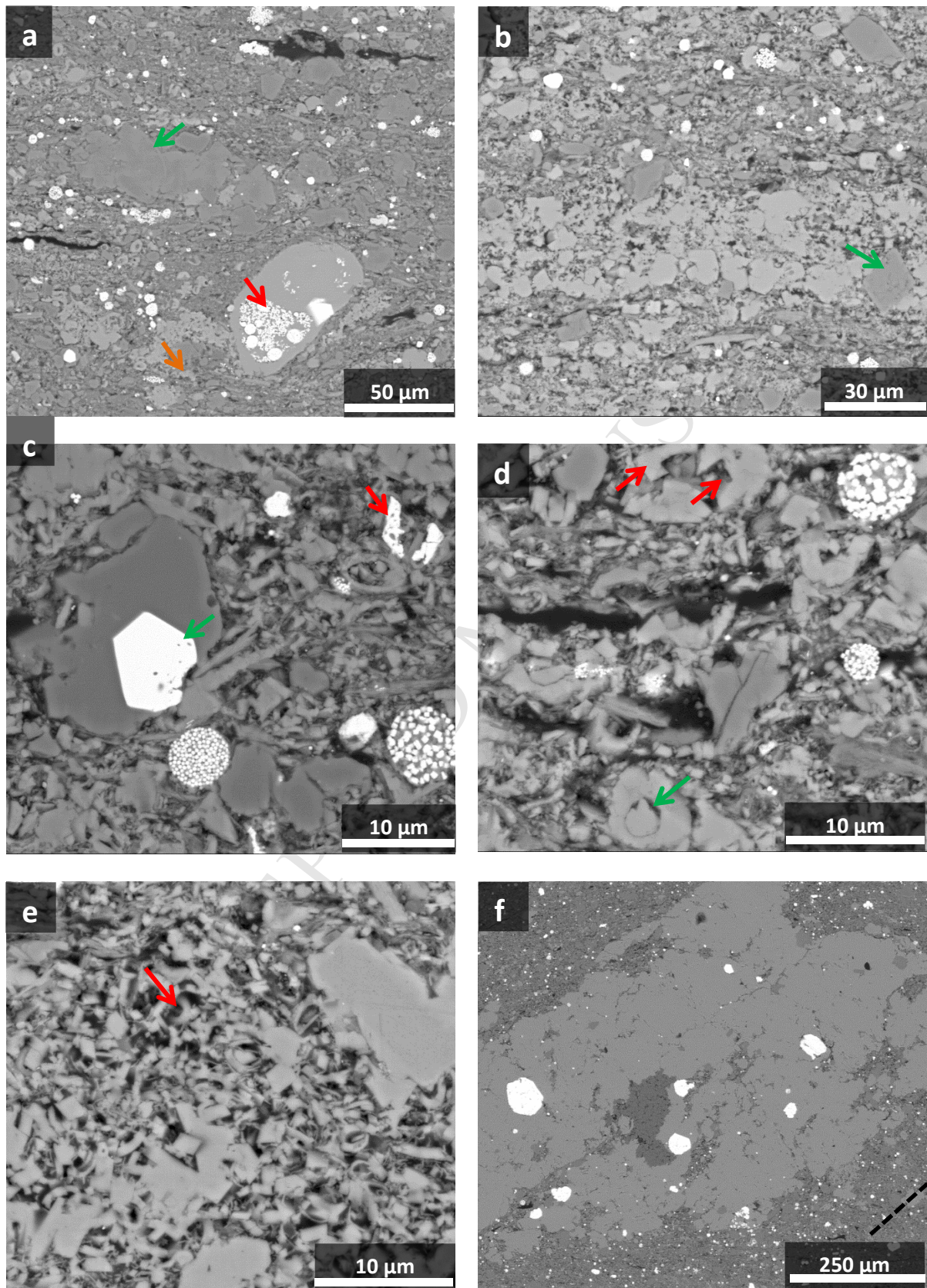


Figure 8 Two column

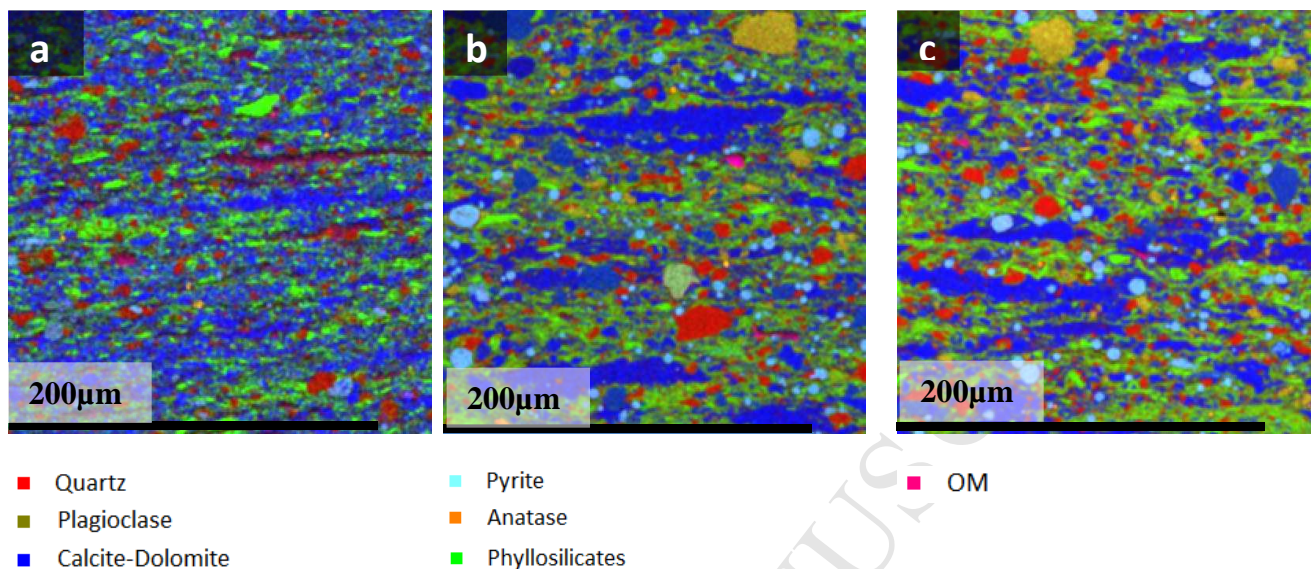


Figure 9 Two column

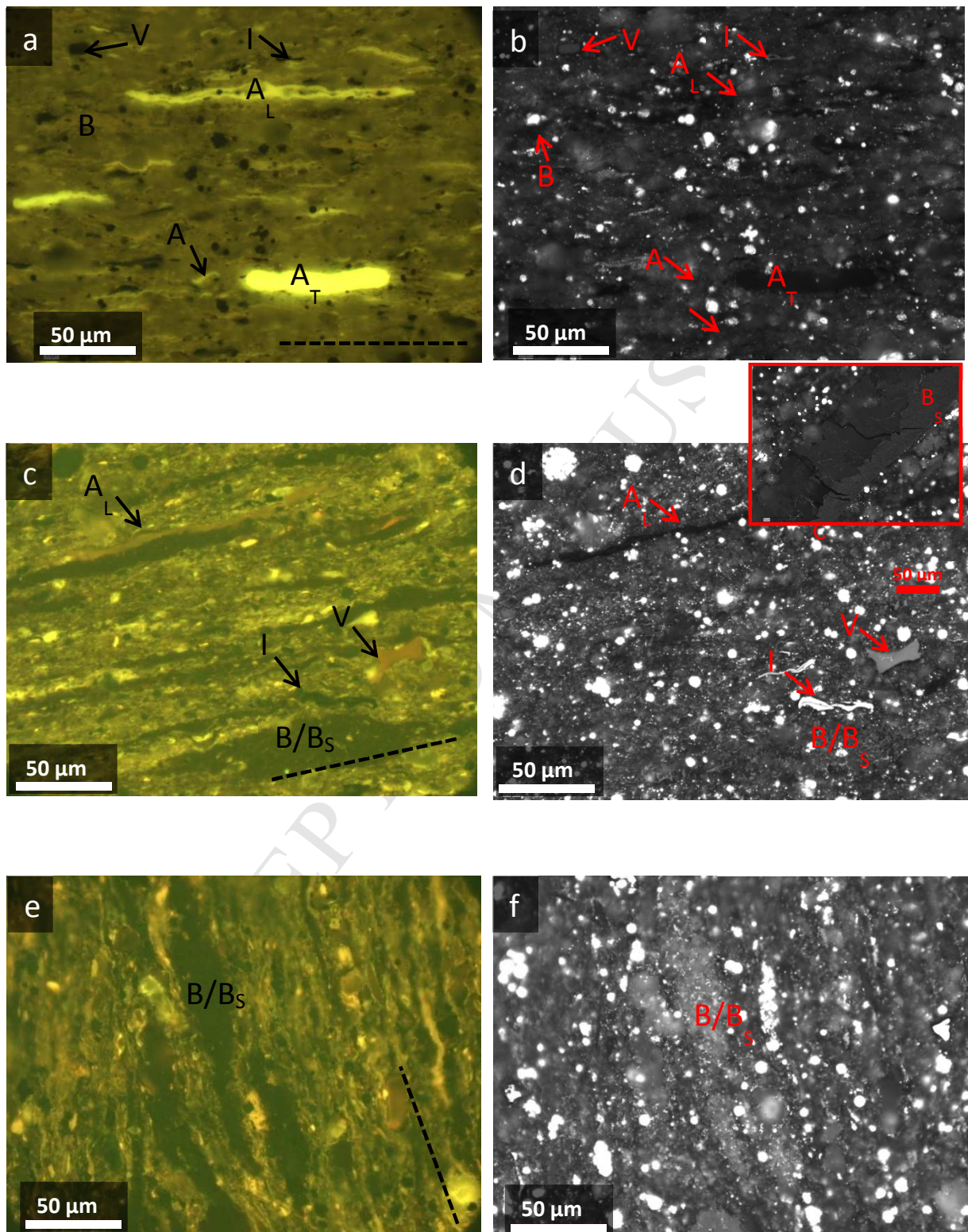


Figure 10 Two column

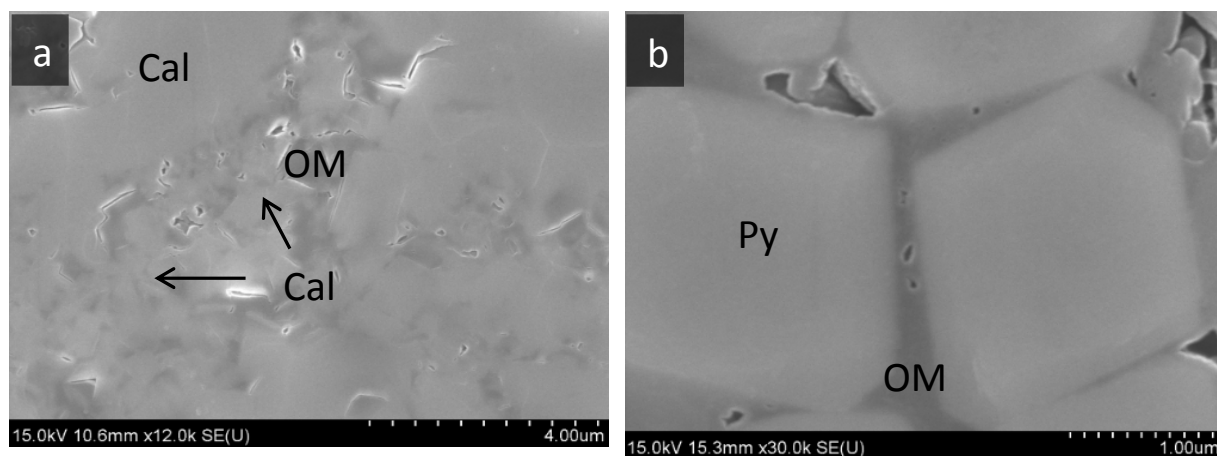


Figure 11 Two column

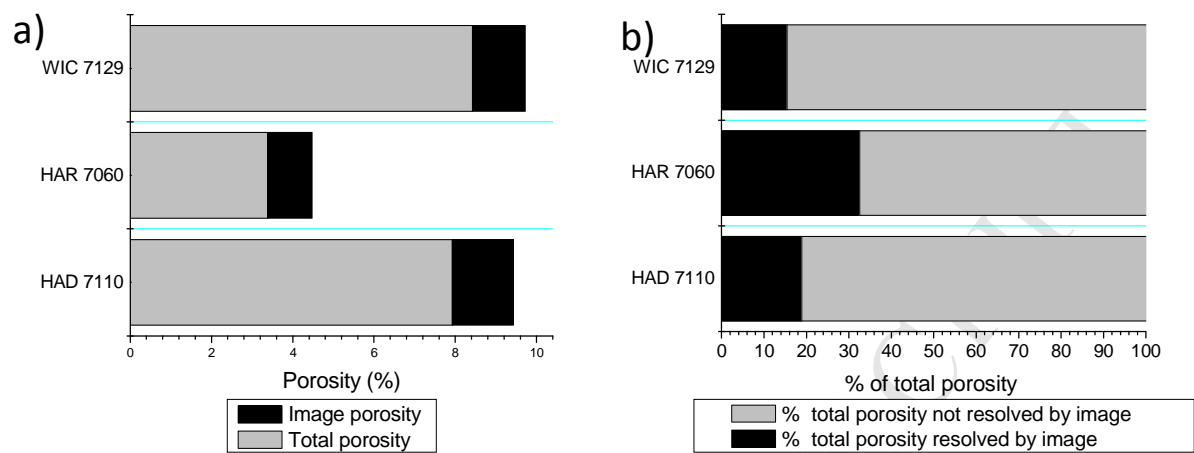


Figure 12 Single column

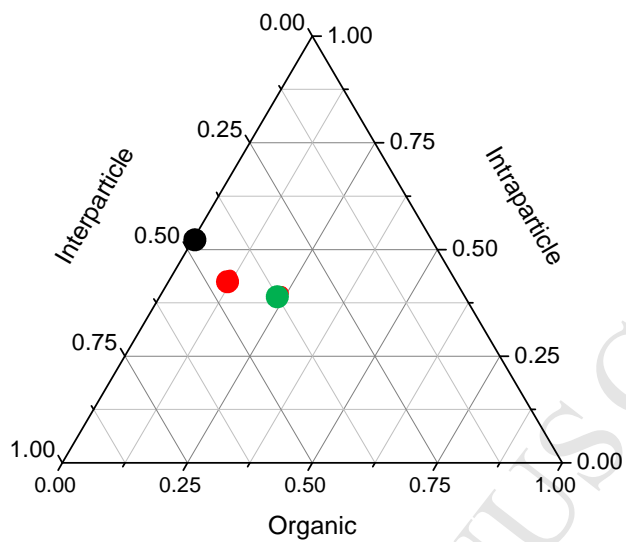


Figure 13 Two column

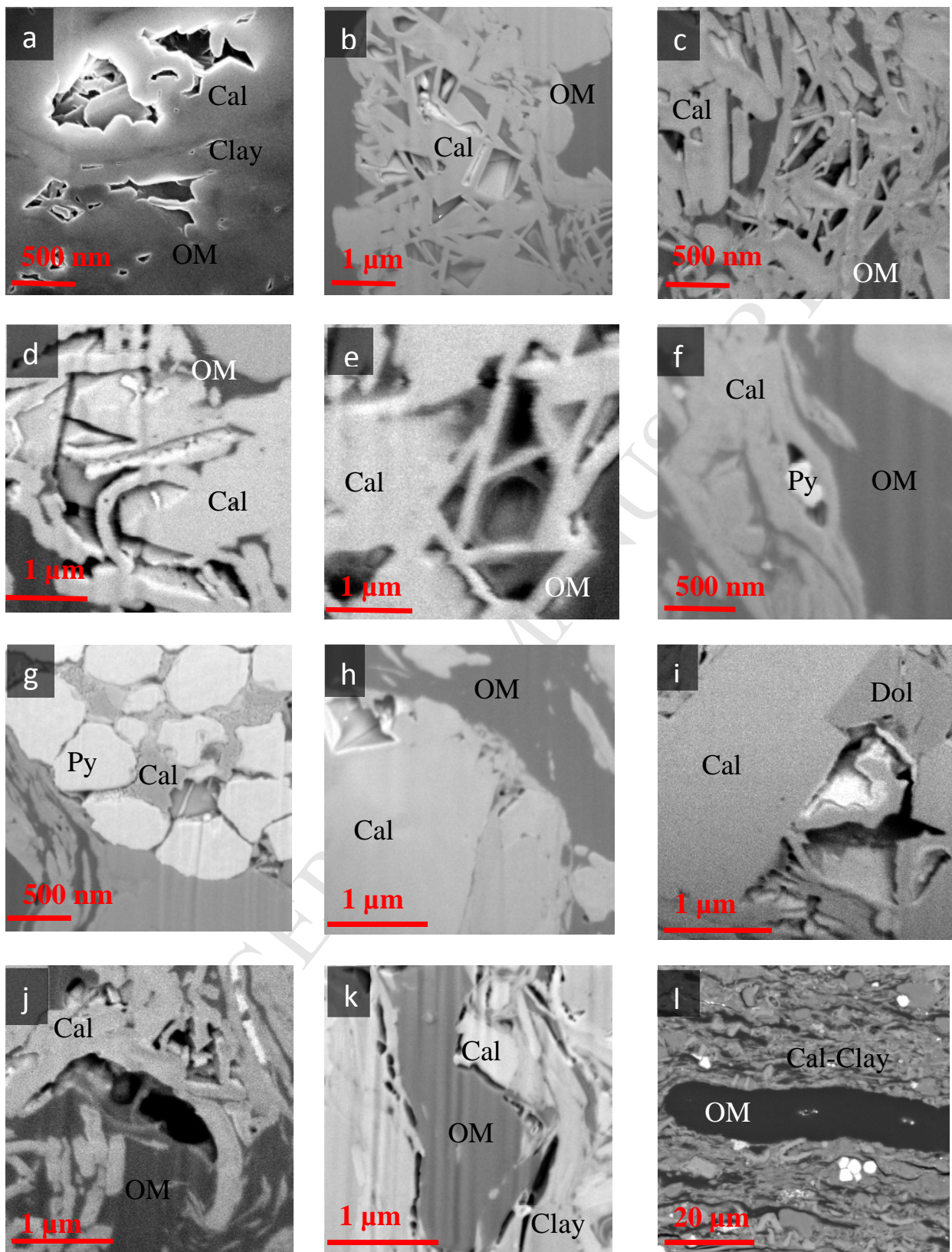




Figure 14 Two column

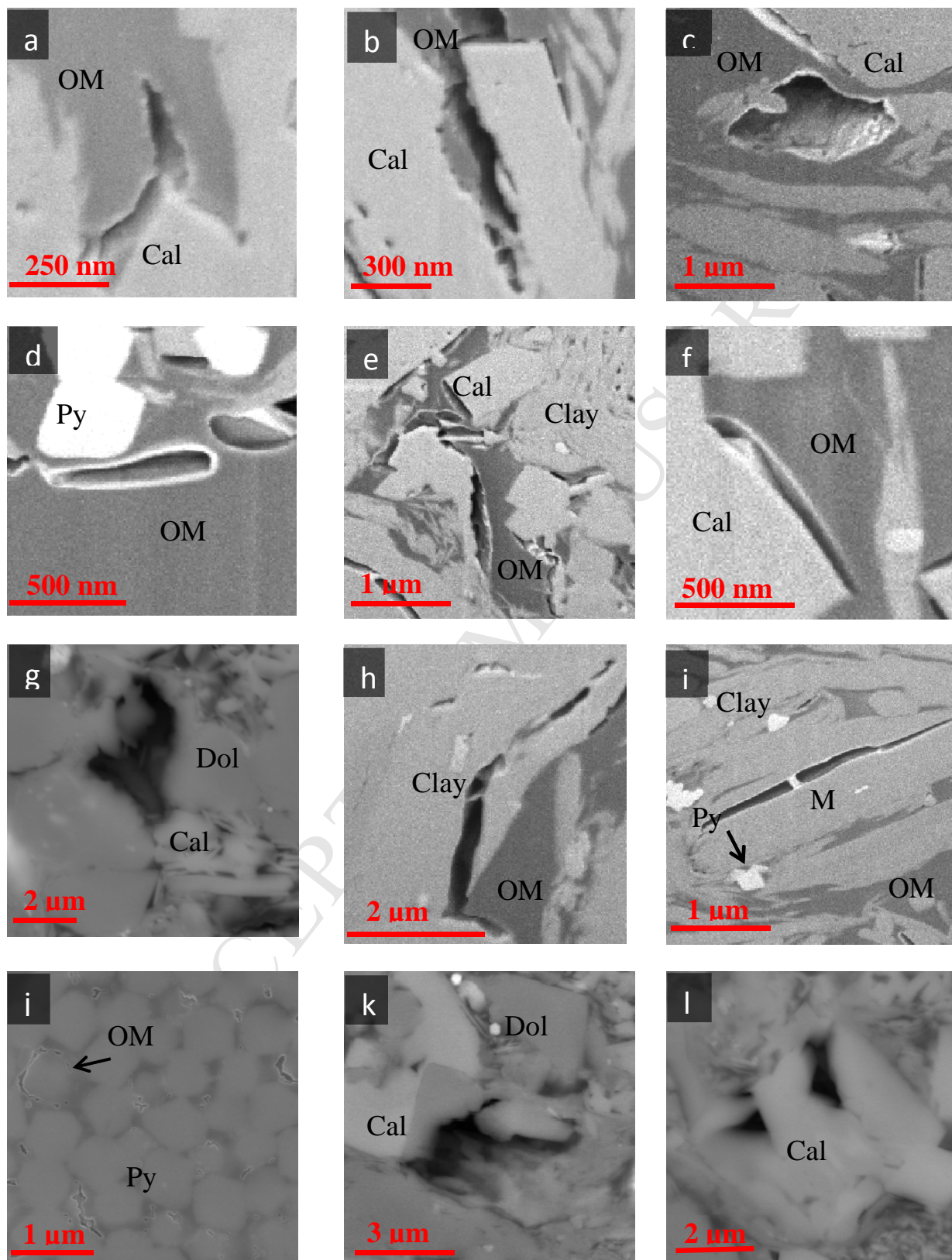


Figure 15 Two column

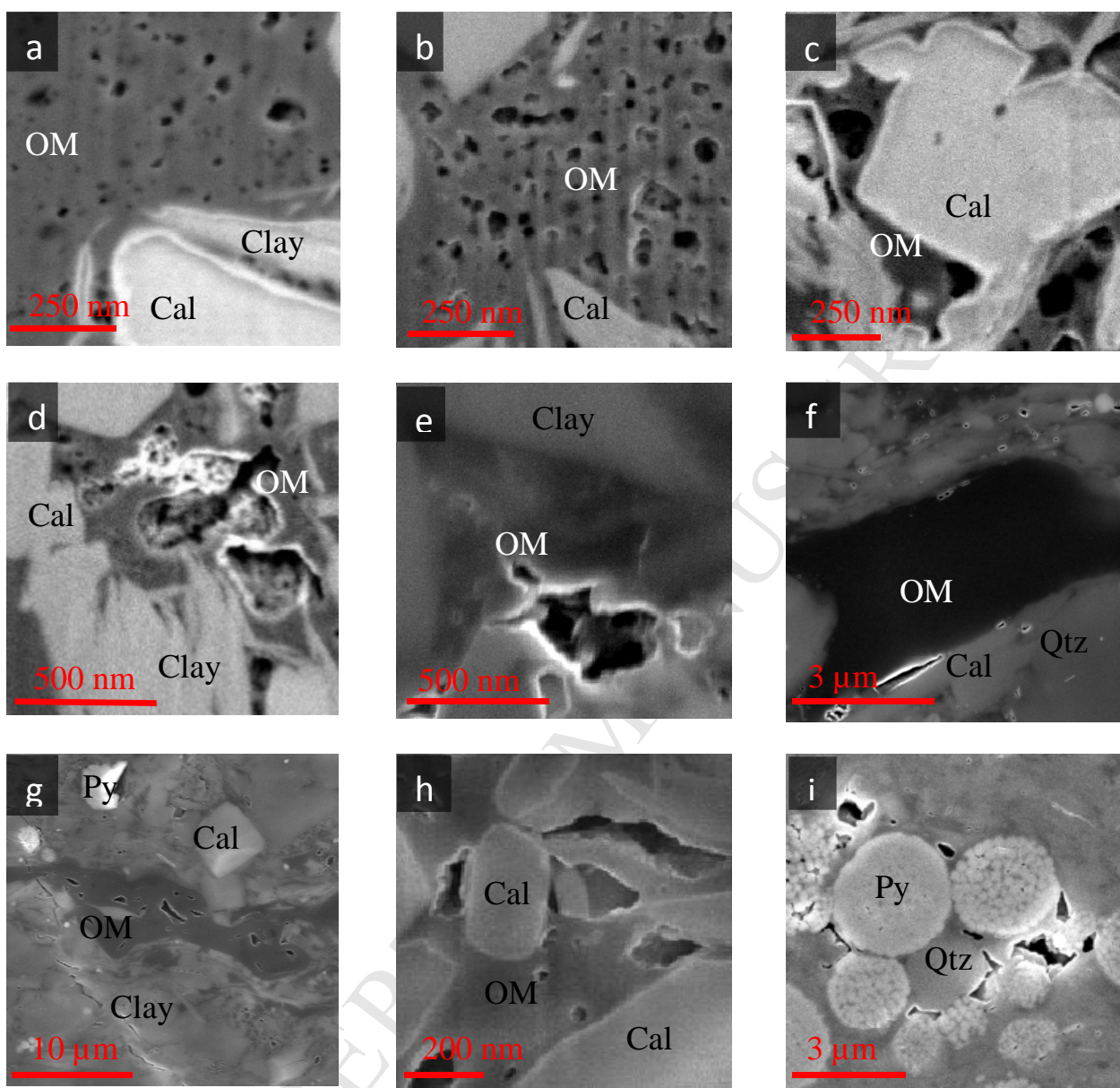
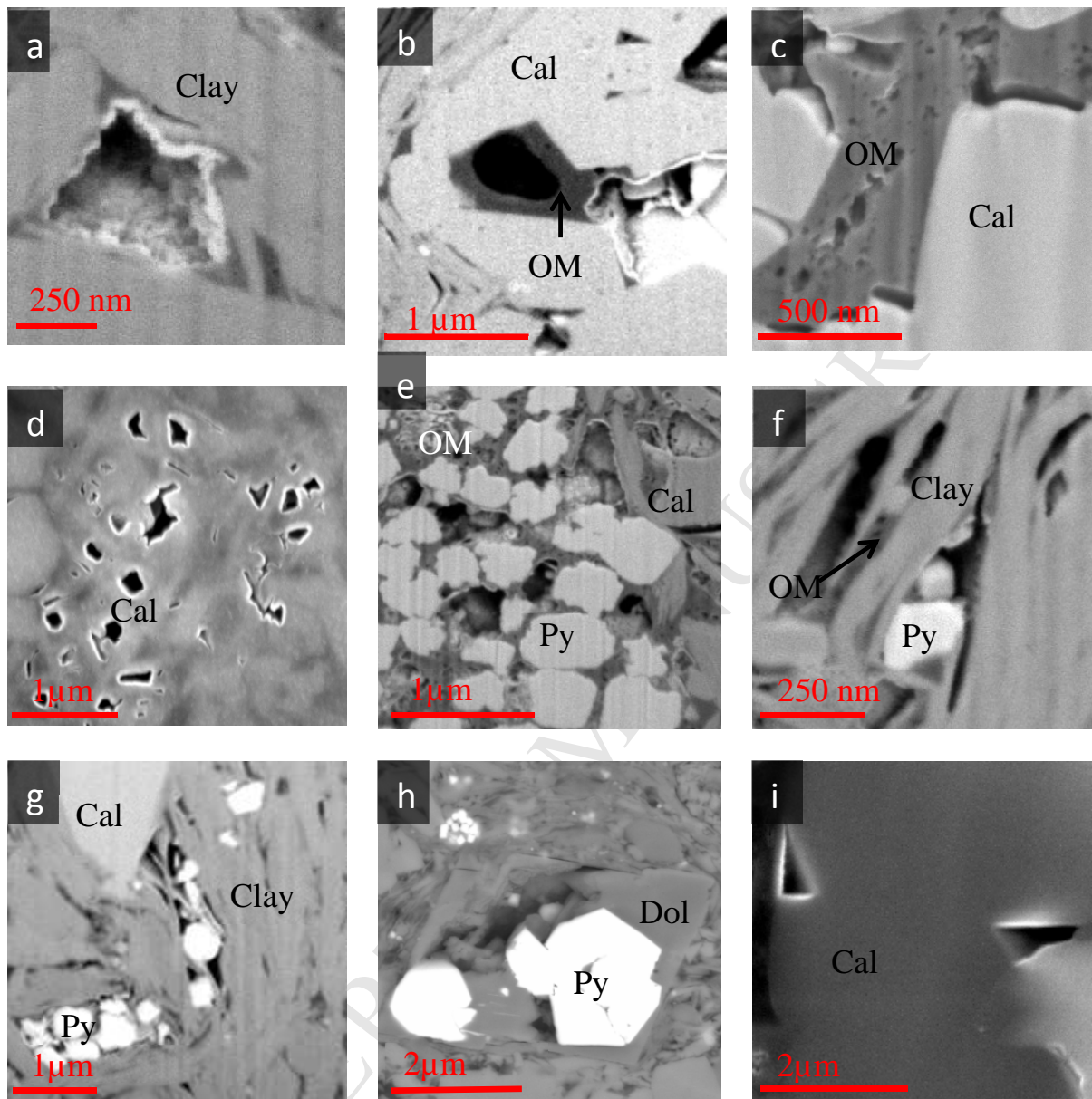


Figure 16 Two column



Highlights: Mathia et al. Microscopic, Petrophysical and Geochemical Characterisation of the Lower Toarcian Posidonia Shale: Implications for Porosity Evolution in an Organic-rich, Calcareous Shale

Porosity of organic-rich, calcareous Posidonia Shale halves in oil window and doubles in gas window

Porosity changes driven by carbonate diagenesis and retention/gasification of bitumen

Pores quantifiable by SEM (> ca. 50 nm) only account for 14-25% of total porosity

Macroporosity of single organic particles in gas window range from 0-40%

Much of porosity generated in gas window is in micro- and mesopores