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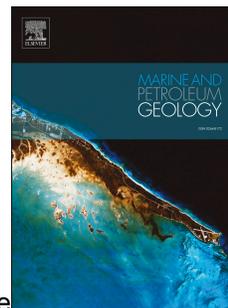
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1 Organic petrography and pore structure characterization of low-mature and gas-mature marine
2 organic-rich mudstones: insights into porosity controls in gas shale systems.

3

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11

12 **Abstract-** Analyses of both type II organic-rich low-mature mudstones from the Kimmeridge
13 Clay Formation (Yorkshire, England) and gas-mature mudstones from the Vaca Muerta formation
14 (Argentina) were performed using petrographic and SEM observations to characterize the organic and
15 inorganic components of the rocks and their relationship with porosity. The porosity analyses using
16 nitrogen adsorption measurements and mercury intrusion porosimetry were then evaluated as a
17 function of both composition and thermal maturity. Despite the absence of variation in the pore size
18 distribution and the total pore volume with maturity, which is controlled by total organic carbon
19 content (TOC), this study demonstrates that the pore network of these marine mudstones varies
20 considerably with thermal maturity. Contrary to low-mature samples, whose porosity depends
21 essentially on mineral interparticle pores, the porosity of thermally-mature rocks is mainly influenced
22 by organic-matter-hosted pores located within secondary solid bitumen. Organic matter (OM)
23 porosity, which is rare in the low-mature stage, appears to increase during thermal maturation in
24 response to the thermal cracking of kerogen and oil, to become predominant in gas-mature rocks. It
25 can therefore be considered that thermal maturation is a major process for the development of the OM
26 porosity. However, the OM of high-TOC (>5.5 wt.%) gas-mature samples contains smaller pores than
27 gas-mature low-TOC mudstones probably due to a difference in the original OM composition between

1 these high- and low-TOC samples. By analogy with the Kimmeridge Clay formation, which is often
2 considered as time equivalent in terms of OM composition (Uliana et al., 1999), the high-TOC Vaca
3 Muerta samples appear to have originally contained greater proportions of oil-prone amorphous OM
4 and thus a better OM intrinsic quality for oil generation. This difference of OM composition and
5 petroleum potential between Vaca Muerta marine mudstones appears to have dramatically influenced
6 the OM-hosted pore genesis during maturation. Consistent with other studies, these results show that
7 thermal maturity is not the only process that can explain OM-hosted pore genesis in gas shale systems.
8 The OM composition can greatly influence the evolution of this porosity during maturation. Organic
9 composition and OM thermal maturity may therefore have a complementary effect, explaining the
10 diversity of trends observed on porosity in natural formations.

11

12 **Keywords:** shales porosity, thermal maturity, organic matter, organic petrography.

13

14 1. Introduction

15 Gas shale systems have been studied for many years, but the origin and the evolution of their
16 pore systems remains incompletely understood. The difficulty lies in the characterization of the
17 features of these rocks whose size is on the order of nm to μm (Ross and Bustin, 2009; Chalmers and
18 Bustin, 2008; Chalmers et al., 2012; Loucks et al., 2012). The porosity of these mudstones is generally
19 subdivided into macropores (pore width >50 nm), mesopores (pore width between 2–50 nm) and
20 micropores (pore width < 2 nm, Sing, 1985) and grouped into three pore classes (Loucks et al., 2012),
21 namely: interparticle pores between mineral grains, intraparticle mineral-hosted pores, and
22 intraparticle organic matter (OM) pores. Quantitative assessments of pore volume and pore size
23 distribution provided by SEM imaging (Curtis et al., 2012; Loucks et al., 2012; Fishman et al., 2012;
24 Ko et al., 2018) and gas adsorption techniques (Chalmers et al., 2012; Kuila et al., 2012; Pan et al.,
25 2015; Tian et al., 2015) revealed that OM porosity is a significant component of the pore networks of
26 gas-mature mudstones. A multitude of factors seem to be responsible for OM-hosted pore genesis and
27 stability in mudstones. Organic richness, OM composition, and OM thermal maturity are the most
28 commonly cited mechanisms (Loucks et al., 2012; Curtis et al., 2012; Ko et al., 2016; Katz and

1 Arango, 2018). However, there remains a lack of a clear understanding of the respective contribution
2 of these factors to the porosity (Katz and Arango, 2018).

3 In recent years, the effect of thermal maturity has received special attention due to the growing
4 recognition of its involvement in the genesis of OM-hosted pores (Chalmers and Bustin 2008; Curtis
5 et al., 2012; Loucks et al., 2012; Chen and Xiao, 2014; Ko et al., 2016). Previous studies have shown
6 that type II OM is mainly non-porous from the immature stage to the early oil window (Loucks et al.,
7 2009; Bernard et al., 2012; Curtis et al., 2012). However, some pores are commonly observed in
8 mudstones rich in type III OM (Reed, 2017). Most of these OM-hosted pores appear to be inherited
9 from the original structures of cellulose and woody fragments (Reed, 2017). Nevertheless, OM pores
10 are widely observed in shales containing type II OM from the late oil window to the overmature stage
11 (Bernard et al., 2012; Loucks et al., 2012). It is thus commonly assumed that OM-related porosity
12 increases with thermal maturity in response to the thermal cracking of type II kerogen (Bernard et al.,
13 2012; Loucks et al., 2012; Chen and Xiao, 2014; Ko et al., 2016, 2018). With increasing thermal
14 maturity some by-products called solid bitumen can be formed during the thermal cracking of pre-
15 existing bitumen into oil and gas or from the transformation of a pre-existing liquid oil into gas (Tissot
16 and Welte, 1984; Lewan, 1993; Behar et al., 1997; Reed et al., 2014). Solid bitumen is the dominant
17 maceral in thermally-mature mudstones (Hackley and Cardott, 2016; Hackley, 2017). The carbon-rich
18 residue formed from the secondary cracking of liquid oil (so called pyrobitumen) is considered to be
19 the main contributor to the porosity in thermally-mature mudstones (Bernard et al., 2012; Milliken et
20 al., 2013; Hackley and Cardott, 2016; Hackley, 2017). The bubble-like morphology of some OM-
21 pores in gas-mature rocks has been interpreted as evidence that this porosity stems only from the
22 formation of gas bubbles within pyrobitumen formed after the secondary cracking of liquid oil
23 (Bernard et al., 2012; Milliken et al., 2013). This hypothesis remains nevertheless controversial (Reed
24 et al., 2014) and some evidence shows that pores in OM can form earlier, in the oil window (Juliao et
25 al., 2015).

26 An increase in OM porosity with thermal maturity has not been systematically and clearly
27 observed, suggesting that the relationship between maturity and OM-hosted porosity is not
28 straightforward (Schieber, 2010; Fishman et al., 2012; Curtis et al., 2012; Löhr et al., 2015; Milliken et

1 al., 2013). Variations as a function of the OM composition and especially the importance of maceral
2 types have been noted in the last few years (Fishman et al., 2012; Loucks et al., 2012; Milliken et al.,
3 2013; Cardott et al., 2015; Ko et al., 2017, 2018). For a given maturity, the OM-hosted porosity can
4 vary greatly between and within rocks of the same formation (Curtis et al., 2012; Loucks et al., 2012;
5 Milliken et al., 2013; Tian et al., 2015). Moreover, in oil-mature and gas-mature mudstones from the
6 Marcellus formation ($R_o = 1.0\%$ and 2.1% , Milliken et al., 2013), high-TOC samples ($TOC > 5.6$
7 wt.%) exhibit a reduced pore volume due to smaller pores compared to low-TOC samples. Similar
8 trends were observed for higher TOC samples ($TOC > 12$ wt.%) in the gas window from the Gufeng,
9 the Longtan and the Dalong formations ($R_o = 2.34\text{--}2.64\%$, Pan et al., 2015). These observations
10 suggest that thermal maturity alone is not sufficient to understand the evolution of porosity in
11 mudstones. The OM typology, its state of preservation and the maceral composition may also
12 influence the development of the OM-hosted porosity (Fishman et al., 2012; Mastalerz et al., 2013;
13 Cardott et al., 2015; Ko et al., 2017, 2018). Many differential compaction phenomena influencing the
14 fabric and the texture of rocks are commonly used to explain these observations such as differences in
15 the relative timing of compaction and cementation or variations in TOC and clay mineral contents
16 (Milliken et al., 2013; Pan et al., 2015; Ko et al., 2017). This issue leads us to ask the following
17 questions. What is the importance of the OM composition compared to compaction/cementation
18 phenomena? What is its contribution to the pore systems of gas-mature mudstones?

19 In order to better understand the different parameters influencing the nature, structure and the
20 distribution of pores in gas-source rocks, this study investigated low-mature and gas-mature source
21 rocks presenting various organic contents from the Kimmeridge Clay Formation (KCF) and the Vaca
22 Muerta Formation (VMF) respectively. These two formations are often considered as equivalent in
23 terms of OM composition and depositional environment (Uliana et al., 1999). This study first
24 documented the overall organic and inorganic composition and thermal maturation of these mudstones
25 to compare their pore structure as a function of OM maturity and mineral composition; then the
26 organic matter composition of both low-mature and gas-mature mudstones was investigated using
27 Rock-Eval, petrographic observations and palynofacies analysis; and finally their pore structure was
28 characterized with high resolution SEM imaging techniques, mercury intrusion porosimetry, and low-

1 pressure nitrogen adsorption measurements. Based on these results, the relationships between organic
2 geochemistry, mineralogy and porosity were then examined and compared as a function of thermal
3 maturity. In the present study, the terminology ‘mudstones’ was used according to the
4 recommendations of Lazar et al. (2015) to refer to rocks containing more than fifty percent of mud-
5 size grains (<62.5 μm , clay and silt).

6 **2. Samples and methods**

7 2.1. Geological settings

8 Twenty-one samples were obtained from drill cores from the Kimmeridge Clay Formation
9 (KCF) and 12 from the Vaca Muerta Formation (VMF) (Tab.1, Figs.1, 2). The VMF is a marine
10 deposit developed in an ancient backarc embayment known as the Neuquén Basin (Argentina, Fig.1)
11 (Legarreta and Uliana, 1991; Uliana et al., 1999; Legarreta and Villar, 2011; Kietzmann et al., 2011,
12 2014). This formation consists of a succession of black shales, marls and dark calcareous siltstones
13 interbedded with organic-rich mudstones and wackestones developed from the Tithonian to the Early
14 Valanginian during a global eustatic highstand (Fig.2, Legarreta and Uliana, 1991; Kietzmann et al.,
15 2011, 2014). Mineralogy exhibits variations depending on the basin location (Garcia et al., 2013).
16 Generally, quartz (16–63 wt.%) and plagioclase (1–28 wt.%) are the most abundant components
17 (Garcia et al., 2013; Kietzmann et al., 2016). The proportion of carbonates is inversely correlated to
18 the quartz content and fluctuates greatly over the formation (0–51 wt.%, Kietzmann et al., 2016).
19 Higher clay mineral content is generally observed in the southwestern part of the basin, where it does
20 not exceed ~30 wt.% (Garcia et al., 2013; Kietzmann et al., 2016). These mudstones are characterized
21 by high type II OM contents and are marked by variations in the OM composition (Uliana et al., 1999;
22 Kietzmann et al., 2014). The kerogen is mainly composed of marine amorphous OM associated with
23 variable amounts of marine microplankton and terrestrial materials in relation to changes in eustasy
24 (Uliana et al., 1999; Legarreta and Villar, 2015). These fluctuations restricted the sea bottom water
25 circulation which temporarily favored euxinic conditions and the preservation and the accumulation of
26 the OM (Legarreta and Uliana, 1991; Uliana et al., 1999). The studied mudstones were collected in the
27 central basin from a borehole located in the thickest and deepest zone of the formation in the east of
28 the fault system of Los Chihuidos (VMF-Well, Fig.1). Samples were collected between 2647 and 2808

1 meters and selected to cover a wide range of TOC throughout the thickness of the formation (Fig.2).
2 These mudstones are considered to reach the gas window with a vitrinite reflectance (%Ro) of ~1.65%
3 (Legarreta and Villar 2011).

4 The KCF consists of organic-rich marine mudstones alternating with marls developed from the
5 Kimmeridgian to the Tithonian in several European basins (Figs.3, 4, Rawson and Riley, 1982; Herbin
6 et al., 1991). The immature part of the formation outcrops in England, on the south coast (Dorset) and
7 in Yorkshire (Fig.3). The studied samples were collected from two holes located in the Cleveland
8 Basin, Marton and Ebberston (Yorkshire, England, Fig.3). These mudstones are characterized by high
9 type II OM contents (2–30 wt.% of Rock-Eval[®] 6 TOC, Fig.4) accumulated in a shallow shelf regime
10 under low energy and anoxic to suboxic conditions (Rawson and Riley, 1982; Herbin et al., 1991).
11 These rocks have just reached the limit of the oil window with a vitrinite reflectance of ~0.5%
12 (Ramanampisoa and Disnar, 1994). The formation is marked by pronounced cyclic variations in the
13 OM content and quality (in terms of oil-proneness) related to climate and eustatic fluctuations at the
14 Milankovitch scale (Oschmann, 1988; Ramanampisoa and Disnar, 1994; Desprairies et al., 1995;
15 Boussafir et al., 1995a, b; Lallier-Vergès et al., 1995). According to these variations, different organic
16 cycles of several orders have been distinguished by Oschmann (1988). The studied samples were
17 selected in cycle I of Marton and Ebberston (Fig.4). The OM composition and its variations
18 throughout this cycle were well-documented two decades ago (Oschmann 1988; Herbin et al., 1991;
19 Ramanampisoa and Disnar, 1994; Boussafir et al., 1995a; Lallier-Vergès et al., 1995, 1997). This
20 third-order cycle is characterized by facies variations (on a decametric to metric scale) from marly
21 shales, mudstones, bituminous mudstones and coccolithic limestones (and conversely) in parallel with
22 changes in the oxygenation of the dispositional environment and organic productivity (Oschmann
23 1988). While the organic-rich facies of the cycle contain mainly a marine and highly oil-prone
24 phytoplanktonic OM, the others are composed of organic compounds with a lower quality for oil
25 generation (Boussafir et al., 1995a; Lallier-Vergès et al., 1995, 1997). Marton and Ebberston samples
26 were selected throughout the whole thickness of cycle I between 128.15-129.20 and 69.11-70.65
27 meters deep respectively (Fig.4) to cover a wide range of TOC and OM compositions.

28 2.2. Mineralogy and organic geochemistry

1 Rock-Eval pyrolysis is a classical method for determining the amount, type, HC-quality and
2 maturity of OM preserved in source-rocks and sediments. Depending on the estimated OM content, 50
3 to 60 mg of dried sediment was used for new Rock-Eval 6[®] (Vinci Technologies, Rueil Malmaison)
4 analysis. The pyrolysis program under inert gas (helium) started with an isothermal stage (2 min.
5 200°C). Then, the oven temperature was raised at 30 °C/min to 650 °C (held 3 min). The oxidation
6 phase corresponds to an isothermal stage at 400 °C, then the temperature was raised at 30 °C min⁻¹ to
7 850 °C (held 5 min) under purified air.

8 The significance of classical Rock-Eval parameters was explained by Espitalié et al. (1985a,
9 b). The specific parameters given by the new Rock-Eval 6 device were presented by Lafargue et al.
10 (1998). The Rock-Eval parameters used here were: (i) total organic carbon (TOC, wt.%), which
11 expresses the quantity of OM calculated from the spectrum integration of S₁, S₂, S₃ (respectively, free
12 hydrocarbons, pyrolyzable hydrocarbons, CO and CO₂ produced by the breakdown of kerogen under
13 inert gas flux), and S₄ peaks (CO and CO₂ produced by pyrolysis and oxidation of residual carbon
14 under purified air flux); (ii) the hydrogen index (HI, mg HC /gTOC), i.e. the amount of hydrocarbon
15 (HC) produced during pyrolysis (S₂); (iii) the oxygen index (OI, mg CO₂ /gTOC), which is calculated
16 from the S₃ peak and represents the oxygenated quality of OM; (iv) T_{max}, a well-established OM
17 maturity indicator (Espitalié et al., 1985a,b), that is the temperature of the maximum amount of
18 hydrocarbons produced during pyrolysis.

19 Inorganic constituents were analyzed by X-ray diffraction (XRD) carried out on crushed
20 samples (< 250 µm) under Cobalt radiation (INEL[®] diffractometer, CPS120 curved detector). The
21 samples chosen for these analyses were selected throughout the entire Marton, Ebberston and VMF
22 series to cover a wide range of depth and TOC contents. Relative mineral percentages were semi-
23 quantified using the area under the curve for major diffraction peaks of each mineral and were then
24 corrected using 4 artificial standard samples (laboratory mixtures with known abundances of mineral
25 standards). This method, based on Fisher and Underwood (1995), assumes that there is a quantifiable
26 relationship between peak area and the relative abundance of each mineral and that the factors are
27 constant. This allows conversion from XRD to mineral abundances (Fisher and Underwood, 1995).
28 The results were then normalized to 100% after TOC contents determined by Rock Eval pyrolysis.

1 Based on the analysis of standard samples, the reproducibility averaged ± 3.7 wt.% for quartz, ± 4.9
2 wt.% for total carbonate, ± 1.3 wt.% for pyrite, ± 3.2 wt.% for gypsum, ± 4.4 wt.% for total clay and \pm
3 8.3 wt.% for albite.

4 2.3. Petrography

5 Petrographic observations were carried out on bulk rock polished sections (Leica® DMRX
6 microscope) under oil immersion using reflected and UV-fluorescence light to identify the different
7 macerals. VMF and KCF polished sections were made from small sample blocks impregnated with
8 epoxy resin. The KCF thin sections used in this study were previously analyzed in Boussafir et al.,
9 1995a; Boussafir and Lallier-Vergès, 1997. In the present study, palynofacies analysis (transmitted
10 light microscopy under oil immersion) was carried out on KCF isolated OM and the associated metal
11 sulphides of each sample (classical HF/HCl treatment, according to Boussafir et al., 1995a, b). This
12 microscopical examination enabled the relative proportion of the organic components to be assessed.

13 Scanning electron microscope (SEM) observations were carried out on six polished thin
14 sections using a SEM Merlin Zeiss® equipped with an in-lens secondary electron detector to image
15 the samples' pore network. Two intermediary-TOC samples (~ 5.5 wt.%, Blc 23, Eb 30, Tab.1) and
16 two relatively high-TOC samples (> 11.2 wt.%, Blc 30 Eb 40, Tab.1) were selected in Marton and
17 Ebberston to ensure the representativeness of SEM observations throughout the KCF. For the VMF
18 two samples with relatively high and representative TOC contents (94B, 5.0 wt.% and 102R, 6.7 wt.%
19 Tab.1) were selected. These polished thin sections were first mechanically polished to facilitate broad
20 beam argon-ion milling. Then, each section was milled through a two-step process. Thin sections were
21 milled first using a source operated at 5 kV for 1 hour with a 4° tilt angle and a current of 220 μ A, and
22 then using a source operated at 2 kV for 30 min (220 μ A). The thin sections were then coated with
23 carbon to prevent electrostatic charging and improve the SEM image quality. Observations were
24 conducted using backscattered (BSE) and secondary electrons (SE) under a current ranging from 10kV
25 to 13 kV at a working distance of ~ 7.7 mm to 8.5 mm.

26 2.4. Pore structure

27 The total pore volume and the PSD of macropores and large mesopores were measured by
28 mercury intrusion porosimetry (MIP) using a Micrometrics® Autopore IV 9500 porosimeter. About

1 1.5 g of sample was crushed into fragments (~2 mm in diameter), degassed under vacuum at 105°C for
2 24 h and intruded with mercury up to 60,000 psia (414 MPa). The equilibration time was set to 10 s.
3 Penetrometers with a stem volume of 0.390 cm³ were used for the analysis. The pore throat radius was
4 calculated assuming cylindrical pores by the Laplace-Washburn equation (Washburn, 1921).
5 Measurements were then corrected for conformance errors (Sigal, 2009, see in text).

6 Low-pressure nitrogen adsorption measurements were carried out on a Quantachrome®
7 NOVA 2200^e apparatus at -196.15°C to measure the pore size distribution (PSD), the specific surface
8 area and the volume of mesopores to large micropores. About 1 g of sample was powdered (<250 μm)
9 and outgassed under vacuum at 105 °C for 24 h before analysis. Adsorption-desorption isotherms were
10 obtained under the relative pressure P/P_0 ranging from 0.003 to 0.987. An equilibration time of 100 s
11 was applied during the analysis. The total pore volume was determined after the liquid molar volume
12 adsorbed at the relative pressure P/P_0 of 0.987. The specific surface area was determined using the
13 Brunauer, Emmett and Teller method (BET) for adsorption in the best linear range between the
14 relative pressure P/P_0 0.03 and 0.33 (Brunauer et al., 1938). A minimum of 15 points was used for the
15 BET surface-area analysis. The PSD was determined using the Barrett, Johner and Halenda (BJH)
16 method (Barrett et al., 1951) applied from the adsorption isotherm to avoid tensile strength effect
17 phenomena that occur during desorption. Note that the plot of $dV/d(r)$ versus the pore diameter was
18 preferred to the plot of $dV/d\log(r)$ versus pore diameter to display the PSD. The plot of $dV/d\log(r)$
19 versus the pore diameter is frequently used to display the PSD because it better shows the relative
20 contribution of pores, over any ranges of pore sizes, to the total pore volume (Tian et al., 2013). The
21 plot of $dV/d(r)$ versus the pore diameter reflects, however, more accurately the concentrations of pores
22 of various size, and provides thus, a complementary information to the plot of cumulated pore volume
23 versus pore diameter (Tian et al., 2013). The pore volume and the specific surface area of micropores
24 were calculated from the t-plot method using two models: the universal t-curve based on the Harkins-
25 Jura model (De Boer et al., 1966) and the Carbon black model (Magee 1995; Tian et al., 2015). The
26 Harkins-Jura model, the one most frequently used in the community, is based on standard siliceous
27 materials (De Boer et al., 1966). Nevertheless, the Carbon black model is more specific for carbon-
28 rich materials (Magee 1995) and should be more appropriate for the estimation of micropore volume

1 in gas-mature samples where the porosity is often associated with OM. The lowest detection limits for
2 the pore volume and the specific surface area were 10^{-4} cm³/g and 10^{-2} m²/g respectively.

3 Clarkson et al., (2013) suggested that pore throats obtained by MIP are similar to pore bodies
4 for some pore geometries including silt pores. In theory low-pressure nitrogen adsorption
5 measurements and MIP should thus give similar results. Accordingly, pore throat size is often
6 considered to be similar to pore size in shales (Wang et al., 2014). Kuila and Prasad (2011) showed
7 that PSD curves from MIP and nitrogen adsorption exhibit a good correlation. Therefore, pore throat
8 size from MIP was used as pore size in this study for convenience when comparing the nitrogen
9 adsorption data.

10 3. Results

11 3.1. Mineralogy

12 Mineralogical data from XRD analysis are shown in Tab.2 and Fig.5. Quartz, calcite, clay
13 minerals, feldspar and pyrite are the main mineral compounds in KCF and VMF samples (Tab.2,
14 Fig.5). Both the VMF and the KCF formations show similar carbonate contents ranging from 6.6 to 29
15 wt.% \pm 4.9 wt.% and relatively high pyrite contents (0.2–6.4 wt.% \pm 1.3 wt.%, Tab.2). However, some
16 differences can be noted. KCF samples are 10 to 20 wt.% richer in clay minerals (\sim 53.0 wt.% \pm 4.4
17 wt.%) than VMF rocks (\sim 26.0 wt.% \pm 4.4 wt.%, Tab.2, Fig.5) and are thus argillaceous mudstones.
18 VMF samples which contain higher amounts of feldspar (\sim 24.0 wt.% \pm 8.3 wt.%) and quartz (28.0
19 wt.% \pm 3.7 wt.%, Tab.2, Fig.5) are siliceous mudstones. Traces of gypsum are observed in KCF
20 samples (Tab.2) as previously noted by Desprairies et al. (1995).

21 3.2. Organic geochemistry

22 Organic geochemistry data from Rock Eval pyrolysis are shown in Tab.1 and Fig.6 and their
23 variations with depth are illustrated in Fig.7. All samples are organic-rich with TOC contents higher
24 than 2 wt.% (Tab.1; Fig.7). VMF samples exhibit low S_2 ($<$ 2.2 mg/g rock), HI ($<$ 49 mg/g TOC) and
25 OI ($<$ 20 mg/g TOC) values regardless of TOC content (Tab.1; Fig.7C). As such, these samples plot
26 near the origin in the pseudo-Van Krevelen diagram and the type of kerogen is non-identifiable
27 (Fig.6). The high T_{max} values (\sim 500°C) indicate a high maturity of OM corresponding to the gas
28 window (Fig.6B, Fig.7C). The RC/TOC ratio is close to 1 (Tab.1), indicating the OM of VMF samples

1 is mainly composed of residual OM with a low residual petroleum potential (low HI and S₂ values)
2 (Tab.1, Fig.7C).

3 The high HI (~527 mg/gTOC in Ebberston, ~452 mg/g in Marton) and low OI values (~20
4 mg/gTOC) of KCF samples show they are Type II kerogen (Tab.1, Fig.6A). The low production index
5 (< 0.1) and T_{max} values (< 435°C) indicate their low maturity (Fig.6B). The RC/TOC ratio, far smaller
6 than 1, (< 0.62), indicates that these samples contain a great fraction of pyrolyzable OM (Tab.1).
7 Consistent variations of TOC, HI and S₂ values are observed in KCF samples (Fig.7A and B). OI
8 values exhibit a negative correlation with TOC in Marton (Fig.7B). Some very high-TOC samples (Eb
9 19, Eb 40 and Blc 30) exhibit higher pyrite contents (Tab.1 and Tab.2).

10 3.3. Petrographic observations

11 The results of petrographic observations are shown in Figs.8, 9 and 10 and SEM images are
12 presented in Figs.11 and 12. In petrographic observations of VMF samples, OM is mainly comprised
13 of highly reflective (grey) non-fluorescent granular particles often associated with pyrite or embayed
14 against carbonate (Fig.8). Some of these particles show a fracture-filling texture (Fig.8B) or form
15 abundant groundmass (Fig.8A) with pitted surface texture (Fig.8C). No identifiable biological
16 structures are present, corroborating the high maturity of OM. These particles have been identified as
17 secondary solid bitumen which is the dominant organic component in thermally mature organic-rich
18 mudstones (Hackley and Cardott, 2016; Hackley, 2017). In SEM images, this residual OM appears as
19 particles hosting nanometer-scale spongy pores (Figs.11F, H). A continuous spongy OM-hosted pore
20 network is observed inside these carbon-rich residues (Fig.11). These spongy pores are abundant,
21 closely spaced and exhibit subangular shapes (Figs.11E, H). The subangular spongy pores are the most
22 abundant (Fig.11E, H) but many oval pores (bubble-like pores) are also observed (Fig.11 A, B, D).
23 These OM-hosted pores appear to be mainly composed of mesopores and macropores with diameter
24 smaller than 200 nm (Fig.11H); the larger pores probably come from the merging of smaller pores.
25 Some pores are located between OM and mineral grains (Fig.11F). These mineral/OM pores cannot be
26 classified as OM-hosted pores and are interpreted as mineral interparticle pores containing relics of
27 OM. The residual porous OM is dispersed in a fine and compact mineral matrix, which appears in the
28 SEM images to be mainly composed of clay mineral sheet aggregates, quartz and calcite grains

1 (Fig.11 Some interparticle macropores are located between quartz, calcite grains or clay-sheets
2 (Fig.11) while some intraparticle macropores are located inside pyrite framboids and calcite grains
3 (Figs.11C, D). Most of the clay mineral aggregates are located near the OM (Fig.11A, B, D). In these
4 thermally-mature samples, only a few OM particles are non-porous or exhibit a low porosity
5 (Fig.11G). Some devolatilization cracks were also observed in the OM (Fig.11B). Some of the large
6 macropores (orange arrows, Fig.11) and the microfractures observed in these samples are interpreted
7 as artefacts due to sample preparation.

8 KCF mudstones show a relatively heterogeneous OM distribution. In these immature samples,
9 OM is composed of several terrestrial and marine macerals dispersed in a fine mineral matrix (Figs. 9
10 and 10). In SEM images, this mineral matrix appears to be composed of clay mineral aggregates,
11 quartz, calcite-grains, pyrite framboids (Fig.12) and some microfossil remains (Fig.12 A, D, F).
12 Terrestrial macerals, mainly represented by inertinite (Fig.9), form a large proportion of the structured
13 OM (~15%, Fig.13). Phytoclasts, observed in palynofacies include some cuticular fragments, woody
14 fragments and various debris of plant tissues (Fig.10 E–J). The predominant marine amorphous OM
15 (AOM) (~75%) is supplemented by a minor contribution of structured organic components derived
16 from preserved phytoplanktonic organic-walled and algal spores (~10%, Fig.13, Fig.10 K, L). This
17 structured marine OM is present as brightly fluorescent thin bodies identified as *Tasmanite* spores
18 (Fig.9). Three distinct types of AOM were identified: brown, orange and black AOM (Fig.10 A-D).
19 Black AOM is the least abundant amorphous fraction (~10%, Fig.13). Brown AOM, identified as
20 alginite in polished sections, is present as brightly fluorescent thin elongated bodies (yellow-colored
21 under UV excitation, Fig.9). Orange AOM is generally associated with pyrite framboids (Fig.10A). In
22 polished sections, these macerals are observable as thick elongated bodies oriented parallel to the
23 bedding with a low brown/orange fluorescence (Fig.9). Abundant in high-TOC samples (Fig.9B, C),
24 these organic particles, so called 'bituminite' (Kus et al., 2017), were previously described in the KCF
25 (Boussafir et al., 1995b; Boussafir and Lallier-Vergès, 1997).

26 The abundance of these particles exhibits significant variations with TOC. In samples with TOC
27 values < 6 wt.% the OM is rather composed of sparse fragments of inertinite with some alginites and
28 rare *Tasmanite* algal bodies (Fig.9A). Samples with very high TOC values (> 6 wt.%) show an

1 increase in abundance of the fluorescent elongated organic particles including both alginites and
2 bituminites (Fig.9B, C). After normalization with TOC, palynofacies observations show that orange
3 AOM and pyrite contents dramatically increase with TOC and HI values (Fig.13; Tab.1) while brown
4 and black AOM contents remain relatively stable (Fig.13). In SEM images, the OM is composed of
5 elongated lamellar masses of kerogen particles (Fig.12). This OM constitutes a homogenous gel with
6 well-defined boundaries cementing mineral grains, clay mineral sheets and pyrite framboids (Fig.12).
7 Some horizontal fractures (Fr, Fig.12), shrinkage OM pores (Fig.12A) and rare OM-hosted mesopores
8 with irregular shapes are visible (orange arrow, Ar, Fig.12). Such fractures and some of the OM-
9 hosted pores are interpreted as artefacts due to sample preparation after retrieval from subsurface and
10 thus may not be present in the subsurface (Chalmers et al., 2012; Tian et al., 2015). The OM in these
11 low-mature samples is thus mainly non-porous. Most of the macropores and mesopores are $< 4 \mu\text{m}$ in
12 diameter and seem located between clay sheets, inside microfossil remains or between calcite, and
13 quartz grains (Fig.12A, C, D). Some intraparticle pores are observed inside pyrite framboids (Fig.12B,
14 E).

15 The relationships between TOC, quartz and clay mineral contents are shown in Fig.14. Clay
16 mineral content exhibits no clear relationship with TOC contents in either of the formations (Fig.14).
17 A negative linear correlation between TOC and quartz contents is observed in the VMF ($R^2=0.70$,
18 Fig.14). A weaker negative linear correlation exists in the KCF between quartz and TOC ($R^2=0.57$,
19 Fig.14). The relationships between organic carbon contents and the specific surface area are shown in
20 Fig.15. VMF and KCF samples do not plot in the monolayer equivalent model trend such as Peru
21 margin and Black-Sea sediments (Fig.15, Hedges and Keil, 1995). This model represents the quantity
22 of organic carbon that can be contributed by organo-clay interactions as a function of the specific
23 surface area. VMF and KCF sediments thus contain organic carbon that cannot have been contributed
24 solely by organo-clay interactions. Compared with Peru margin and Black-Sea sediments, our results
25 suggest that other additional mechanisms have allowed the OM to be well-preserved in the KCF and
26 VMF formations (Hedges and Keil, 1995).

27 3.4. Porosity and pore size distribution

1 Data obtained from mercury intrusion porosimetry (MIP) are listed in Tab.3. MIP
2 measurements revealed a connected total porosity ranging from 15.69 to 23.40% in the KCF and from
3 16.69 to 28.68% in the KCF (Tab.3). Cumulative intrusion as a function of TOC and PSD are shown
4 in Fig.16 and Fig.17. A significant number of pores are located in the 50–1000 μm pore size range for
5 the KCF sample and in the 100–1000 μm for the VMF samples (Fig.16 A, C). Nevertheless, these
6 large macropores which largely contribute to the total porosity were never seen in SEM and
7 petrographic observations. The largest pores imaged by SEM are about 6 μm in diameter in both
8 formations. The presence of pores $> 6 \mu\text{m}$ is considered as conformance errors due to surface
9 roughness, cracks and filling of the container (Sigal, 2009; Klaver et al., 2012). In order to provide
10 more realistic MIP data, mercury intrusion curves, porosity and pore volumes were thus corrected by
11 excluding pores greater than 6 μm in diameter and by subtracting the first part of the intrusion data
12 from the total (Fig.16 A, C). Corrected porosity and pore volumes are listed in Tab.3 and corrected
13 PSD and cumulative intrusion curves are shown in Fig.17. After corrections, the total porosity ranges
14 from 3.37 to 9.98% and the total pore volume ranges from 1.89 to 5.57 $\text{cm}^3/100\text{g}$ for KCF samples
15 (Tab.3). For VMF samples, their total porosities vary between 0.59 and 2.87% and the pore volume
16 ranges from 0.35 to 1.63 $\text{cm}^3/100\text{g}$ (Tab.3), suggesting a very low macro- and mesoporosity ($>6 \text{ nm}$).
17 The bulk and the skeletal density of all samples decrease with increasing TOC likely due to the
18 difference in density between OM and minerals (Tab.3). KCF and VMF samples are mainly composed
19 of mesopores less than 30 nm in diameter with a great number of pores measuring less than 15 nm
20 (Fig.17). Only a few pores are in the 50 nm to 6 μm pore-size range in both formations (Fig.17). These
21 macropores account for $\sim 15.63\%$ of the total pore volume in the KCF samples and for only $\sim 7.71\%$ in
22 the VMF samples (Tab.3), suggesting a less abundant macroporosity in the VMF samples than in the
23 KCF samples. The total pore volume and thus the porosity of KCF and VMF mudstones decrease with
24 increasing TOC (Tab.3, Fig.16 B, D). KCF samples with more than 6 wt.% of TOC exhibit a lower
25 number of pores in the 8 to 30 nm pore size range, and thus a lower porosity and total pore volume
26 (Tab.3, Fig.16B, Fig.17). Nevertheless, these high-TOC samples can contain a significant amount of
27 pores of less than 8 nm in diameter, such as Eb 19 or Eb 40 (Fig.17). However, some of these small
28 pores may be due to the additional creation of pore space during the crushing process at a high

1 mercury pressure (up to 414 MPa) (Sigal, 2009; Comisky et al., 2011), and therefore these results must
2 be interpreted with caution. VMF samples which contain more than 6 wt.% of TOC exhibit a lower
3 porosity and total pore volume than samples with lower TOC contents due to a smaller number of
4 mesopores in the 8–30 nm pore size range (Tab.3).

5 Data obtained from low-pressure nitrogen adsorption measurements are listed in Tab.4. The
6 pore size distributions (PSD) are shown in Fig.18. VMF exhibits total pore volumes varying from 1.97
7 to 4.57 cm³/g (Tab.4). In the KCF, total pore volumes range from 2.24 to 5.62 cm³/g (Tab.4). The two
8 models commonly used in the community for the t-plot method, the Harkins-Jura and the Carbon
9 black models, provide comparable micropore surface areas and pore volumes (Tab.4). Although the
10 Carbon black model is more specific for carbon-rich materials (Magee, 1995) and the Harkins-Jura
11 model for siliceous materials (De Boer et al., 1966), the two models give similar results for these
12 marine mudstones. This result suggests that these models are both useful t-plot models to evaluate
13 micropore volume in marine mudstones and that their results can be easily compared. KCF samples
14 exhibit low micropore volumes (< 0.50 cm³/100g, Tab.4) and low specific surface areas (< 9.3 m²/g,
15 Tab.4). In these low-mature samples, micropores account for less than 15.2% of the total pore volume
16 (Tab.4). VMF mudstones exhibit higher micropore volumes (0.50–1.10 cm³/100g, Tab.4) and higher
17 micropore specific surface areas (7.5–21.0 m²/g, Tab.4), suggesting a higher microporosity. In these
18 thermally-mature rocks, micropores account for 8.4 to 31.1% of the total pore volume (Tab.4). Despite
19 this slightly higher microporosity in the VMF, total pore volumes of KCF and VMF are mainly
20 provided by mesopores. Cumulative pore volumes show that the total pore volume is mainly provided
21 by pores > 10 nm in diameter in both formations (Fig.18 D, E, F). PSD defined by low-pressure
22 nitrogen adsorption analyses revealed that abundant micropores less than 8 nm are present in KCF and
23 VMF samples (Fig.18 A, B, C), but have a low contribution to the total pore volume (Fig. 18 D, E, F).
24 VMF samples show slightly higher specific surface areas than KCF samples (~21.0 m²/g in the VMF,
25 ~17.0 m²/g in the KCF, Tab.4).

26 Total pore volumes and specific surface areas of KCF and VMF exhibit significant variations
27 with TOC, but different trends are observed in the two formations (Fig.18, Fig.19 A, B, E, F). OM
28 content exerts thus a strong control on porosity which depends on the thermal maturity of these marine

1 mudstones (Fig.19). In KCF samples, the specific surface area, the total pore volume (Fig.19 A, B)
2 and the content of small mesopores and micropores (< 10 nm) decrease simultaneously with increasing
3 TOC (Fig.17, Fig.18 B, C). Similar trends are observed for the cumulated pore volumes in the 10-100
4 nm pore size range (Fig.18 E, F), suggesting the decrease in the number of pores > 10 nm in diameter
5 with increasing TOC. KCF samples can be divided into two groups according to the texture of clay
6 minerals in SEM observations (Fig.19C, I, J). In lower clay samples, identified as group 1,
7 phyllosilicate aggregates appear mainly isolated, dispersed in the mineral matrix with a more random
8 orientation and accompanied by heterogeneous diffuse organo-mineral aggregates (Fig.19C, D, J). In
9 clay rich-samples, identified as group 2, the phyllosilicate aggregates are parallel to each other, more
10 compact, with some interlayer pores (Fig.19C, D, I). In this group, the OM is mainly composed of
11 laminar pure OM without or with fewer insertions of clays. For both groups, the total pore volume
12 strongly increases with quartz, carbonate and albite contents. In spite of the lower clay mineral
13 contents of VMF samples, their specific surface area increases with increasing TOC content (Fig.19F).
14 However, the evolution of pore volume as a function of TOC appears more complex since no
15 relationship can be discerned between differential pore volumes and TOC contents (Fig.18 A, D). The
16 total pore volume (Fig.19 E) and the cumulated pore volume (Fig.18A) first increase with TOC
17 contents but a lack of correlation is observed above 5.5 wt.%. That trend appears to be associated with
18 the presence of smaller pores in organic-rich mudstones as evidenced by the decrease in the mesopore
19 volume and the increase in the micropore volume above 5.5 wt.% of TOC (Fig.19E) and the high
20 content of mesopores less than 2 nm in diameter in very high-TOC samples (Fig.18A). In contrast with
21 low-mature samples, the total pore volume of VMF rocks exhibits no correlation with clay, quartz,
22 feldspar and carbonate contents (Fig.19 G, H). Despite similar pore volumes and PSD, VMF and KCF
23 mudstones exhibit therefore different pore characteristics.

24 **4. Discussion**

25 4.1. Organic petrography, porosity and pore size distribution

26 Petrographic and Rock Eval analysis show that KCF samples consist of low-mature organic-
27 rich argillaceous mudstones with a high potential for oil generation ($HI \approx 500$ mg HC/g TOC, Tab.1,
28 Figs.5, 6) while VMF samples consist of gas-mature siliceous mudstones mainly composed of a

1 residual OM with a low residual petroleum potential ($RC/TOC > 0.90$, low HI values, Tab.1, Figs.5,
2 6). This substantiates the %Ro of ~1.65% determined by Legarreta and Villar (2011) in the VMF and
3 the %Ro of ~0.50% obtained by Ramanampisoa and Disnar (1994) in KCF mudstones. In KCF
4 samples, the OM components identified in petrographic observations can be grouped into three classes
5 according to their origin: (1) the brown AOM (alginite macerals) (Figs. 9, 10) which are derived from
6 the selective preservation of resistant cell-walls of green microalgae and bacterial biomacromolecules
7 (Largeau et al., 1984); (2) terrestrial particles including spores, woody and cuticular fragments and
8 black AOM (Figs.9, 10) derived from bacterial macromolecules mixed with altered lignaceous debris
9 (Boussafir and Lallier-Vergès, 1997); (3) the orange AOM interpreted as bituminite macerals (Figs.9,
10 10, Boussafir et al., 1995b; Boussafir and Lallier-Vergès, 1997).

11 Previous studies suggest that these macerals have high hydrocarbon potentials and
12 nanoscopically amorphous and homogeneous ultrafine structures in TEM observations, and are
13 derived from phytoplanktonic lipidic remains preserved by natural vulcanization (Ramanampisoa and
14 Disnar, 1994; Boussafir et al., 1995b; Boussafir and Lallier-Vergès, 1997). In the KCF, periods of
15 high productivity allow the metabolizable OM to enter the anoxic zone, favoring the development of
16 sulphate-reducing organisms and thus the production of H_2S (Lallier-Vergès et al., 1995; Boussafir et
17 al., 1995a; Boussafir and Lallier-Vergès, 1997). Most of this H_2S diffuses from the sea sediments,
18 while a part reacts with the reactive metals present in sediments to form sulphides (commonly pyrite)
19 (Boussafir et al., 1995a; Boussafir and Lallier-Vergès, 1997). The excess of H_2S is then in part
20 incorporated as organosulfur compounds in the metabolizable OM by natural vulcanization to form
21 bioresistant amorphous OM known as orange AOM (Boussafir and Lallier-Vergès 1997). These
22 processes of natural sulfurization have allowed the preservation of a large amount of metabolizable
23 OM explaining why KCF mudstones are not close to the monolayer equivalent field in the TOC versus
24 specific surface area diagram (Fig.15). Furthermore, this also explains the strong association of these
25 hydrogen-rich amorphous OM with pyrite (Figs.9, 10, 13) and the relative increase of the OM quality
26 in terms of oil-proneness with increasing TOC (Tab.1, Fig.13). In SEM images, such OM exhibits a
27 homogenous and gelified texture with well-defined boundaries and manifests a very low primary
28 porosity (Fig.12). In the high-TOC samples (≥ 5.4 wt.%, Tab.1), the amorphous OM represents more

1 than 85% of TOC based on observations with SEM (Fig.13). These amorphous and homogeneous
2 particles have lost their inherited biological structure due to reorganizations during preservation
3 processes (Boussafir and Lallier-Vergès, 1997; Boussafir et al., 1995a and b), probably explaining
4 their low primary porosity. Furthermore, the increase in the pore volume, the porosity and the specific
5 surface area with decreasing TOC (Fig.16B, Fig.17B-F, Fig.18B-F) suggests that the porosity of these
6 low-mature mudstones is not provided by these rare OM-hosted pores. On the contrary, the gel formed
7 by this amorphous OM appears to fill the interparticle mineral porosity, reducing the pore volume
8 (Fig.12, Fig.19A, B). Most of the porosity in these low-mature rocks is thus composed of mineral-
9 associated pores which are not filled by OM (Fig.12). The strong increase in the pore volume with
10 quartz, calcite and albite contents (Fig.19D) indicates that the pores located between mineral grains
11 (Fig.12) largely contribute to the total porosity. Nevertheless, the behavior of the pore volume as a
12 function of quartz, calcite and albite contents seems to be influenced by the texture of the clay
13 minerals (Fig.19C, D, I, J). The slightly higher clay mineral contents of group 2 (Fig.19C) seem to
14 have favored the presence of thick phyllosilicate aggregates, parallel to each other, more compact,
15 with some interlayer pores (Fig.19I). In samples with relatively low clay mineral contents (group 1),
16 clay minerals, mainly isolated, dispersed in the mineral matrix with a more random orientation and
17 with the presence of heterogeneous diffuse organo-mineral aggregates appear to be less favorable to
18 the presence of interlayer-pores between them (Fig.19J). This observation suggests that clay mineral
19 texture can influence the porosity of low-mature marine mudstones. However, the origin of this
20 difference of texture and the link with clay mineral contents is unclear and further investigations are
21 required.

22 VMF samples exhibit very different features. The generation of hydrocarbons with increasing
23 maturity has led to the formation of a residual OM identified as secondary solid bitumen (Fig.8). This
24 carbon-rich residue (often called pyrobitumen) was probably formed during the secondary cracking of
25 liquid oil into gas (Tissot and Welte, 1984; Lewan, 1993; Behar et al., 1997; Bernard et al., 2012;
26 Reed et al., 2014). The large predominance of pyrobitumen was previously noted in most thermally
27 mature mudstones (Bernard et al., 2012; Hackley and Cardott, 2016; Hackley, 2017). In SEM and

1 petrographic observations, this “grainy” OM exhibits a highly-developed and interconnected OM-
2 hosted porosity compared to the KCF immature organic “gel” (Figs.11, 12). These nanometer-size
3 OM-hosted pores exhibit variable shapes (Fig.11). While most of them are subangular spongy OM
4 pores, abundant oval pores (bubble-like) are visible in some OM particles (Fig.11). Similar pores have
5 been commonly described in thermally-mature mudstone reservoirs (Loucks et al., 2012; Curtis et al.,
6 2012; Bernard et al., 2012; Hackley and Cardott 2016; Ko et al., 2016, 2017). These oval and
7 subangular spongy pores are often considered to be formed in secondary solid bitumen/or pyrobitumen
8 during gas generation and expulsion from the end of the oil window to the dry gas zone (Bernard et
9 al., 2012; Ko et al., 2016). Not all the OM in the VMF is porous: some sparse and rare OM particles,
10 probably kerogen (inertinite) are non-porous or exhibit a very low porosity (Fig.12G). Similar
11 observations were made in thermally mature KCF, Woodford and Marcellus mudstones (Fishman et
12 al., 2012; Curtis et al., 2012; Hackley and Cardott, 2016), suggesting that residual kerogen evolves
13 differently from pyrobitumen with increasing maturity. Contrary to the KCF, the strong increase in the
14 specific surface area with TOC (Fig.19F) demonstrates that the porosity of gas-mature mudstones is
15 mainly provided by these OM-hosted pores. On the contrary, the absence of correlation between TOC
16 and mineral contents (Fig.19G, H) suggests that the interparticle pores identified between clay sheets,
17 calcite and quartz grains (Fig.8) do not significantly contribute to the pore volume.

18 OM from the thermally mature VMF rocks is dominated by secondary solid bitumen (Figs.8,
19 12). Due to the high maturity of these samples, this precursor OM is unidentifiable but previous
20 studies have shown the presence of a KCF-like type II OM (Uliana et al., 1999; Legarreta and Villar,
21 2011, 2015). OM of low-mature VMF mudstones is mainly composed of hydrogen-rich type II OM
22 derived from the early diagenesis of phytoplankton and algal bacterial contributions (orange and
23 brown AOM observed in KCF) with variable amounts of alginite and terrestrial relics (Uliana et al.,
24 1999; Legarreta and Villar, 2011, 2015). Highly oil-prone amorphous OM content increases with TOC
25 content (3 to 12 wt.%, Legarreta and Villar, 2011, 2015), leading to fluctuations of HI (\approx 650 mg
26 HC/g TOC, Legarreta and Villar, 2011, 2015) and OI ($<$ 30–40 mg CO₂/g TOC, Legarreta and Villar,
27 2011, 2015) as a function of TOC as observed in KCF mudstones (Tab.1). Therefore, in the present
28 study VMF and KCF mudstones exhibit: (1) similar high pyrite contents which attests to natural

1 sulfurization processes (Tab.2); (2) a similar absence of correlation between clay and TOC contents
2 (Fig.14); (3) similar high TOC contents compared to their specific surface areas (Fig.15, Hedges and
3 Keil, 1995) showing the low contribution of organo-clay interactions regardless of vulcanization
4 (orange AOM) and selective preservation processes (brown AOM). These formations thus contain two
5 different stages of maturity of the similar precursor organic material which may allow comparison of
6 their OM-hosted porosity as a function of maturity.

7 Previous work has demonstrated that clay minerals can act as catalysts in the acid-catalyzed
8 cracking of kerogen into hydrocarbons during thermal maturation (Tannenbaum and Kaplan, 1985;
9 Pan et al., 2009). Differences in clay mineral contents appear to mainly influence the kinetics of
10 hydrocarbon generation during the low stage of maturation (Tannenbaum and Kaplan, 1985). We can
11 assume that variations in clay mineral content may lead to a different evolution of OM porosity in
12 some formations during the oil generation stage. The catalytic influence of clays is, however, minor in
13 higher maturation stage such as the gas window for our VMF samples (Tannenbaum and Kaplan,
14 1985). However, if we admit some catalytic effect in this higher maturation stage, and despite the
15 lower clay mineral content of the Vaca Muerta samples (Tab.2, Fig.5), most of the OM is integrated
16 with or closely associated to clay mineral aggregates (Fig.11A, B and D) as for the KCF. We can
17 therefore assume that the catalytic effect of clay might be similar in the KCF and VMF formations and
18 that the difference in mineralogy between these formations probably had a limited impact on OM
19 porosity in these gas-mature samples.

20 4.2. Thermal maturity involvement in OM-hosted pore genesis

21 With a pore volume ranging between 2.0 and 5.6 cm³/100g (Tab. 4), KCF and VMF samples
22 exhibit a good storage capacity. The hydrous pyrolysis experiments of Chen and Xiao (2014) suggest
23 that porosity and pore volumes increase with increasing maturity and thus thermally-mature
24 mudstones will exhibit a higher porosity than low-mature rocks. Surprisingly, pore volumes
25 determined from nitrogen adsorption show similar trends for both formations despite their difference
26 in maturity (Tab.4). This observation suggests that the relationship between thermal maturity and total
27 pore volume is not straightforward.

1 The porosity of both formations appears to be mainly mesoporous. The few number of
2 mesopores in the 7-100 nm pore size range account for the most part of the pore volume (Fig.18). KCF
3 and VMF samples contain, however, abundant mesopores and micropores less than 8 nm in diameter
4 which have a low contribution to the total pore volume (Figs.17, 18). The presence of these very small
5 mesopores (< 8 nm) and micropores has been previously noted in many gas shale systems (Chalmers
6 and Bustin, 2008; Chalmers et al., 2012; Tian et al., 2015). The contribution of micropores to the total
7 pore volume determined from nitrogen adsorption is higher in thermally-mature VMF mudstones
8 (~21.0%) than in the KCF (~4.9 - 8.7%, Tab.4). MIP measurements reveal that the macropores
9 observed in SEM images do not greatly contribute to the porosity of KCF (10.6-22.8%, Tab.3) and
10 VMF mudstones (Figs.11, 12 and 17). This may explain the low porosity and the low pore volumes of
11 VMF samples measured using MIP (Tab.3): the main part of the porosity of these thermally-mature
12 mudstones is below the detection limit of MIP measurements. This was especially true for VMF
13 samples in which macropores account for less than 9% of the total pore volume obtained by MIP
14 (Tab.4). Moreover, VMF samples show slightly higher specific surface areas (Tab.4). This result is
15 quite surprising in view of the mineralogical compositions of these two series. Contrary to the
16 observations, the higher content of clay minerals in KCF samples (Fig.5) is expected to give them a
17 greater specific surface area. This difference is likely related to the greater microporosity of VMF
18 samples. This suggests a greater contribution in the KCF of the macropores observed between mineral
19 grains and clay mineral aggregates in SEM images (Fig.12). The higher thermal maturity and the
20 greater depth of gas-mature samples have probably allowed a greater mineral matrix compaction than
21 in low-mature KCF mudstones, thus probably reducing the number of macropores. Moreover, the
22 presence of some mineral/OM pores and abundant solid bitumen (Figs.8, 11) suggests that the original
23 mineral pores were partially filled during petroleum generation. Located between mineral grains
24 (Fig.11F), these 'modified mineral pores' are considered as original mineral pores, filled first by
25 petroleum which was later extracted leaving behind residual solid bitumen and smaller pores (Ko et
26 al., 2016, 2017). It can therefore be assumed that this process has also contributed to the progressive
27 decrease in the number of primary macropores in thermally-mature samples.

1 The more fully developed spongy OM-hosted pores in gas-mature rocks suggests that they are
2 essentially controlled by thermal maturation. This observation substantiates the common model of
3 organic-hosted pore genesis which holds that the porosity increases during maturation in response to
4 the volume lost during expulsion of the liquid and gaseous hydrocarbons produced by the thermal
5 primary and secondary cracking of the OM (Jarvie et al., 2007; Chalmers and Bustin, 2008; Loucks et
6 al., 2012; Curtis et al., 2012). Recent studies show that these OM-hosted pores first formed in solid
7 bitumen since the oil window (Juliao et al., 2015; Ko et al., 2016; Hackley and Cardott 2016) may
8 further developed progressively to the dry gas zone and become predominant in gas-mature mudstones
9 such as the VMF samples (Jarvie et al., 2007; Chalmers and Bustin, 2008; Loucks et al., 2012; Curtis
10 et al., 2012; Chen and Xiao, 2014; Hackley, 2017; Ko et al., 2018). Nevertheless, while OM appears to
11 be the major contributor to the total pore volume of these thermally-mature mudstones, the total pore
12 volume does not increase linearly with TOC (Fig.19E). This suggests that other factors than maturity
13 are working.

14 While the OM-hosted porosity increases strongly with thermal maturity (Curtis et al., 2012;
15 Loucks et al., 2012; Chen and Xiao, 2014; Ko et al., 2017; Hackley, 2017), this gain in volume may be
16 counteracted by the decrease in the interparticle pores by compaction and diagenetic processes
17 (Charpentier et al., 2003; Day-Stirrat et al., 2008; Milliken et al., 2013). The combination of these
18 processes may not lead to a systematic variation in the total pore volume as a function of thermal
19 maturity (Tab.3). Consequently, TOC may sometimes have a stronger control on these parameters than
20 thermal maturity as previously observed in other studies (Milliken et al., 2013; Pan et al., 2015).

21 4.3. Secondary OM-hosted pores vs primary organic porosity

22 In contrast with SEM observations in low-mature KCF mudstones which reveal a very low
23 primary OM-hosted porosity, the presence of very porous OM in immature to low-mature samples
24 (Ro: 0.35-0.50%) has been previously noted in the Woodford shale, in the Monterey or in Stuart
25 Range formations (Löhr et al., 2015). This suggests that some specific OM may contain abundant
26 primary OM-hosted pores inherited from their biological structure. Similar observations were recently
27 made in the Eagle Ford, the Wilcox group and the Smithwick shales (Reed, 2017). Reed (2017)

1 suggested that this primary OM porosity is closely tied to the presence of terrestrial organic matter,
2 probably inherited from the original structures of cellulose and woody fragments. The low content of
3 these terrestrial organic materials in KCF samples (less than 15% of the TOC, Fig.13) and the small
4 area covered by SEM images probably may not allow the observation of these porous OM in the
5 present study. Furthermore, even if we assume that non-observed primary OM-hosted pores exist in
6 low-mature KCF mudstones, these pores do not significantly contribute to the total pore volume, as
7 shown by the decrease in porosity, the total pore volume and the specific surface area with increasing
8 TOC (Fig.16B, Fig.19A).

9 While the difference in OM-hosted porosity between low-mature KCF and thermally-mature
10 VMF mudstones is clearly illustrated in the present study, Fishman et al. (2012) demonstrated that in
11 the offshore KCF mudstones, the size and abundance of this primary porosity varies with the maceral
12 composition but is largely similar regardless of maturity variation between 0.5–1.3%Ro. Similar
13 observations were also noted in the Woodford shale, in the Monterey or the Stuart Ranges formations
14 (Löhr et al., 2015). A hypothesis can be proposed to explain this difference with gas-mature rocks
15 from the VMF. As suggested by Fishman et al. (2012), the plastic nature of the clay-rich KCF
16 mudstones (Tab.2, Fig.5) could allow a greater compaction of pores developed during hydrocarbon
17 generation. The secondary OM porosity in KCF mudstones may thus have not been preserved like the
18 VMF mudstones which exhibit a higher content of rigid minerals (quartz and feldspar, Tab.1, Fig.3)
19 and allow a better preservation of pores during compaction (Day-Stirrat et al., 2008; Schieber, 2010).
20 Nevertheless, further investigations are needed to understand the connections which may exist
21 between mineral compositions, compaction and secondary OM-hosted pores.

22 4.4. TOC and OM composition controls on pore genesis

23 Although thermal maturation appears to have significant effect on OM-hosted genesis, this
24 process alone is insufficient to explain the decrease in the pore size with increasing TOC in thermally-
25 VMF mature samples with TOC values greater than 5.5 wt.% (Fig.19E). Similar trends were also
26 previously observed in Marcellus mudstones (Milliken et al., 2013) and the Permian mudstones of the
27 Lower Yangtze region (Pan et al., 2015). This observation may explain the lower pore volumes and

1 MIP porosity of the two very high-TOC samples (7.3 wt% and 9.1 wt., Fig.16D). Contrary to the
2 lower-TOC samples (< 5.5 wt.%) which contain larger pores, the main part of the porosity of these
3 high-TOC samples (> 5.5 wt.%) is below the detection limit of MIP. These samples contain a higher
4 proportion of mesopores and macropores below the MIP detection limit (Tab.3). The difference in the
5 OM composition between high- and low-TOC samples could explain these pore-size variations as a
6 function of TOC. In KCF mudstones, the increase of orange AOM content is responsible for higher
7 values of HI and petroleum potential (S_2) and corresponds to periods of anoxia favorable to natural
8 sulfurization processes (Boussafir et al., 1995a). These periods are marked by slightly lower quartz
9 content (Fig.14). By comparison, low-TOC samples correspond to periods marked by a greater
10 proportion of quartz and terrestrial OM inputs (Figs.13, 14), responsible for the decrease in the OM
11 quality with respect to oil generation and in the TOC content (Fig.7 A, B). Similar variations were
12 previously documented in low-mature VMF mudstones (Legarreta and Uliana, 1991; Uliana et al.,
13 1999; Legarreta and Villar, 2011, 2015). Similar variations in the original OM composition as a
14 function of TOC can thus be expected in VMF mudstones and three explanations can be suggested: (1)
15 As previously mentioned (Milliken et al., 2013; Pan et al., 2015), the smallest OM-pores of organic
16 rich samples may represent a more complete pore network collapse after petroleum migration caused
17 by a higher hydrocarbon production (or higher petroleum potential); (2) Alternatively, higher TOC
18 samples from the VMF probably contained a greater content of well-preserved highly oil-prone OM
19 which are less prone to the production of large *in-situ* OM mesopores during maturation. Well-
20 preserved and more hydrogen-rich type II macerals (e.g., high HI values) produce liquid
21 hydrocarbons, richer in light constituents, that are easy to migrate outward while more degraded and
22 less oil-prone (e.g., low HI values) type II macerals produce heavier and more viscous oils (richer in
23 asphaltenes, Tissot and Welte, 1984). During the secondary cracking of these viscous oils, abundant
24 secondary solid bitumens and essentially gaseous HC are produced, which may result in a greater
25 amount of mesoporosity. This may explain why TOC and pore volume are not systematically
26 positively correlated. Moreover, some macerals such as inertinite (Fig.11G) do not appear to develop
27 pores with increasing maturity. This may explain the variations in porosity observed between nearby
28 organic regions of the same sample in Woodford mudstones (Curtis et al., 2012). Changes in the

1 relative proportion of these non-porous macerals may thus explain some variations between these
2 samples. The importance of maceral types has been previously emphasized to explain porosity
3 variations (Fishman et al., 2012; Loucks et al., 2012; Milliken et al., 2013; Cardott et al., 2015; Ko et
4 al., 2017, 2018); (3) A close link seems to exist between the production of gas and OM-hosted pore
5 genesis from the oil window to the dry gas zone (Bernard et al., 2012; Milliken et al., 2013). Spongy
6 pores in thermally-mature samples seem form from the nucleation and the expulsion of gaseous
7 hydrocarbons produced by the thermal cracking of OM (Chalmers and Bustin, 2008; Loucks et al.,
8 2012; Curtis et al., 2012; Bernard et al., 2012; Milliken et al., 2013). Moreover, artificial maturation
9 experiments have shown that the quantity of gas (CO, CO₂, CH₄, C₂-C₅) generated during the thermal
10 diagenesis of OM can vary greatly between type I, II or III kerogen (Behar et al., 1992; Behar et al.,
11 1997). It may be appropriate to assume that slight fluctuations in the OM composition may have led to
12 the production of various quantity of gas during thermal maturation resulting in variations of the
13 amount of spongy pores formed in residual OM between samples. This may explain in part why high-
14 and low-TOC samples in the VMF exhibit different pore sizes.

15 In gas shale systems composed of a heterogeneous OM, this different evolution of OM
16 porosity during maturation may mask the effect of thermal maturity. That could explain why porosity
17 appears to be mainly controlled by TOC in some formations such as the Marcellus (Milliken et al.,
18 2013) or in the Lower Yangtze region (Pan et al., 2015) and suggests therefore that thermal maturity
19 and OM composition have a complementary effect, explaining the complexity and the diversity of
20 trends observed in natural gas shale systems.

21 **5. Summary and conclusions**

22 The pore structure and the geochemistry of rocks from the Kimmeridge Clay Formation and
23 the Vaca Muerta Formation were investigated and the following conclusions are drawn.

- 24 - KCF rocks are low-mature marine mudstones mainly composed of amorphous and less-porous
25 marine OM while VMF samples are gas-mature marine mudstones mainly composed of
26 porous secondary solid bitumen.

- 1 - The OM composition of KCF samples manifests variations. High-TOC samples contain higher
2 lipidic phytoplanktonic fractions and thus have a higher petroleum potential than low-TOC
3 samples. Similar variations were observed in low-mature VMF mudstones.
- 4 - Pore size distributions show a predominance of pores smaller than 30 nm and the pore volume
5 ranges between 2 and 5 cm³/100g regardless of the degree of maturity. Nevertheless, pore
6 networks in gas shale vary significantly with thermal maturity. The porosity of low-mature
7 mudstones is dominated by inorganic interparticle pores while the main contributor to the
8 porosity of thermally mature rocks is the porous secondary solid bitumen. OM porosity, low in
9 the immature stage, appears to be formed in solid bitumen and increases during thermal
10 diagenesis in response to hydrocarbon generation, becoming predominant in thermally mature
11 rocks.
- 12 - Although the porosity of gas-mature mudstones is mainly controlled by OM, surprisingly no
13 linear correlation is observed between TOC and total pore volume for samples with TOC
14 greater than 5.5 wt.%. This observation appears to be tied to the decrease of the number of
15 pores with increasing TOC. Differences in the composition of the precursor OM between
16 high- and low-TOC samples may explain these pore-size variations. This suggests that other
17 controlling factors such as OM composition can influence OM-hosted pore genesis. Three
18 hypotheses can be put forward: (1) a stronger framework compaction of high-TOC samples in
19 response to volume lost during the expulsion of a greater amount of hydrocarbons (higher
20 petroleum potential); 2) The presence of well-preserved and more hydrogen-riche type II OM
21 in high-TOC samples that is less favorable to the production of viscous oils and abundant
22 porous secondary solid bitumen and thus less favorable to the formation of large mesopores
23 (3) Variations in the quantity of gas generated during thermal maturation due to different
24 composition of the precursor OM between high- and low-TOC samples may have led to
25 variations in the quantity of pores formed in residual OM in response to gas nucleation and
26 expulsion.

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1 **Figures and tables**

2

3 Tab.1. Main parameters from Rock Eval pyrolysis for Vaca Muerta (VMF) and Kimmeridge Clay

4 samples (KCF). TOC: Total Organic Carbon (wt.%). S₁: free hydrocarbons (mg HC/g of rock). S₂:5 pyrolyzable hydrocarbons (mg HC/ g of rock). T_{max}: temperature of the S₂ peak (°C). HI: Hydrogen6 Index (mg HC/g of TOC). OI: Oxygen Index (mg CO₂/g of TOC). RC: Residual Carbon.

Sample no.	Formation-well	Depth (m)	TOC (wt.%)	S1 (mg HC/g rock)	S2 (mg HC /g rock)	Tmax (°C)	HI (mg HC/g TOC)	OI (mg CO ₂ /g TOC)	RC/TOC**
Eb 3	KCF-Ebberston	69.11	8.3	0.9	52.7	425	636	18	0.47
Eb 4	KCF-Ebberston	69.14	7.1	0.2	37.2	428	528	17	0.57
Eb 8	KCF-Ebberston	69.48	6.4	0.7	39.6	429	616	20	0.49
Eb 11	KCF-Ebberston	69.9	4.2	0.3	24.6	428	586	21	0.51
Eb 19	KCF-Ebberston	69.98	10.6	0.4	61.5	428	580	15	0.52
Eb 28	KCF-Ebberston	70.01	3.2	0.1	7.9	434	249	20	0.78
Eb 30	KCF-Ebberston	70.03	5.4	0.1	18.9	432	353	18	0.71
Eb 32	KCF-Ebberston	70.05	6.6	0.2	30.5	429	462	17	0.62
Eb 34	KCF-Ebberston	70.12	12.6	0.5	80.4	425	638	18	0.48
Eb 38	KCF-Ebberston	70.25	13.4	0.9	81.3	423	607	17	0.50
Eb 40	KCF-Ebberston	70.28	15.9	0.9	97.7	424	613	19	0.49
Eb 48	KCF-Ebberston	70.65	6.0	0.1	27.3	428	456	18	0.62
		Mean	8.3	0.4	46.6	427	527	18	0.56
	KCF-Ebberston	Min	3.2	0.1	7.9	423	249	15	0.47
		Max	15.9	0.9	97.7	434	638	21	0.78
Blc 2	KCF-Marton	128.15	3.0	0.1	13.3	433	439	25	0.63
Blc 4	KCF-Marton	128.25	3.2	0.1	13.8	431	428	27	0.62
Blc 8	KCF-Marton	128.28	2.9	0.1	12.4	433	427	26	0.64
Blc 13	KCF-Marton	128.40	3.0	0.1	12.3	434	414	22	0.65
Blc 23	KCF-Marton	128.65	5.6	0.3	29.8	432	537	15	0.56
Blc 30	KCF-Marton	128.75	11.2	1.5	70.2	428	628	15	0.48
Blc 31	KCF-Marton	128.78	6.9	0.5	42.2	432	615	18	0.49
Blc 43	KCF-Marton	129.10	2.2	0.1	6.7	433	307	31	0.74
Blc 50	KCF-Marton	129.20	2.1	0.1	5.7	433	275	30	0.76
		Mean	4.4	0.3	22.9	432	452	23	0.62
	KCF-Marton	Min	2	0	6	428	275	15	0.48
		Max	11	1	70	434	628	31	0.76
93X	VMF-well	2647	2.1	0.3	0.8	/	38	19	0.95
94B	VMF-well	2668	5.0	1.2	2.2	/	43	5	0.94
95G	VMF-well	2685	3.6	0.5	0.6	/	16	15	0.97
96Z	VMF-well	2697	7.3	1.1	1.8	515*	25	5	0.96
97U	VMF-well	2710	3.9	0.5	0.9	/	23	11	0.97
98M	VMF-well	2720	5.5	0.7	1.4	/	25	6	0.97
99W	VMF-well	2734	5.4	0.8	1.3	507*	24	7	0.96
100C	VMF-well	2747	3.2	0.3	0.8	/	26	9	0.97
101E	VMF-well	2764	4.3	0.3	1.7	/	39	6	0.96
102R	VMF-well	2769	6.7	1.1	1.3	488*	19	4	0.97
103K	VMF-well	2789	9.1	1.2	1.6	500*	18	2	0.96
104P	VMF-well	2794	1.3	0.1	0.7	/	49	20	0.90
		Mean	4.8	0.7	1.3	502	29	9	0.96
	VMF-well	Min	1.3	0.1	0.6	488	16	2	0.90
		Max	9.1	1.2	2.2	515	49	20	0.97

7 /: unmeasurable Tmax due to a flat S2 peak. *: Tmax values which appear to be correct despite a low

8 S2 peak. **RC/TOC: the closer this ratio is to unity, the greater the amount of residual carbon (RC) is.

- 1 Tab.2. Mineralogical composition obtained using X-ray diffraction analysis (in weight %) for
 2 Kimmeridge Clay (Ebberston, Marton boreholes) and Vaca Muerta samples (VMF).

Sample no.	Well	Depth (m)	Quartz (wt.%)	Carbonate (wt.%)			Total carbonate (wt.%)	Gypsum (wt.%)	Albite (wt.%)	Total clay (wt.%)	Pyrite (wt.%)
				Calcite	Siderite	Dolomite					
Eb 4	Ebberston	69.14	15.9	8.5	0	0	8.5	2.0	2.5	57.6	6.4
Eb 19	Ebberston	69.98	8.7	17.6	0	0	17.6	0.8	3.0	53.6	5.7
Eb 28	Ebberston	70.01	19.8	22.4	0	0	22.4	0	6.1	46.6	2.0
Eb 40	Ebberston	70.28	7.8	13.8	0	0	13.8	1.4	1.5	54.6	5.0
Eb 48	Ebberston	70.65	15.8	19.5	0	0	19.5	1.0	1.9	54.8	1.0
	Min		7.8	8.5	0	0	8.5	0	1.5	46.6	1.0
	Max		19.8	22.4	0	0	22.4	2.0	6.1	57.6	6.4
	Mean		13.6	16.4	0	0	16.4	1.0	3.0	53.4	4.02
Blc 2	Marton	128.15	19.7	16.3	4.6	0	20.9	1.1	2.6	52.5	0.2
Blc 13	Marton	128.40	21.5	19.7	4.4	0	24.1	1.7	0	49.0	0.7
Blc 30	Marton	128.75	14.3	15.0	0	0	15.0	0.8	6.2	46.0	6.4
Blc 31	Marton	128.78	14.3	17.0	1.0	0	18.0	0.6	2.7	54.1	3.5
Blc 50	Marton	129.20	12.4	6.5	13.7	0	20.2	1.1	3.8	59.1	1.3
	Min		12.4	6.5	0	0	15.0	0.8	0	46.0	0.2
	Max		21.5	19.7	13.7	0	24.1	1.7	6.2	59.1	6.4
	Mean		16.4	14.9	4.7	0	19.6	1.1	3.1	52.1	2.42
94B	VMF	2668	31.5	10.0	0.3	0.5	10.8	0	21.1	30.0	1.6
96Z	VMF	2697	15.6	28.8	0.2	0	29.0	0	23.6	22.2	2.4
98M	VMF	2720	33.7	14.2	0.1	0	14.3	0	22.8	22.1	1.6
100C	VMF	2747	39.1	8.1	0	0	8.1	0	26.4	21.7	1.5
102R	VMF	2769	27.7	12.8	0.2	0	13.0	0	27.9	23.3	1.4
103K	VMF	2789	22.1	6.5	0.1	0	6.6	0	24.6	36.1	1.6
	Min		15.6	6.5	0	0	6.6	0	21.1	21.7	1.4
	Max		39.1	28.8	0.3	0.5	29.0	0	27.9	36.1	2.4
	Mean		28.3	13.4	0.1	0.1	13.6	0	24.4	25.9	1.7

3

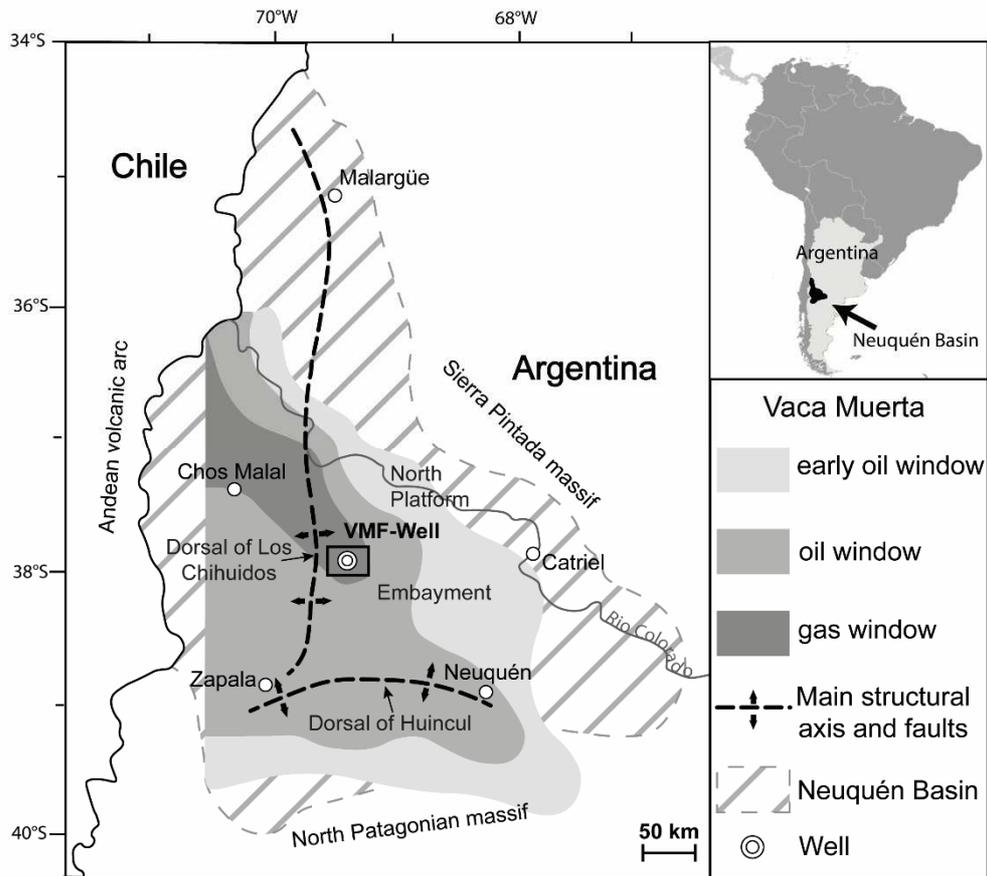
1 Tab.3. Porosity measurements obtained from mercury intrusion porosimetry including raw data and
 2 corrected data from surface roughness for Vaca Muerta (VMF) and Kimmeridge Clay mudstones
 3 (Marton, Ebberston boreholes). Contribution of macropores corresponds to the contribution to the total
 4 pore volume of macropores ranging between 50 nm - 6 μ m in diameter. PV: pore volume. TP: Total
 5 porosity.

Sample no.	Well	Raw data				Corrected data			
		PV (cm ³ /100g)	TP (%)	skeletal density (g/cm ³)	bulk density (g/cm ³)	PV (cm ³ /100g)	TP (%)	Cumulated PV at 50 nm (cm ³ /100g)	Contribution of macropores (%)
Eb 4	Ebberston	9.93	19.58	2.45	1.97	3.06	6.04	0.55	17.99
Eb 19	Ebberston	10.51	18.60	2.17	1.77	3.10	5.48	0.40	12.97
Eb 28	Ebberston	10.10	19.76	2.44	1.96	5.06	9.91	0.64	12.59
Eb 40	Ebberston	12.16	19.01	2.06	1.56	3.00	4.70	0.52	17.24
Eb 48	Ebberston	13.05	23.40	2.34	1.79	5.57	9.98	0.97	17.37
Mean		11.15	20.07	2.29	1.81	3.96	7.22	0.61	15.63
Blc 2	Marton	9.72	19.49	2.49	2.01	2.61	5.23	0.28	10.80
Blc 13	Marton	8.35	16.91	2.44	2.02	2.39	4.85	0.27	11.12
Blc 30	Marton	10.59	18.84	2.19	1.78	1.89	3.37	0.43	22.84
Blc 31	Marton	8.33	15.69	2.24	1.88	2.14	4.03	0.49	22.75
Blc 50	Marton	10.13	20.13	2.49	1.99	3.07	6.09	0.33	10.63
Mean		9.42	18.21	2.37	1.94	2.42	4.71	0.36	15.63
93X	VMF	16.31	28.68	2.47	1.76	1.63	2.87	0.15	8.91
96Z	VMF	16.59	28.49	2.40	1.72	0.36	0.61	0.03	8.26
98M	VMF	15.96	28.10	2.45	1.76	1.31	2.29	0.09	6.69
103K	VMF	9.76	16.69	2.33	1.70	0.35	0.59	0.02	7.00
Mean		14.65	25.49	2.41	1.73	0.91	1.59	0.07	7.71

6

7 Tab.4. Porosity measurements obtained by nitrogen adsorption analysis including BET specific surface areas (S_{BET}) and total pore volumes (P_{vol}) for Vaca
 8 Muerta (VMF) and Kimmeridge Clay samples (Marton, Ebberston boreholes). Comparison of the two models frequently used in the community for the T-plot
 9 methods: the universal t-curve based on the Harkins-Jura model and the Carbon-black model specific for carbon-rich materials. V_{micro} : micropore volume.
 10 S_{micro} : micropore specific surface area. S_{ext} : external specific surface area ($S_{\text{micro}} = S_{\text{BET}} - S_{\text{ext}}$). V_{micro} contribution (%) is the contribution of the micropore
 11 volume to the total pore volume (%).

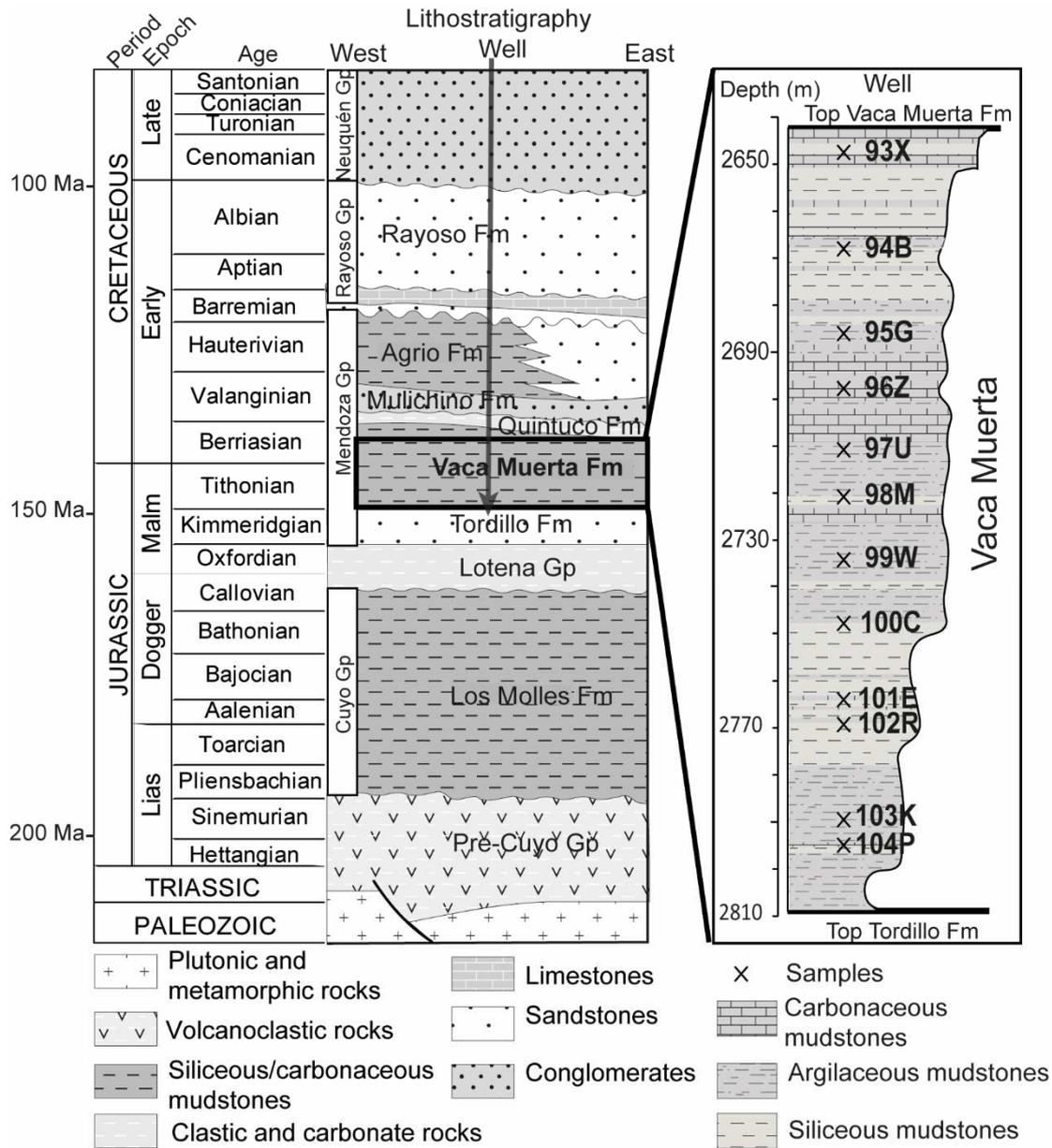
Sample no.	Well	TOC (%)	T-plot methods										
			S_{BET} (m^2/g)	P_{vol} ($\text{cm}^3/100\text{g}$)	Harkins-Jura model				Carbon black model				V_{micro} contribution (%)
					S_{micro} (m^2/g)	S_{ext} (m^2/g)	V_{micro} ($\text{cm}^3/100\text{g}$)	V_{ext} ($\text{cm}^3/100\text{g}$)	S_{micro} (m^2/g)	S_{ext} (m^2/g)	V_{micro} ($\text{cm}^3/100\text{g}$)	V_{ext} ($\text{cm}^3/100\text{g}$)	
93X	VMF	2.1	13.52	2.24	9.72	3.80	0.50	1.74	10.29	3.23	0.50	1.74	22.4
100C	VMF	3.2	17.54	2.76	15.99	1.54	0.80	1.96	16.06	1.48	0.80	1.96	29.0
94B	VMF	5.0	22.64	3.51	11.46	11.18	0.60	2.91	9.18	13.46	0.40	3.11	11.4
98M	VMF	5.5	21.07	3.57	7.39	13.68	0.30	3.27	7.48	13.59	0.30	3.27	8.4
102R	VMF	6.7	23.36	3.54	16.03	7.33	0.80	2.74	15.43	7.93	0.80	2.74	22.6
96Z	VMF	7.3	19.37	2.68	12.52	6.84	0.60	2.08	12.16	7.20	0.60	2.08	22.4
103K	VMF	9.1	29.92	3.54	23.43	6.49	1.10	2.44	21.01	8.92	1.10	2.44	31.1
Mean		5.6	21.1	3.1	13.8	7.3	0.7	2.4	13.1	8.0	0.6	2.5	21.0
Eb 4	Ebberston	7.1	15.53	4.42	4.85	10.68	0.10	4.32	4.79	10.75	0.10	4.32	2.3
Eb 19	Ebberston	10.6	12.06	3.63	7.42	4.65	0.40	3.23	7.22	4.85	0.40	3.23	11.0
Eb 28	Ebberston	3.2	33.96	5.41	9.28	24.68	0.50	4.91	9.86	24.09	0.50	4.91	9.2
Eb 38	Ebberston	14.4	10.32	2.82	1.61	8.70	0.10	2.72	1.36	8.95	0.10	2.72	3.5
Eb 40	Ebberston	15.9	9.59	3.17	1.29	8.30	0.10	3.07	1.12	8.47	0.10	3.07	3.2
Eb 48	Ebberston	6.0	20.01	5.62	0.73	19.28	0.00	5.62	0.57	19.44	0.00	5.62	0.0
Mean		9.5	16.9	4.2	4.2	12.7	0.2	4.0	4.2	12.8	0.2	4.0	4.9
Blc 2	Marton	3.0	19.93	3.63	6.97	12.96	0.40	3.23	7.75	12.18	0.40	3.23	11.0
Blc 13	Marton	3.0	22.29	4.33	1.74	20.55	0.10	4.23	1.80	20.50	0.10	4.23	2.3
Blc 23	Marton	5.6	17.53	3.73	2.26	15.27	0.10	3.63	1.60	15.92	0.10	3.63	2.7
Blc 30	Marton	11.2	5.80	1.97	5.00	0.80	0.30	1.67	5.01	0.78	0.30	1.67	15.2
Blc 31	Marton	6.9	8.87	3.01	5.72	3.14	0.30	2.71	5.66	3.21	0.30	2.71	10.0
Blc 50	Marton	2.1	28.56	4.57	7.38	21.18	0.40	4.17	9.25	19.31	0.50	4.07	10.9
Mean		5.3	17.2	3.5	4.8	12.3	0.3	3.3	5.2	12.0	0.3	3.3	8.7



1

2 Fig.1. Location of the Vaca Muerta Formation and the studied area (VMF-Well) in the Neuquén

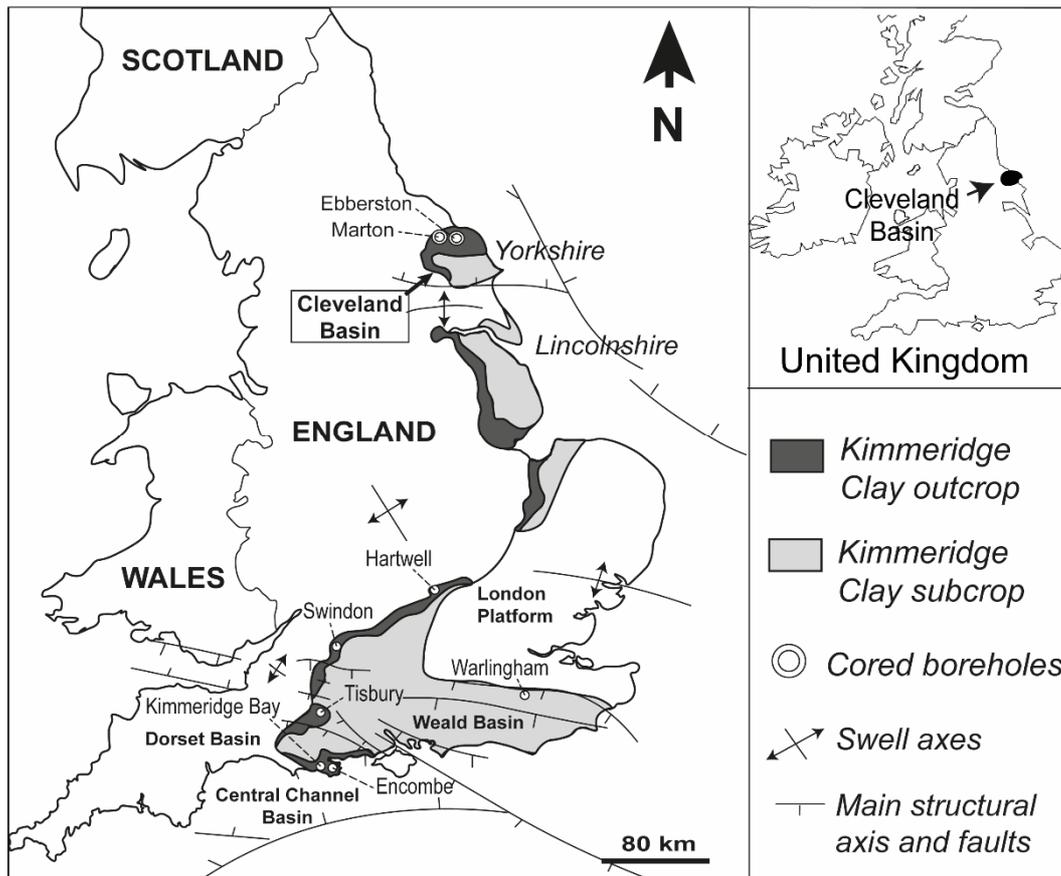
3 Basin, central-west Argentina (from Legarreta and Villar, 2011).



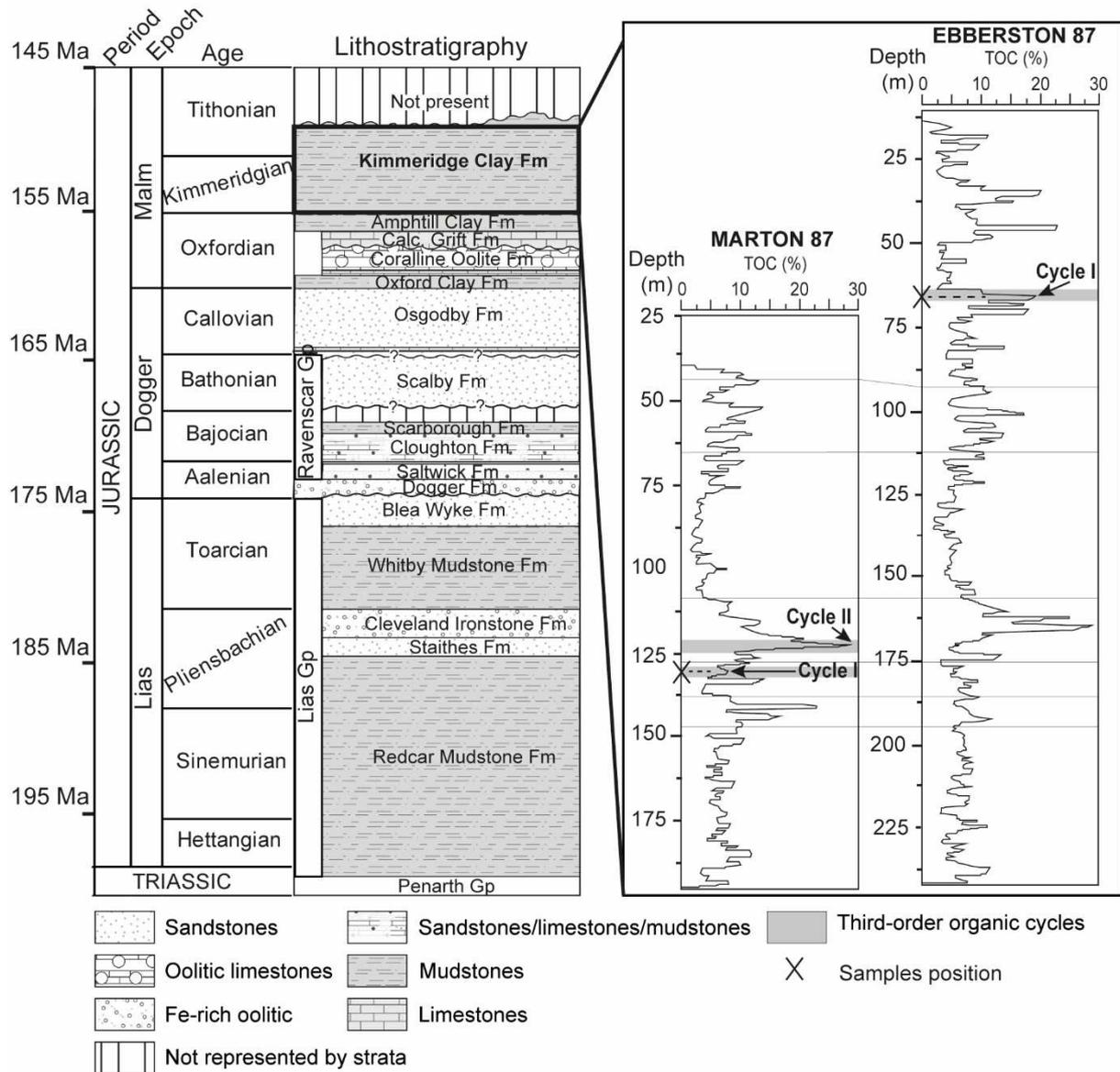
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2 Fig.2. Chronostratigraphy of the Neuquén Basin in the studied area and distribution of samples in the

3 investigated well. Lithostratigraphy after Howell et al. (2005) and Vergani et al. (2011).

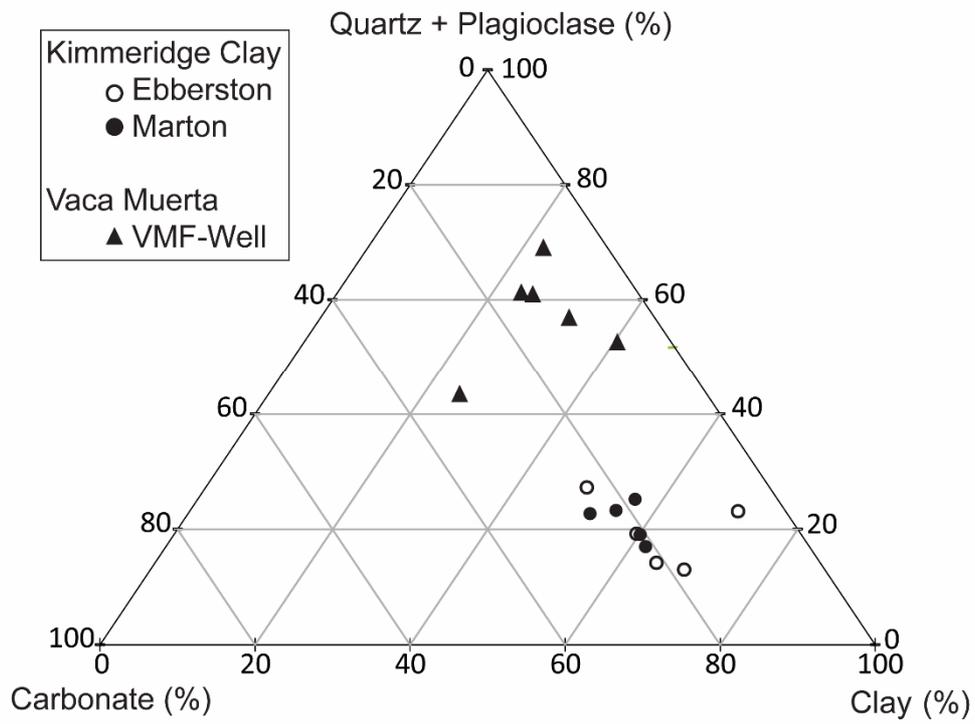


- 1 Fig.3. Location of the Kimmeridge Clay formation outcrops, Marton and Eberston Holes in the
- 2 Cleveland Basin (Northeast of England) (from Ramanampisoa and Disnar, 1994; Herbin et al., 1991).

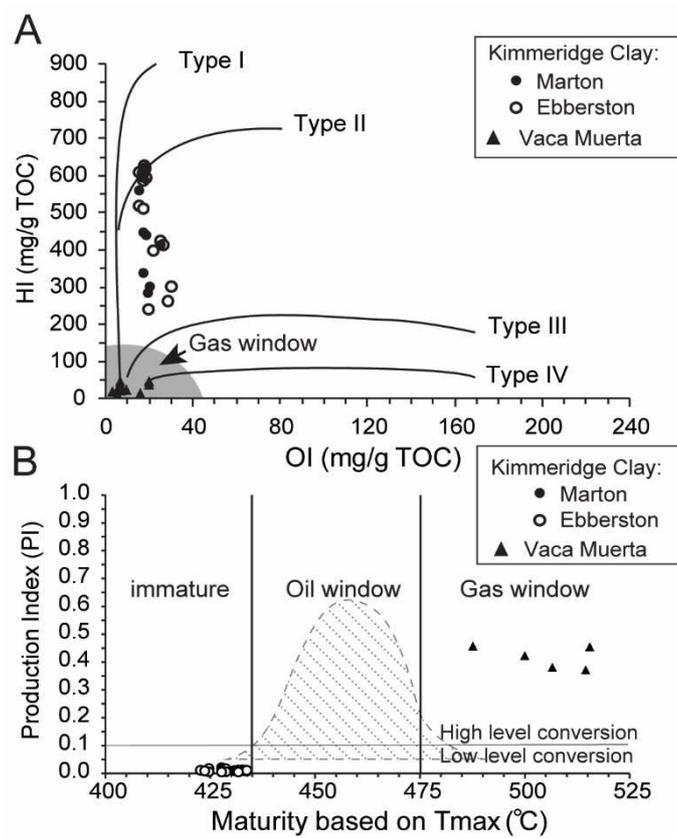


1
2 Fig.4. Simplified stratigraphic column of the Cleveland Basin (Northeast England, from Powell, 2010)
3 and total organic carbon distribution with depth in Eberston and Marton boreholes with studied short-
4 term organic cycles and sample locations (from Herbin et al., 1991).

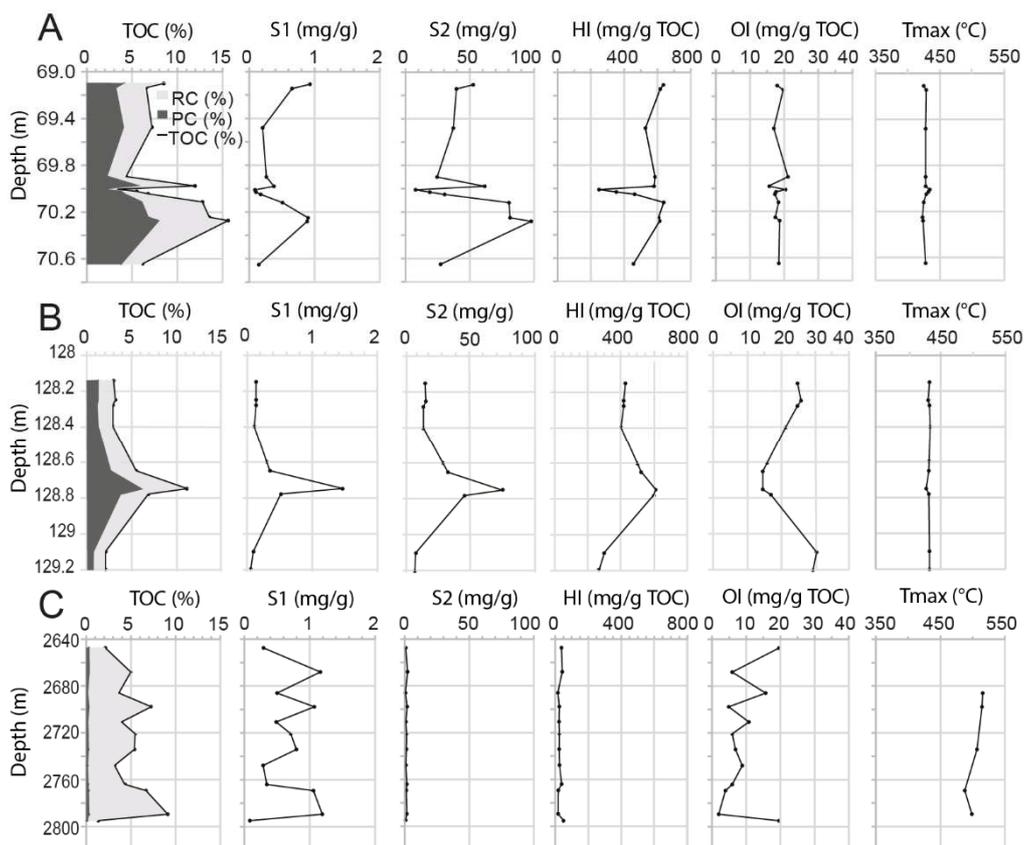
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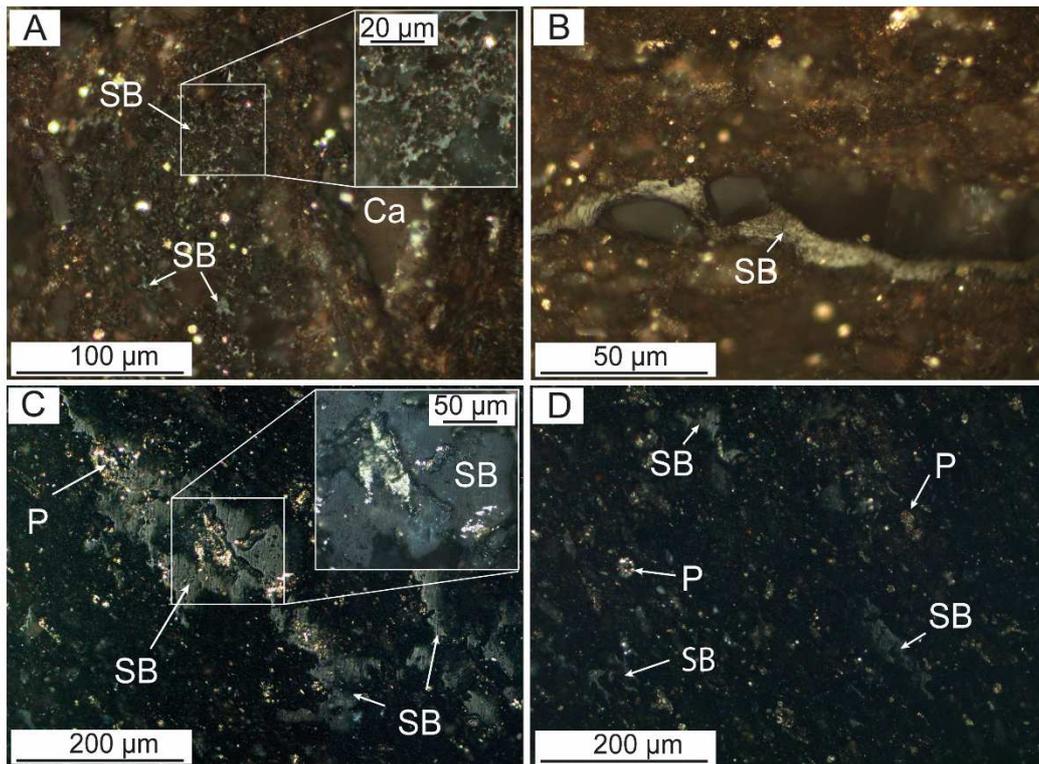
2 Fig.5. Mineralogical ternary diagram based on the normalized data from Tab.1 (in weight %).



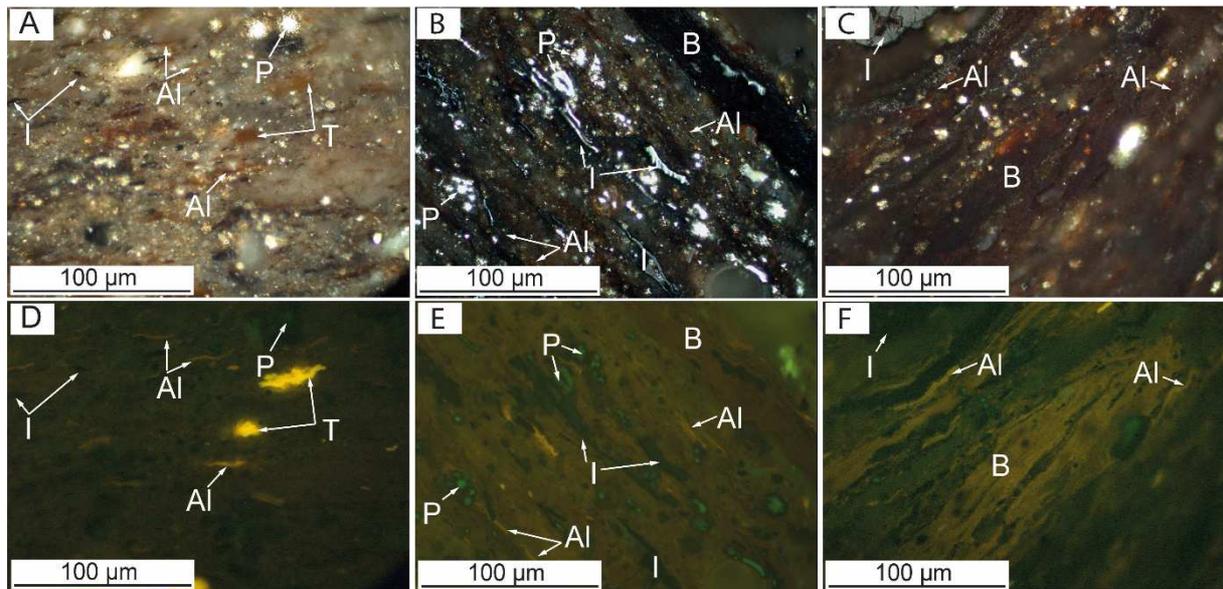
- 1 Fig.6. A) Pseudo-Van Krevelen diagram of Vaca Muerta and Kimmeridge Clay samples. B)
- 2 Production index as a function of T_{max} (data from Tab.2).



1 Fig.7. Evolution of the main petrographic parameters with depth in Ebberston (A), Marton (B)
 2 (Kimmeridge Clay formation) and in the Vaca Muerta formation (C) (data from Tab.2). RC: Residual
 3 Carbon. PC: pyrolizable carbon (in weight %).

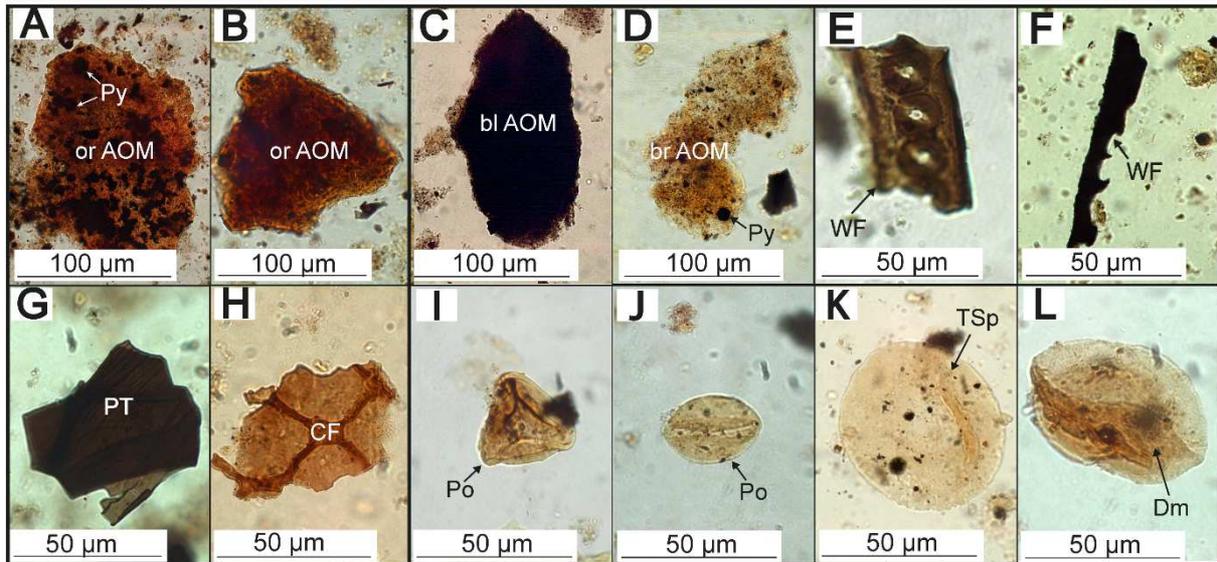


1
 2 Fig.8. Incident white light photomicrographs (oil immersion) of thermally-mature (~1.65%) organic-
 3 rich Vaca Muerta mudstones (TOC = 5.0 wt.%). A) Vaca Muerta sample showing solid bitumen (SB)
 4 network. Insert in A shows solid bitumen embayed against small euhedral crystals of carbonates. B)
 5 Photomicrographs showing a solid bitumen streak (grey-white). C-D) Solid bitumen accumulations
 6 with a granular/pitted surface texture. P: pyrite. Ca: carbonate.

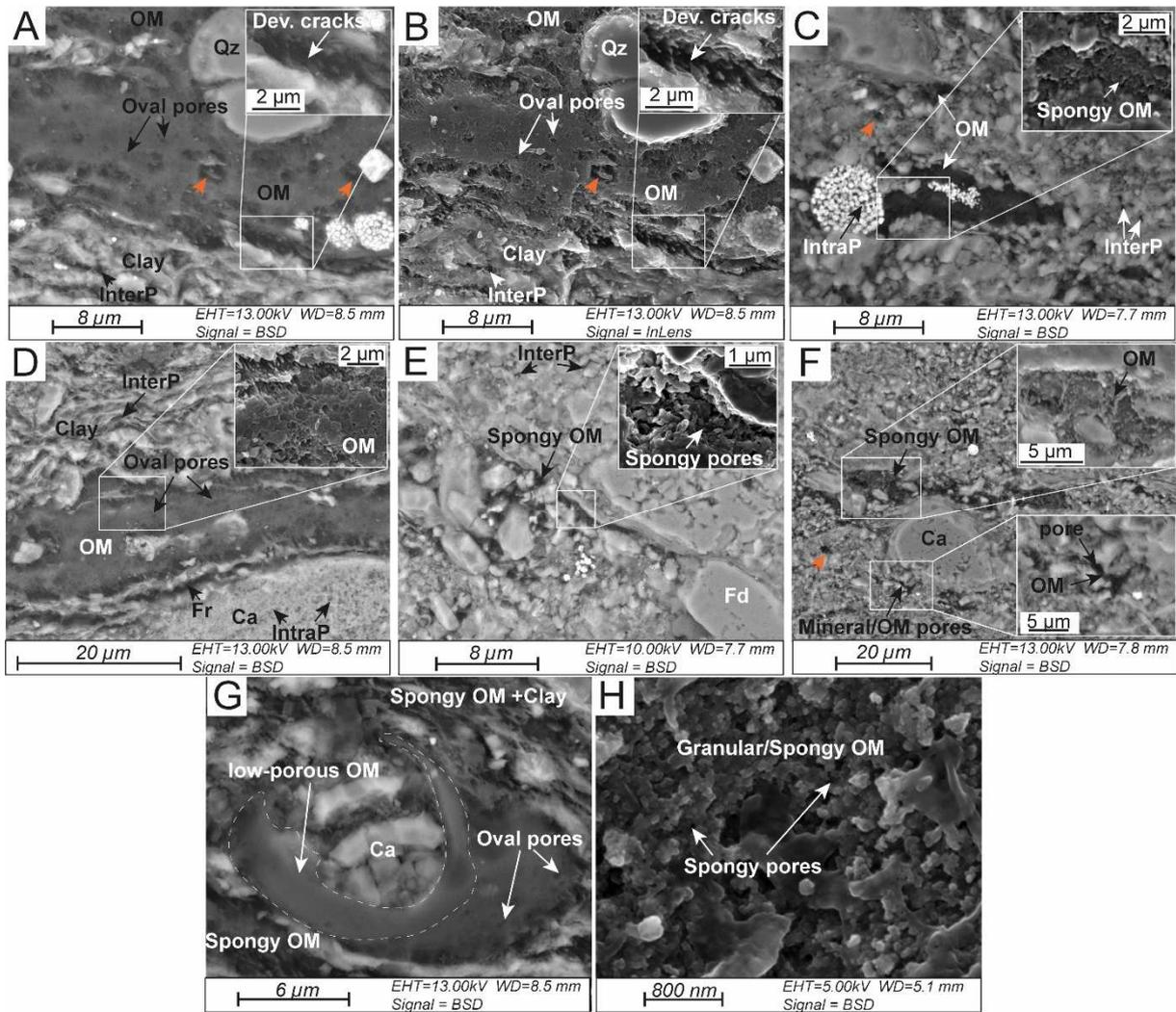


1 Fig.9. Incident white light (A-C) photomicrographs (oil immersion) of organic-rich Kimmeridge clay
 2 mudstones (A, TOC= 5.6 wt.%; B =10.9 wt.%; C, TOC =15.9 wt.%). D-F) Same field as A, B and C
 3 under UV-fluorescence light. Al: lamellar alginite macerals. T: *Tasmanite* algal body. B: elongated
 4 bodies of dark/brown amorphous organic matter identified as 'bituminite' macerals. I: inertinite
 5 fragments. P: pyrite framboids.

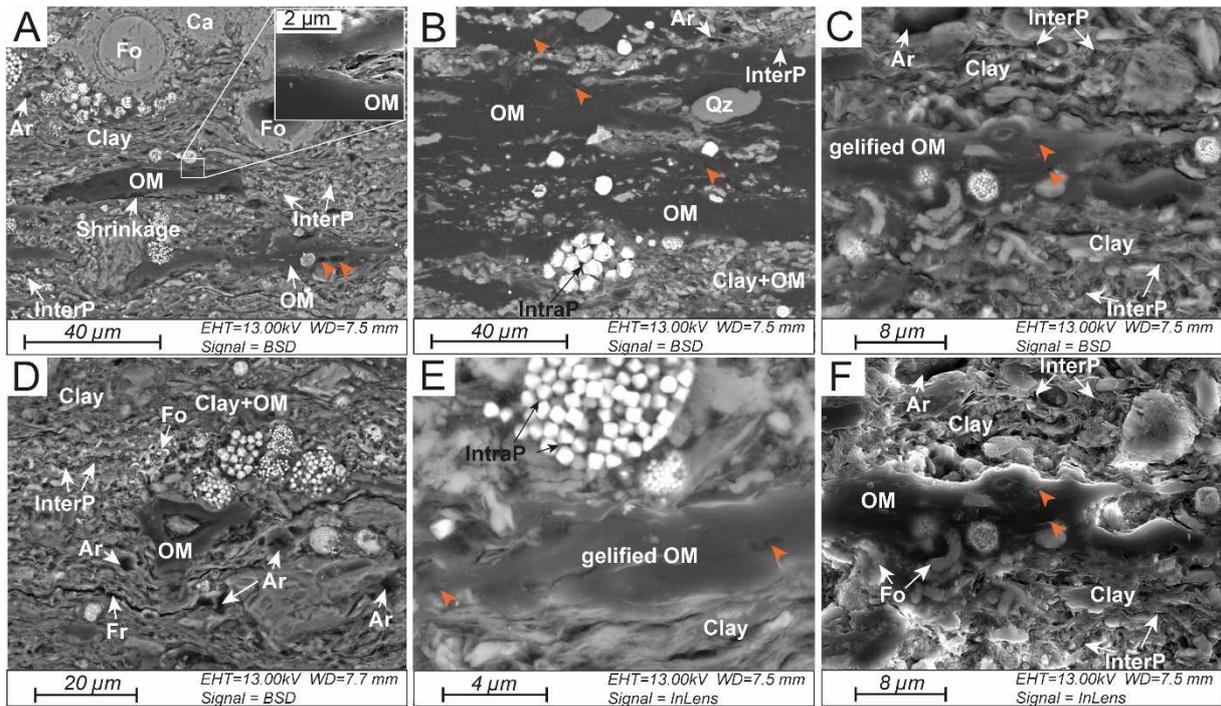
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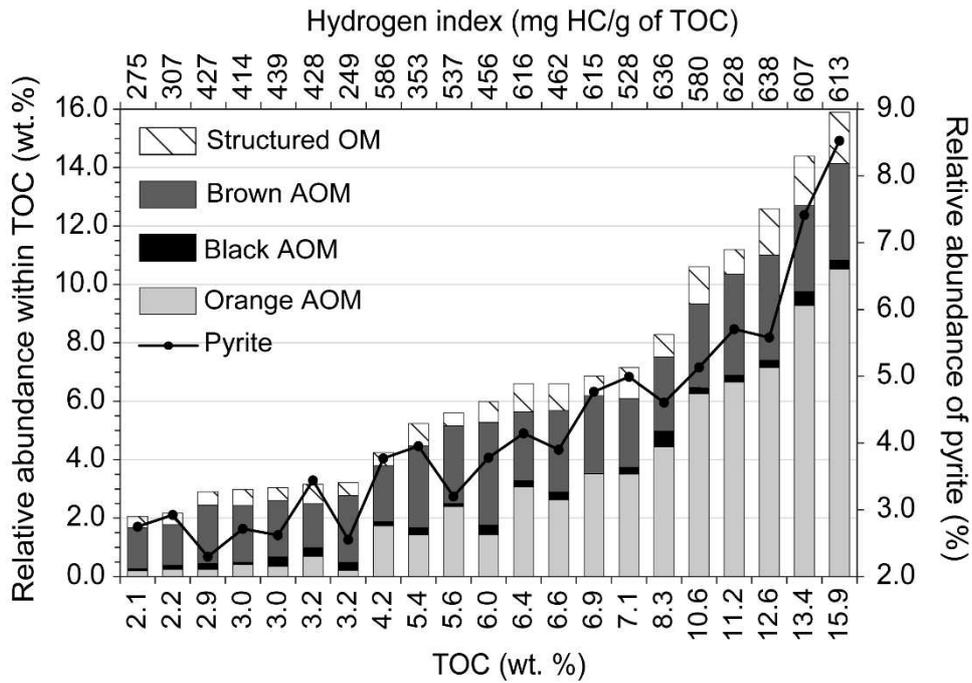
1 Fig.10. Different types of amorphous organic matter (A-D) and isolated structured organic matter (E-
 2 L) observed in Kimmeridge Clay samples by optical microscopy (transmitted light, oil immersion). A,
 3 B): orange amorphous organic matter (or AOM) with black pyritic inclusions (Py). C: black
 4 amorphous organic matter (bl AOM). D: brown amorphous organic matter with pyrite and oxidized
 5 debris inclusions. E: woody oxidized fragment (WF). F: opaque oxidized debris from plant tissue
 6 (WF). G: gelified membranes of plant tissue (PT). H: cuticular fragments (CF). I and J: pollen grains
 7 (Po). K: well preserved *Tasmanite*-like megaspore (Tsp). L: degraded megaspore (Dm).



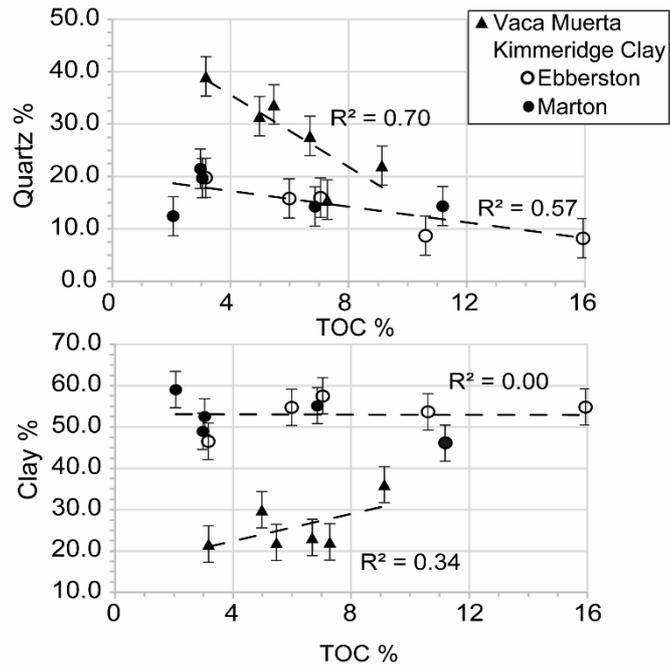
1 Fig.11. Scanning electron microscope images of broad ion beam milled thin sections of thermally-
 2 mature ($R_o \approx 1.65\%$) organic-rich Vaca Muerta samples (A-B, TOC=6.7 wt.%; E-H, TOC=5.0 wt.%).
 3 A, B, D) Backscattered electron (BSE) and secondary electron (SE) images showing a continuous
 4 spongy organic matter(OM)-hosted pore network with abundant oval pores. Insert in B shows the
 5 presence of some devolatilization cracks (Dev.cracks). C, E-F) BSE images showing spongy/ granular
 6 organic matter accumulations embayed in the mineral matrix. H and inserts in C-E show SE images of
 7 spongy subangular OM-hosted pores. Insert in F shows BSE images of pores located between mineral
 8 and residual OM interpreted as mineral/OM pores. G) BSE image showing a relatively low-porous
 9 organic matter area. Ca: calcite. Qz: quartz. InterP: interparticle pores. IntraP: intraparticle pores. Fr:
 10 microfracture. Some of the large macropores (orange arrows) and the microfractures observed in these
 11 samples are interpreted as artefacts due to sample grinding and polishing.



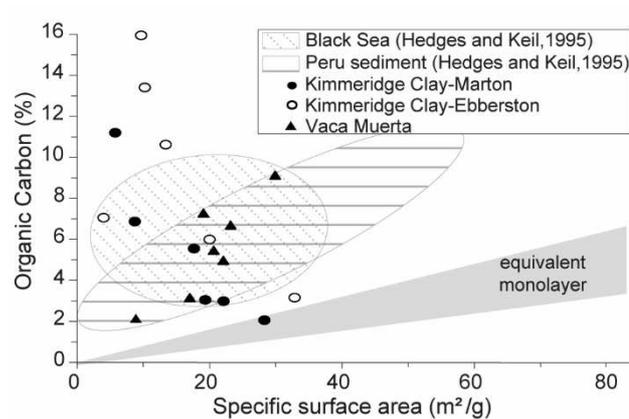
1 Fig.12. Scanning electron microscope images of broad ion beam milled thin sections of low-mature
 2 ($R_o \approx 0.5\%$) organic-rich Kimmeridge Clay samples (A: TOC=15.9 wt.%; B: TOC=11.2 wt.%; C-F:
 3 TOC=5.6 wt.%). A-E) BSE images showing a gelified non-porous organic matter (OM). F and insert
 4 in A show SE images of non-porous and homogeneous OM. Fr: microfracture. Ca : carbonate. Qz :
 5 quartz. InterP: interparticle pores. IntraP: intraparticle pores. Fo: microfossil debris. Rare intraparticle
 6 pores are present in OM (orange arrows). Some of the large macropores (Ar) and the microfractures
 7 (Fr) observed in these samples are interpreted as artefacts due to sample grinding and polishing.



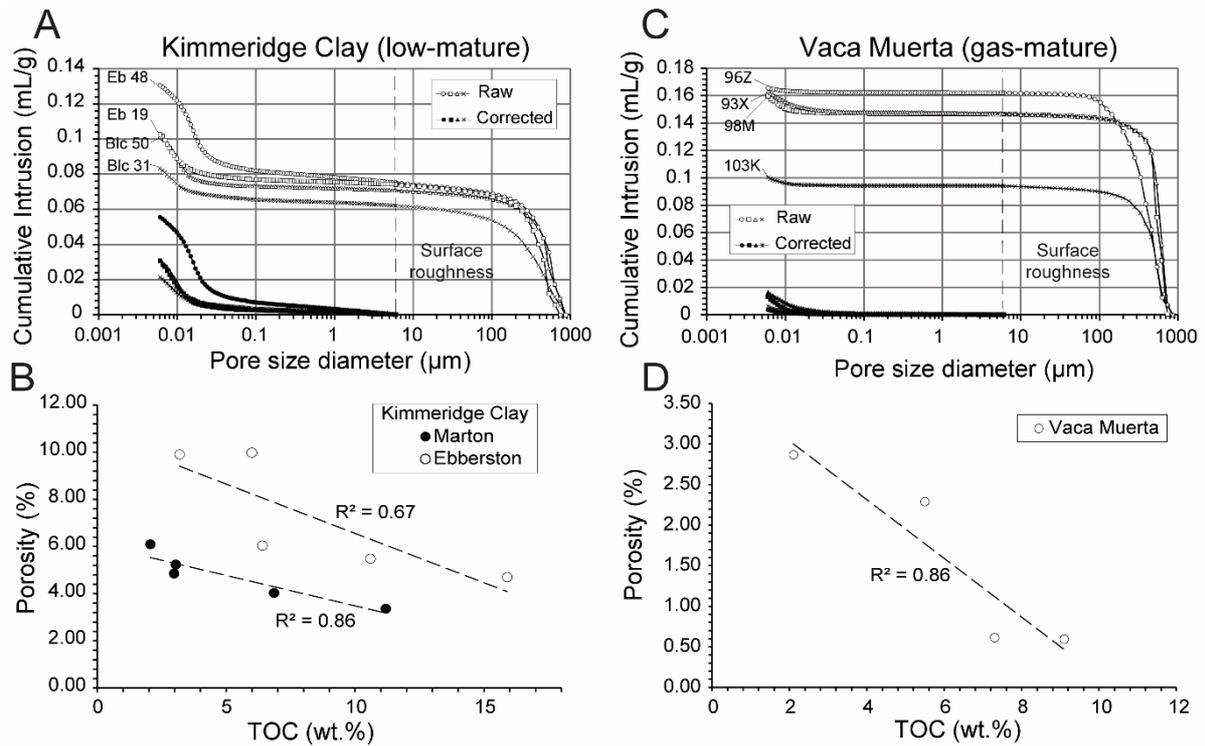
- 1 Fig.13. Palynofacies composition versus TOC contents and hydrogen index of Kimmeridge Clay
- 2 samples (including Marton and Ebberston samples). AOM: amorphous organic matter. Structured
- 3 OM: structured organic matter composed of various phytoclasts including woody fragments, cuticular
- 4 fragments and other plant tissues, pollen grains, spores and preserved phytoplankton.



- 1 Fig.14. Relationships between silica, clay minerals and TOC contents in Kimmeridge Clay (Marton and Eberston holes) and Vaca Muerta samples (in weight %).
- 2

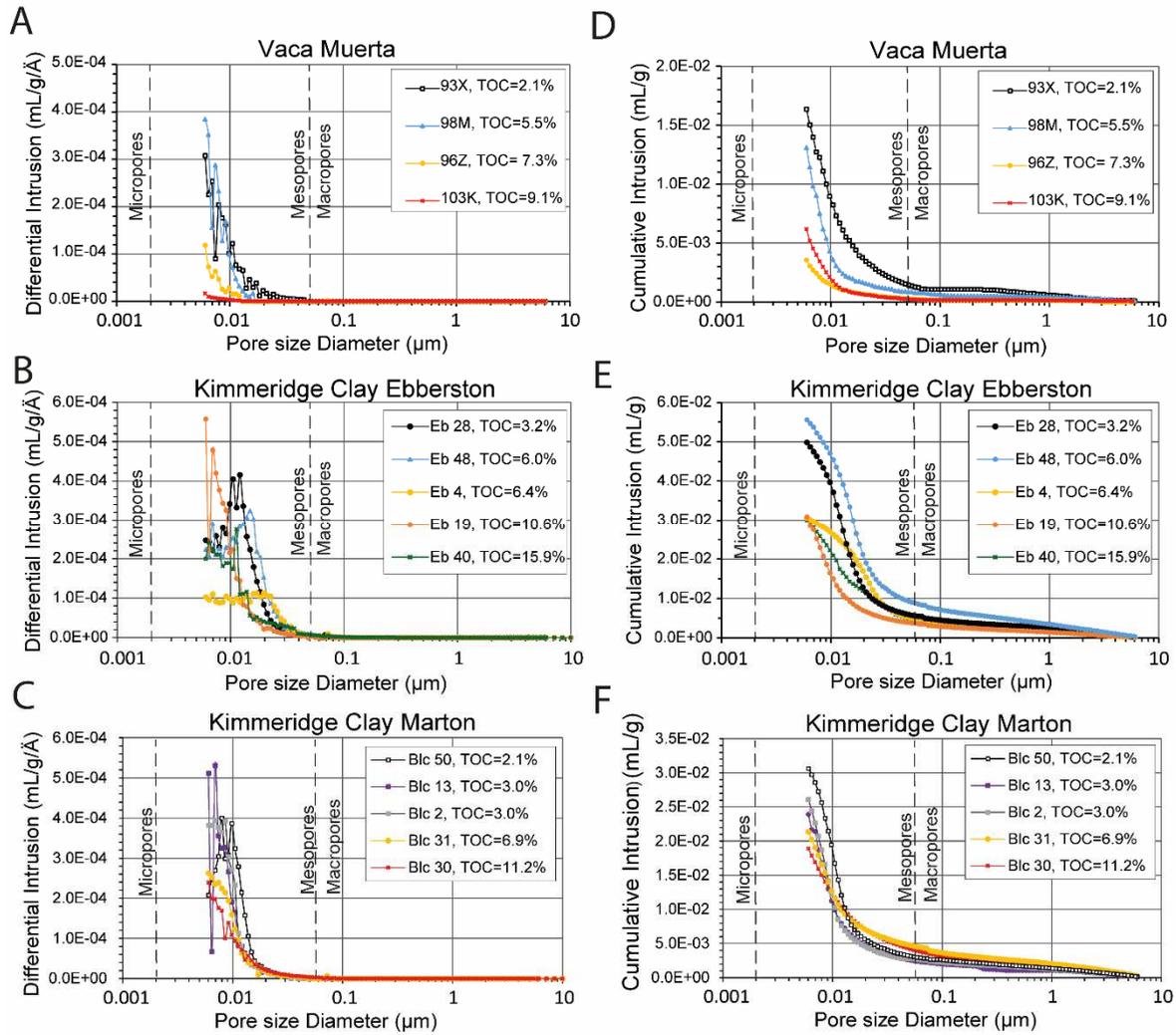


- 1 Fig.15: Organic carbon content as a function of specific surface area of Kimmeridge Clay and Vaca
- 2 Muerta samples. Comparison with the monolayer equivalent model from Hedges and Keil, (1995).



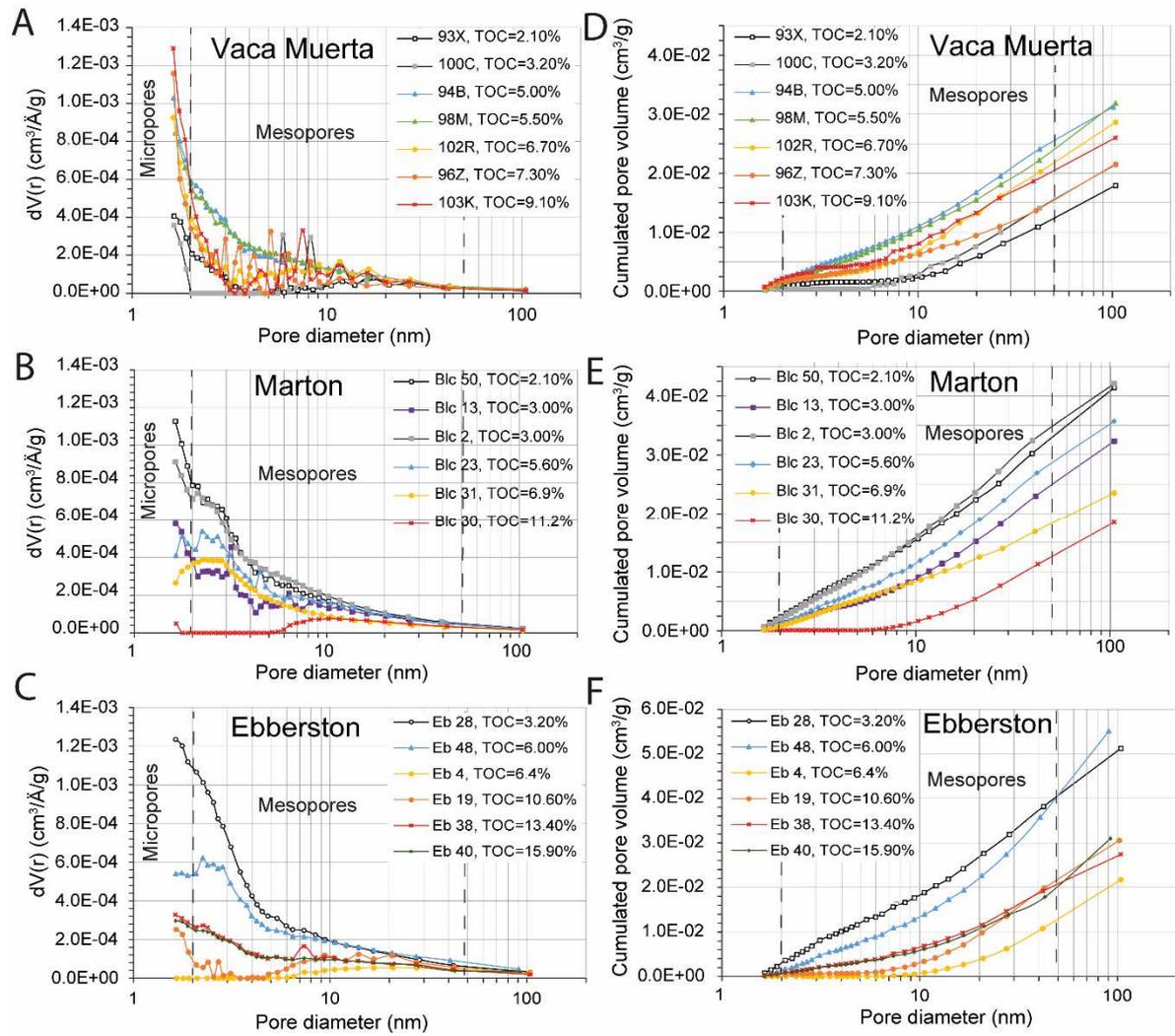
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2 Fig.16. A, C) Examples of cumulative intrusion curves derived from mercury intrusion porosimetry as
 3 a function of pore size diameter before and after correction of conformance errors for Kimmeridge
 4 Clay and Vaca Muerta samples. B, D) Evolution of porosity as a function of TOC after correction.

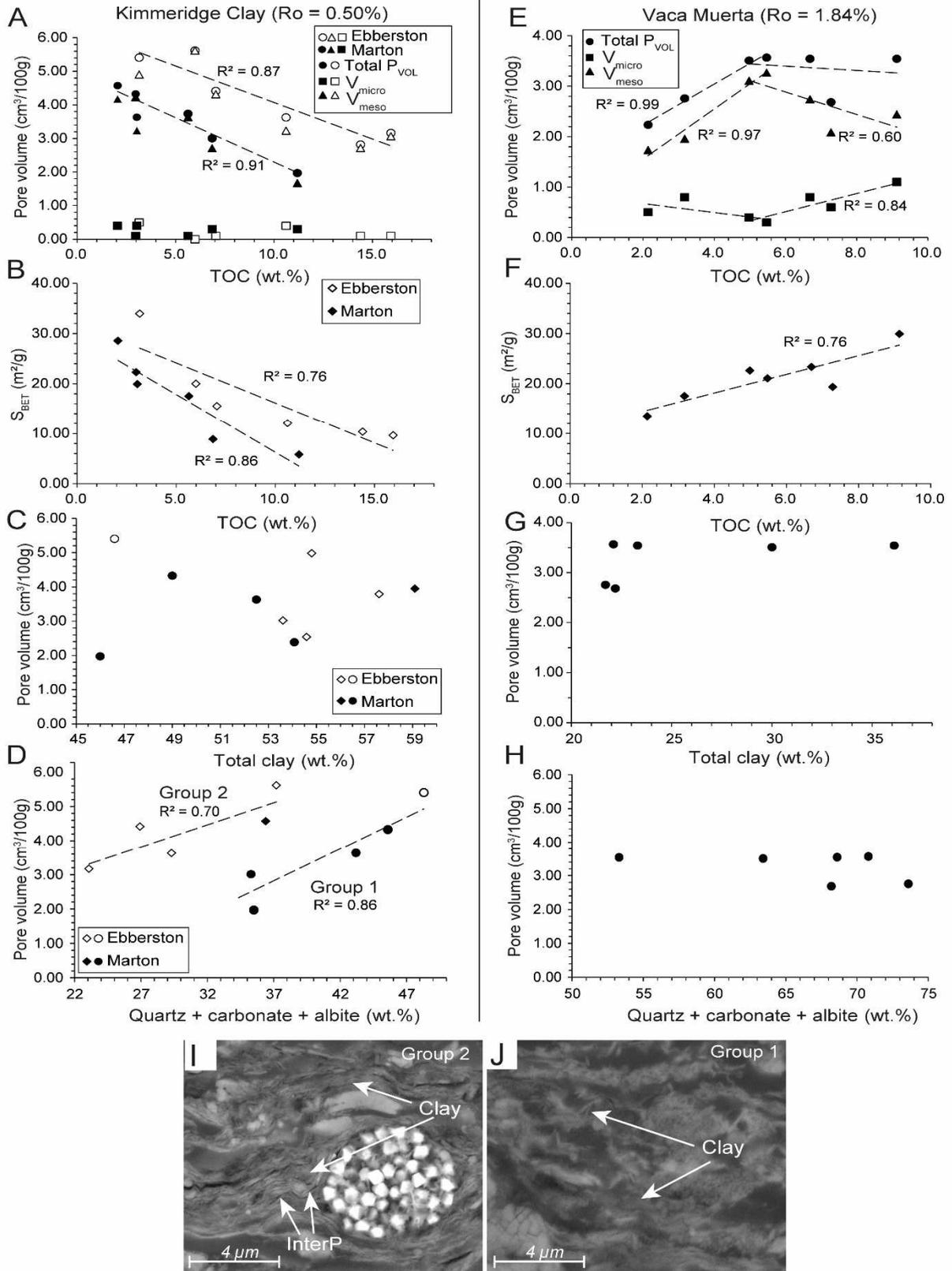


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2 Fig.17. Pore size distributions and cumulated pore volumes (after corrections) derived from mercury
 3 intrusion porosimetry measurements as a function of TOC (in weight %) for Vaca Muerta and
 4 Kimmeridge Clay rocks.



1 Fig.18. Pore size distributions and cumulated pore volumes derived from the nitrogen adsorption
 2 branch for the isotherms of Kimmeridge Clay (Marton, Eberston) and Vaca Muerta mudstones (BJH
 3 model) as a function of TOC (in weight %).



1 Fig.19. A-H) Pore volumes and specific surface areas from nitrogen adsorption measurements as a
 2 function of TOC, clay, quartz, carbonate and albite contents for Vaca Muerta and Kimmeridge Clay
 3 (Marton, Eberston) mudstones. Micropore (V_{micro}) and mesopore (V_{meso}) volumes were obtained from

- 1 the T-plot method using the Carbon black model. C-D) The dots represent samples with relatively low
- 2 clay mineral contents (group 1) and the diamonds stand for samples with relatively high clay mineral
- 3 content (group 2). I-J) SEM images of broad ion beam milled thin sections of low-mature Kimmeridge
- 4 Clay samples showing differences in the texture of clay minerals between the group 1 (J) and 2 (I).
- 5 InterP: interparticle pores.

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Highlights

- Shale pore networks vary significantly with thermal maturity.
- The porosity of immature shales is dominated by mineral interparticle pores.
- The porosity of gas-mature rocks is dominated by OM-hosted pores.
- A decrease in pore size with increasing TOC is observed in gas-mature samples.
- The higher oil-prone quality of high-TOC samples can influence OM-pores genesis.