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High-frequency (20 MHz) NMR and Modified Rock-Eval Pyrolysis Methods as an Integrated Approach to Examine Producibility in Kerogen-Rich Source-Reservoirs

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Abstract

The geochemical and petrophysical complexity of source-reservoirs in Liquid-Rich Unconventional plays (LRU) urges for the implementation of alternative analytical protocols for initial play assessment. In this study, samples from selected source-reservoirs in the USA and the UK were analyzed by high frequency-nuclear magnetic resonance (HF-NMR relaxometry), followed by hydrous pyrolysis, and modified Rock-Eval pyrolysis methods (multi-heating rate methods, MHR). The analytical protocol here presented attempts to better qualify and quantify different petroleum fractions (mobile, heavy hydrocarbons, viscous, solid bitumen), and thus provide valuable and refined information about producibility of target intervals during appraisal stages.

Modified Rock-Eval Pyrolysis (MHR). Briefly, the pyrolysis oven program had four temperature ramps (at 50 °C/min) and isothermal plateaus (maintained isothermal for 15 minutes) at 200°C, 250°C, 300°C and 350°C, with a fifth and last ramp of 25°C/minute to 650°C. HF-NMR Relaxometry Hydrogen NMR measurements were made with a special 22MHz spectrometer from MR Cores equipped with a 30-mm diameter probe. The T2 data were acquired using the CPMG sequence with an echo time spacing of TE=0.07 ms. The T1 data were acquired using an inversion-recovery sequence. Selected samples (Kimmeridge Clay, Green River Shale) were subjected to hydrous pyrolysis experiments. Crushed rock chips (2-4 g, 1-3mm top size) were loaded into mini-reactor vessels (25-35 mL internal volumes). Rock chips were covered with deionized water and the reactor was placed in a gas chromatograph oven at the chosen temperature, generally for 72h.

Initial results show how the hydrocarbon fractions interpreted from NMR regions are in good agreement with those from MHR pyrolysis analysis in terms of hydrocarbon mobility/productibility. Results from hydrous pyrolysis experiments show that an exception to this general agreement between NMR and MHR estimates occurs for the Kimmeridge Clay samples, where MHR shows an increase of > 90% in producible hydrocarbon yields vs. minimal to no presence of mobile hydrocarbons in NMR T1-T2 maps. Ongoing experiments will clarify the role of pore structure and networks in these discrepancies of

producible oil estimates when comparing pyrolysis with NMR-based techniques. This multi-step, multidisciplinary approach provides an opportunity to use it as a screening analysis to identify zones of higher OIP and predict fluids mobility prior to drilling. The novelty of our study is the integration of laboratory-derived analytical data (HF H-NMR, MHR and Hydrous Pyrolysis, organic petrography) to assess the proportion of the OIP that is producible prior to drilling or completions.

Introduction

Liquid-rich plays are unconventional resource systems that contain large quantities of in-situ producible oil from the organic-rich shales themselves or from associated organic-lean facies (e.g., carbonates and siltstones; Jarvie, 2012, 2014). A full characterization of liquid-rich or shale-oil resources is no easy task due to their highly variable characteristics, such as numerous geochemical and petrophysical characteristics that make a liquids-rich resource producible. Among those characteristics, a proper initial assessment of the quantity of producible oil-in-place (OIP) is arguably one of the most important (Jarvie et al., 2012). Current methodologies to evaluate OIP rely mostly on petrophysical modeling, charge models, and direct measurements on rocks analyzed in the lab, usually via open-system programmed pyrolysis.

Open-system programmed pyrolysis, commonly known as Rock-Eval pyrolysis (Espitalie et al., 1977) has been the industry's workhorse of source-rock screening for over 40 years. Although originally developed for source-rock evaluation of immature to marginally mature samples (e.g., Espitalie et al., 1985; Peters, 1986), customizing the pyrolysis program to best suit the geochemical and geological characteristics of particular hydrocarbon plays (e.g., shale-oil plays) is a trivial task in newer versions of pyrolysis instruments (e.g., Romero-Sarmiento et al., 2015; Carvajal-Ortiz & Gentzis, 2018). The need for customized pyrolysis programs is in response to the complex nature of liquid-rich unconventional plays (LRU) (Abrams et al., 2017; Carvajal-Ortiz & Gentzis, 2018). Despite the availability for over 20 years of customizable pyrolysis programs that would yield better characterization results (e.g., Trabelsi et al., 1994; Sanei et al., 2015), most analytical protocols for geochemical screening and assessment of LRU plays rely heavily on the analysis of as-received and solvent-extracted powdered material, using a single pyrolysis program (initial isotherm at 300°C for 3-5 minutes, followed by a ramp of 25°C/min to 550°C or 650°C, depending on the instrument used), regardless of the nature of the LRU play (e.g., Collins & Lapierre, 2014; Raji et al., 2015; Dang et al., 2016; Piedrahita & Aguilera, 2017). The greatest challenge this analytical methodology faces is the uncertainty to determine how much of the extractable bitumen can be truly considered as part of the OIP, and thus contribute to producibility.

Only a few recent well-documented studies have implemented the use of modified pyrolysis programs that are better suited for the evaluation of LRU plays. For instance, Romero-Sarmiento et al. (2016) presented an example of the advantages of such customized pyrolysis programs, where modified pyrolysis methods, jointly with Thermal-Extraction Gas Chromatography (TE-GC), showed an improved understanding of geochemical properties of the Doig Formation in Canada as a LRU play. Similarly, Abrams et al. (2017) proposed a non-pyrolysis high-resolution thermal extraction methodology (referred to as MiSTE) to better map out zones of high OIP that could be an indication of zones of higher likelihood for producibility.

Thus, the complexity of organic-rich source-reservoirs in LRU plays requires the implementation of alternative techniques for initial play assessment, in addition to pyrolysis-based protocols. One such alternative is nuclear magnetic resonance (NMR). Few studies have attempted to integrate geochemical screening techniques and hydrogen NMR for the assessment of LRU plays (e.g., Washburn & Birdwell, 2013; Washburn et al., 2015; Birdwell & Washburn, 2015). In what is perhaps the only documented use of modified, multi-heating rate (MHR) programmed-pyrolysis methods in tandem with hydrogen NMR, Romero-Sarmiento et al. (2017) used NMR T1-T2 maps and the T1/T2 ratio to distinguish bitumen, oil,

and organic matter in the Vaca Muerta Formation, Argentina. The study correlated TOC obtained from a modified Rock-Eval pyrolysis method (the IFPEN Shale Play® method) to ‘solid echo’ signal intensities calculated by hydrogen NMR relaxometry. Similarly, Piedrahita & Aguilera (2017) proposed a model to estimate the oil saturation index, OSI ($S1 \times 100 / \text{TOC}$) from NMR logs and back-calculate S1 (and OIP) for evaluation of producible oil in shale plays.

A main challenge in hydrogen NMR and geochemical screening studies is to better define the cut-offs (both in T1-T2 mapping and pyrolysis parameters) for producible OIP. In this study, high frequency (22 MHz) NMR relaxometry (HF-NMR) of original samples and their residues obtained following hydrous pyrolysis (HP) tests at different temperatures was used in tandem with multiple-heating rate pyrolysis (MHR) as an alternative approach to investigate producibility estimates from the free/adsorbed hydrocarbons present in source-reservoir intervals. The proposed analytical protocol could provide improved and complementary estimates of the hydrocarbons that are likely to be produced.

Methods

Sample selection

Samples were selected from thermally-immature outcrops (in which the organic matter has not experienced the thermal stress required to enter the threshold for economic hydrocarbon generation) of the Upper Jurassic Kimmeridge Clay Formation in the UK and the Green River Shale Formation in the USA. The sample labeled as APM is a laminated lacustrine oil shale from the informal Mahogany zone of the Eocene Green River Formation. The sample was collected from outcrops at the Anvil Points Mine in the Piceance Basin in western Colorado. The Kimmeridge Clay Formation sample, labeled KC-1, was collected from an outcrop in the type area on the Dorset coast of England. Both samples were collected by M. Lewan and aliquots were provided by the USGS Petroleum Geochemistry Research Laboratory in Denver, CO. For additional information on sample mineralogy and organic matter (kerogen) properties, see Birdwell & Washburn (2015a, b) and Washburn et al. (2017).

Both formations exhibit supreme organic-richness and oil-proneness, as well as contrasting behaviors upon exposure to thermal stress (e.g., Green River Shale not entering the threshold for hydrocarbon generation until vitrinite reflectance values of ~0.90% relative to KC-1 entering the oil window at Ro_{eq} of ~0.60%). These characteristics make an excellent substrate matter for experiments on thermal maturation and hydrocarbon quantification.

Hydrous Pyrolysis

Samples examined herein were subjected to HP experiments. A complete description of the hydrous pyrolysis method with SwageLok™ mini-reactors was recently provided by Hackley & Lewan (2018). Crushed rock chips (2–4 g, 1–3 mm top size) were loaded into SwageLok™ mini-reactor vessels (25–35 mL internal volumes). The rock chips were covered with deionized water and the reactor was placed in a gas chromatograph oven at the selected temperatures (300°C, 330°C, 360°C) for 72 h. Solid rock residue from each experiment was collected for MHR pyrolysis, hydrogen NMR measurements, and organic petrography analysis.

Multi-heating rate pyrolysis (MHR)

About 60 mg of crushed rock chips were analysed using a Rock-Eval 6® Turbo analyzer and 90 mg of crushed samples using a Rock-Eval 7S® analyzer (Vinci Technologies, France). The Rock-Eval 7S® was used because of its sulfur detection capabilities and ability to directly quantify the total organic sulfur (TOS) in whole-rock samples, which is a critical parameter that directly influences thermal conversion of organic matter into hydrocarbons. Our MHR pyrolysis program was similar to the one described by Abrams et al. (2017), with minor modifications. Briefly, the pyrolysis oven program started at a temperature of 80°C and immediately ramped to 200°C at a rate of 50°C/minute and maintained isothermal for 15 minutes. The second ramp was to 250°C with 50°C/minute and maintained isothermal

for 15 minutes. The third ramp was with 50°C/minute to 300°C and maintained isothermal for 15 minutes, followed by a fourth ramp of 50°C/minute to 350°C and maintained isothermal for 15 minutes. Fifth and the last ramp was to 650°C with 25°C/minute.

HF-NMR Relaxometry

Hydrogen-NMR measurements were made at Core Laboratories with a special 22MHz spectrometer from MR Cores, equipped with a 30 mm diameter probe. The NMR probe size allowed for measurements on samples of any shape or form that can be loaded into sample vials. The T2 data were acquired using the Carr-Purcell-MG (CPMG) sequence with an echo time spacing of 0.07 ms. The T1 data were acquired using an inversion-recovery sequence. The T1-T2 correlation data were acquired using a pulse sequence of combining T1 and T2 data acquisitions, where the amplitude was determined from the first echo, then processed using an Optimized Truncated Singular Value Decomposition (OTSVD) inversion method to obtain the 2D T1-T2 map. All analysis were performed at room temperature of 22°C.

Organic petrography

Detailed sample preparation and analysis procedures are described in the ASTM D7708 standard test method (2014) and by Hackley et al. (2015). Briefly, whole-rock (WR) samples were crushed to 20 mesh (850 µm or 0.85 mm size) particles. Ground particles were placed in specially-designed plastic molds (1.5 in. or 3.8 cm in diameter) where they were mixed with epoxy resin and hardener (ratio of 2:1) to harden overnight. Sample grinding and polishing was performed using Buehler EcoMet/AutoMet 250 automated polishing equipment. Reflectance in oil (Ro) and fluorescence analyses were performed using a Carl Zeiss Axio Imager A2m microscope, equipped with a white halogen light source (from a 12 V/100 W halogen lamp with stabilized current) and a UV light (fluorescence) source (from a high pressure 100 W mercury lamp with stabilized current). A sapphire standard (%Ro-0.595) was used for the reflectance analysis. The latter allows for the observation of the fluorescence colors of oil-prone OM (alginite, sporinite, dinoflagellates, etc.) when in the oil window.

Argon Ion Milled-Scanning Electron Microscopy (AIM-SEM)

A representative portion of the sample was polished with a Leica EM TIC3x argon ion mill in order to create a flat, artifact-free surface suitable for analysis with backscattered electrons. To document the characteristics of the sample backscattered electron, secondary electron, and/or backscattered electron images with superimposed secondary electron images were taken using a FEI Quanta FEG250 Scanning Electron Microscope operating at relatively low beam energy (10kV-15kV), in a high pressure (~60 Pa or 0.09 psi) vacuum chamber environment. Using relatively low beam-energy and high pressure chamber environment mode helps to avoid the evaporation of any volatiles that may be associated with the organic matter. A benefit of backscattered electron imaging is that it is easier to identify specific mineral grains; this is because the various 'grey-levels' of the image are a function of the density of the minerals. The higher density minerals are white (e.g., pyrite) and the lowest density grains (e.g., organic matter) are black.

Results and Discussion

Organic petrography

Green River shale (APM)

Native solid bitumen in the original APM sample occurs as thin (5-10 µm) lamellae parallel to bedding (Figure 1a). Low-gray reflecting organic matter (OM) resembling vitrinite (huminites per ICCP, 1998) is less abundant (Figure 1b). The original sample contains abundant Type I kerogen, occurring primarily as strongly fluorescent telalginite, liptodetrinite, and weakly fluorescing amorphous organic matrix (AOM) (Figure 1c-d). Both the fluorescence colors and the measured Ro (%Ro of huminites is 0.25) confirm the low maturity level of the organic matter in this sample (Mukhopadhyay, 1994).

Kimmeridge Clay Formation (KC-1)

The original KC-1 sample contains abundant grey-color bitumen matrix (Figure 2a; %Ro is ~0.20) and AOM with a reddish tint (Figure 2a). Dispersed terrestrial inertinite (fusinite) and inertinized telalginite (Figure 2b) are common but vitrinite is present in trace amounts. Some micrinite having granular texture is present as a result of the early conversion of the AOM. The golden-yellow to greenish-yellow fluorescing colors of telalginite (Figure 2c-d) confirm the lower level of thermal stressed experienced by the organic matter in this sample (Mukhopadhyay, 1994).

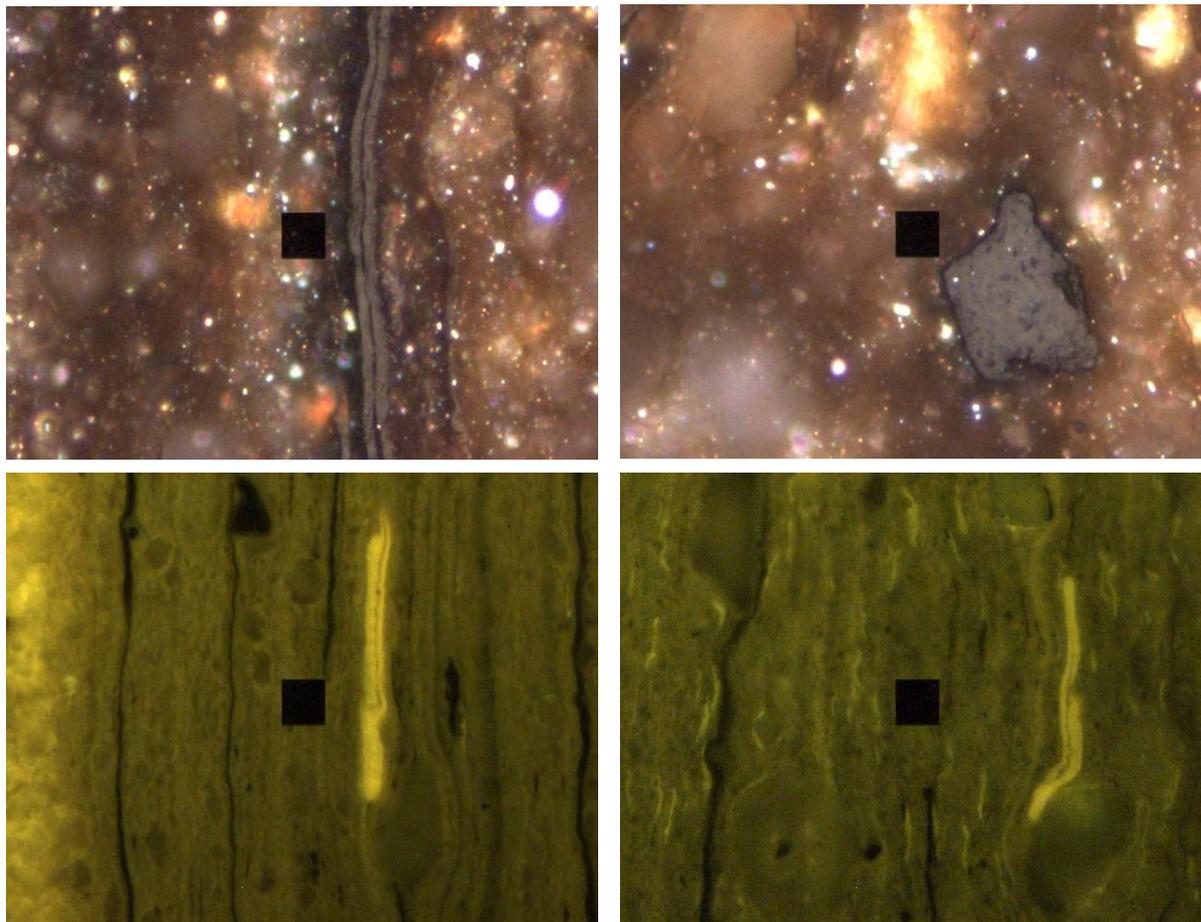


Figure 1 (a-d). Reflected white and UV light microphotographs of the immature Green River sample APM. White light photos show thin lamellae of native bitumen (5 μm thick, top left photo-a) as well as a huminite particle (%Ro=0.25; top right photo-b). UV light photos (bottom photos c-d) reveal the presence of telalginite and liptodetrinite, embedded in a fluorescing amorphous matrix. The black square is used here as a scale, with each side is 10 μm .

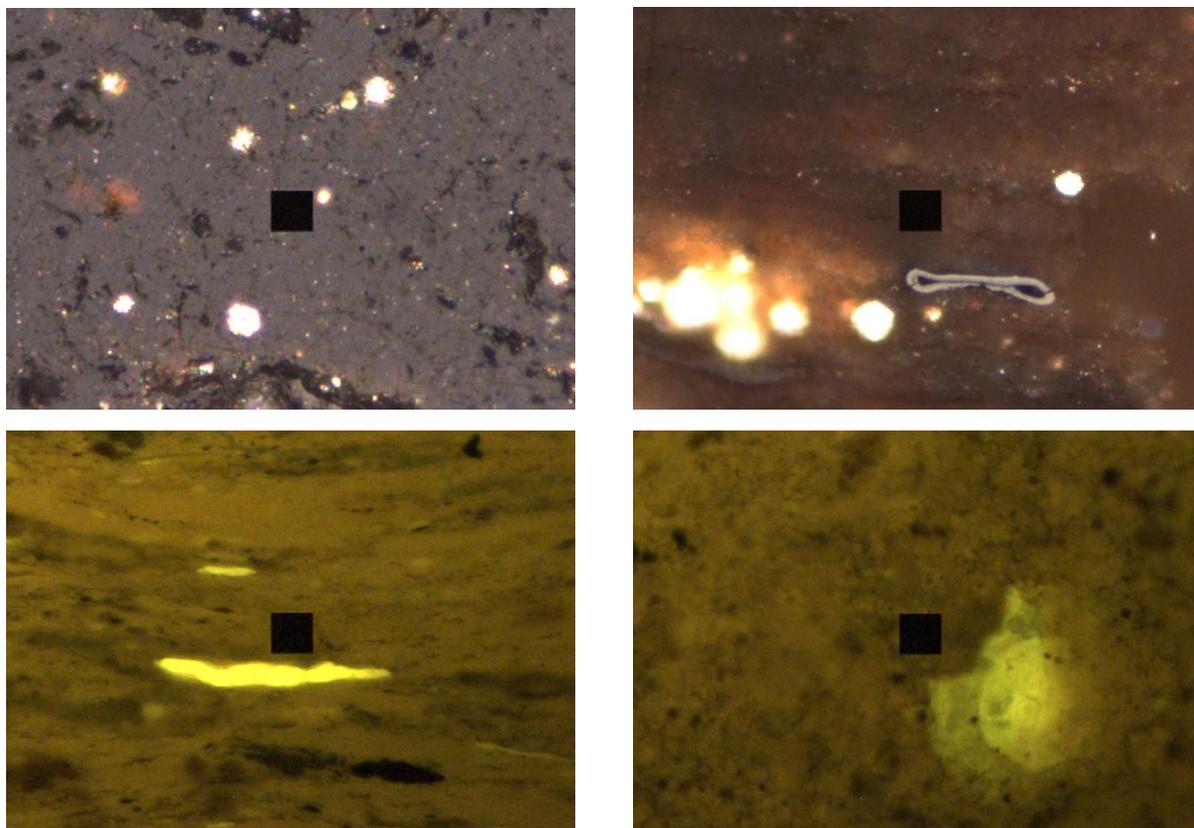


Figure 2 (a-d). Reflected white and UV light microphotographs of the immature Kimmeridge Clay sample KC-1. White light photos show massive native bitumen matrix with grey color (top left photo-a) as well as inertinite particles (top right photo-b). UV light photos (bottom photos) reveal the presence of golden-yellow fluorescing telalginite (lower left-c), another type of greenish-yellow telalginite (parallel to bedding, lower right-d), and weakly-fluorescing amorphous organic matrix. The black square is used here as a scale, with each side μm .

NMR and MHR

The total quantity of hydrocarbons detected from each analysis is listed in Table 1. Figure 3a shows the pyrograms of two analyses performed on the same sample (KC-360, from the HP experiment performed at 360°C) using the Rock-Eval 7S[®] instrument. The pyrogram in the upper panel comes from the analysis performed using the Basic/Bulk-Rock pyrolysis method (initial isotherm at 300°C for 3 minutes, followed by a ramp of $25^{\circ}\text{C}/\text{min}$ to 650°C). The lower panel comes from the analysis performed using the modified pyrolysis method (MHR) as described in the Methods section. From the values shown in Figure 3a and Table 1, it is clear that the Basic/Bulk-Rock method, commonly utilized in most play assessment projects, is not the adequate analytical option when evaluating OIP in LRU plays because the Basic-Bulk-Rock pyrolysis method underestimated the S1 compared to the MHR pyrolysis method (68.4 vs 117.1 mg/g), regardless of the instrument used (Romero-Sarmiento et al., 2017; Carvajal-Ortiz & Gentzis, 2018). MHR pyrolysis results separate free/adsorbed hydrocarbons present in LRU intervals into four (4) regions (L1 through L4; Figure 3a) corresponding to each of the isothermal steps of the MHR analysis. Region L1 (distilled at 200°C) was interpreted by Carvajal-Ortiz et al. (2018) to contain the lowest boiling-point hydrocarbons, as confirmed by Thermal Extraction-Gas Chromatography (low boiling-point *n*-alkanes and aromatics), similar to the findings of Abrams et al. (2017). Thus, L1 represents hydrocarbons in intervals with the highest likelihood of being produced from the chemical make-up point of view. Increasing molecular weight (heavier hydrocarbons and non-hydrocarbons) dominate the remaining free/adsorbed hydrocarbon regions in order of increasing distillation temperature ($\text{L2} < \text{L3} < \text{L4}$), thus reducing their likelihood of being produced. Similarly, the HF-NMR T1-T2 maps (Figure 3b) show the

evolution of the different hydrocarbon populations: more relaxed hydrocarbons interpreted here to represent high boiling-point hydrocarbons, Region 2; heavier hydrocarbons or hydrocarbons in smaller pores, Regions 3 & 4; more rigid, viscous hydrocarbons, Region 5 (after Washburn & Birdwell, 2013; Khatibi et al., 2019, and references therein).

Table 1. Pyrolysis and NMR results for all the 8 sample aliquots analyzed. All values are in mg/g. S2-ext= S2 of extracted sample. The number in the sample ID corresponds to the hydrous pyrolysis temperature experimented by each sample (in °C) prior to NMR and MHR pyrolysis analysis.

Sample ID	Method	L1	L2	L3	L4	OIL (S1, Σ L1-L4, or Σ NMR 2-5)	S2	S2-Ext.
KC-1	BASIC					3.34	262.32	212.71
	MHR	2.37	3.21	5.88	29.74	41.2	228.88	
	NMR					32.45	235.1	
KC-300	BASIC					39.71	248.24	36.01
	MHR	26.1	20.08	20.69	23.19	90.06	198.49	
	NMR					41.73	190.2	
KC-330	BASIC					48.01	175.86	21.32
	MHR	32.52	31.72	29.32	27.48	121.04	109.51	
	NMR					26.8	141.9	
KC-360	BASIC					68.43	87.52	15.32
	MHR	47.88	33.35	21.91	13.97	117.11	34.67	
	NMR					92.58	59	
APM	BASIC					5.42	192.82	180.72
	MHR	2.93	2.43	3.59	8.55	17.5	182.94	
	NMR					16.32	101	
APM-300	BASIC					9.29	159.5	110
	MHR	5.46	6.67	7.33	8.17	27.63	144.14	
	NMR					31.89	119	
APM-330	BASIC					16.38	121.62	26.14
	MHR	8.56	11.49	11.84	11.88	43.77	99.73	
	NMR					49.7	55.1	
APM-360	BASIC					12.5	25.31	6.7
	MHR	6.84	5.07	4.25	4.05	20.21	16.45	
	NMR					32.26	24.9	

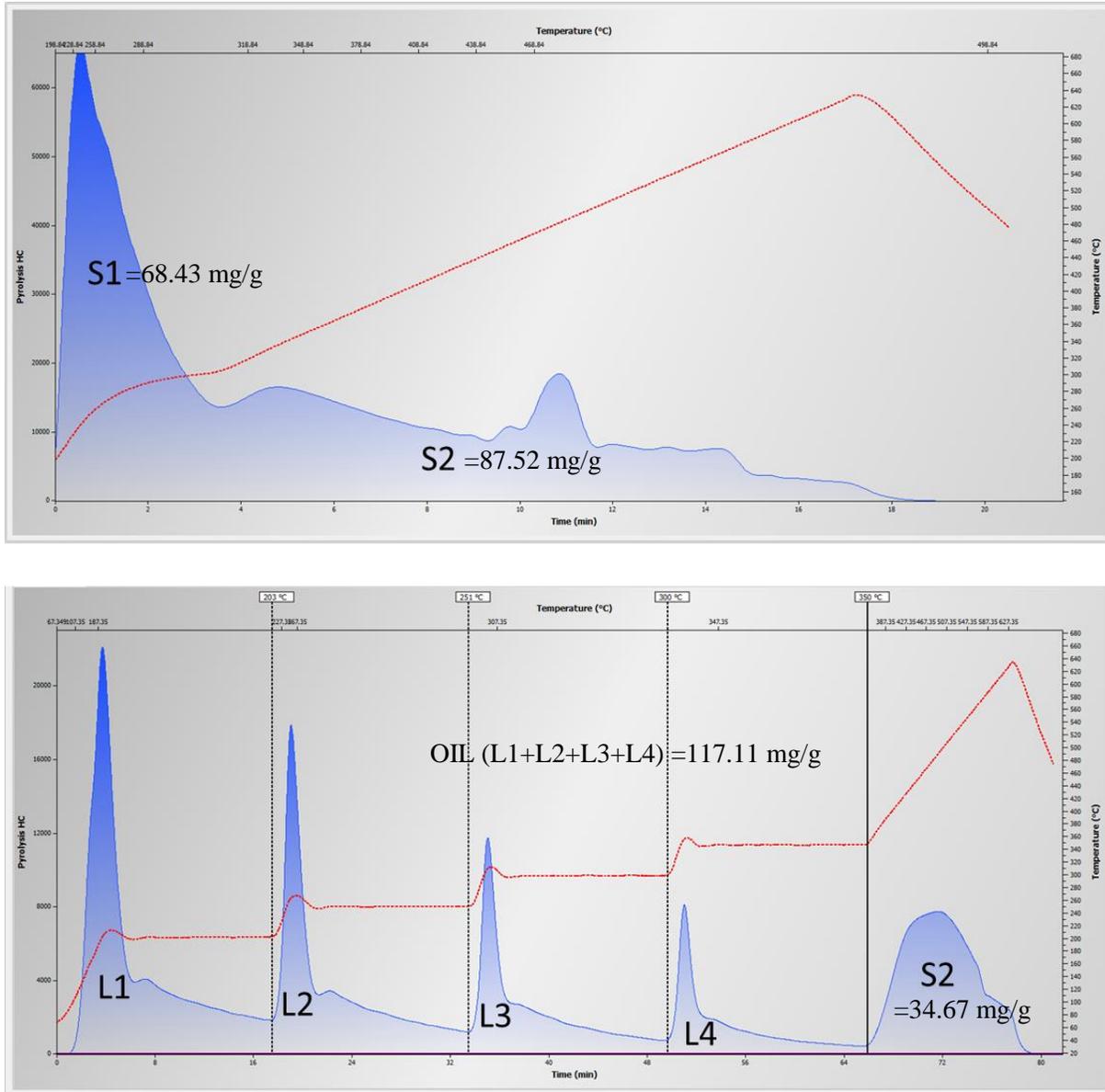
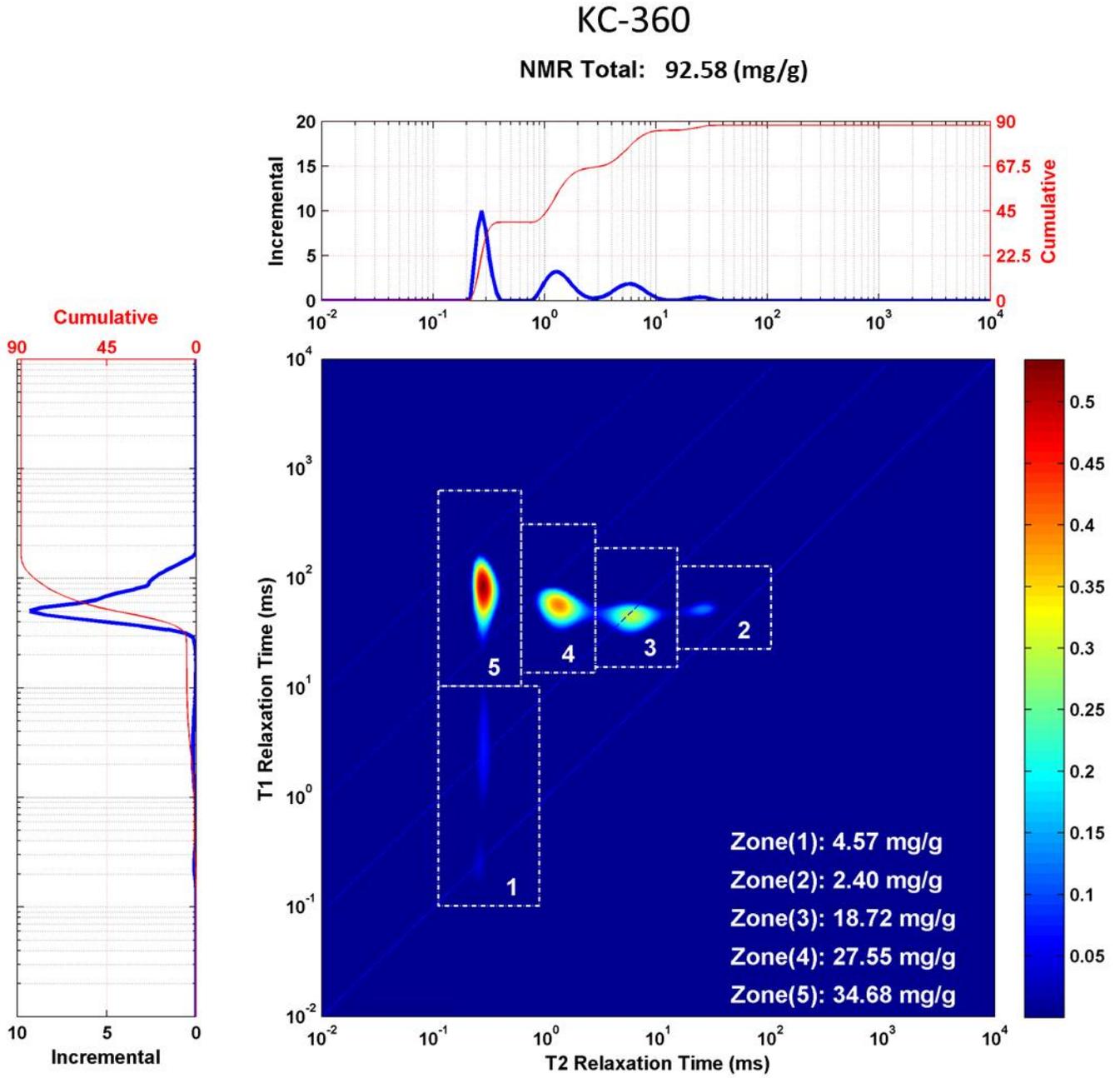


Figure 3a. Rock-Eval 7S[®] Pyrograms of the KC-360 sample using the Basic/Bulk-Rock pyrolysis program (upper panel) and the Multi-Heating Rate (MHR) program (lower panel). S1= free/adsorbed hydrocarbons; S2= reactive kerogen or remaining hydrocarbon potential; L1-L4, free/adsorbed hydrocarbon fractions from MHR.



Map Version 1.0

Figure 4b. NMR T1-T2 relaxation map of the same KC-360 sample shown in Figure 3a. Total NMR OIL is shown. Zone 1= water signals; Zones 1 through 5 are relaxed hydrogen likely from hydrocarbons. Relaxation time decreases to the left. Zone 2= more relaxed, Zone 5= more rigid. Rigid solid signal was removed from the map. Color bar values are in mg Hydrogen per g. Color scale is a quantitative expression of the NMR data, in mg Hydrogen per g. Red color indicates higher values and blue lower values.

The fraction “OIL” listed in Table 1 is thought to contain the total amount of OIP (in mg/g) as detected by modified pyrolysis methods, such as the Reservoir Pyrolysis and Shale Play methods (Trabelsi et al., 1994; Romero-Sarmiento et al., 2015), and the MHR method ($OIL=L1+L2+L3+L4$) (Carvajal-Ortiz et al., 2018). The OIL quantities from MHR pyrolysis are compared in Table 1 to the total amount of more relaxed hydrocarbon fluids (zones having longer T2 relaxation time) in the T1-T2 map from NMR and to the S1 quantities from Basic/Bulk-Rock pyrolysis analysis. Figure 4 shows the bar graphs of OIL quantities from each of the analysis performed using the three methods. Figure 4 also shows the quantities of reactive kerogen (S2) detected by the three methods. The comparison amongst the samples are also shown in the same figure.

The Green River Shale samples (APM samples, lower-left panel) show a good agreement between the quantities of OIL from NMR and MHR pyrolysis (with differences being between 1-12 mg/g) but they also show some discrepancies between the quantities detected for reactive kerogen (S2, lower-right panel) with differences sometimes as high as 90 mg/g (sample APM, the immature sample). Conversely, the Kimmeridge Clay samples (KC samples, upper panels) show some discrepancies between the quantities of OIL from NMR and MHR pyrolysis (with differences being between 20-97 mg/g) but they also show a good agreement between the quantities detected for reactive kerogen (S2, upper-right panel) with differences as low as 7-8 mg/g and as high as 32 mg/g. It is possible that these discrepancies, for the same type of organic matter at different maturities and between types of organic matter, may be related to the composition of the hydrocarbon fluid generated from the different types of reactive kerogen (Jin et al., 2012) and the type of porosity developed upon maturity. This is a matter of ongoing investigation.

Of the eight samples analyzed, the Kimmeridge Clay sample from the HP experiment at 330°C (KC-330) shows the highest discrepancy between MHR pyrolysis results and both Basic/Bulk-Rock pyrolysis and NMR values (for both OIL and Reactive kerogen). Figure 5 shows the Rock-Eval 7S[®] pyrograms of both pyrolysis methods, Basic/Bulk-Rock and MHR, and the NMR T1-T2 map for sample KC-330. The NMR signal, after removal of the rigid solid signal, is only able to clearly differentiate between two hydrocarbon zones, Zones 2 & 3, with a total OIL =24.63 mg/g. This value is half of that measured using the Basic/Bulk-Rock pyrolysis method ($S1=48.01$ mg/g) and almost six-times lower than OIL from MHR pyrolysis (121.04 mg/g). Pore size (as seen in the AIM-SEM photos in Figure 6) does not seem to be an obvious cause of this discrepancy. Figure 6 shows the same T1-T2 map and the pyrogram from MHR pyrolysis shown in Figure 5, but also includes two AIM-SEM images of the original sample (KC-1) and the KC-330 sample. The difference in pore availability and sizes between the samples is striking: sample KC-1 shows virtually no porosity present while, after maturing through hydrous pyrolysis for 72 hrs @ 330°C, pore space is created throughout the sample, especially in places where organic matter appeared to occupy space in the original KC-1 sample.

In the case of the KC-1 samples, it is possible that the fluid is more viscous than that in the APM samples. Fluid composition affected the NMR measurements, leading to an underestimation of the OIL content. As mentioned earlier in this discussion, the L1 fraction from MHR pyrolysis has been interpreted to contain the lowest boiling-point hydrocarbons (Abrams et al., 2017; Carvajal-Ortiz et al., 2018) and is the fraction with the highest likelihood of being produced. If the amount of liquid hydrocarbons detected in the L1 portion of the MHR pyrolysis is compared with zones 2 and 3 from NMR, the difference for sample KC-330 decreases to <6 mg/g. This comparison between L1 from MHR pyrolysis and the more relaxed liquid hydrocarbon fractions from NMR (Zones 2, 3 and 4, if present) is shown for all the KC samples in the bar graphs in Figure 7. This figure shows that, for the Kimmeridge Clay samples, HF-NMR at room temperature (22°C) tends to underestimate the amount of producible hydrocarbons. It is only able to differentiate the very lowest boiling-point hydrocarbons from very rigid solids (S2), leaving behind undifferentiated - but potentially producible - liquid hydrocarbons. Such hydrocarbons are likely trapped in very small pores, although this is not likely the case in these KC-1 samples. Alternatively, these liquid hydrocarbons may have a particular chemical make-up and fluid properties masking them from NMR

detection at room temperature, thus require NMR analysis at higher temperatures to be detected. The latter hypothesis is a matter of ongoing investigation.

This underestimation of producible liquid hydrocarbons seen in the matured Kimmeridge Clay samples could also be related to the temperature at which NMR measurements were taken (room temperature). Since NMR molecular relaxation is heavily impacted by viscosity of the fluid, pore size, and surface affinity (all factors present in LRU plays), producible oil present in very small pores (probably not seen under AIM-SEM in Figure 6) could be mistaken as rigid to semi-rigid solid by NMR because it is viscous for NMR standards or has a chemical make-up that masks it under room temperature NMR measurements.

This variation in temperature during NMR measurements was explored by both Romero-Sarmiento et al. (2017) and Carvajal-Ortiz et al. (2018). In particular, Carvajal-Ortiz et al. (2018) analyzed samples from the Wolfcamp, Woodford, and Meramec formations at six different temperatures: 22°C, 45°C, 50°C, 55°C, 60°C, and 65°C. They concluded that, for naturally generated fluids found in the aforementioned formations, about 60-80% of the hydrocarbons in the less relaxed zones of the T1-T2 maps for experiments held at 65°C (equivalent to Zones 3 & 4 in APM and KC samples presented here) have a higher likelihood of being produced than previously thought based on HF-NMR measurements held at room temperature (22°C). Ongoing experiments at different temperatures, similar to those in Carvajal-Ortiz et al. (2018) above, will decipher whether experimental conditions play a significant role in Kimmeridge Clay analysis, as they did for the Woodford and Meramec analysis and will shed some light on the causes of such a large discrepancy in the amount of producible oil detected by NMR and MHR pyrolysis methods.

Conclusions

- Current resource assessments using Basic/Bulk-Rock pyrolysis on as-received material and on solvent-extracted material tend to either underestimate or overestimate the OIP present in LRU plays. The need for modified pyrolysis methods, such as MHR, combined with HF-NMR, is required for a complete characterization of true OIP.
- HF-NMR Zones 2 +3 and MHR pyrolysis (L1 fraction) are in good agreement in terms of HC quantities, when HF-NMR measurements are taken at room temperature (22°C). L1 contains the lowest-boiling-point hydrocarbon fraction, which is easily producible from the chemical make-up point of view, but is not the only producible fraction found in LRU plays.
- HF-NMR at room temperature appears to underestimate the amount of OIP for certain types of organic-rich LRU resources. Therefore, NMR analysis at higher temperatures is required to determine whether any of the less relaxed hydrocarbons in Zones 3 & 4 could be mobilized and produced, thus providing a better correlation between HF-NMR and MHR pyrolysis data.

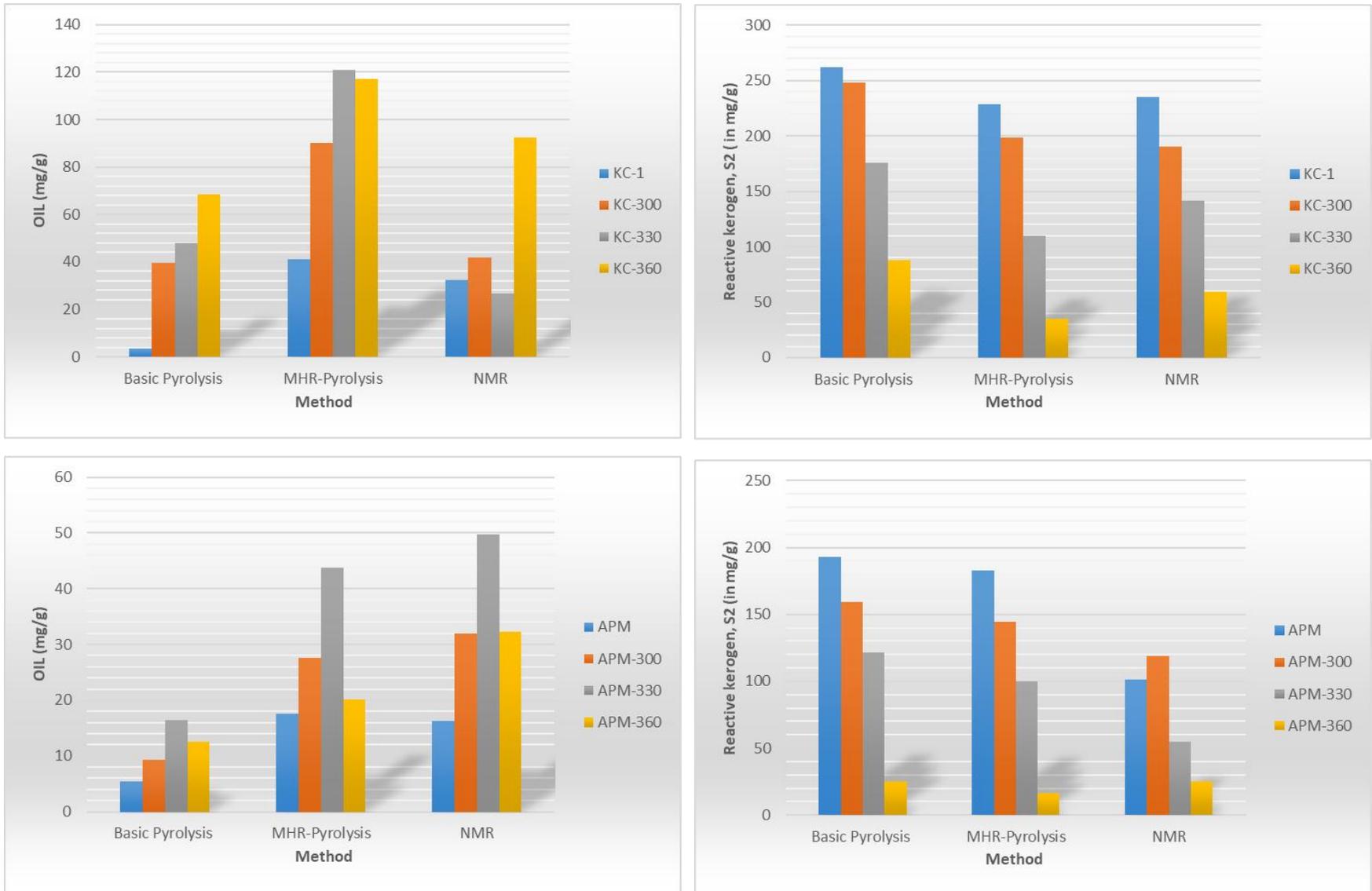


Figure 5. Bar graphs of OIL yields and reactive kerogen (S2) quantified with the three different techniques here discussed for both the Green River (APM samples, lower panel) and Kimmeridge Clay samples (KC samples, upper panel).

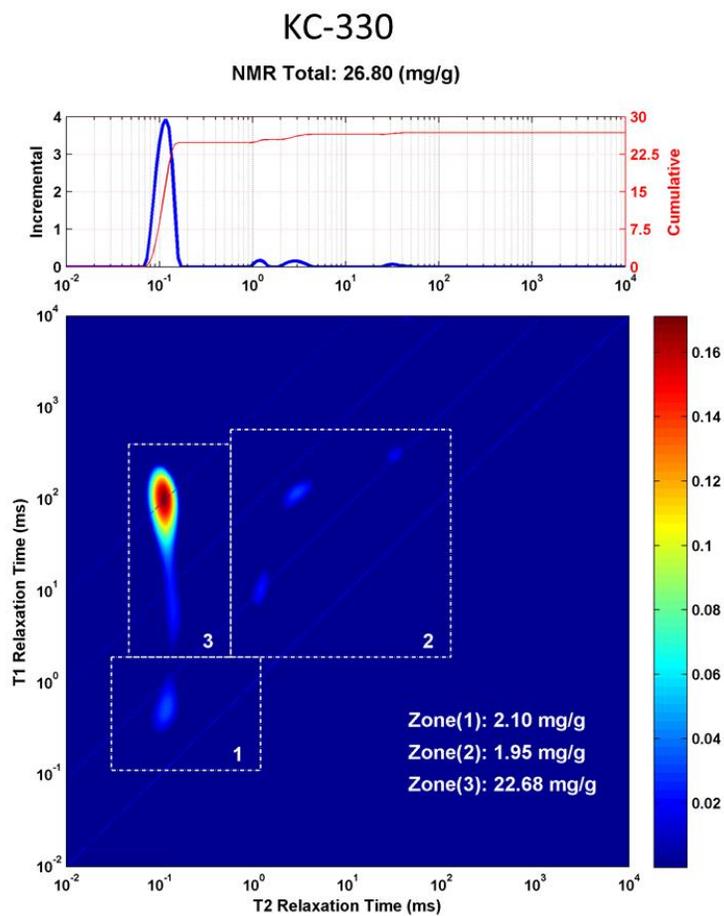
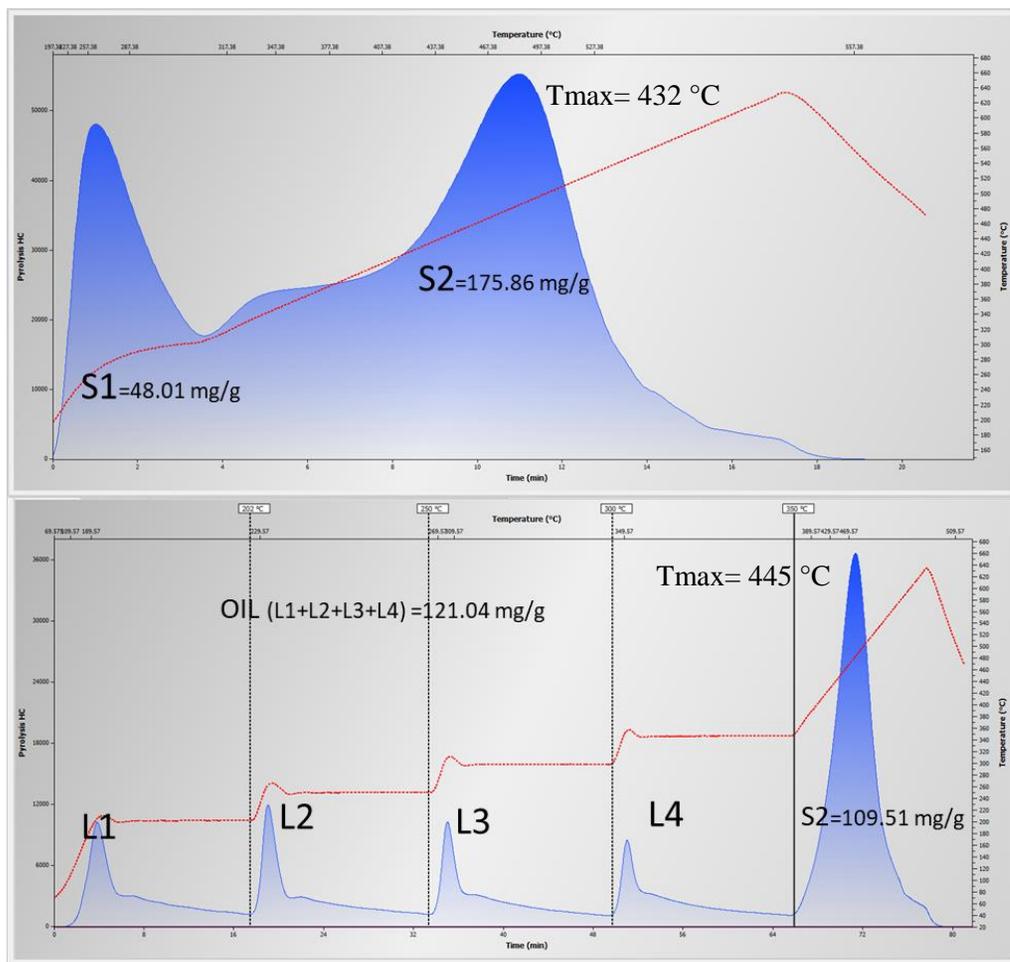


Figure 5. Pyrograms from Basic/Bulk-Rock and MHR pyrolysis and T1-T2 maps from NMR of the Kimmeridge Clay sample from the $330\text{ }^{\circ}\text{C}$ hydrous pyrolysis experiment (KC-330). Quantities detected are shown.

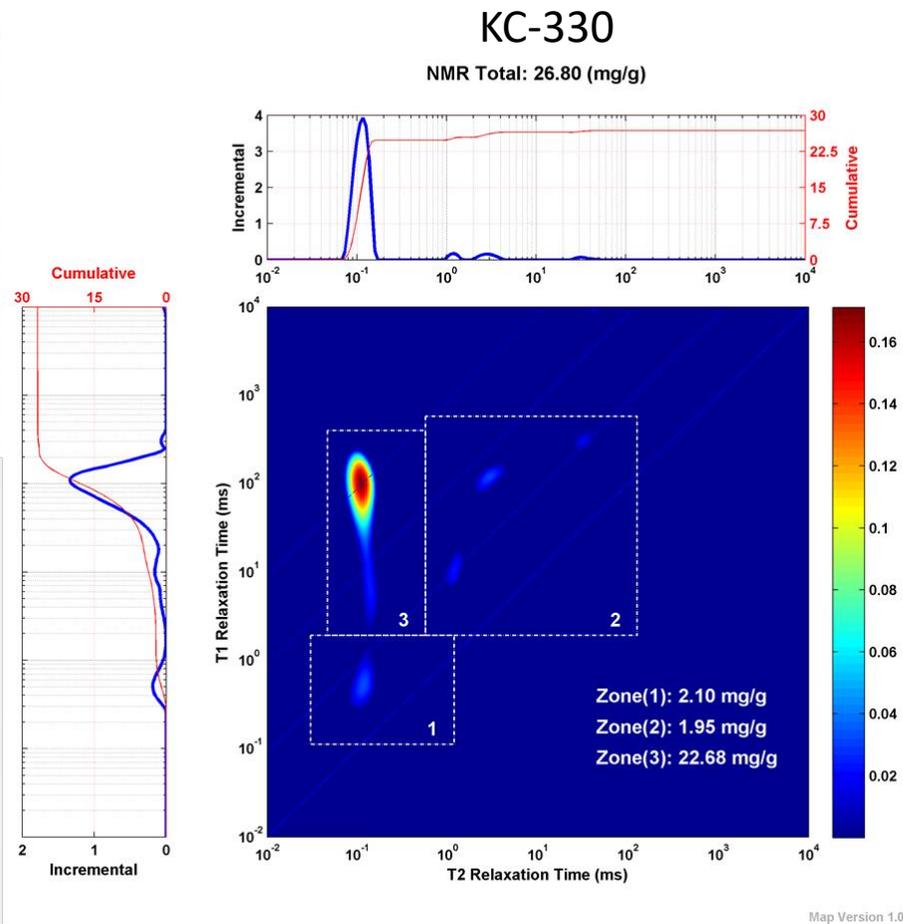
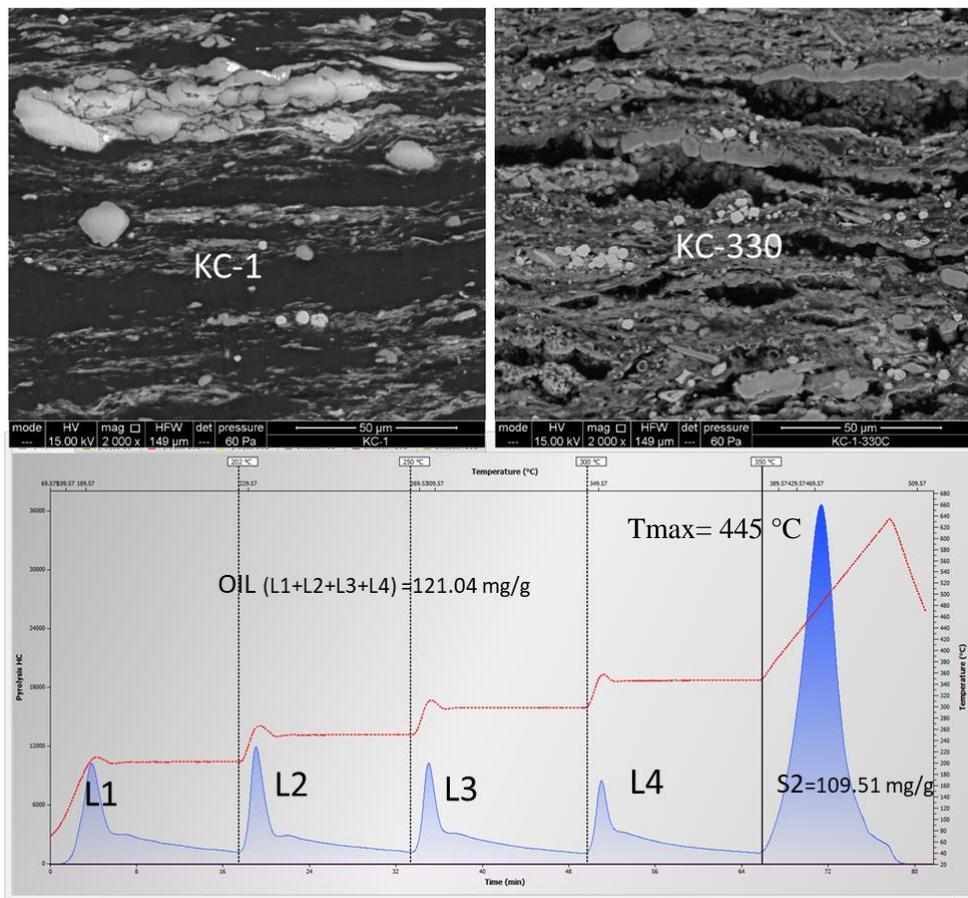


Figure 6. Pyrogram from MHR pyrolysis, AIM-SEM photos (for both KC-1 and KC-330), and T1/T2 maps from NMR of the Kimmeridge Clay sample from the 330°C hydrous pyrolysis experiment (KC-330). AIM-SEM images are derived from mixed secondary electron (SE) and Back Scattered (BS) ones.

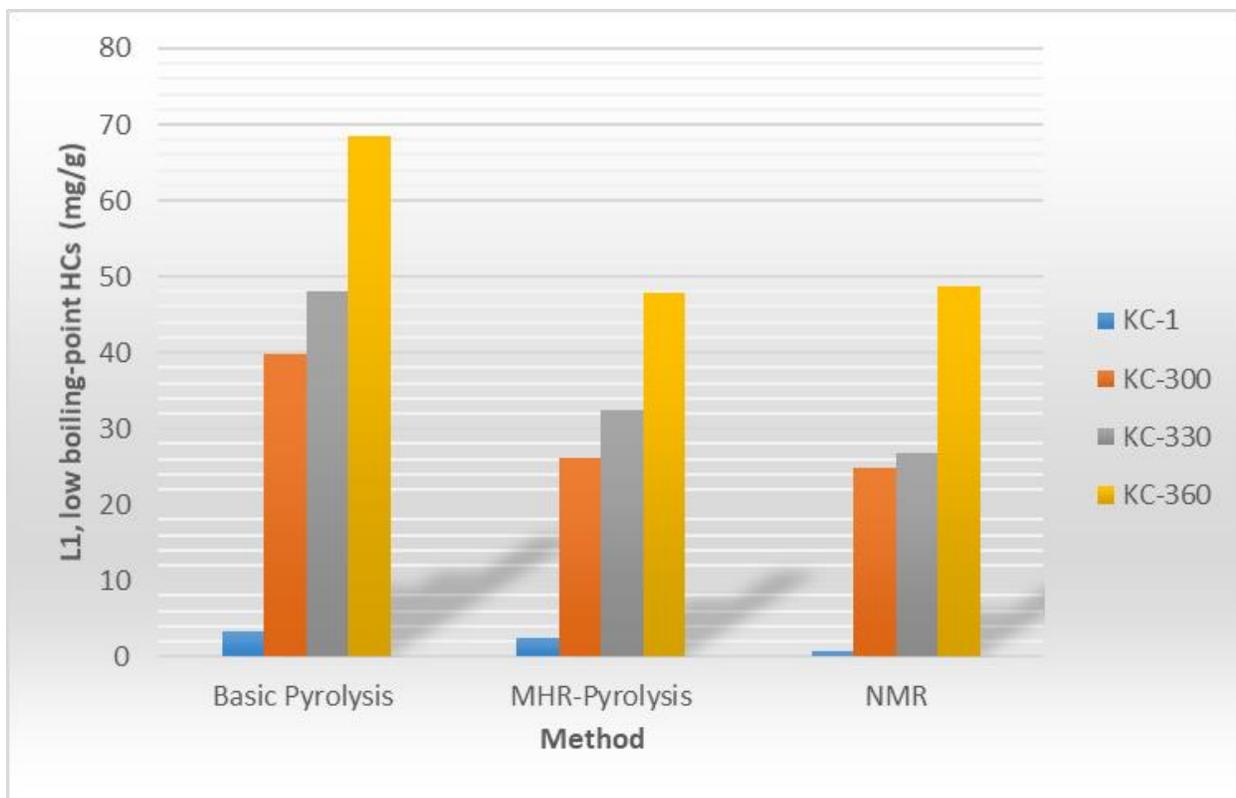


Figure 7. Kimmeridge Clay samples bar graphs of the lowest boiling-point saturate and aromatic hydrocarbons L1 in MHR, compared to total hydrocarbons detected from the Basic/Bulk-Rock pyrolysis method, and with the more T2-relaxed fractions from NMR. The more relaxed NMR fractions show a better agreement with L1 values than with the OIL values for analysis from the KC-330 and KC-360 samples. Basic/Bulk-Rock pyrolysis continues to differ from the NMR and MHR estimates.

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