Impact of oil-prone sedimentary organic matter quality and hydrocarbon generation on source rocks porosity: artificial thermal maturation approach.

*Amélie Cavelan [a**], Mohammed Boussafir [a*], Claude Le Milbeau [a], Fatima Laggoun-Défarge [a].*

(a) Université d'Orléans, ISTO, CNRS UMR 7327, 45100, Orléans, France

Supplementary data: full description of methods and complementary results

* Corresponding author: mohammed.boussafir@univ-orleans.fr.

** Currently at currently at Université de Lorraine, CNRS, LIEC, F-54000, Nancy, France

This document contains full details of the operating conditions for Rock Eval, Gas chromatography-mass spectrometry (GS-MS), Gas Chromatography with thermal Conductivity Detector analyses (GC-TCD), Scanning Electron Microscope (SEM) observations as well as the table of all biomarker ratios used in the Figures of the manuscript (Complementary Table.1) and the distribution of the alkanes, hopanes, steranes, monoaromatic (MAS) and triaromatic steroids (TAS) of artificially matured Kimmeridge Clay samples (Complementary Figures.1, 2 and 3) and naturally oil-matured sample from the Viking Graben (VK1).

SUPPLEMENTARY MATERIAL AND METHODS

Gas Chromatography with thermal Conductivity Detector (GC/TCD)

After maturation, the gold cells were sealed in glass bottles (25 cm^3) and pierced under vacuum. 2 cm^3 of gases were then sampled in the bottle with a gastight syringe and injected in a Gas Chromatography with thermal Conductivity Detector (GC/TCD). Gas composition was determined using a Perkin Elmer® Clarus 580 gas chromatograph fitted with a Supelco® Carboxen 1010 Plot® Capillary column (30 m × 0.53 mm i.d., 0.15 µm film thickness). (for more details about the operating conditions,

see Cavelan et al.(Cavelan et al., 2019)). During the analysis, the temperature was (1) held 5 min at 35°C; (2) increased to 240°C at 20°C.min^{-1}; (3) held for 40 min at 240°C. To avoid any contamination between samples, the machine was purged between each analysis with an isothermal temperature held 25 min at 240°C. Helium was the carrier gas. Samples were injected splitless. The injector temperature was set at 240°C. For the identification and quantification of gas, calibration curves were made using standard gases (H_2O, CH_4, CO_2, C_2H_6, C_3H_8, C_4H_{10} and C_5H_{12}). The number of moles of gas was quantified by assuming ideal gas behavior and by comparison between their respective peak areas on chromatograms and calibration curves.

Rock Eval

50-60 mg of total powdered and dried KCF mudstones were analyzed using a new Rock-Eval® 6 (Vinci Technologies, Rueil Malmaison) pyrolizer before and after thermal maturations to determine the total organic carbon (TOC) and oil-generation potential (hydrogen index, HI, mg/g of TOC). The pyrolysis program starts by an isothermal stage at 200°C, held 2 min under inert gas (helium); then, the temperature was raised to 650°C at 30°C.min^{-1} (held 3 min). The oxidation phase involved an isothermal stage

at 400°C under purified air. The oven temperature was then raised at 30°C.min^{-1} to 850°C (held 5 min). The significance of the parameters used in this study was explained by Espitalié et al.(Espitalié et al., 1985a, 1985b) and Lafargue *et al.*(Lafargue et al., 1998). Two parameters were used in the present study: (i) the total organic carbon (TOC, wt%), which accounts for the quantity of OM calculated from the integration of the amount of thermo-evaporated free hydrocarbons (S1 peak), hydrocarbons produced by kerogen pyrolysis (S2), S_3CO and S_3CO_2 produced by the breakdown of kerogen under inert gas and S_4CO and S_4CO_2 produced by the oxidation and the pyrolysis of residual carbon under purified air; (ii) the hydrogen index (HI, mg HC.g^{-1} TOC), which represents the amount of HC quality produced during pyrolysis (calculated from the S2 peak).

Gas chromatography-mass spectrometry (GC-MS)

To enable extraction of the preserved lipidic component of the studied samples before and after thermal maturation, ≈1g of total pulverized samples was extracted with a dichloromethane/methanol (1/1) mixture using ultrasonication. The extracts were dried, weighed and desulfurized on copper prior to being separated by a

deactivated silica gel (5% with water) chromatography column. Elution with heptane recovered the aliphatic fractions (SAT). Subsequent elution with a mixture of heptane/toluene (3/1) and (2/2) recovered the aromatic fractions (ARO). Finally, the polar fraction was recovered by elution with methanol. Each fraction was dried and weighed. The quantity of asphaltenes was calculated by mass difference between the total extract and the sum of the ARO, SAT and the polar fractions. Asphaltenes were counted with the polar fraction to obtain the total NSO fraction (total fraction of compounds rich in heteroatoms such as Nitrogen, Sulfur and Oxygen). The SAT and ARO fractions were analyzed by gas chromatography-mass spectrometry (GC-MS) using a Trace-GC Ultra gas chromatograph (GC) equipped with a Thermo Trace-Gold 5 MS capillary column (60 m × 0.25 mm i.d, 0.25 film thickness) and coupled to a TSQ Quantum XLS mass spectrometer (MS). The apparatus was fitted with an AS 3000 auto sampler (Thermo Scientific). The operating conditions were as follows: (1) temperature was held 1 min at 80°C, (2) the temperature increased to 120°C at 30°C.min^{-1} and from 120°C to 300°C at 3°C. min^{-1}. The final isotherm was held at 300°C during 68 min. The sample was injected in splitless mode. The injector temperature was set at 280°C. Helium was the carrier gas. The mass spectrometer

was operated in the electron ionization mode at 70 eV ionization energy. Samples were analyzed in the m/z 50-600 scanning range. SAT and ARO compounds were identified by comparing the mass spectra and retention times with available published data. The calculation of SAT and ARO compounds concentrations and molecular ratios was based on peak area integrations. Squalane was used as internal standard. Depending on the OM-richness of the samples, different amounts of standard were added to improve the assessment of SAT and ARO concentrations.

Scanning Electron Microscopy (SEM)

Petrographic observations were carried out on bulk polished rock sections of the studied artificially matured Kimmeridge Clay samples using scanning electron microscope (SEM). After thermal maturation, the rock sections were prepared by mechanical polishing (abrasive grinding paper up to P4000 and alumina polishing suspensions up to 0.04 µm) perpendicular to bedding to facilitate broad beam argon-ion milling. The rock sections were then argon-ion milled using a Gatan PECS model 682 at 5 kV for 1 h with a 4° tilt rock angle and a sample rotation speed set as 20 rpm and then 30 min at 2 kV. Previous works showed that the intense heat create on the

surface of the sample due to longer and more aggressive ion milling conditions may artificially increase the thermal maturity of samples (Mastalerz and Schieber, 2017). This may result in an artificial increase of the organic porosity at the surface of polished samples due to the early and fast devolatilization of light organic compounds. It's the reason why we have limited argon-ion milling to 1h and 30 minutes at a relatively low intensity. The sections were finally coated with carbon and fixed to SEM stubs with a carbon paste to improve image quality in preventing electrostatic charging effects.

COMPLEMENTARY RESULTS

Table S1. New Rock Eval 6 S2 (mg HC/g of rock), main biomarker ratios of artificially matured (Kimmeridge Clay) and naturally matured rocks (VK1: Viking Graben sample. VMF: Vaca Muerta samples). These data are plotted in the Figs.8 and 9 of the manuscript. The methyldibenzothiophene ratio (MDBT), the methylphenanthrene ratio (MPI-1) and the dimethylphenanthrene ratio (DPR) served to the calculation of the mean calculated vitrinite reflectance ratio (Rc) presented in the Tab. 1 of the manuscript (equation in Appendix 1).

		S2	MDBT	MPI-1	DPR	20S/ (20S+R)^3	22S/ (22S+R)^3	Pr/n-C_{17}	Ph/n-C_{18}	Pr/Ph
M2	Raw	12.4	0.36	0.33	0.17	0.12	0.34	3.01	1.48	1.14
M23		30.6	0.37	0.3	0.16	0.17	0.42	3.38	1.47	1.07
E38		86.4	0.35	0.39	0.17	0.1	0.39	1.78	2.29	0.9
E40		95.3	0.3	0.4	0.2	0.14	0.35	2.24	2.56	0.73
Mean			**0.35**	**0.36**	**0.18**	**0.13**	**0.38**	**2.60**	**1.95**	**0.96**
M2	325°C	9.1	1.19	0.82	0.27	0.36	0.49	1.06	0.68	1.30
M23		24.5	1.21	0.74	0.28	0.30	0.50	0.95	0.55	1.62
E38		78.9	1.40	0.70	0.26	0.46	0.50	0.95	0.90	1.15
E40		84	1.22	0.56	0.29	0.43	0.51	0.92	0.87	1.17
Mean			**1.26**	**0.71**	**0.28**	**0.39**	**0.50**	**0.97**	**0.75**	**1.31**
M2	350°C	7.7	3.88	0.71	0.33	0.54	0.55	0.64	0.35	1.13
M23		19.4	3.44	1.01	0.36	0.50	0.54	0.72	0.44	1.44
E38		75.8	2.94	0.98	0.34	0.54	0.60	0.62	0.66	0.76
E40		76.1	2.62	0.92	0.40	0.53	0.58	0.68	0.66	1.28
Mean			**3.22**	**0.91**	**0.36**	**0.53**	**0.57**	**0.67**	**0.53**	**1.15**
M2	390°C	2	5.89	1.45	0.66			0.05	0.05	0.38
M23		5.6	6.17	1.50	0.70			0.06	0.05	0.63
E38		20.2	5.99	1.44	0.57			0.03	0.03	0.46
E40		26.3	6.07	1.52	0.55			0.02	0.03	0.31
Mean			**6.03**	**1.48**	**0.62**			**0.04**	**0.04**	**0.445**
M2	440°C	0.3	7.24	1.87	0.97					
M23		0.6	7.12	1.93	0.90					
E38		2.6	7.60	2.56	1.10					
E40		5.7	7.34	2.29	0.92					
Mean			**7.33**	**2.16**	**0.97**					
M2	470°C	0.2	*	*	*					
M23		0.2	*	*	*					
E38		1.3	7.98	0.50	4.50					
E40		1.5	8.04	0.80	4.30					
Mean			**8.01**	**0.65**	**4.40**					
VK1		6.6	1.99	0.78	0.29	0.4	0.53	1.06	0.78	0.77
VMF1		2.2	*	*	*					

VMF2	1.3	*	*	*

*: unquantifiable due to too low concentrations. [1] 20S and 20R are epimers at C-20 in the C29 5α,14α,17α steranes. 22S is C32 17α21β 22S hopane and 22R is C32 17α21β 22R hopane. Pr: pristane. Ph: phytane.

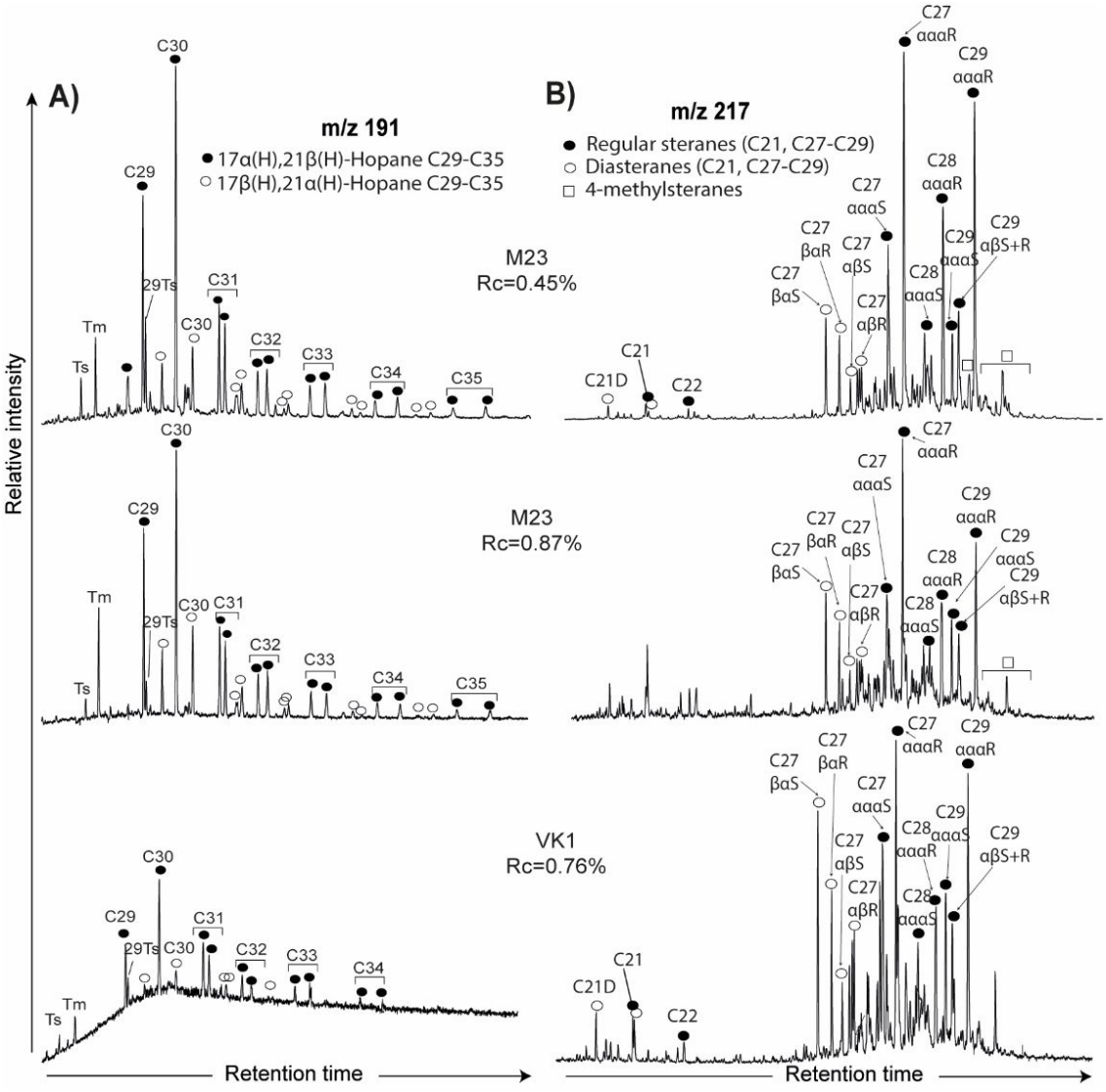

Figure S1. Mass chromatograms showing the distribution of A) hopanes (m/z 191) and B) regular steranes, diasteranes (m/z 217) and 4-methysteranes in artificially matured Kimmeridge clay mudstones at different thermal maturities. Ts: 18α(H)-22,29,30-trisnorhopane. Tm: 17α (H)-22,29,30–trisnorhopane.

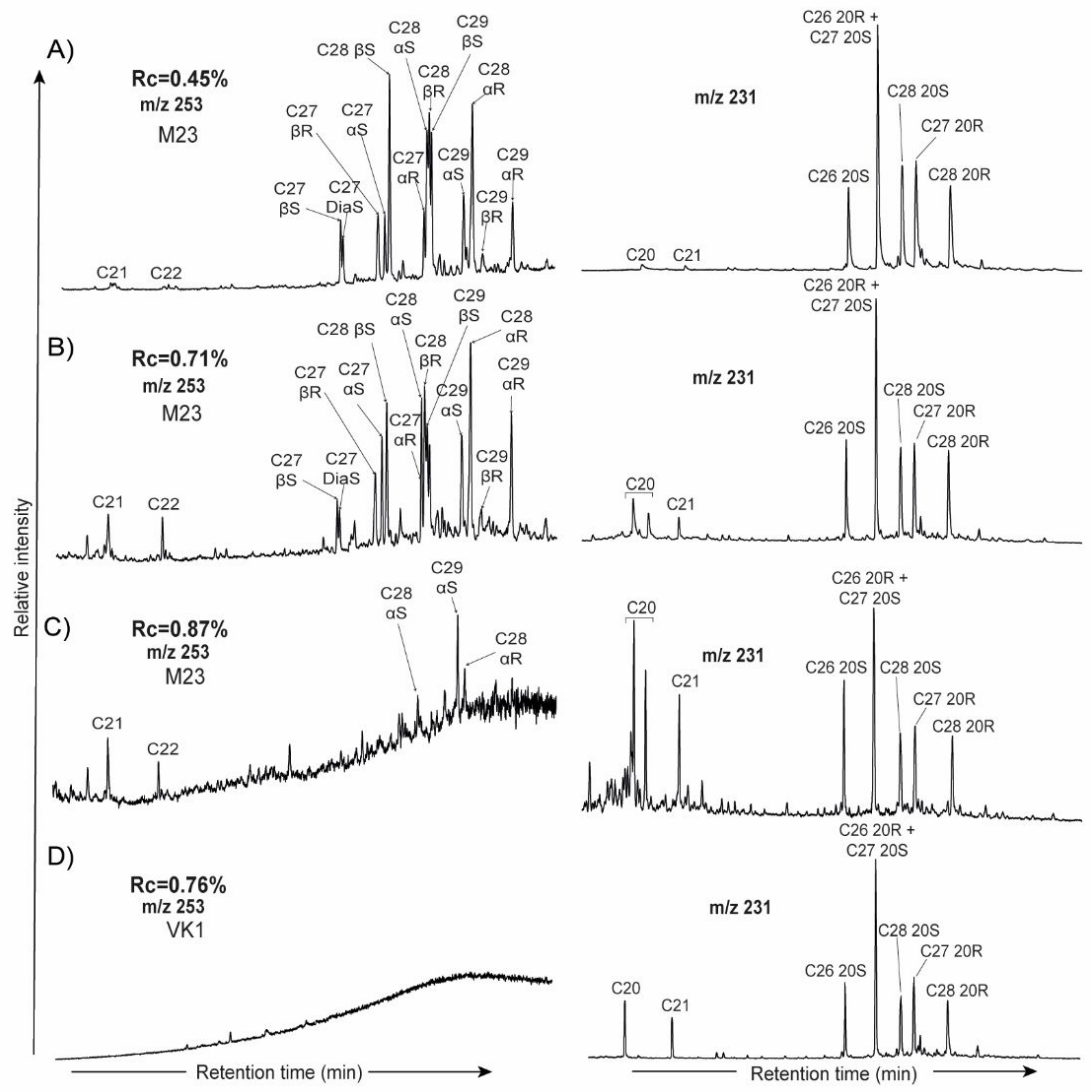

Figure S2. Mass chromatograms showing the distribution of monoaromatic (m/z 253) and triaromatic steroids (m/z 231) in artificially matured Kimmeridge clay samples in A) the immature stage, B) the beginning of the oil generation stage, C) the peak of oil generation, D) in naturally matured sample. VK1: Viking Graben. Note the progressive decrease of the monoaromatic steroid concentrations and the increase of the relative proportion of short-chain triaromatic steroids with increasing maturity in artificially matured samples.

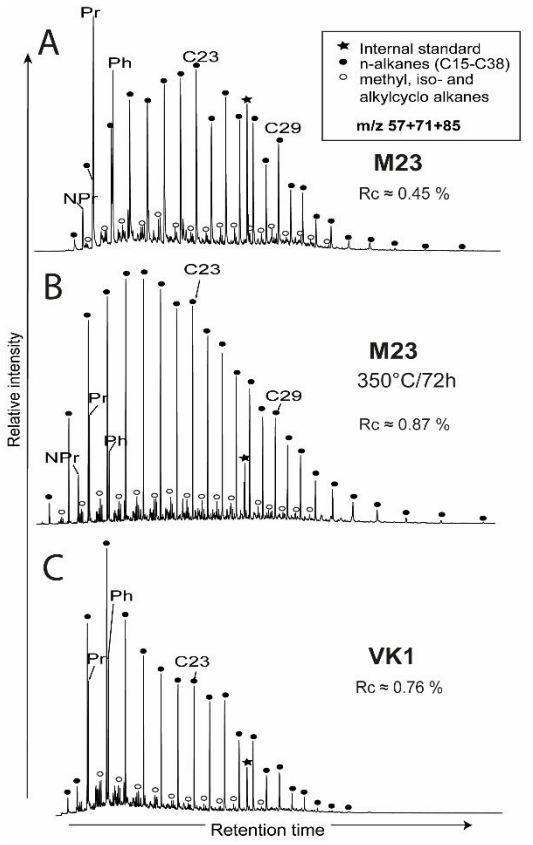

Figure S3. Mass chromatograms showing the distribution of n-alkanes, methyl, iso- and alkylcyclo-alkanes (m/z 57+71+85) in artificially matured Kimmeridge clay samples in A) the immature stage, B) the oil generation stage and C) in naturally matured sample. VK1: Viking Graben. Note the progressive decrease of $>C_{29}$ alkanes concentration, the increase of $<C_{23}$ alkanes with increasing maturity in artificially matured samples.