

SYMPOSIUM ON GEOCHEMISTRY AND CHEMISTRY OF OIL SHALE  
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GEOCHEMISTRY AND PYROLYSIS OF OIL SHALES

By

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There is no geological or chemical definition of an oil shale. Any rock yielding oil in commercial amount upon pyrolysis may be considered as an oil shale. The composition of the inorganic fraction may vary from a shale where clay minerals are predominant, such as the Lower Jurassic shales of Western Europe (particularly France and West Germany), to carbonates with subordinate amounts of clay and other minerals, such as the Green River shales of Colorado, Utah and Wyoming.

The organic fraction is mainly an insoluble solid material, kerogen, which is entirely comparable to the organic matter present in many petroleum source rocks (1,2). Figure 1 shows the elemental composition of the Green River shales, the Lower Toarcian shales of the Paris Basin and West Germany and also various oil shales from different origins. A large number of core samples from the Green River and the Paris Basin shales was taken at various burial depths. They cover the diagenesis, catagenesis and metagenesis stages of thermal evolution (1) (the latter stage was available from the Green River shales only). The diagram shows that these two shales series constitute typical evolution paths of type I and type II kerogens according to the definition of Tissot et al. (3). Furthermore, other oil shale kerogens belong either to type I, such as Coorongite and Keroseene shales (Australia), Torbanite (Scotland and S. Africa) and bogheads; or to type II, such as Kukersite (USSR), Irati (Brazil) and Messel (W. Germany) shales; Tasmanite (Australia) shows an intermediate elemental composition. The evolution path of humic coals is also shown in Figure 1 for comparison. It has obviously a lower hydrogen content than any of the oil shale kerogens, unless they have been deeply altered by thermal evolution.

Infrared spectroscopy (Figure 2 and Table I) of the kerogens (4) from oil shales shows that all of them are rich in aliphatic bands at 2900 and 1450  $\text{cm}^{-1}$  related to chainlike and cyclic saturated material. However, kerogens of type I, such as Green River shales and Torbanite, contain a larger proportion of long aliphatic chains, marked by the absorption bands at 720  $\text{cm}^{-1}$ .

TABLE I  
RELATIVE IMPORTANCE OF ALIPHATIC BANDS IN INFRARED SPECTROSCOPY  
OF SOME KEROGENS FROM SELECTED OIL SHALES (ARBITRARY UNITS)

Type	Sample	IR Aliphatic bands ( $\text{cm}^{-1}$ )			
		K <sub>2900</sub> C-H	K <sub>1450</sub> CH <sub>2</sub> +CH <sub>3</sub>	K <sub>1375</sub> CH <sub>3</sub>	K <sub>720</sub> (CH <sub>2</sub> ) <sub>n</sub> n>4
I	Green River shale	136.6	11.2	1.5	1.3
	Torbanite	103.5	10.8	2.1	1.1
II	Toarcian shales	73.0	10.0	2.5	0
	Kukersite	72.7	11.5	2.8	0.4
	Messel shales	76.0	9.6	3.7	0.2

The total oil yield obtained from the shale upon pyrolysis is usually measured by the standard Fischer assay. However, it is possible to obtain a fast and accurate measurement of the oil yield by using the Rock Eval. source rock analyzer (5), which operates on small quantities of rock, such as 50 or 100 mg. Figure 3 shows the comparison between the value obtained from the Rock Eval pyrolysis and the yield of the Fischer assay on the Toarcian shales of the Paris Basin.

A series of experiments has been carried out to observe the generation of the different classes of oil constituents. Aliquots of two kerogens from the Green River Shales (type I) (6) and the Lower Toarcian shales of the Paris Basin (type II) (7) were heated at a constant heating rate of 4°C  $\text{min}^{-1}$  to different final temperatures ranging from 375°C to 550°C. A humic coal from Indonesia

(type III) was also used for comparison (8). These various samples have experienced a comparable thermal history in geological conditions: they belong to the final stage of diagenesis (1) (vitrinite reflectance between 0.4 and 0.5%). The mass balance of the organic fraction is shown in Figure 4 as a function of the final temperature. At 375°C, most of the organic material is still made of kerosene. With increasing final temperature an increasingly large fraction is converted to oil which condenses in a cold trap, leaving a solid residue or char. The non-recovered fraction is assumed to be mainly carbon dioxide, water and light hydrocarbons non-condensable in the cold trap.

A somewhat different behavior is observed according to the type of kerogen: the Green River shale (type I) requires higher temperatures, as the maximum rate of conversion occurs ca. 475°, versus 425-450°C for the Paris Basin shale (type II) and the humic coal (type III). Furthermore, the conversion ratio and the composition of the products are different: the total conversion ratio (condensate plus non-recovered products) decreases from over 80% for type I, to 55% for type II and only 35% for coal. The amount of oil (condensate) generated is relatively high in kerogens from oil shales: 62% for type I and 47% for type II, whereas it is low (less than 12%) for coal. This is partly due to an important generation of carbon dioxide and water from humic coals. The relative proportion of hydrocarbons (saturated, unsaturated, aromatics) compared to N, S, O - compounds also decreases from type I to type III.

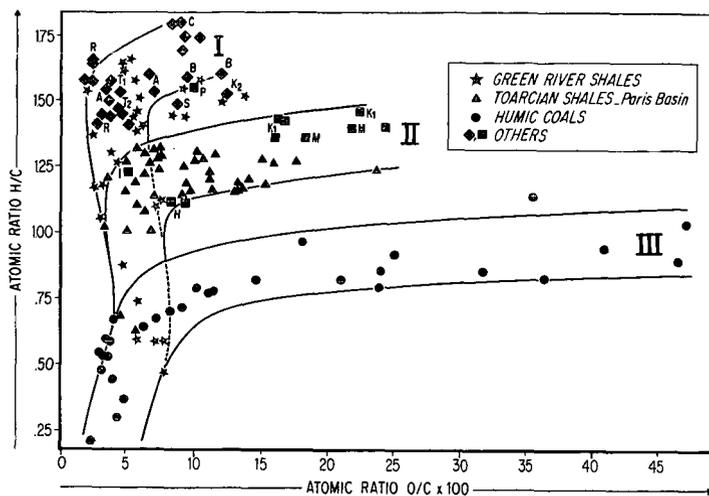
The total amount and composition of the hydrocarbons generated is shown in Figure 5. The Green River oil shale (type I) produces mainly linear or branched hydrocarbons, whereas the Paris Basin shale (type II) generates mainly cyclic - particularly aromatic - hydrocarbons. The percentage of aromatics is also important in coal pyrolysis, but the absolute amount is much smaller. The bottom part of Figure 6 shows the distribution of n-alkanes in shale oils: it is regularly decreasing from C17 to C30 in the oil derived from type II kerogen, which is a fluid synthetic oil; it is relatively flat up to C30 (type I) or even increasing towards a C25-C29 maximum (type III) in the two other synthetic oils which have a waxy character. Furthermore, a slight predominance of the odd-numbered molecules (C25, C27, C29) noted in the oil derived from humic coal points to a contribution of natural waxes from higher plants to the organic material.

A direct pyrolysis-gas chromatography of the kerogens was also performed and is presented in Figure 7 (9). The chromatograms taken at pyrolysis temperature of 475°C show the total distribution of hydrocarbons, with the relative importance of long chain molecules up to C30 in types I and III. It also shows the importance of low-boiling aromatics (B: benzene; T: toluene; X: xylenes) generated from humic coal (type III) as compared to those generated from oil shales (types I and II).

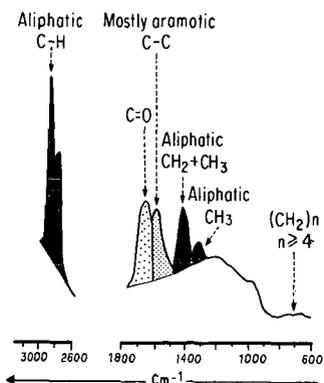
Composition of the solid organic residue of pyrolysis was also analyzed in order to follow the progressive change from the immature kerogen to the final char. Figure 8 presents the elemental composition of the solid organic fraction corresponding to the experiments reported in Figure 4. Artificial evolution of the two types of oil shale kerogen and the humic coal is represented by the elemental composition and the final temperature of pyrolysis. The artificial evolution paths corresponding to types I and II are reasonably comparable to the natural evolution paths observed in geological situation (10, 11), where the Green River and Paris Basin shales are buried at depth (this path is marked by bands I and II, respectively, in Figure 8). The major loss of hydrogen occurs ca. 475-500°C for type I and ca. 400-475°C for type II kerogen; this remark is in agreement with a comparable delay in their respective conversion ratio reported in Figure 4. The behavior of coal is somewhat different from that of oil shale kerogen: its artificial evolution does not duplicate the natural evolution path of humic coals. This is possibly due to the higher oxygen content of the initial sample and to its preferential elimination as water (a hydrogen consuming process) during pyrolysis, as compared to geological situations, where oxygen is mostly eliminated as carbon dioxide.

A confirmation of the inadequacy of pyrolysis to simulate the natural evolution of coal is provided in Figure 9, where two parameters of the Rock Eval pyrolysis are presented. The hydrogen index (5) is plotted as a function of a thermal evolution parameter  $T_{max}$  (temperature of pyrolysis corresponding to the maximum rate of release of organic compounds). The hatched bands marked I, II and III correspond to the natural evolution paths (under burial in geological situation) of the Green River Shales (10), the Paris Basin and W. Germany Toarcian (11), and humic coals (12), respectively. Again, the artificial evolution paths of type I and type II oil shale kerogens are reasonably comparable to the natural evolution paths, whereas the deviation is important for coal. The graph points to an early loss of hydrogen, possibly used for oxygen elimination through water generation; thus the hydrogen index, which measures the potential for further hydrocarbon generation, is lowered at an early stage of thermal evolution as compared to its behavior in geological situation.

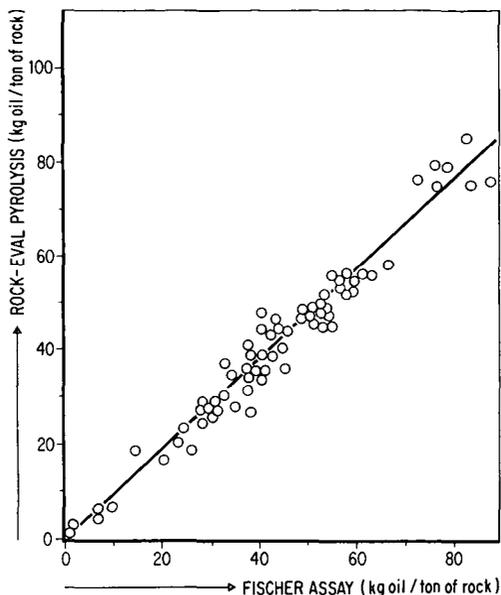
Another aspect of the comparison between pyrolysis and natural evolution of the organic matter is shown in Figure 10. In the Paris Basin, Lower Jurassic shales have been mined as oil shales where they are outcropping, whereas in the central part of the basin they were submitted to sufficient burial to generate bitumen in large amounts (11); in turn, a small fraction of that bitumen migrated to form small oil fields. Figure 10 presents the global composition of a) shale oil generated by laboratory pyrolysis, b) natural bitumen generated at depth in the shale acting as a source rock, and c) crude oil accumulated in a small field. The global composition of shale oil (non-aromatic



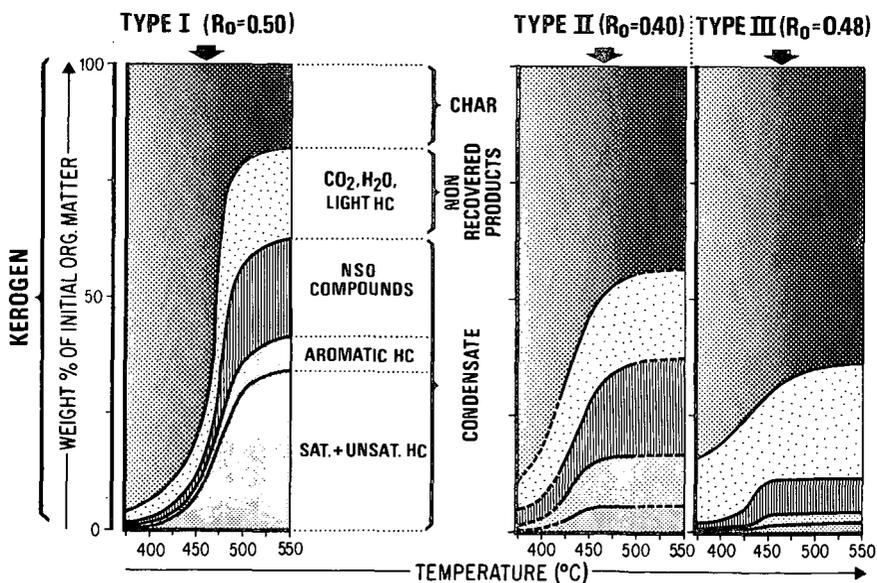
1. Van Krevelen diagram showing the elemental composition of oil shale kerogens. The organic constituents of the Green River shales and the Toarcian shales of the Paris Basin are typical kerogens of Types I and II, respectively. Other oil shales belong to either Type I (★) or II (◆) or III (●); A: Autun boghead, Permian, France; B: Moscow boghead, Permian, USSR; C: Coorongite, Recent, Australia; H: Marahunite, Tertiary, Brazil; I: Irati shales, Permian, Brazil; K<sub>1</sub>, K<sub>2</sub>: Kukersite, Paleozoic, USSR; M: Messel shale, Eocene, W. Germany; R: Kerosene shale, Permian, Australia; S: Tasmanite, Permian, Australia; T<sub>1</sub>: Torbanite, Carboniferous, Scotland; T<sub>2</sub>: Torbanite, Permian, Australia. The evolution path of humic coals (type III) is shown for comparison.



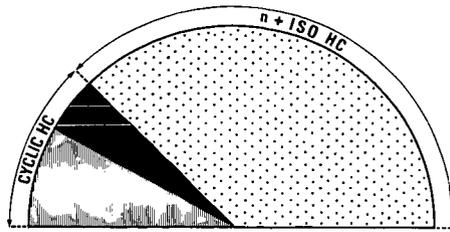
2. Typical infra-red spectrum of the kerogen isolated from lower Toarcian shales, Paris Basin.



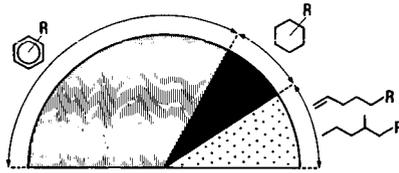
3. Correlation between oil content obtained by Fischer assay and by Rock-Eval pyrolysis.



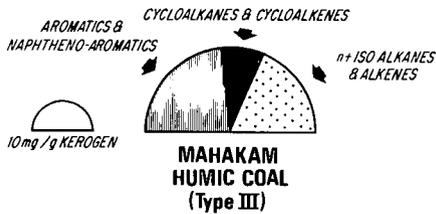
4. Pyrolysis of kerogens at a standard heating rate of  $4^{\circ} \text{ min}^{-1}$  up to different final temperatures. Mass balance of recovered and non recovered products plus residual char.



**GREEN RIVER SHALE (Type I)**

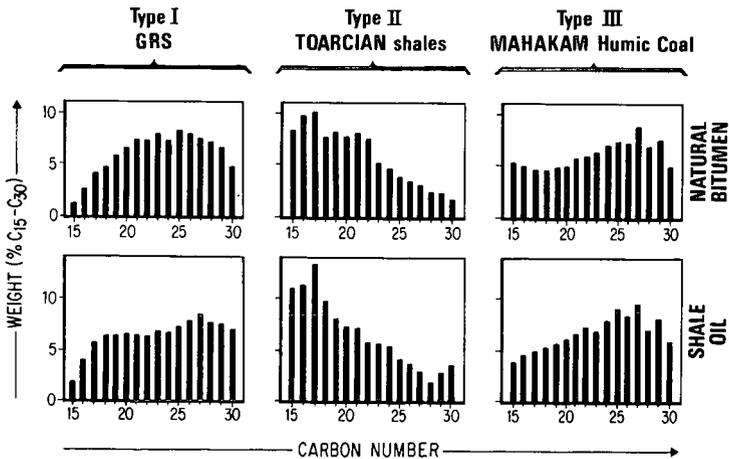


**TOARCIAN SHALE (Type II)**

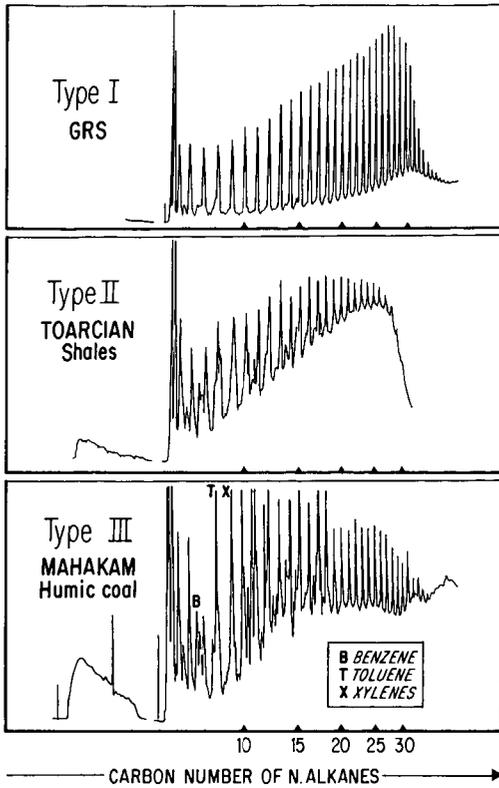


**MAHAKAM HUMIC COAL (Type III)**

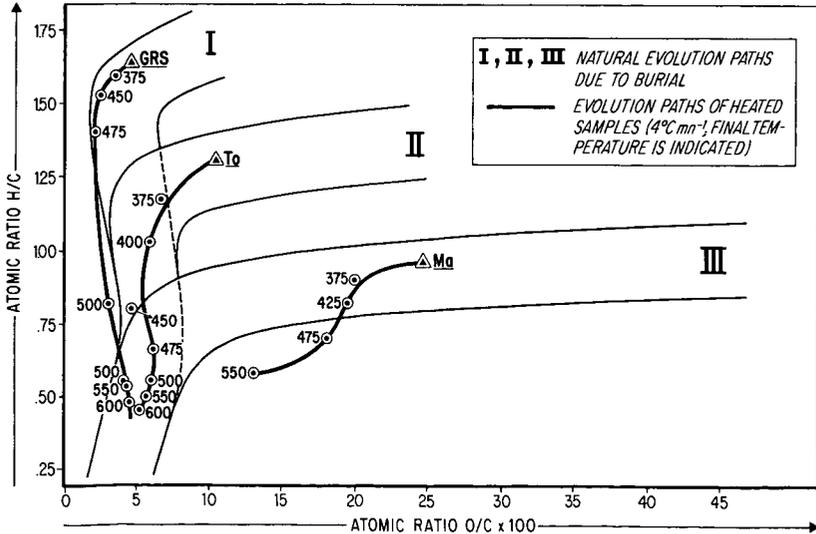
5. Hydrocarbons generated from the two main types of oil shales by pyrolysis at  $4^{\circ} \text{ min}^{-1}$  rate up to  $500^{\circ} \text{ C}$ . Hydrocarbons generated from a humic coal (type III) are shown for comparison.



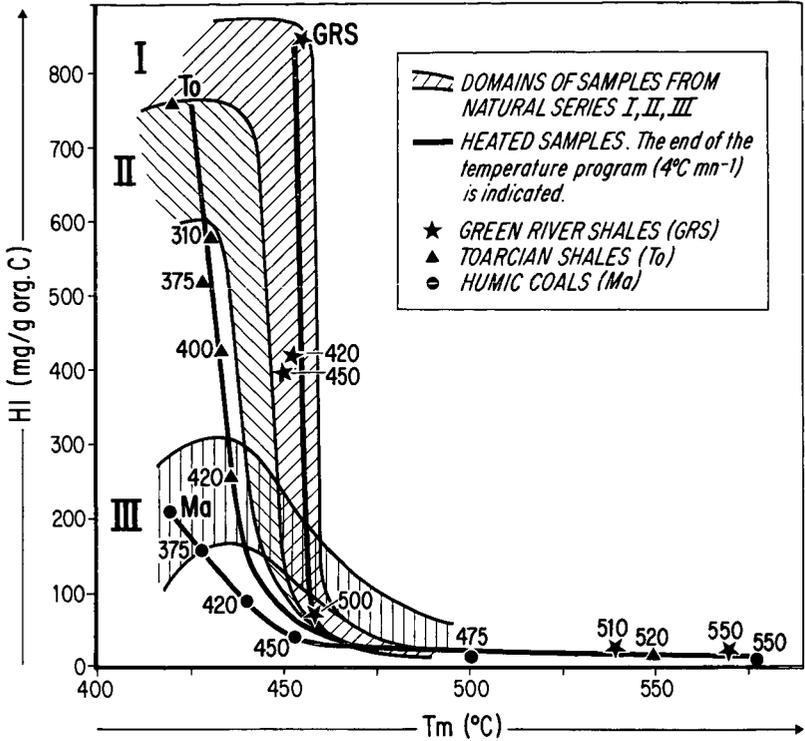
6. Comparison of the normal alkane distribution in shale oil generated by pyrolysis and in bitumen from geological samples with an equivalent stage of thermal evolution.



7. Pyrolysis — Gas chromatography at 475° C. The chromatogram shows total hydrocarbons.



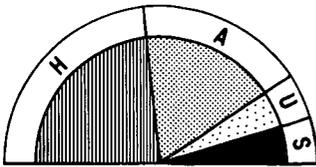
8. Evolution paths of heated samples compared to natural evolution paths of series I, II, III.



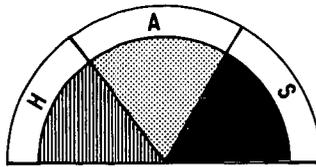
9. Evolution of hydrogen index versus  $T_{max}$  of Rock-Eval pyrolysis in natural series I, II, III (hatched) and in heated samples (identified by final temperature of pyrolysis).

## Type II ORGANIC MATTER

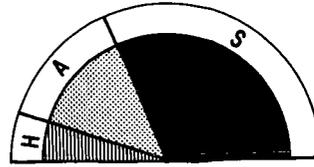
H NSO COMPOUNDS     
  U UNSATURATES  
 A AROMATICS     
  S SATURATES



SHALE OIL



NATURAL BITUMEN



POOLED OIL

10. Composition of shale oil, natural bitumen present at depth and pooled oil, all derived from lower Jurassic shales, Paris Basin.

hydrocarbons, aromatic hydrocarbons, N,S,O - compounds) shows some similarities with that of natural bitumen, especially the high content of N,S,O - compounds, as compared to the content in pooled oil. This similarity is also observed in Figure 6 where the n-alkanes distribution of three shale oils is compared with that of three natural bitumens of comparable stage of thermal evolution.

There are two major causes for the differences observed between shale oil and crude oil. One is due to generation by pyrolysis of compounds unusual in natural bitumens and crude oils, such as unsaturated hydrocarbons (olefins): Figure 10. Nitrogen hetero-compounds are also much more abundant than they are in natural bitumen or crude oils. The other difference is due to the migrated character of pooled oil which results in a preferential migration of hydrocarbons, especially saturates, and a retention of most of the N,S,O - compounds in the source rock (1). Thus natural bitumen has an intermediate composition, separated from shale oil by the conditions of pyrolysis and from pooled oil by migration across sedimentary beds.

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