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Some predicted effects of minerals on the generation of petroleum in nature

Shengyu Yang and Brian Horsfield

GFZ German Research Centre for Geosciences, Telegrafenberg, 14473 Potsdam, Germany

Abstract

The presence of some minerals can strongly influence the composition of laboratory pyrolysates. The question is whether similar effects may also occur in nature, thereby influencing gas-oil ratio and other bulk compositional characteristics. A series of experiments have been conducted at varying heating rates to examine this issue. Three source rocks which vary significantly in mineralogy (a quartz-rich, a calcite-rich and a clay-rich sample), namely the Alum Shale, Bowland Shale, and Toolebuc Shale, respectively, were tested by Rock-Eval pyrolysis, open system pyrolysis gas chromatography and bulk kinetics parameters in order to check for the existence or otherwise of mineral matrix effects (MME). Kerogen and whole-rock samples were then pyrolyzed at 3 heating rates using closed system (MSSV) pyrolysis to examine the heating rate dependency on hydrocarbon aromaticity, gas-oil ratio and total yield. The solvent extract of one Bowland Shale sample was used as a reference material for the natural system when extrapolating the results from laboratory experiments to nature. A comparison of the natural reference sample with kerogen- and whole-rock pyrolysates using Fourier Transform - Ion Cyclotron Resonance Mass Spectrometry was also made, providing insights into NSO compounds in laboratory and natural environments. The MME in Alum Shale, Toolebuc Oil Shale and Bowland Shale has negligible, weak and strong influences on Rock-Eval, PyGC and bulk kinetics results, respectively. MME on the hydrocarbon aromaticity total yield are heating rate dependent, with decreasing heating rates, the effect is weakened. Bowland kerogen pyrolysate resembles natural products more in certain NSO class ratios compared with its whole-rock counterpart. The MME is speculated to be induced by the fast heating rates and higher temperatures in the laboratory, and it is concluded that the effects do not occur in the geological maturation process.

1. Introduction

Petroleum consists of an exceedingly complex mixture of hydrocarbons and non-hydrocarbons, extending from methane to macromolecular aggregates. The relative proportions of these components are quite variable and depend initially on the nature of the kerogen in the parent source rock and its level of maturity at the time of expulsion, and subsequently upon the pressure and temperature conditions of the source-carrier-reservoir system during expulsion, migration and accumulation. While the role played by diagenetic minerals on reservoir quality is well known, for example the formation of clays from feldspars or the conversion of smectite to illite^{1,2}, it remains unclear as to whether bulk petroleum composition is strongly influenced by retention and/or catalytic processes in source rocks. It has been suggested that clay minerals can be used in the search for oil due to its importance in petroleum generation and expulsion³. For instance, clay can effect isomerization, disproportion of hydrogen and polymerization of unsaturated hydrocarbons^{4,5}, and might,

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3 therefore, be responsible for the presence of aromatics and the absence of olefins in petroleum^{6,7}. Mango⁸
4 proposed that the transition metals, captured from sedimentary waters by chlorophyll, are the catalytic agents
5 that convert *n*-alkane biolipids into the rearranged light hydrocarbons in petroleum. At the molecular level,
6 diasterane/sterane ratios for biomarkers are commonly related to clay content^{9,10}, because clays catalyse the
7 formation of diasterane precursors. The high heterogeneity of both organic matter and minerals in gas shales
8 argues that organic-inorganic interactions may be quite different depending on the depositional environment¹¹.
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12 The purported importance of organic-inorganic interactions during petroleum formation in nature stems
13 largely from pyrolysis experiments. For example, Jurg and Eisma¹² produced hydrocarbons by decarboxylating
14 a fatty acid mixed with kaolinite in the presence and absence of water; Shimoyama and Johns¹³ produced the
15 same using montmorillonite. Beta cleavage produced a hydrocarbon with two carbon atom atoms less than the
16 parent fatty acid when pyrolysis was conducted in the presence of calcium carbonate¹⁴. So called Mineral
17 Matrix Effects (MME)¹⁵ can bring about changes in the gas-oil ratio, gas wetness and fluid aromaticity
18 pyrolysates, as reported from laboratory open- and closed-system experiments including Rock-Eval^{16,17},
19 pyrolysis-GC¹⁸, pyrolysis-FT IR¹⁹, pyrolysis-GC/MS²⁰, bulk kinetics determination^{21,22}, PhaseKinetics modelling
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For clay minerals, two main mechanisms are active: (1) due to the high surface area²⁵, they tend to adsorb heavy compounds generated in pyrolysis, hence influence the pyrolysis maturity indicator (T_{max}), composition and quantity of the pyrolysate²⁶, as well as the kinetics of the reaction, (2) a selective catalytic feature of the clay minerals can change the gas-oil ratio (GOR), aromaticity, oxygen index (OI) and other compositional features of the products^{27,28}. It has to be pointed out that not every source rock in pyrolysis experiments necessarily has to suffer from the MME. Horsfield and Douglas¹⁸, Horsfield, Dembicki and Ho²⁶ and Katz¹⁶ concluded that MME varies according to the TOC content and mineralogy of the samples under investigation. A very high TOC (>6%) or low clay content can decrease even avoid the MME²⁹. Tannenbaum and Kaplan³⁰, Pan, et al.³¹ and Lewan, Dolan and Curtis²⁴ emphasized that the presence of liquid water in the pyrolysis system could significantly attenuate the activity of the clay catalysing function, although Eglinton, et al.³² and Behar, et al.³³ noted that the function of water in pyrolysis is limited.

One of the most significant differences between laboratory pyrolysis and geological maturation lies in the heating rate. Geological heating rates normally fall in the range 10^{-10} to 10^{-12} K/min, while a typical laboratory pyrolysis heating rate is not slower than 10^{-1} K/min. Having said that, the slowest experimental heating rate is 300°C over 6-years, or 10^{-5} K/min³⁴. Retort yield from Green River Shale is reported to decrease at lower heating rates³⁵. From a petroleum generating kinetics perspective, during non-isothermal pyrolysis of immature oil shale and coal, the onset and T_{max} of organic transformation reactions are shifted to higher temperatures with increasing rate of heating^{36,37}. For the MSSV pyrolysis of Duvernay Shale, aromaticity and the unresolvable GC "hump" decrease with decreasing heating rates³⁸. Similarly, pyrolysates are always richer in polar and aromatic compounds than petroleum³⁹ and are higher in gas wetness⁴⁰ compared with natural products irrespective of the type of pyrolysis being employed. Karabakan and Yürüm⁴¹ reported the influence of heating rate to MME, but instead of using kinetic derived temperatures they simply heated samples to certain fixed temperatures under different heating rates which is less meaningful in a geological sense.

Because, for example, when a marine sample was heated to 400°C with a heating rate of 0.1K/min it could reach a transformation ratio (TR) of 100%, but the sample which was heated under 10K/min could only reach about 50% TR till 400°C. The comparison of these pyrolysates does not reflect the heating rate dependency in pyrolysis; it is mainly controlled by maturity instead. Only the products that were generated at the same TR are directly comparable.

It would represent a significant step forward if MME in pyrolysis experiments could be extrapolated to geological systems by consideration of heating rate as a parameter. In this paper, we evaluate the MME on three types of source rocks which have significantly different mineralogies (a quartz-rich, a calcite-rich and a clay-rich sample) using Rock-Eval, open pyrolysis and bulk kinetic modelling. Two types of samples with strong MME were applied to a closed-system (MSSV) pyrolysis to investigate the heating rate dependency of MME on aromaticity, GOR and bulk generation amounts. The projected changes in MME as a function of heating rate were firstly extrapolated from laboratory to nature, and the predictions compared with the results of thermovaporisation of a natural bitumen sample. The ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrum (FT-ICR MS) technique, which has been applied to identify acids and heteroatom compounds in crude oil⁴², petroleum distillates⁴³, asphaltene⁴⁴, oil sand⁴⁵ and coal extracts⁴⁶, etc., was first induced into MME research here to compare the major compound classes present in whole-rock and kerogen pyrolysates with those in natural bitumen to elucidate whether MME occurs in nature.

2. Samples and Analytical Methods

2.1 Samples

Three immature whole-rock samples from the Alum Shale, Toolebuc Oil Shale and Bowland Shale, as well as their kerogen concentrates were studied in this research using pyrolysis (Table 1). The solvent extract of one mature Bowland Shale was used as a reference.

Table 1. Generalized information and Rock-Eval & TOC data of the samples tested in the research.

Sample Name	Location	Age	Mineralogy	Sample type	Tmax (°C)	HI (mg HC/g TOC)	OI (mg CO ₂ /g TOC)	TOC (%)
Alum Shale	Middle Sweden	Early Ordovician	Quartz-rich (80%)	whole-rock	418	357	4	16.7
				kerogen	420	356	6	41.1
Toolebuc Oil Shale	Northeastern Australia	Early Cretaceous	Calcite-rich (+45%)	whole-rock	417	457	24	13.1
				kerogen	421	426	31	52.5
Bowland Shale	Northern England	Late Carboniferous	Clay-rich (+50%)	whole-rock	431	194	10	3.17
				kerogen	426	302	4	24.2

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3 The Alum Shale sample taken from a core drilled in Central Sweden is of Early Ordovician age. This marine
4 shale was deposited in an inner shelf facies and is characterized by an enrichment of uranium (>200ppm) which
5 was diffused from seawater across the sediment/water interface ⁴⁷. Quartz (80%) is a major mineralogical
6 component, together with K-feldspar (18%) ⁴⁸.

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10 As one of the most important oil shale plays in Australia, the marine Toolebuc Formation of Early
11 Cretaceous age underlies about 484,000 km² of the Eromanga and Carpenteria Basins in Queensland and
12 adjacent states ⁴⁹. The outcrop Toolebuc Oil Shale samples studied here comes from Julia Creek where the oil
13 shale was deposited in an epicontinental sea environment ⁵⁰ and has a calcite content over 45% ⁵¹.

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16 The Namurian (Late Carboniferous) Bowland Shale sample is from 31.02m in the Carsington Dam
17 Reconstruction C4 borehole, which was drilled in the Widmerpool Trough, Northern England. Thin section
18 observation and carbon isotope research have previously shown that this Bowland Shale sample is a thin-
19 bedded carbonate-bearing clay-rich mudstone, its bulk $\delta^{13}\text{C}_{\text{org}}$ value of -28.8 ‰ indicating that the kerogen is
20 derived from marine planktonic algae ⁵². The mineralogy of the marine Namurian Bowland Shale in Northern
21 England is characterized by a high concentration of clay (+50%) and a moderate content of quartz (22.1±3.9 %)
22 ^{53, 54}. Among the clay minerals, kaolinite is the most abundant, constituting 20.8±7.5 % of the total minerals;
23 montmorillonite and illite contents are low.

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29 The reference Bowland Shale core sample was taken from 1,404 metres depth in Old Dalby. The whole-
30 rock sample has an HI of 188 mg/g TOC which is similar to the pyrolyzed whole-rock (HI: 194 mg/g TOC; see
31 results section). With a T_{max} of 437°C, the shale is considered to be an early oil-window matured sample which
32 is suitable as a reference for comparing artificial and natural products.

33 34 35 **2.2. Analytical Methods**

36 37 38 **2.2.1 Kerogen isolation and screening**

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40 Kerogen concentrates were isolated from whole-rock samples by (1) crushing the shale sample to sub-
41 millimetre size, (2) treating with hydrochloric acid/6N hydrofluoric acid [2:1] for one week at room
42 temperature and (3) sieving to 10-500 microns.

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45 Rock-Eval and TOC analyses were performed using a Rock-Eval 6 and Leco SC-632 Analyser respectively
46 following established procedures.

47 48 49 **2.2.2 Pyrolysis gas chromatography (PyGC)**

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51 PyGC was performed using the Quantum MSSV-2 Thermal Analysis System[®] interfaced with an Agilent GC-
52 6890A ⁵⁵. Milligram quantities of each sample were loaded into a small open glass tube and heated under
53 flowing helium; free hydrocarbons were vented for 3 minutes during an isothermal purge at 300°C, after which
54 the C₂₊ pyrolysis products generated during heating from 300°C to 600°C were collected in a cryogenic trap
55 (liquid nitrogen). Methane passed through the trap and passed through the GC column to the Flame Ionisation
56 Detector (FID). Trapped products were then liberated by removing the cooling agent and heating the trap to
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3 300°C. An HP-Ultra 1 dimethylpolysiloxane capillary column connected to the FID was employed using helium
4 as carrier gas. Quantification of individual compounds and boiling range splits was conducted by external
5 standardisation with n-butane.
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7 8 2.2.3 Bulk kinetics 9

10 Bulk pyrolysis was performed using a Source Rock Analyser® (SRA) at three different heating rates (0.7, 2
11 and 5 K/min) following established procedures³⁶. The discrete activation-energy (E_a) distribution optimization
12 with a single frequency factor (A) as well as geological extrapolation were performed using the KINETICS 2000®
13 and KMOD® programmes. The corresponding temperatures of Transformation Ratio (TR) 30%, 50% and 70% for
14 each of the three different heating rates (0.7, 2 and 5 K/min) were selected for MSSV pyrolysis and
15 measurement of pyrolysate composition.
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19 20 2.2.4 Micro scale sealed vessel (MSSV) pyrolysis-GC 21

22 As described by Horsfield, Leistner and Hall⁵⁵, milligram quantities of samples were sealed in glass
23 capillaries and artificially matured to temperatures corresponding to 30, 50 and 70 TR for each of the heating
24 rates 0.7, 2 and 5 K/min respectively. The tubes were then cracked open using a piston device coupled with the
25 injector, and the released products were swept into the GC using a flow of helium. Quantification was
26 performed by external standardisation using *n*-butane.
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30 31 2.2.5 Thermovaporisation-GC 32

33 Around 10 mg of coarsely crushed reference shale was weighed into MSSV glass capillary tubes, which
34 were then sealed by an H₂ flame after having reduced the internal volume with pre-cleaned quartz sand. After
35 introduction into the Quantum MSSV-2 Thermal Analysis System, the external surfaces of the tube were purged
36 for 5 min at 300°C, during which time volatiles were mobilised within the tube; thereafter the tube was cracked
37 open by a piston device to transfer the products into a liquid nitrogen-cooled trap. The composition of these
38 volatiles was analysed as described under PyGC.
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42 43 2.2.6 MSSV-FT-ICR MS 44

45 Aliquots of MSSV pyrolysates were extracted using dichloromethane and methanol (V/V 9:1). Mass analyses
46 were performed in negative ion ESI mode with a 12 T FT-ICR mass spectrometer equipped with an Apollo II ESI
47 source, both from Bruker Daltonik GmbH. Nitrogen was used as drying gas at a flow rate of 4.0 L/min and a
48 temperature of 220 °C and as nebulizing gas with 1.4 bars. The sample solutions were infused at a flow rate of
49 150 µL/h. The capillary voltage was set to 3000 V and an additional CID (collision-induced dissociation) voltage
50 of 70 V in the source was applied to avoid cluster and adduct formation⁵⁶.
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3 A Soxhlet extractor was used for extraction of the reference sample bitumen. Core sample material (20 g) was
4 filled in an extraction tube and extracted with a solvent mixture of dichloromethane and methanol (v/v = 99:1)
5 at 40 °C for 24 h. The bitumen was then analysed by FT-ICR MS as described above.
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8 **3. Results and discussion**

9 **3.1 The existence of MME**

10 **3.1.1 Rock-Eval and TOC**

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16 Significant differences in maturity parameters and organic matter type identification indices can be found
17 between Bowland and Toolebuc whole-rock-kerogen pairs while Alum Shale sample pairs seem to be less
18 influenced by MME (*Table 1 and Figure 1*). The clay-rich Bowland whole-rock sample manifests higher T_{max}
19 (*Figure 1a*), higher OI (*Figure 1b*) and lower HI (*Figure 1b*) than its kerogen counterpart and these make the
20 Bowland whole-rock samples seem to be more mature and more terrestrial in origin as when compared with
21 the kerogen. By comparison, the calcite-rich Toolebuc Oil Shale whole-rock sample was influenced by a less
22 significant MME, and in the opposite way to that of the Bowland samples, namely the Toolebuc whole-rock
23 signature looks less mature and has a better organic matter type (*Figure 1*). A negligible MME in T_{max} and OI
24 was noted for the quartz -dominated Alum Shale samples.
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31 The MME induced by clay minerals in these Rock-Eval tests resemble those reported by Dembicki, et al.
32 ⁵⁷, Espitalié, Makadi and Trichet ¹⁷ and Heller-Kallai, et al. ⁵⁸ who concluded (1) the retention of relatively heavy
33 compounds on clay minerals is responsible for the increase of T_{max} and decrease of HI in whole-rock samples
34 and (2) the selective catalytic effect of acid minerals in generating CO₂ ⁵⁹ explains why the OI of whole-rock
35 sample was shifted to higher values. The impact of MME on the calcite-rich Toolebuc Oil Shale samples
36 supports the work of Katz ¹⁶ who reported carbonate mineral can enhance the HI and hinder the OI.
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39 **3.1.2 PyGC**

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42 The PyGC analysis of source rocks is a technique which can make a quick evaluation of kerogen structure
43 ^{57, 60} and relate that structure to bulk petroleum composition by means of Petroleum Type Organofacies ⁶¹.
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46 As a Lower Palaeozoic marine shale, it is not typical for the Alum Shale to be rich in low molecular weight
47 and aromatic pyrolysis products, e.g., xylene and toluene (*Figure 2 and 3*), this unique characteristic could be
48 induced either by an unusual precursor biota or by effects related to the presence of uranium (ionizing
49 radiation, oxygen incorporation) ⁶². Negligible differences in the pyrolysates of Alum whole-rock and kerogen
50 can be observed which implies the quartz does not bring about MME because of its inert nature, possibly
51 combined with the already aromatic nature of the pyrolysate (*Figure 2 and 3*).
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56 The pyrolysate of Toolebuc Oil Shale belongs to the Low Wax P-N-A (Paraffinic-Naphthenic-Aromatic) oil
57 Petroleum Type Organofacies (*Figure 3. a*)⁶¹. Thiophenic sulphur compounds generated from the carbonate oil
58 shale are more abundant than in either of the two clastic sediments (*Figure 3. b, d*). Although the differences of
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3 kerogen and whole-rock pyrolysates are not significant (*Figure 2*), it still can be recognised that the kerogen
4 products are more aromatic than the whole-rock counterpart (*Figure 3*).
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7 In contrast, pronounced differences can be found between the clay-rich Bowland Shale whole-rock
8 pyrolysis products and its kerogen pyrolysate, i.e., aromatic compounds are more abundant, and there is an
9 increased complexity of the compound mixture in whole-rock products, when compared with kerogen that was
10 heated alone (*Figure 2*). Different from the calcite-rich Toolebuc Oil Shale, Bowland Shale kerogen generates
11 more high molecular (*Figure 3a*) and aliphatic products (*Figure 3 b-d*).
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15 The preferential catalytic effect of clay minerals on low molecular weight aromatic and branched
16 hydrocarbons has been attributed to cracking *via* a carbonium-ion intermediate which forms on the Lewis acid
17 sites of the clay⁶³. The MME induced by carbonate minerals was considered as less significant and opposite to
18 clay minerals^{20,64}.
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20 21 3.1.3 Bulk kinetics 22

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24 The activation energy distribution and frequency factor of Alum Shale kerogen degradation seem not to
25 be influenced by the intimate presence of minerals during pyrolysis (*Figure 4*). Toolebuc kerogen shows slightly
26 more refractory characteristics compared with the whole-rock, and the Bowland Shale kerogen's activation
27 energy distribution was shifted to obviously lower values when MME was eliminated (*Figure 4*). These
28 preferential shift features of illite, calcite and clay minerals on bulk kinetic parameters are in agreement with
29 the stated effects of mineral matrices when building kinetic models^{21,22}.
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33 An instructive way of comparing the differences in kinetic parameters noted above is to apply them to a
34 geological heating rate, here chosen to be 3K/million year (*Figure 5*). Considering a TR of 50% for example, the
35 geological temperature shifts between whole-rock-kerogen pairs of Toolebuc Oil Shale and Bowland Shale are
36 5°C and 17°C, respectively (*Figure 5*). It is clear that these variations can lead to huge differences in the
37 estimated timing of hydrocarbon generation, expulsion and accumulation.
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40 41 3.2 The heating rate dependence of MME 42

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44 With decreasing heating rates, the GC "hump" (unresolved complex mixture) and alkene/alkane ratios of
45 both Toolebuc and Bowland pyrolysates decrease, which is in agreement with previous studies on the heating
46 rate dependency of pyrolysis products^{38,65}. Here, we discuss how aromaticity, GOR and total yield were
47 influenced by heating rates with and without minerals..
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50 51 3.2.1 Aromaticity 52

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54 For the pyrolysates of samples artificially matured to TR 50%, the lower the heating rate is, the lower is
55 the aromaticity (benzene, toluene, xylenes and tetramethylbenzene compared with nearby normal alkanes).
56 The biggest change is seen for the Bowland Shale whole-rock sample (*Figure 6*). Changes of the Bowland whole-
57 rock pyrolysates are bigger than those of their kerogen counterparts, pointing to the stronger heating
58 dependence on organic-inorganic interactions than on the thermal degradation of kerogen. By way of contrast,
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3 the aromaticities of Toolebuc whole-rock and kerogen samples seem to not be strongly controlled by heating
4 rates at all, ostensibly because MME are weak (*Figure 7a*).
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6 7 3.2.2 Gas-oil ratio

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9 Differences in GOR between the whole-rock and kerogen samples is another important compositional
10 influence caused by MME¹⁸. The GOR of both Toolebuc and Bowland samples increase with decreasing heating
11 rate (*Figure 7b*). The volatile generation in closed system pyrolysis was contributed by kerogen and oil cracking,
12 a slower heating rate which allows longer time for cracking is possibly the reason why GOR is elevated with
13 decreasing heating rate⁶⁶. GOR of the clay-rich Bowland whole-rock sample changes much more significantly
14 with varying heating rates compared with the other pairs (*Figure 7b*) because of MME.
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18 19 3.2.3 Generated Product Yield

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21 Significant differences in bulk generation product yields (including unresolved complex mixture in the GC
22 “hump”, normalized by TOC) can be found between whole-rocks and kerogen concentrates of Toolebuc and
23 Bowland samples (*Figure 7c*). Whole-rocks of the Toolebuc Oil Shale possess higher bulk generation/TOC than
24 their kerogen counterparts while Bowland Shale samples show the opposite trend (*Figure 7c*), which correlates
25 with HI changes caused by the MME (*Figure 1*). Gross hydrocarbon generation by kerogen samples is roughly
26 independent of heating rate, which is consistent with the prerequisite of kinetic theory^{38, 67}. In contrast, the
27 quantity of whole-rock product depends on heating rate especially in the case of the Bowland Shale samples
28 (*Figure 7c*). It seems that with decreasing heating rate, the MME on bulk generation amount can be diminished,
29 and whole-rock generation yields can approach those of its kerogen counterpart. It has to be pointed out that
30 the “pseudo HI” in MSSV pyrolysis (*Figure 7c*) is not directly comparable to Rock-Eval derived HI because: (1)
31 the highest TR in MSSV pyrolysis is 70% in this research, while Rock-Eval HI is achieved when TR has reached
32 100%; (2) MSSV products were introduced to the GC column where part of the pyrolysate is retained at the GC-
33 interface, whereas very little pyrolysate is lost during direct FID ignition in Rock-Eval³⁹; and it should be noted
34 that (3), coke can be formed in the low-pressure closed-system MSSV pyrolysis but only at high TR. The first
35 two of these factors explain why “pseudo HI” in MSSV is much lower than the HI provided by Rock-Eval.
36 Anyway, the gross hydrocarbon quantity variation induced by MME in both of these systems should be similar.
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45 46 3.3 Geological calibration and the validity of laboratory-based kinetic predictions

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48 The aliphaticity of thermal extracts from the natural bitumen in Bowland Shale is always higher than
49 artificial pyrolysis products generated from the immature starting material (*Figure 8a*). With slower heating
50 rates, aliphaticities of both whole-rock and kerogen pyrolysates increase. In the logarithmic coordinates system,
51 the changing rate of whole-rock products is obviously faster than kerogen pyrolysates which implies that in a
52 geological heating rate the differences between these two materials become smaller, in another words, the
53 aliphaticity difference is very likely to have disappeared completely. Geological extrapolation trend lines from
54 artificial pyrolysis show that the prediction of aliphaticity roughly matches that of the natural rock bitumen
55 chosen here for calibration, although, geometrically speaking, there are many possibilities for smoothing the
56 trend lines from the limited dataset shown here.
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3 From the perspective of gross hydrocarbon yield, the heating rate independency of kerogen breakdown
4 implies that the quantity predicted in the laboratory using kerogen is comparable to the geological situation
5 (*Figure 8b*). Obviously, this is not the case for direct measurements on whole-rock samples; but using
6 extrapolated data, the slower the heating rate, the closer the generation amount of Bowland whole-rock is to
7 its kerogen counterpart (*Figure 8b*). This observation could be explained by deducing that the MME on gross
8 hydrocarbon generation is quantitatively heating rate dependent and a slower pyrolysis heating rate could
9 reduce the effectiveness of MME on hydrocarbon retention. Another possible explanation relies on the impact
10 of MME on kinetics. A prerequisite for applying bulk kinetic derived TR evolution according to temperature to
11 MSSV pyrolysis is the uniformity of kinetic features in open- and closed-system pyrolysis⁶⁸, if the whole-rock
12 suffers from a heavy MME this prerequisite might be not valid anymore, thus leading to erroneous
13 temperature assignment in MSSV TR calculation, causing differences in predicted hydrocarbon compositions at
14 a given TR.
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21 **3.4 Insights into heteroelement geochemistry**

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23 The distribution of elemental classes in source rock extracts and crude oil revealed by FT-ICR MS is largely
24 determined by deposition environment^{42, 69}, maturity^{56, 70} and secondary alteration effects such as migration
25 fractionation⁷¹, biodegradation^{72, 73} and thermochemical sulphate reduction⁷⁴. Here we examined pyrolysates
26 to see if MME affects heteroelement distributions.
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30 The pyrolysates of Bowland kerogen and whole-rock samples show a decrease in oxygen and increase in
31 nitrogen compounds with increasing TR (*Figure 9*) thereby resembling changes noted for natural solvent
32 extracts of Type II source rocks with increasing thermal maturity⁵⁶. The gross oxygen, nitrogen and sulphur
33 composition of kerogen and whole-rock pyrolysates are rather similar which is surprising considering that
34 significant MMEs have described earlier. However, a detailed comparison of the compound class ratios of
35 O_1/O_2 , N_1/N_{2-4} and N_1O_1/N_1O_2 demonstrates significant differences do indeed occur (*Figure 10*). Kerogen
36 pyrolysates show much higher ratios in O_1/O_2 , N_1/N_{2-4} and a lower N_1O_1/N_1O_2 ratio. Although it was reported
37 that O_2 class distribution can be changed by contamination and biodegradation^{72, 73}, all samples were tested by
38 the sample instrument on the same day, these factors can be safely excluded. Since the values of the
39 compound class ratios are small and relatively constant with increasing TR, it can be demonstrated that no
40 significant heating rate dependency occurs within either kerogen or whole-rock samples. More importantly,
41 the O_1/O_2 , N_1/N_{2-4} and N_1O_1/N_1O_2 ratios of the natural Bowland Shale extract being used for calibration are 0.31,
42 0.30 and 0.59 respectively which are rather close to kerogen products but not whole-rock pyrolysates (*Figure*
43 *10*). Since the reference sample is in the early oil window maturity and occurs within a thick shale layer (over
44 20m), very limited expulsion is anticipated. The low ratios of O_1/O_2 and N_1/N_{2-4} of whole-rock sample appear to
45 be caused by the catalytic effect of minerals which tends to bring about condensation of oxygen and nitrogen
46 atoms into aromatic ring systems.
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56 The great resemblance of kerogen pyrolysates and shale extract in the three compound class ratios
57 implies that though kerogen MSSV pyrolysis can't accurately reflect the occurrence of NSO compounds in
58 natural bitumens, it does provides better prediction than whole-rock pyrolysis. The vast differences between
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3 artificially heated whole-rock and naturally matured shale extract on both elemental gross compounds and
4 compound class ratios manifest that MME caused by clay minerals on NSO generation is heating rate related,
5 and that is why the extreme slow geological heating generates similar product as kerogen pyrolysate although
6 there are minerals in the shale. In brief, MME on both hydrocarbon and NSO compounds generation are
7 obviously heating rate dependent and the slower the heating rate is, the weaker the effects of MME. Thus, it
8 can be speculated that the MME only exists in a laboratory environment, but is not significant in the geological
9 maturation process.
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13 **Conclusion**

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16 1. The MME in the quartz-rich Alum Shale, calcite-rich Toolebuc Oil Shale and clay-rich Bowland Shale has
17 negligible, weak and strong effluence on Rock-Eval, PyGC and bulk kinetics result respectively. Kerogen type,
18 maturity, organic facies and kinetics can be influenced accordingly.
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21 2. MME on the hydrocarbon aromaticity and generation amount are heating rate dependent, with
22 decreasing heating rate, the effect is weakened. The heating rate dependency of whole-rock pyrolysate GOR is
23 stronger than MME and gets enhanced when heating rate is slowed down.
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26 3. Neither the Bowland kerogen nor the whole-rock pyrolysates show similar gross elemental
27 composition as natural products. However, kerogen pyrolysate resembles natural products more in certain NSO
28 class ratios compared with whole-rock pyrolysate, which implies MME on NSO compounds is diminished in a
29 geological situation.
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32 4. The MME is speculated to only exist in the laboratory environment, not in a geological maturation
33 process. The MME doesn't change kinetic of hydrocarbon generation nor the composition of products in nature;
34 it only affects laboratory pyrolysis results in assessing kerogen type, maturity, organic facies or kinetics.
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39
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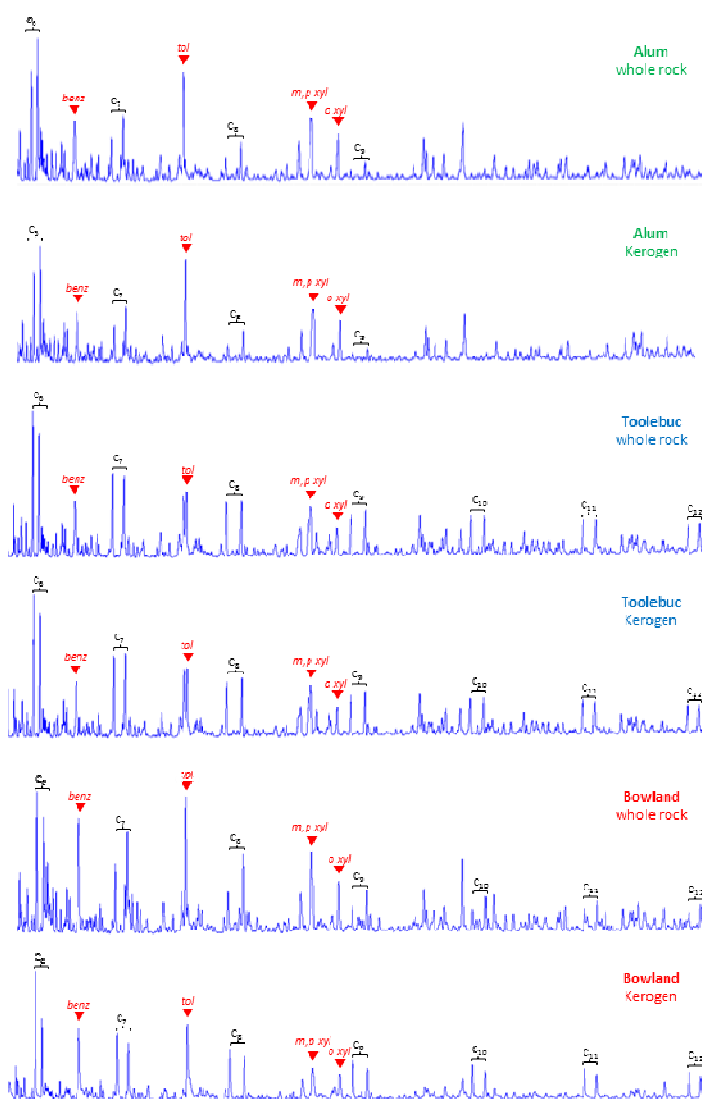


Figure 2. Comparison of PyGC maps on whole-rock and kerogen pairs. Bowland Shale pyrolysate shows an obviously higher aromatic compounds concentration compared with its kerogen counterpart. (benz: benzene, tol: toluene, m,p xyl: meta- and para-xylene, o xyl: ortho-xylene.)

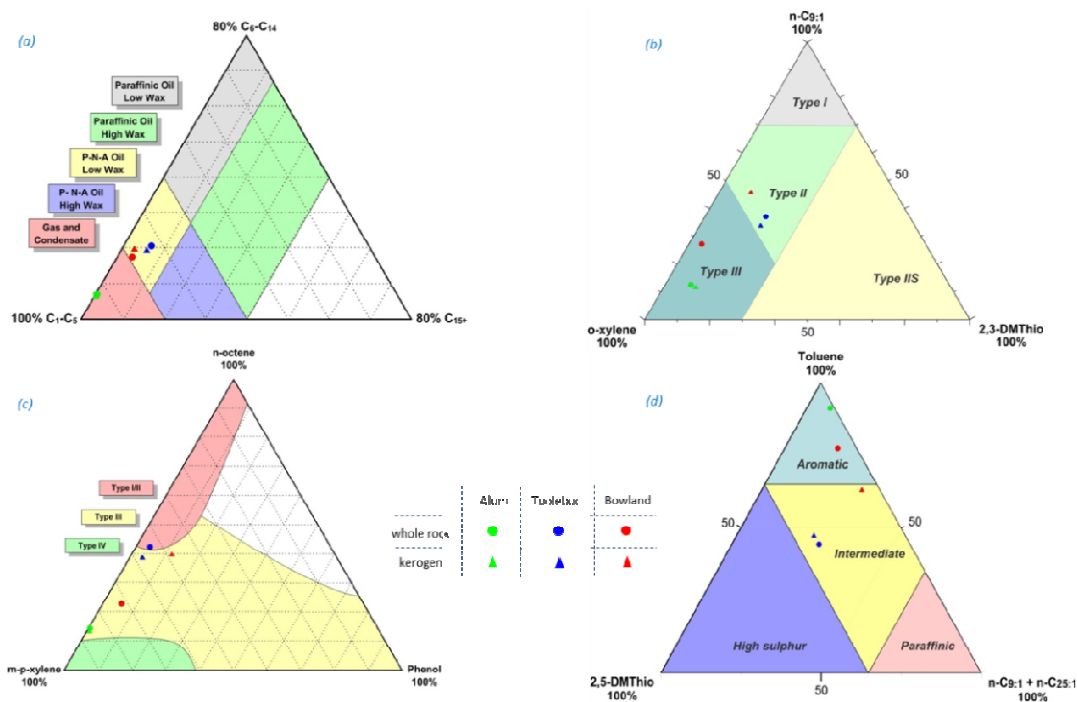


Figure 3. Quick classification on the pyrolysates of both whole-rock and kerogen concentrates.

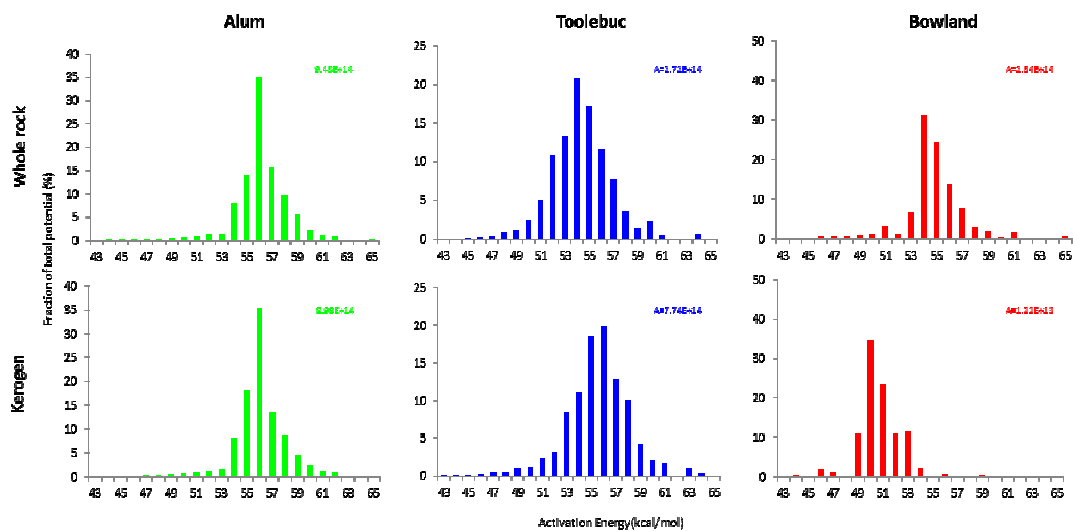


Figure 4. Bulk kinetic parameters of whole-rock and kerogen samples. Negligible (Alum Shale), Small (Toolebac Oil Shale) and significant (Bowland Shale) differences can be figured out.

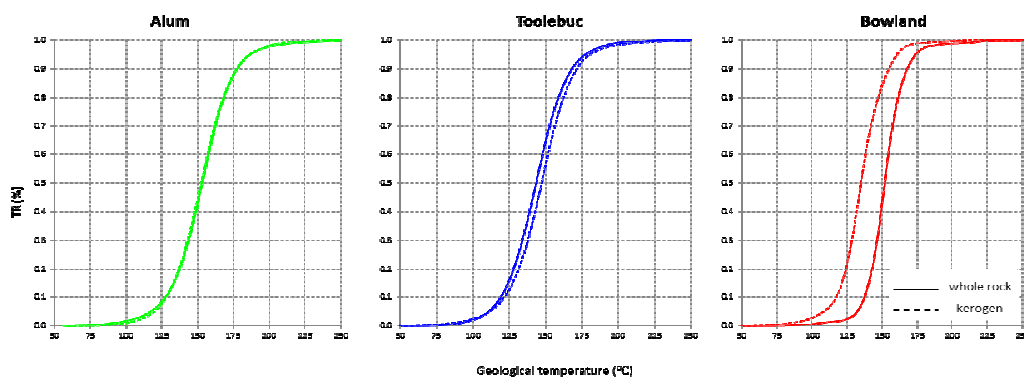


Figure 5. Geological extrapolation (heating rate: 3K/million year) of bulk kinetics parameters and comparison of comparison on whole-rock and kerogen samples.

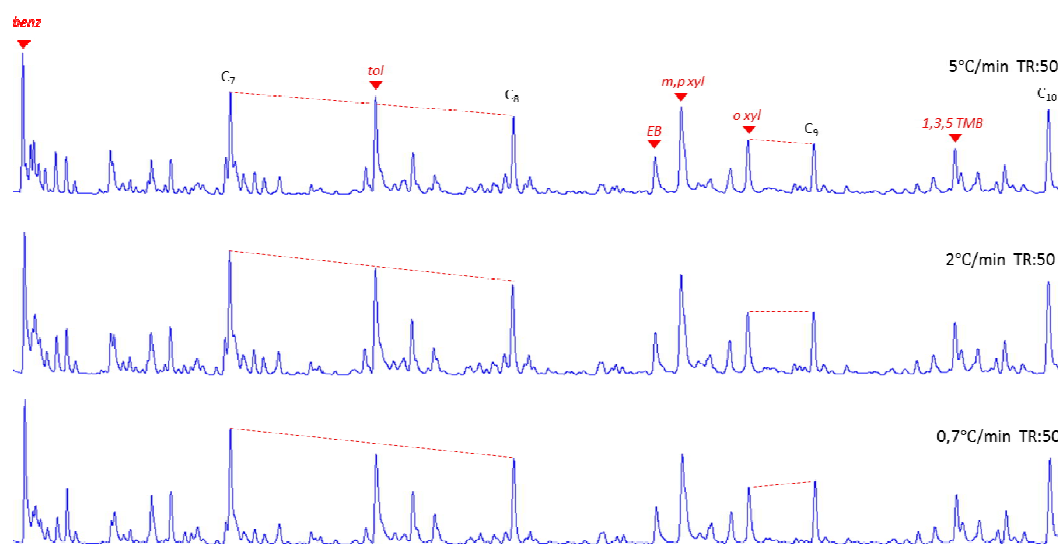


Figure 6. Pyrolysate GC maps of Bowland whole-rock sample at different heating rates when all heated to TR:50 manifest that the slower the heating rate is, the more aliphatic products can be generated. benz: benzene, tol: toluene, EB: ethylbenzene, xyl: xylene, TMB: tetramethylbenzidine.

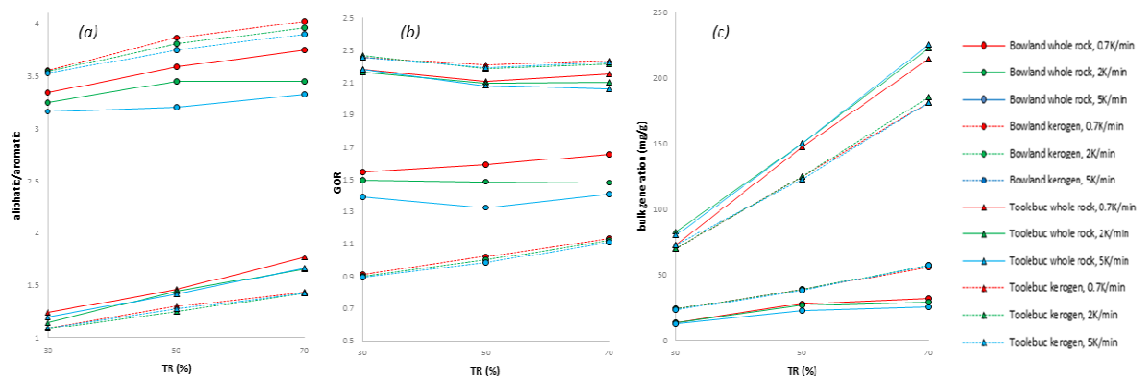


Figure 7. Aliphatic/aromatic compounds ratio, GOR and bulk hydrocarbon generation/TOC variations of Bowland Shale and Toolebuc Oil Shale samples in all three heating rates. Aliphatic compounds include all normal alkenes and alkanes from C₁-C₃₀. Aromatic compounds are composed of benzene, toluene, ethyl benzene, xylenes, tetramethylbenzidines, naphthalene, and branched naphthalenes.

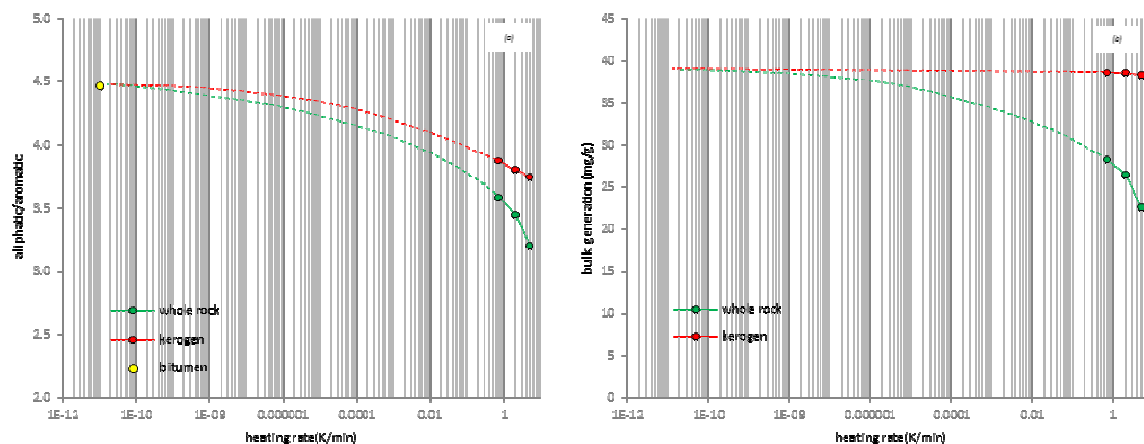


Figure 8. The variation trends of aliphatic/aromatic ratios, GOR and bulk generation according to changing heating rates on Bowland Shale samples when they are heated to TR 50%. Natural bitumen reference was shown in figure 8a.

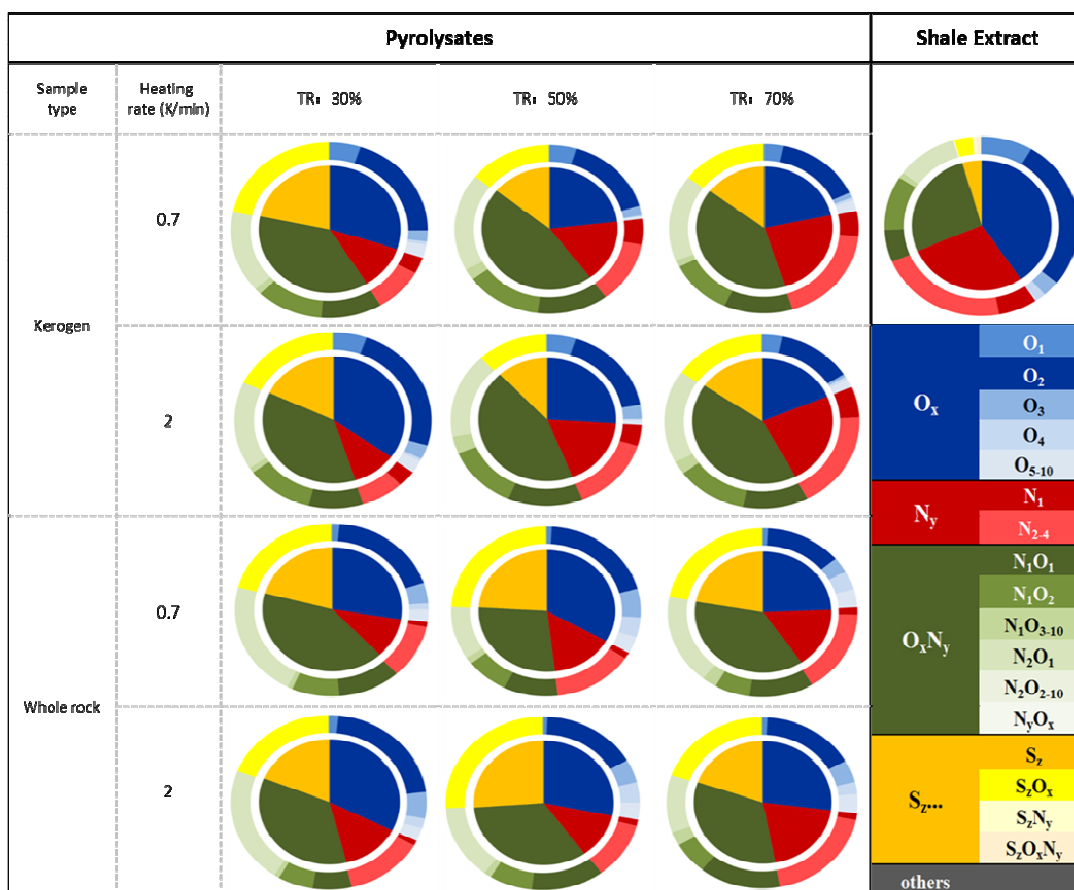


Figure 9. Elemental class distribution pie charts of pyrolysates and matured shale extract in the negative ESI spectra assigned with molecular formulas.

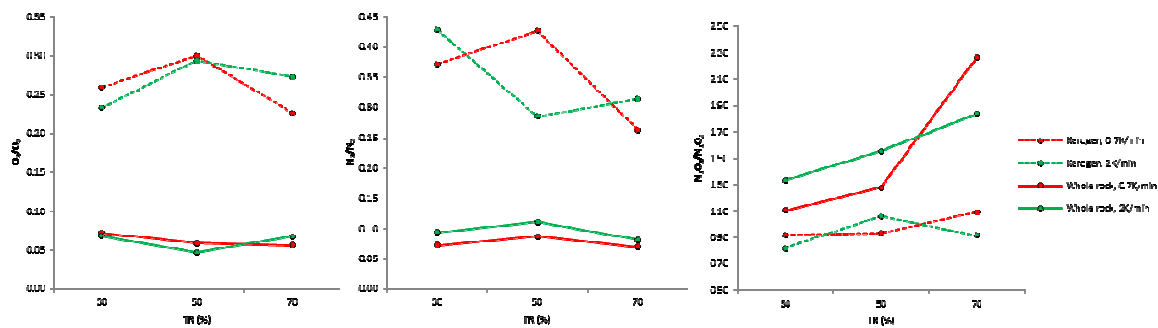


Figure 10. "Class" comparison of kerogen and whole-rock pyrolysates.