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Amélie Cavelan, Mohammed Boussafir. Does grain size influence hydrocarbons generation and mesoporosity during artificial thermal maturation of an organic-rich mudstone?. *Journal of Petroleum Science and Engineering*, 2022, 208 (Part C), pp.109643. 10.1016/j.petrol.2021.109643 . insu-03373772

HAL Id: insu-03373772

<https://insu.hal.science/insu-03373772>

Submitted on 11 Oct 2021

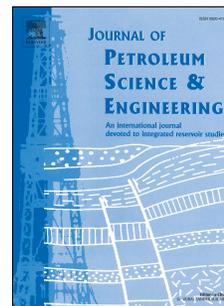
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Journal Pre-proof

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PII: S0920-4105(21)01276-6

DOI: <https://doi.org/10.1016/j.petrol.2021.109643>

Reference: PETROL 109643

To appear in: *Journal of Petroleum Science and Engineering*

Received Date: 14 April 2021

Revised Date: 7 September 2021

Accepted Date: 7 October 2021

Please cite this article as: Cavelan, A., Boussafir, M., Does grain size influence hydrocarbons generation and mesoporosity during artificial thermal maturation of an organic-rich mudstone?, *Journal of Petroleum Science and Engineering* (2021), doi: <https://doi.org/10.1016/j.petrol.2021.109643>.

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Author statement

Amelie Cavelan: Investigation - Original draft preparation- Redaction - Writing - Review & Editing. **Mohammed Boussafir:** Project administration - Conceptualization - Supervision- Review & Editing - Funding acquisition.

Journal Pre-proof

1 **Does grain size influence hydrocarbons generation and mesoporosity during artificial thermal**
2 **maturation of an organic-rich mudstone?**

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9
10 **Highlights**

- 11 • The effect of sample grain sizes on laboratory thermal maturations is investigated.
- 12 • The use of small blocks, rocks fragments, and powder were compared
- 13 • The use of small blocks lowered the amount of the generated hydrocarbons.
- 14 • Lower pore sizes and volumes are measured for the small blocks
- 15 • The impact of the sample grain sizes differs between thermal maturation systems

16 **Abstract**

17 To assess how the grain size/rock fabric of laboratory-matured shale samples impact oil, gas production,
18 and the formation of pores during laboratory thermal maturation, cores (4.5 mm*1 cm) of bulk rock,
19 millimetric equidimensional rock fragments (3*3 mm), and fine grind powder (<200µm) were obtained
20 from an organic-rich mudstone (Kimmeridge Clay Fm. "KCF", Yorkshire, UK) and artificially matured
21 under anhydrous conditions. The composition of the organic matter (OM), porosity, and thermal
22 maturity were characterized using nitrogen adsorption, Rock-Eval® VI pyrolysis, GC/TCD (Gas-
23 Chromatography/Thermal Conductivity Detector), and GC/MS (Gas Chromatography/Mass
24 Spectrometry). While only a few differences in geochemical composition and porosity exist between
25 rock fragments and powders, a greater gap is observed with the cores. Probably due to lower surface
26 contact between the organic components themselves and clay mineral surfaces (which can act as a

27 catalyst of oil and gas generation) less intense OM thermal degradation processes were observed for the
28 cores. The use of cores rather than powder and fragments results in: (i) the production of lower
29 extractible OM concentrations; (ii) lower amounts of gas (C₁-C₅ and CO₂); (iii) lower pore volumes and
30 smaller pore sizes during maturation. This preliminary work highlights the importance of considering
31 the fabric of the rock being artificially matured and shows that the use of cores with an intact rock fabric
32 (e.g. cores), closer to natural conditions, could be more suitable when studying OM thermal degradation
33 and porosity. In comparison with previous works, this also demonstrated that depending on the
34 maturation system used (e.g. semi-confined, confined) the differences in the amount of hydrocarbons
35 generated and porosity observed between powder and cores during maturation could differ significantly
36 and find their origin in different processes.

37 **Keywords:** Artificial thermal maturation, rock fabric, mesoporosity, mudstone.

38 1. Introduction

39 A further understanding of the variation of the porosity of mudstones during maturation is
40 necessary to predict the spots favorable for successful exploitation of shale oil and gas (Clarkson et al.,
41 2013; Katz and Arango, 2018; Ross and Bustin, 2009). To better explain how OM composition and
42 thermal maturity affect organic-rich mudstone porosity, laboratory thermal maturations were
43 increasingly used these last years since they ensure to obtain rocks of different thermal maturity from
44 the same initial immature sample (Cao et al., 2021; Cavelan et al., 2019a, 2020a; Chen and Xiao, 2014;
45 Guo et al., 2017; Han et al., 2019; Ko et al., 2016, 2018; Song et al., 2020, 2021; Tan et al., 2021; T.
46 Wang et al., 2021; Y. Wang et al., 2021; Xu et al., 2021). Initially used to calculate kinetic parameters,
47 assess variations of the kerogen structure, mass balance, or quantify oil generation potential, this method
48 significantly improved our knowledge about oil and gas generation mechanisms and hydrocarbon
49 expulsion processes (Behar et al., 2010, 2008, 2003, 1997, 1992; Behar and Vandenbroucke, 1986; Hou
50 et al., 2021; Landais et al., 1994; Lewan, 1997; Michels et al., 1994; Monthieux et al., 1985) and their
51 relation with the formation of pores and the storage capacity of shale reservoirs (Cavelan et al., 2019a;

52 Chen and Xiao, 2014; Guo et al., 2017; Han et al., 2019; Ko et al., 2018; Song et al., 2020, 2021; T.
53 Wang et al., 2021; Y. Wang et al., 2021; Xu et al., 2021). Today several conventional and MBE (material
54 balance equation) models used to estimate the gas sorption capacity of kerogen at different thermal
55 maturity are still partly based on the knowledge acquired during these experiments (Alafnan, 2021;
56 Alafnan et al., 2020; Ambrose et al., 2012; Ungerer et al., 2015). However, the experimental conditions
57 (open, semi-confined, confined, the chosen duration/temperature, hydrous/anhydrous conditions, rock
58 fabric) chosen for these maturations is known to influence OM thermal degradation processes (Behar et
59 al., 2003; Cavelan et al., 2020a; İnan, 2000; Landais et al., 1994; Michels et al., 1995; Monthieux, 1988;
60 Shao et al., 2018; Song et al., 2021; Suárez-Ruiz et al., 1994). The mineral phase, and especially clay
61 minerals, is known to act as a support medium of the OM and a catalyzer during its thermal
62 transformations (Tannenbaum et al., 1986; Tannenbaum and Kaplan, 1985; Tissot and Welte, 2013).
63 The relative distribution of OM and minerals in rocks, the size of the OM domains, and the degree of
64 confinement of the system may influence oil and gas generation during burial (Michels et al., 1995,
65 1994; Suárez-Ruiz et al., 1994). In particular, during artificial maturation, OM diagenetic processes can
66 be affected by the physical and morphological properties of the pyrolyzed sample (İnan, 2000; Shao et
67 al., 2018; Song et al., 2021; Suárez-Ruiz et al., 1994). Probably due to better confinement achieved in
68 core samples, these works observed different compositions and contents of hydrocarbons generated by
69 the OM after the maturation of cores and powdered samples. In particular, they showed that the use of
70 core samples may favor the expulsion of oil (Shao et al., 2018; Song et al., 2021). Considering the effect
71 that the thermal degradation of OM can have on the development of mudstone porosity (Cavelan et al.,
72 2020b; Chen and Xiao, 2014; Curtis et al., 2012; Fishman et al., 2012; Guo et al., 2017; Hackley and
73 Cardott, 2016; Han et al., 2019; Katz and Arango, 2018; Klaver et al., 2015; Ko et al., 2018; Löhr et al.,
74 2015; Loucks et al., 2009; Mastalerz et al., 2013; Milliken et al., 2014; Song et al., 2021, 2020; T. Wang
75 et al., 2021; Y. Wang et al., 2021; Xu et al., 2021), we can suppose that the use of different rock particle
76 sizes during artificial maturation may affect the thermal degradation of the OM, leading to different
77 OM-hosted pore development. Indeed, Song et al. (2021) demonstrated that semi-closed pyrolysis of

78 type-II lacustrine mudstones gives different results in terms of hydrocarbon retention-expulsion
79 mechanisms and pore development when performed on a powdered sample or cores.

80 Recent computation works for estimating the gas storage capacity of kerogen in shales are based
81 on porosity parameters and in particular on Langmuir isotherms and Langmuir volumes which depend
82 on the kerogen composition but also the porosity formed during maturation (Alafnan, 2021; Alafnan et
83 al., 2020; Ambrose et al., 2012; He et al., 2019; Memon et al., 2020; Ungerer et al., 2015). The pore size
84 distributions of shales may also largely influence gas-in-place calculation (Tolbert and Wu, 2015).
85 Differences in specific surface area, pore-volume, or pore size distribution obtain between different
86 thermal maturation conditions for the same maturity may, therefore, lead to differences in gas storage
87 capacity and gas in place recovery estimations. Recent numerical works also demonstrated that the
88 properties of the pore network such as the pore radius or the composition of the oils acquired during
89 thermal maturation greatly influence the oil transport in shale micro-fractures and nanopores (Cui,
90 2019a). For example, the increase in the amount of generated asphaltenes may enhance the permeability
91 of organic pores but reduce the permeability of inorganic pores and micro-fractures (Cui, 2019a), while
92 the radius of pores and fractures controlled the permeability of shales that may impact pre-Darcy flow
93 phenomena mechanisms (Cui, 2019b; Cui and Si, 2021). Therefore, an inaccurate estimation of these
94 parameters (oil composition, oil quantity, pore sizes, etc.) linked to the choice of thermal maturation
95 parameters could, for example, lead to an inaccurate estimation of the flow capacity/properties of the
96 studied shale formation. However, to our knowledge, only Song et al. (2021) studied the impact of the
97 rock fabric on the evolution of shale porosity during laboratory thermal maturation. This is insufficient
98 to determine to which extent these results can be applied to all experimental thermal maturation works
99 since they could depend on the maturation system used (semi-confined).

100 It is, therefore, necessary to better understand how these maturation conditions, which often
101 differ from one study to another, affect the maturation of OM and the resulting porosity. To that end,
102 cores, rock fragments, and powder of an immature mudstone from the Kimmeridge Clay Fm. (Yorkshire,
103 UK) were artificially matured in autoclaves. The composition of the OM, thermal maturity, and

104 mesopore structure with increasing maturity were determined using nitrogen adsorption and bulk
 105 geochemical characterizations (Rock-Eval VI pyrolysis, GC-TCD (gas chromatography-thermal
 106 conductivity detector), and GC-MS (gas chromatography-mass spectrometry). The obtained data were
 107 compared with naturally matured rocks from the Vaca Muerta Fm. (Cavelan et al., 2020b, 2019b) to see
 108 which artificial sample series is closest to natural trends.

109 2. Methods

110 2.1. Sample

111 Three cores (4.5 mm*1 cm), rock fragments “RF” (3*3 mm), and powder “PO” (<250µm) were
 112 obtained from one immature mudstone from the Kimmeridge Clay Fm. (Yorkshire, UK). The properties
 113 of this sample are presented in Tab.1. For each sample type, 1g was firstly oven-dried at 105°C for 12
 114 hours, placed separately in gold tubes before being introduced into high-pressure autoclaves in stainless
 115 steel. Each sample was then laboratory- matured under confined and anhydrous conditions at 325°C,
 116 390°C, and 470°C for 72 hours (600 bars, external hydrostatic pressure) with the protocol defined by
 117 Cavelan et al. (2019b).

118 2.2. Rock-Eval

119 To determine the hydrogen index (HI, mg HC./g TOC), T_{max} , and total organic carbon (TOC, wt.%)
 120 contents of samples after maturation, 60 mg of each sample were crushed into powder and analyzed
 121 using new Rock-Eval 6[®] pyrolysis with the same procedure described in (Cavelan et al., 2019a). TOC
 122 was calculated from the integration of peaks S₁, S₂, S₃CO, S₃CO₂, S₄CO, and S₄CO₂ (see Espitalie et al.,
 123 1985). The HI represents the amount of pyrolyzed hydrocarbons and was calculated with the following
 124 equation (equation 1):

$$125 \quad HI (mgHC/g TOC) = \frac{S_2 * 100}{TOC} \quad (equation 1)$$

126 With S_2 the amount of hydrocarbons generated by the thermal cracking of the kerogen during the
127 pyrolysis. The T_{max} is often used as a maturity indicator and is derived from the T_{pic} which is the
128 temperature of the peak oil production during pyrolysis (see Espitalie et al., 1985).

129 2.3. Gas chromatography

130 After maturation, 2 cm³ of gas were sampled with the protocol described in (Cavelan et al., 2019a) and
131 injected in GC-TCD (Perkin Elmer® Clarus 580; Column Supelco® Carboxen 1010 Plot® Capillary:
132 length: 30 m, film thickness: 0.15 μ m, internal diameter 0.53 μ m). Gas quantification was made using
133 calibration curves and the areas of the peak of each gas on chromatograms. Then, 1g of all artificially
134 matured samples was crushed into powdered and extracted in solvent (dichloromethane: methanol (1:1))
135 using ultrasonication. The extractible part of the OM (EOM) was then separated on a silica gel
136 chromatography column and the fraction of aromatic (ARO), saturated (SAT), and polar hydrocarbons
137 were then recovered separately by elution with different solvents using the protocol of Cavelan et al.
138 (2020b). Asphaltene contents were obtained by the difference between the mass of the total extract and
139 the mass of the recovered polar hydrocarbons, ARO and SAT. The compounds rich in Nitrogen, Sulfur,
140 or Oxygen (NSO) represents the sum of the asphaltenes and polar hydrocarbons. The molecular
141 composition of ARO and SAT were determined using a GC-MS Trace-GC Ultra (Column: Thermo
142 Trace-Gold 5 MS, length 60 m, internal diameter 0.25 mm, film thickness 0.25 μ m fitted by a mass
143 spectrometer TSQ Quantum XLS. Compounds of interest in the ARO fraction were identified using
144 retention times and mass spectra and quantified using their peak areas on ion-specific chromatograms.
145 Squalane was the internal standard. Values of equivalent vitrinite reflectance (R_c , %) were then
146 calculated using the methyl dibenzothiophene ratios (MDTR), the dimethylphenanthrene ratios (DMPR),
147 and the methylphenanthrene index (MPI-1) with the equation described by Radke et al. (1986) and
148 Boreham et al. (1988). The mean of these three obtained R_c values is the mean R_c (%). Before and after
149 maturation 60 mg of each sample were powdered and dried before being pyrolyzed using the Rock-
150 Eval® VI method (Espitalié et al., 1985a, 1985b) to obtain : (i) the content of total organic carbon

151 (TOC, in weight % of the rock); (ii) the oil-prone quality of the OM expressed as a Hydrogen Index (HI,
152 mg of HC per g of TOC).

153 2.4. Vitrinite reflectance

154 To confirm the calculated vitrinite reflectance values obtained from biomarker ratios (Rc), vitrinite
155 reflectance (Rv) was measured on fragments and cores after thermal maturation. Measurements were
156 carried on polished rock sections made from cores and fragments using the preparation and calibration
157 protocol described in (Cavelan et al., 2020b). For each sample, each Rv value is the mean of 50 random
158 measurements.

159 2.5. Nitrogen adsorption measurements

160 After maturation, the volume, the distribution of the pore sizes (PSD), and the BET surface area were
161 measured using nitrogen adsorption (Quantachrome® NOVA 2200e). Before analysis, each sample was
162 crushed to a particle size < 250 µm before being oven-dried for 12 hours (110°C). The samples were
163 then outgassed for 24h (105°C) directly in the apparatus. The volume of pores accessible to nitrogen
164 was determined using the liquid molar volume of nitrogen adsorbed at the relative pressure (P/Po) =
165 0.99 with the following equation (equation 2):

$$166 \text{ Pore volume (cm}^3\text{/g)} = \frac{\text{amount of N}_2 \text{ adsorbed at } \frac{P}{P_0}=0.99 \text{ (cm}^3 \text{ STP/g)}}{647 \text{ (N}_2 \text{ liquid volume ratio at 77 K)}} \quad (\text{equation 2})$$

167 PSDs were calculated on the adsorption isotherms using the method of Barrett et al. (1951) (often called
168 the “BJH method”). BET surface areas were calculated using the Brunauer, Emmett, and Teller method
169 applied to the adsorption isotherm (BET) between P/Po 0.03 and 0.33 (Brunauer et al., 1938). Each
170 analysis of BET surface area was done with a minimum of 15 points. Analyses were done at the liquid
171 nitrogen temperature (77K).

172 Preliminary results obtained by CO₂ (Quantachrome - Autosorb-1-MP-6) and N₂ (Micromeritics®
173 ASAP -2420) adsorption measurements using the Dubinin-Radushkevich model (DR), Dubunin-
174 Astakhov between P/Po ranging from 0.0001 to 0.01 (adsorption isotherms), and the Horwath-Kawazoe

175 model between P/Po ranging from 1 to 0.35 showed that the studied samples are predominantly
176 mesoporous. Microporosity (<2 nm) represents less than 8% of the pore volume and specific surface.
177 Therefore, only mesoporosity (2-50 nm) and part of the macroporosity (> 50 nm) were investigated in
178 this work.

179 Three replicates of thermal maturations were made from the same sample for each degree of
180 maturity and each type of rock fabric. The presented results show the mean values and standard
181 deviations obtained for these triplicates.

182 **3. Results and discussion**

183 3.1. Influence of particle size of the pyrolyzed rock on the amount and composition of generated
184 hydrocarbons.

185 Variation of calculated (Rc) and measured vitrinite reflectance (Rv), HI, T_{max}, and concentrations of gas,
186 SAT, NSO, and ARO shows that the three series of samples evolved from the oil to the gas window
187 after heating from 325°C to 470°C (Tab.2, Fig.1). Whatever the rock fabric of the samples, the early
188 stage of oil production was reached after heating at 325°C (Rc ~0.71%). After maturation at 390 and
189 470°C, the decrease of the HI, SAT, ARO, and NSO contents, the increase of C1-C5 hydrocarbons
190 gases, and CO₂ concentrations indicate the entry in the gas window (Tab.2, Fig.1). This is well
191 substantiated by the Rc of 1.28% and 2.41% calculated after heating at 390°C and 470°C (Tab.2).
192 Concerning the extracted OM composition, differences exist between series, especially between the
193 cores and the two other sample types: RF and PO. The few differences observed between the PO and
194 RF are less than 10% and are thus not significant. Even if special care has been taken to sample all series
195 on one small and homogeneous rock, these differences can simply be explained by slight intern
196 variations in the initial composition of the rock or by the slight differences attached to the OM extraction
197 and analyses. These differences are therefore not sufficient to reveal any effect of the sample rock fabric
198 on OM thermal degradation between these series. The experimental thermal maturation of powder and
199 rock fragments gives thus comparable results and can be compared. Moreover, differences are greater

200 with the core series (Fig.1). The cores generated 25% less EOM (including NSO, ARO, and SAT
201 concentrations) during the generation of oil ($R_c \sim 0.71\%$). The relative proportions of ARO, SAT, and
202 NSO are nevertheless similar between RF and PO series ($\sim 14\%$, 18% , and 68% respectively). A similar
203 difference is observed during gas generation. While only a few negligible differences are observed
204 between RF and PO during the condensate wet gas zone ($R_c \sim 1.28\%$) and the dry gas zone ($R_c \sim 2.41\%$),
205 the cores generated $\sim 30\%$ fewer concentrations of C_1 - C_5 and 50% to 84% fewer concentrations of CO_2
206 (Fig.1). All series of samples come from the same immature rock (a mudstone rich in OM) treated with
207 the same experimental protocol, these differences are thus probably influenced by the fabric of the
208 laboratory-matured samples. This supports previous results (İnan, 2000; Shao et al., 2018; Song et al.,
209 2021; Suárez-Ruiz et al., 1994) and confirms that the fabric of the rock affects the thermal maturation
210 of the OM and thus the production of oil and gas. These results are in agreement with the observations
211 of Shao et al. (2018), which shows that after thermal maturation under anhydrous conditions of shale
212 samples from the Eagle Ford, the cores generated less C_1 - C_5 and CO_2 concentrations than powdered
213 samples. However, contrary to our study, Suárez-Ruiz et al. (1994) and Song et al. (2021) found that the
214 cores had the highest oil yield than the powdered series during artificial thermal maturation. Based on
215 previous works (Monthioux, 1988; Monthioux et al., 1985), Suárez-Ruiz et al. (1994) proposed that the
216 increase of the grain size (e.g using cores) favored the retention of the pyrolysis effluents, allowing an
217 increase in (i) the retention time of the compounds in the system; (ii) in the partial pressure of the
218 effluents at the origin of the increase in oil yield during maturation. This assumption is also supported
219 by Song et al. (2021). The thermal maturation of Suárez-Ruiz et al. (1994) and Song et al. (2021), was
220 carried out using an open and semi-closed pyrolysis system respectively, in which the effluents are
221 collected progressively during maturation. In the system of Suárez-Ruiz et al. (1994) no means of
222 confinement is applied on samples, the different degree of confinement of the two sample series during
223 oil generation created by the better ability of the cores to retain oil is therefore very important. In our
224 case, all samples are matured in a confined environment inside sealed gold cells under inert gas and
225 external hydrostatic pressure. This system has two advantages: (i) whatever the rock particle size, the

226 effluents are trapped in contact with the sample during maturation; (ii) although the means of
227 confinement used in this system was not similar to the lithostatic pressure present in natural basins, it
228 permits to reproduce for all series a certain degree of confinement required to accurately reproduce the
229 thermal degradation of kerogen under laboratory conditions (Monthieux et al., 1985). According to these
230 differences of artificial maturation conditions, we can therefore suggest that, in our case, variations in
231 effluents' retention time or in the degree of confinement induced by the sample particle size that is being
232 pyrolyzed are limited. The experimental device used by Song et al. (2021) reproduced both hydrostatic
233 and lithostatic pressure conditions. The degree of confinement used is therefore also different from our
234 experiments. This probably explains why we obtained so different results compared with these studies.
235 However, this highlights the importance of the choice of laboratory thermal maturation conditions.
236 Results from maturations under different conditions are not strictly comparable with each other or with
237 natural samples. Results from laboratory maturation experiments should therefore be interpreted with
238 caution. Concerning our experiments in anhydrous, closed, and confined conditions, the processes at the
239 origin of the variations of oil and gas generation between our sample series are to be found elsewhere.
240 We can suggest that the decrease in the sample particle size has: (i) increased the contact surface between
241 the different OM components favoring the OM thermal degradation and increasing the yield of generated
242 hydrocarbons; (ii) increased the contact surface between the OM and clay minerals. Previous works
243 have indeed shown that the presence of Smectite or Illite (abundant in the Kimmeridge clay, Cavelan et
244 al., 2019a) can act as catalysts for OM thermal degradation reactions (Huizinga et al., 1987;
245 Tannenbaum et al., 1986; Tannenbaum and Kaplan, 1985). They showed that the strong adsorption
246 capacities of these clay minerals and their ability to absorb and retain the heavy polar OM components
247 favor the production of light, gaseous hydrocarbons, and the production of CO₂ during the cracking of
248 OM. Increasing the surface contact between OM, all the effluents and the mineral surfaces have thus
249 probably greatly favored the thermal degradation of the OM in the RF and the PO series compared to
250 the cores during our laboratory simulations. This may explain the higher oil yield of the RF and the PO
251 during oil generation but especially their higher C₁-C₅ and CO₂ concentrations during gas generation

252 (Fig.1). Shao et al. (2018) found comparable results for the Eagle Ford shales but suggested that the
253 higher production of CO₂ was caused by an accelerated carbonates decomposition by the organic acids
254 released by the OM thermal degradation. However, the upper Cretaceous Eagle Ford Shale is composed
255 of carbonates with more than 80 wt% calcite (Ko et al., 2018; Shao et al., 2018). KCF samples contain
256 less than 25% carbonates (Tab.1, Cavelan et al., 2019a), we can therefore conclude that the measured
257 CO₂ is also partly generated from the OM thermal degradation. Comparison with gas-matured Vaca
258 Muerta rocks with similar TOC shows that cores give the closest EOM, ARO, and NSO concentrations
259 during gas generation (Fig.1). The use of cores during artificial maturation may be more suitable to
260 represent natural OM thermal degradation and that the decrease in the sample particle size may create
261 an artificial enhancement of the OM thermal degradation process in the studied laboratory conditions.

262 3.2. Influence on rock mesoporosity

263 After heating at 325°C, the volume of pores and specific surface areas of the cores were low (0.26
264 cm³/100g and 2.0 m²/g respectively) showing a poorly interconnected/low rock porosity. At this
265 maturity stage the PO and the RF exhibit similar specific surface areas, volumes of pores, and PSDs
266 (Fig.2A) which are mainly composed of ~50% of mesopores and macropores (Fig.2B). Then, with
267 increasing maturity the specific surface area and the volume of pores increase in all series due to the
268 appearance of pores with a diameter > 10 nm (Fig.2). This evolution in porosity may mark the formation
269 of OM-hosted pores formed in response to oil and gas production (Bernard et al., 2012; Cao et al., 2021;
270 Cavelan et al., 2020b, 2019a; Chalmers and Bustin, 2008; Curtis et al., 2012; Han et al., 2017; Ko et al.,
271 2018, 2016; Loucks et al., 2009; T. Wang et al., 2021). While a few differences in PSDs, specific surface
272 areas and pore volumes were observed between RF and PO series (Fig.2), for which similar quantity
273 and composition of generated hydrocarbons were observed (Fig.1), significant differences in PSD,
274 specific surface areas, pore volumes, EOM, SAR, ARO, NSO, and gas content exist between core series
275 and the other series. During the production of gas, the pore volume of the cores is systematically lower
276 with fewer pores larger than 10 nm (Fig.2A, B). On the contrary, the cores have larger specific surface
277 areas due to the presence of smaller pores (<10 nm). Cores generated fewer hydrocarbons (liquid and

278 gaseous) during thermal maturation and therefore, have a lower oil and gas yield (Fig.1). The lower
279 conversion of organic compounds in cores, related to the larger sample particle size, seems to lead to
280 less or slower pore development. Thus, for similar thermal maturation conditions and maturity, porosity
281 formed in cores is less developed, poorly connected (explaining why pores are inaccessible to nitrogen
282 and not measurable in the oil window).

283 Comparison with naturally gas-matured Vaca Muerta samples showed once again, that the
284 specific surface area and the PSD of core samples after maturation at 390°C and 470°C are the closest
285 to the natural samples (Fig.2A, B). However, the pore volumes of Vaca Muerta samples are lower than
286 for RF and PO and significantly higher than for the cores (Fig.2A). This may be related to the different
287 mineralogy of the Vaca Muerta rocks (dominated by quartz) and KCF (dominated by clay, Cavelan et
288 al., 2019a) which may influence the pore structure and the ability of the rock to preserve its porosity
289 from deformation during maturation.

290 3.3 General implications

291 Considering these results and previous works (Shao et al., 2018; Song et al., 2021; Suárez-Ruiz et al.,
292 1994), production, retention of hydrocarbons, and the composition of the oil and gas released by an
293 organic-rich mudstone during artificial thermal maturation depend on the rock fabric of the pyrolyzed
294 sample. This generates changes in the evolution of mesoporosity, specific surface areas, and pore
295 volumes. While this confirms the close link existing between the OM thermal degradation reactions and
296 porosity of OM-rich mudstones, it shows the importance of choosing the most appropriate thermal
297 maturation parameters to simulate, as best as possible, the conditions of natural systems. As expected,
298 in the light of our results natural samples seem better represented by core samples, which exhibit the
299 most singular pore volumes and PSD after maturation and the closest features to naturally matured Vaca
300 Muerta rocks. This suggests that confined anhydrous thermal maturation experiments previously carried
301 out on powder and rock fragments may overestimate the amount of hydrocarbons generated and the
302 associated pore volume that develops simultaneously. As observed between these three maturations

303 experiments and according to previous works, it must nevertheless be kept in mind that these results
304 show that the magnitude of these differences is influenced by the artificial maturation conditions (degree
305 and means of containment, hydrous pyrolysis...). Indeed, contrary to our observations in confined
306 environments, in semi-confined conditions, the use of powder seems to underestimate the yields of
307 generated oil and C4-C5 gases and to overestimate the yields of C1-C3 hydrocarbons (Song et al., 2021).
308 Predicting the differences between experimental maturation on powder, fragments or cores is, therefore,
309 not so easy. In recent years, a great number of works that aimed to better understand the physical-
310 chemical processes affecting the OM in source rocks, the porosity, and the storage capacity of
311 unconventional reservoirs were based on laboratory thermal maturation experiments (e.g. Cavelan et al.,
312 2020b, 2020c, 2019a; Gafurova et al., 2021; Guo et al., 2017; Ko et al., 2018, 2016; Song et al., 2020;
313 T. Wang et al., 2021; Wang et al., 2020; Wu et al., 2018; Xu et al., 2021; Yang et al., 2018). Many of
314 these papers compare their results with each other although they often used different thermal maturation
315 systems and sample rock fabrics. It is clear from these results that this could introduce biases into the
316 estimations of hydrocarbon production, permeability, gas storage capacity based on these results. For
317 example, the amount of NSO (including asphaltenes) generated during cores maturation is 35-50%
318 lower during the oil window than for powder and fragments (Fig.1). Recent numerical models showed
319 that the increase in the amount of generated asphaltenes may enhance the permeability of organic pores
320 but reduce the permeability of inorganic pores and micro-fractures of shales (Cui, 2019a). The organic
321 or inorganic pore permeability parameters of the same shale sample estimated by these mathematical
322 models could, therefore, vary greatly for the same thermal maturity depending on the sample rock fabric
323 used. Numerical models showed also that a change in pore sizes, distribution, connectivity, or shape will
324 influence the permeability of the rock and its flow properties (Cui, 2019a, 2019b). Our results show that
325 maturations on powder or fragments lead to different PSD and especially a lower number of micropores
326 than maturations on cores. Recent computations showed that the PSD, and in particular the number of
327 micropores in shales, has a strong influence on the gas in place calculation (Tolbert and Wu, 2015). In
328 our thermal maturation conditions, maturations of powder and fragments may, therefore, lead to an

329 underestimation of the amount of gas in place calculated by these models compared to maturations on
330 cores. In general, models for estimating the gas sorption/storage capacity of kerogen or gas in place in
331 shales use specific surface area or pore volume data based on Langmuir models (Alafnan et al., 2021;
332 Alafnan et al., 2020; Ambrose et al., 2012; Hu et al., 2019; Memon et al., 2020; Tolbert and Wu 2015;
333 Ungerer et al., 2015). The differences in pore volume and sizes observed between our thermal maturation
334 experiments on cores, fragments, and powder, therefore, show that the choice of maturation parameters
335 is crucial to ensure consistent estimates of shale reservoirs' properties. Most recent studies aimed to
336 improve their models for predicting the quality and recoverability of the studied reservoirs using thermal
337 maturation. It is therefore urgent to consider the effect of the experimental conditions used for thermal
338 maturations to move towards standardization of thermal maturation techniques for a better and reliable
339 understanding of the factors affecting hydrocarbon production, yields, and shale porosity (and without
340 introducing biases due to differences in experimental maturation conditions between studies).

341 **4. Conclusions**

342 Laboratory thermal maturations of cores, fragments, and powder from the same organic-rich
343 Kimmeridge Clay mudstone were compared. The results reveal that only a few differences of OM
344 geochemical composition and porosity exist between rock fragments and powder series for each stage
345 of maturation while cores give different results. Probably due to the lower surface contact between the
346 organic components themselves and clay mineral surfaces (which can act as a catalyst for oil and gas
347 generation) in cores, the OM undergoes a less effective thermal degradation characterized by (i) the
348 production of lower SAT, ARO and NSO concentrations during oil production; (ii) lower C₁-C₅ and
349 CO₂ concentrations during gas generation. This is marked by lower/less interconnected pore volume and
350 smaller pores in the cores. This work shows that the amount of oil and gas and porosity may be
351 influenced by the sample particle size used for laboratory thermal maturation. These experiments
352 highlight, therefore, the importance of considering the particle size of the rock that is being pyrolyzed
353 when studying OM thermal degradation and its relation with mudstones porosity. However, if these
354 maturations in a confined and anhydrous environment on powder and fragments overestimate the

355 quantity of oil and C₁-C₅ hydrocarbons generated during thermal maturations compared to samples with
356 an intact fabric (i.e cores), the opposite tendency has been observed in previous maturations in semi-
357 confined environments. The comparison with equivalent (in terms of TOC and OM composition)
358 naturally gas-mature rocks from the Vaca Muerta Fm. show that cores give the closest results to natural
359 trends and appear thus, more suitable for artificial thermal maturation. Indeed, the use of powder or
360 fragments leads to significant variations in composition and amount of generated hydrocarbons, specific
361 surface areas, PSD, and pore volumes which can lead to a significant deviation from natural trends.

362 **Acknowledgments**

363 The authors would like to thank Mrs. Rachel Boscardin, Dr. Rémi Champallier, and Mrs. Nathalie
364 Lottier for their support during experiments. Many thanks for the professional help of anonymous
365 reviewers and editors which have greatly improved the quality of this work. This work was partly funded
366 by the French National Research Agency (ANR) as part of the program “Investments
367 d’Avenir” LabEx VOLTAIRE, 10-LABX-0100. This work was supported by the French council of the
368 region Centre-Val de Loire.

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591 **Tables**

592

593 Tab.1. Location and main properties of the studied sample.

Location					
Basin	Formation	Well		Depth (m)	
Cleaveland Basin (UK)	Kimmeridge Clay	Ebberston87		69.98	
Mineralogy (wt.%)^a					
Quartz	Calcite	Gypsum	Clay	Pyrite	Albite
8.7	17.6	0.8	53.6	5.7	3.0
Rock Eval parameters^b					
TOC (wt.%)	S1 (mgHC/g rock)	S2 (mgHC/g rock)	IH (mgHC/g TOC)	IO (mg CO ₂ /g TOC)	
10.3	0.2	57.4	557	14	
Vitrinite reflectance (%)^b					
0.43					

594 ^a(Cavelan et al., 2019b);^b(Cavelan et al., 2019a)

595

596 Tab.2. Mean calculated vitrinite reflectance (R_c), measured vitrinite reflectance (R_v), TOC, and Hydrogen index (HI) after maturation.

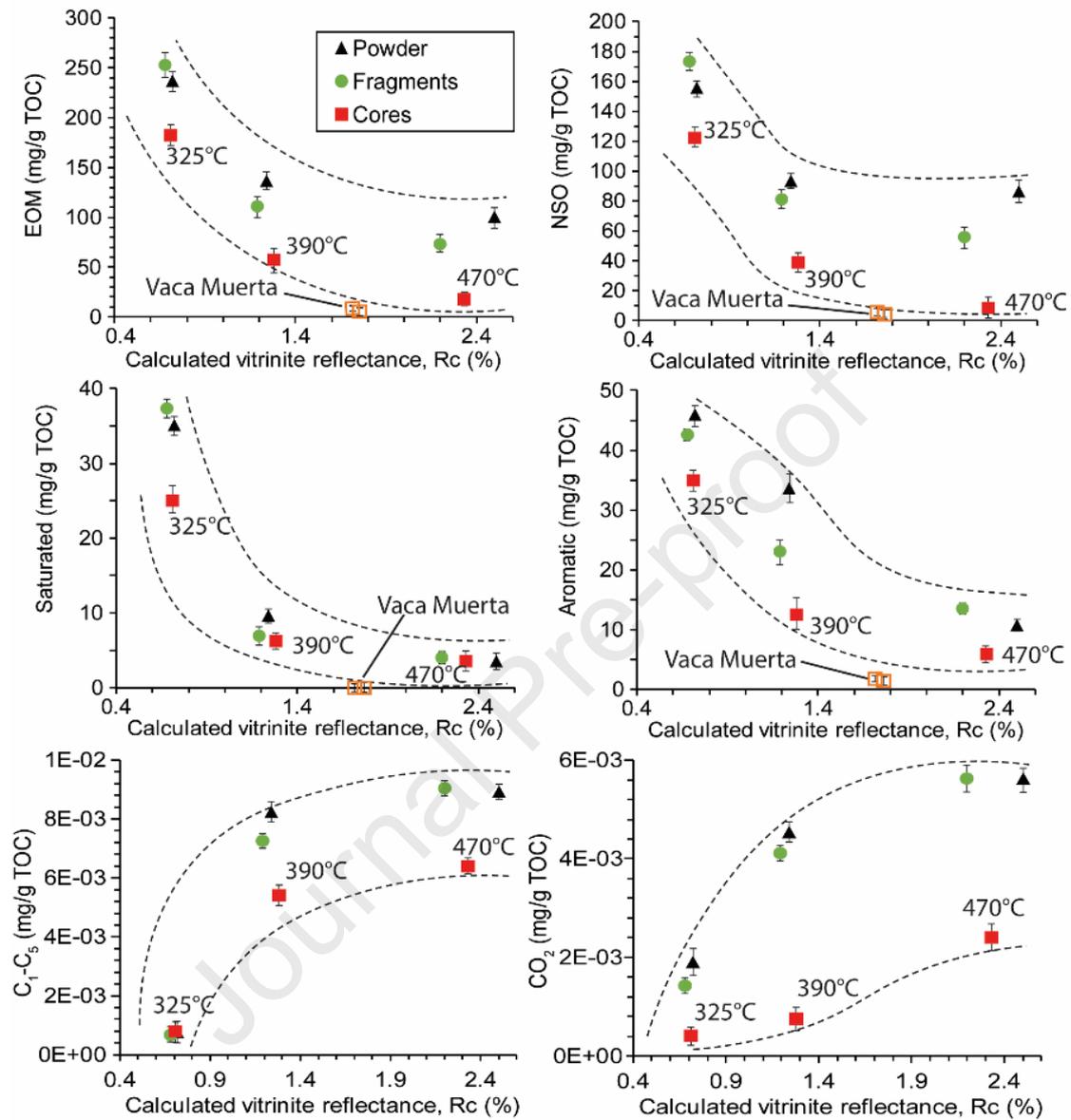
		MDTR ²	R _{MDTR} (%)	Std Dev.	MPI-1 ³	R _{MPI} (%)	Std Dev	DMPR ²	R _{DMPR} (%)	Std Dev	Mean R _c (%)	Std Dev.	HI (mg/g TOC)	TOC (wt.%)	Tmax	R _v (%)	Std Dev.
Powder	325°C	1.5	0.68	0.02	0.81	0.79	0.04	0.28	0.76	0.01	0.74	0.06	481	10.2	442		
Fragments		1.29	0.65	0.03	0.56	0.61	0.02	0.29	0.78	0.03	0.68	0.09	478	10.2	442	0.70	0.04
Cores		1.29	0.65	0.01	0.70	0.71	0.03	0.28	0.76	0.02	0.71	0.05	476	10.1	443	0.68	0.03
Mean		1.36	0.66		0.69	0.70		0.28	0.77		0.71		478	10.2		0.69	
Powder	390°C	6.25	1.29	0.05	1.59	1.33	0.06	0.69	1.28	0.04	1.3	0.03	146	7.2	470		
Fragments		5.99	1.19	0.07	1.36	1.17	0.04	0.87	1.42	0.04	1.26	0.14	151	6.7	un	1.32	0.05
Cores		5.94	1.17	0.05	1.48	1.26	0.05	0.85	1.41	0.06	1.28	0.12	104	8.2	489	1.38	0.04
Mean		6.06	1.22		1.48	1.25		0.80	1.37		1.28		134	7.4		1.35	
Powder	470°C	8.21	2.62	0.10	0.72	2.6	0.13	5.6	2.5	0.13	2.58	0.07	7	7.0	un		
Fragments		7.75	2.20	0.15	0.38	2.79	0.15	2.21	1.96	0.10	2.32	0.43	7	7.6	un	2.34	0.08
Cores		7.90	2.33	0.10	0.3	2.84	0.16	1.77	1.83	0.14	2.33	0.5	15	8.3	un	2.13	0.10
Mean		7.96	2.38		0.47	2.74		3.19	2.10		2.41		10	7.6		2.24	

597 ¹MDTR: ratio of methyl dibenzothiophene (Radke et al., 1986); R_{MDTR} (%) calculated with the equation of Radke, (1988). ²DMPR: ratio of dimethylphenanthrene
598 (Radke et al., 1986) R_{DMPR} was calculated with the equation of Radke (1988). ³MPI-1: index of methylphenanthrene (Radke et al., 1986). R_{MPI-1} calculated with
599 the equation of Boreham et al. (1988) for R_v between 0.3-1.7% and R_v > 1.7%.

600

601 **Figures**

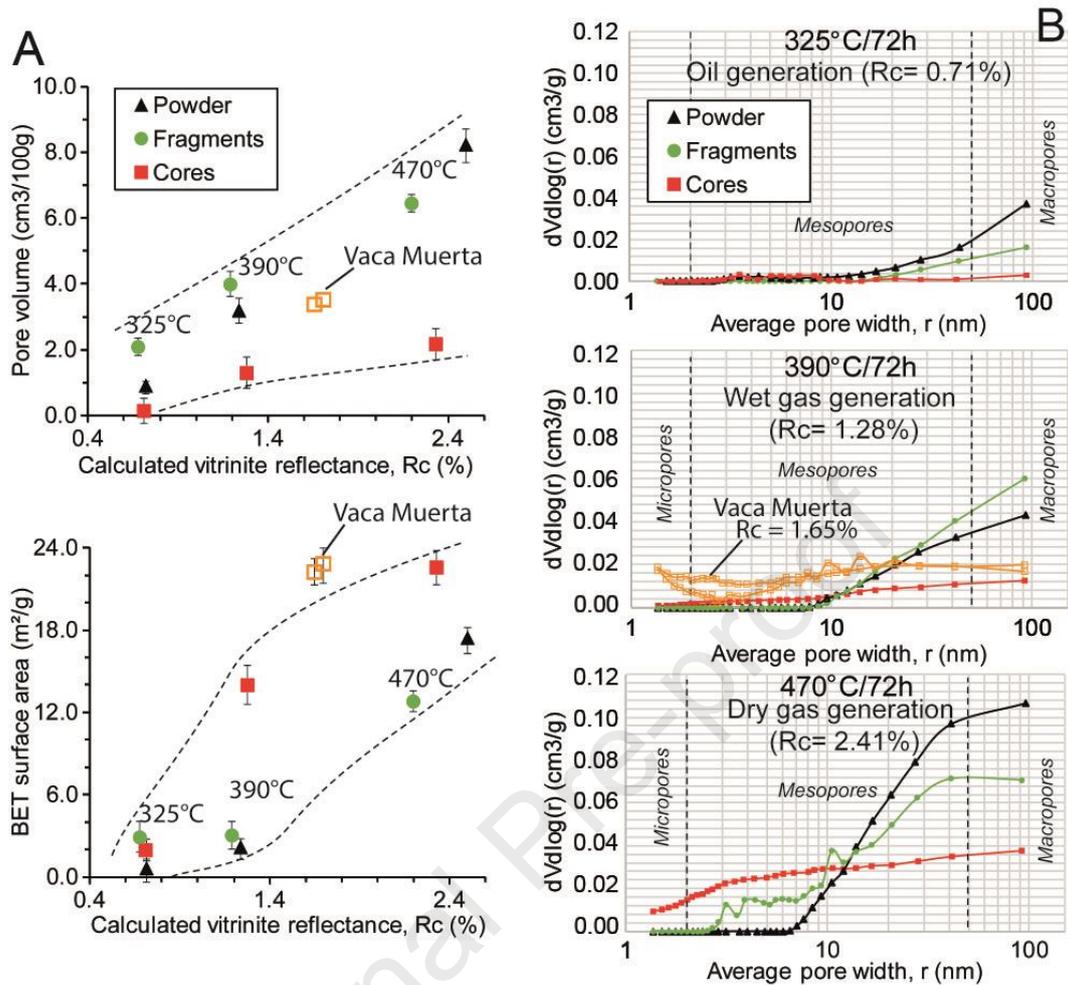
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603

604 Fig.1. Evolution of Extractable Organic Matter (EOM), NSO, saturated, aromatic, C₁-C₅ hydrocarbon
 605 gases, and CO₂ concentrations as a function of the sample type during maturation. Comparison with
 606 Vaca Muerta samples (similar composition of the OM with the Kimmeridge Clay, Vitrinite reflectance
 607 = 1.65 and 1.69%, TOC = 5.0 and 6.7 wt.%, HI = 43 and 19 mg/g HC, Cavelan et al., 2019a).

608



609

610 Fig.2. A) Pore volume, BET surface area, and B) BJH pore size distribution for the different rock fabric
 611 after artificial maturation. B) displays the relative contribution to the total pore volume of pores over
 612 any range of pore sizes. Comparison with Vaca Muerta samples (Cavelan et al., 2020b, 2019b). The
 613 PSD curves presented in the figure are considered to be the most representative among the three
 614 triplicates but PSD curves obtained for each triplicate are comparable (less than 10% of variation).

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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