

## Oxygenic Asphaltization/Kerogenization of Methanol-Soluble Fraction of Asphaltic Crudes: the La Luna Formation (Venezuela)

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**Abstract.** The (non-volatile) methanol-soluble fraction isolated from DMO-118, a typical asphaltic crude from the La Luna formation, was heated at 200 °C in the presence of the air oxygen (O<sub>2</sub>) for periods 0.5 to 10 hours. In the first stage, heating yields an asphaltenes-like product similar to the DMO-118 asphaltenes. In the later stage, heating generates the kerogen-like material similar to the kerogens isolated from the La Luna (QM) source rocks. We used a Fourier Transform Infrared (FTIR) spectroscopy to compare these artificial and natural materials. Kerogenization follows the first-order consecutive reaction kinetics with the asphaltenes-like product as an intermediate. Similar oxygenic kerogenization was observed for other asphaltic DMO crudes as well as non-asphaltic DM crudes of the La Luna formation.

**Keywords:** polar fraction, asphaltenes, kerogen, crude, La Luna, oxygen.

### Introduction

Structureless masses of insoluble organic matter in ancient sedimentary rocks of marine origin are referred to as amorphous kerogen. Phytoplankton and, to a lesser extent, bacteria, are usually considered precursors of amorphous kerogen. This kerogen is one of the main primary sources of crude oil: the oil-prone kerogen, also known as source kerogen. It is firmly established that crude oil produces oil-prone kerogen (during catagenesis) at approximately 50 °C and 150 °C, depending on the geologic age of a particular crude source rock [1]. This temperature range corresponds to the “principal zone of petroleum formation” [2] and to burial depths of approximately 2000 m to 5000 m, depending on the particular temperature gradient [1].

Throughout this report, by “asphaltization” and “kerogenization” we will mean, respectively, the processes involving the conversion of georganic precursor(s) into asphaltenes and kerogen under natural/laboratory conditions [3].

Experimental results from this Laboratory suggest the possible occurrence of low temperature ( $\leq 100^\circ\text{C}$ ) oxygenic kerogenization of asphaltic crudes as one of the formation of pathways of oil-prone (secondary) kerogen associated with bituminous rocks. These crudes must be in contact with a constant supply of atmospheric O<sub>2</sub> such as the ground waters. It is also inferred that this type of kerogenization may be widespread especially in porous and/or fractured carbonate/carbonate-siliceous bitumen-bearing rocks [3, and references therein]. Consequently, an asphaltic crude incorporated into the host rock within the atmospheric O<sub>2</sub>-

rich zone (mainly the groundwater region) can be then converted (through oxygenic kerogenization) into “new” (secondary) oil-prone kerogen. However, almost no attention is paid by petroleum geochemists to this rather controversial issue.

Whilst considerable attention has been devoted in this Laboratory to oxygenic kerogenization of asphaltenes extracted from asphalts and asphaltic crudes (including the La Luna crudes), no/little attention has been given to similar kerogenization of methanol-soluble (polar) fractions of these crudes. It has been pointed out that, in addition to the asphaltene fractions, other asphaltic crude components are probably involved (directly or indirectly) in the artificial kerogen generation during oxygenic kerogenization [3, and references therein]. Namely, previously we noted that non-asphaltic fractions of some asphaltic crudes could be kerogenized by laboratory heating at 200 °C in the presence of air O<sub>2</sub> [3, and references therein].

The objective of the present communication was to carry out the oxygenic transformation of the (non-volatile) methanol-soluble fraction (MSF) of an asphaltic crude to evaluate the probability that asphaltenes/kerogen could be derived by subsurficial heating of the asphaltic crudes in an air atmosphere under appropriate natural conditions. For this purpose, we select several typical asphaltic (heavy) DMO crudes (DMO-115, -116, -118, -119, 120) from the La Luna Formation (Western Venezuela). For comparison, we also studied several typical non-asphaltic (light) crudes (DM-1, -3, -8) [4, and references therein].

## Experimental

**Sample.** The geographical locations of selected DMO/DM crudes and their QM source rocks (bituminous limestones) of Cretaceous age are shown in Fig. 1. The heating experiments at 200 °C in the presence of air oxygen (O<sub>2</sub>) of the methanol-soluble fraction (MSF) of DMO-118 (MSF) have been given the most attention in this work and provide the main background for the ensuing discussion. We also studied other selected DMO/DM crudes (see above), and their polar and MSF fractions.

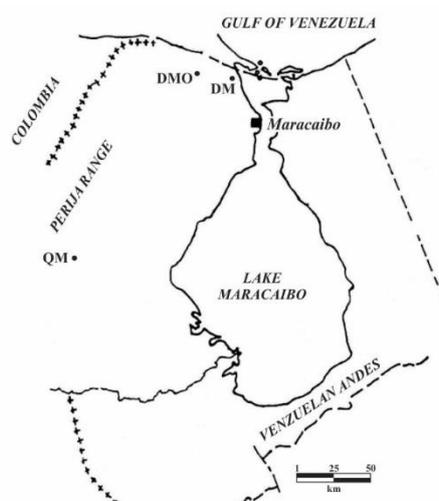


Figure 1. Geological map indicating the QM source rock/DMO/DM crude locations in Western Venezuela [4, and references therein].

**Chemical isolation of kerogen of the QM source rocks.** For comparison purposes, we isolated kerogens from several typical La Luna source rocks: QM-3/-8. The fractionation procedure is similar to that used by Saxby [5] and Premović et al. [6, 7]. The major steps in preparing the demineralized fraction were: the removal of carbonates (the acetate buffer) and silicates (the HF/HCl mixture). This predominantly (>99 %) organic fraction was further extracted (Soxhlet, 72 hrs.) for bitumen with benzene: methanol (6:1, v/v) mixture. The final insoluble residue represents the QM kerogen. The results of this chemical isolation are given in Table 1. Similar results were obtained for QM -1/10/12/14) kerogens.

**Table 1.** The contents [%] of asphaltenes, polar fractions of the QM-3/8 kerogens and the DMO/DM crudes and their MSF's.

Sample	Asphaltenes	Polar fraction	Kerogen	MSF <sup>a</sup>
QM-3	9	9	82	na*
QM-8	7	7	86	na
DMO-115	17	66	-	26
DMO-116	18	58	-	35
DMO-118	18	62	-	30
DMO-119	19	55	-	17
DMO-120	19	51	-	28
DM-1	4	82	-	17
DM-3	4	79	-	8
DM-8	6	81	-	6

<sup>a</sup>Percentage of the polar fraction. The rest is the evaporable part of this fraction. \*na: not analyzed.

**Chemical extraction and separation of DMO/DM asphaltenes and MSF.** The crude sample was dissolved in benzene:methanol (6:1 v/v), centrifuged (2 h) and the supernatant filtered (5 µm pore filter). After solvent evaporation, the crude condensate was refluxed (Soxhlet) for 90 h in *n*-hexane to obtain the insoluble fraction: the DMO/DM asphaltenes and the soluble part: maltene fraction (after solvent evaporation). The maltene fraction was washed several times with benzene:methanol (6:1 v/v) until the wash solution was clear, then dried at 45 °C. The maltene condensate was refluxed (Soxhlet) for 90 h in methanol to obtain the polar fraction. The insoluble is resin. The polar component was then dried at 45 °C for 24 h in a vacuum oven to remove completely solvent (and other volatile components) yielding “pure” MSF. The results of this chemical extraction/separation are given in Table 1. Similar results were obtained for DM-19/43/51/53/63/96/104 crudes. For comparison purposes, we also isolated asphaltenes from these crudes and kerogens of their typical source rocks: QM-3/8, as well as for QM-1/10/12/14.

**Gas chromatography (GC).** GC was performed from MSF on a Packard 417 GC, equipped with a flame ionization detector and an inorganic salt eutectic column. Operating conditions 105-295 °C, 8 °C min<sup>-1</sup>. The results of the chromatographic analyses for selected DMO's and DM-1 are given in Table 2.

**Table 2.** The saturated/aromatic hydrocarbon contents of the MFS's of DMO-118/119/120 and DM-1 crudes.

Crude	Saturated hydrocarbons	Aromatic hydrocarbons
DMO-118	50	48
DMO-119	50	47
DMO-120	40	56
DM-1	62	35

**Heating procedure.** Heating experiments of the whole DMO/DM crude samples and their asphaltenes, polar and MSF's were at  $200\pm 2$  °C for 0.5 to 10 hours. Hereafter, asphaltenes/kerogen-like materials produced from these experiments will be referred to as "artificial asphaltenes (AA) and artificial kerogen (AK)". In the first series of preliminary experiments, we heated the samples of the whole DMO/DM crudes for 6 hours. The results are given in Table 3. Similar results were obtained for DM-19/43/51/53/63/96/104 crudes.

**Table 3.** The percentages of evaporable fractions, AK's and non-kerogenizable fractions isolated from selected DMO/DM crudes after their heating for 6 h in the presence of air at 200 °C.

Crude	Evaporable fraction	AK	Non-kerogenizable fraction
DMO-115	44	20	36
DMO-116	44	20	36
DMO-118	43	16	41
DMO-119	42	20	38
DMO-120	45	20	35
DM-1	66	21	13
DM-3	70	23	7
DM-8	69	25	6

These results show that their polar fractions can be kerogenized as their asphaltenes. For this reason, we also carried out similar heating experiments of the polar fractions of selected DMO's and DM's. The results are given in Table 4. Similar results were obtained for the polar fractions of DM-19/43/51/53/63/96/104 crudes.

These experiments imply that MSF is also possible to kerogenize. For this reason, the final series of heating experiments of MSF's were carried out as follows.

**Table 4.** The contents (%) of the evaporable fractions, AK and non-kerogenizable fractions of selected DMO/DM crudes after heating of their polar fractions for 6 h in the presence of air at 200 °C.

Crude	Evaporable fraction	AK	Non-kerogenizable part
DMO-115	71	26	3
DMO-116	63	35	2
DMO-118	68	30	2
DMO-119	74	17	9
DM-120	70	28	2
DM-1	80	17	3
DM-3	91	8	1
DM-8	94	5	1

The MSF samples were placed on the glass plates (2 cm × 2cm × 0.2 cm). Each plate was heated (in an electric resistance furnace) at 190, 200 and 210 °C in the presence of air O<sub>2</sub> during 0.5, 1, 2, 3, 4, 6 and 10 h. After heating, the heating products were extracted (Soxhlet) with methanol, then with n-hexane and finally with benzene. Two fractions were separated by these chemical treatments:

- a) insoluble in methanol and n-hexane but soluble in benzene: AA;
- b) insoluble residue: AK; and,
- c) no or little no-resin-like material was detected.

**Table 5.** Amounts of MSF (%), AA (%) and AK (%) after the heating of MSF-118 at 200 °C in the presence of the air O<sub>2</sub> for 0.5 to 10h (see also Fig. 2).

Heating time (h)	MSF	AA	AK
0	100	0	0
0.5	74	23	2
1	38	55	16
2	10	65	35
4	1,1	37	65
6	0	21	81
10	0	5	97

The results of the heating experiments for MSF-118 are given in Table 5/Fig. 2. Similar results were obtained for MSF's of other selected DMO/DM crudes.

Apart from the common features, MSF's of asphaltic crudes in question cover a rather narrow range of chemical properties/gross composition. Chromatographic analyses of these fractions indicate that they are predominantly composed of soluble (non-volatile) saturated/aromatic hydrocarbons, very likely high molecular weight polymers. Their saturated hydrocarbon contents vary from ca. 35 % (DMO-120) to 65 % (DMO-115) and their aromatic hydrocarbon contents range from 35 % (DMO-115) to 65 % (DMO-120), Table 2.

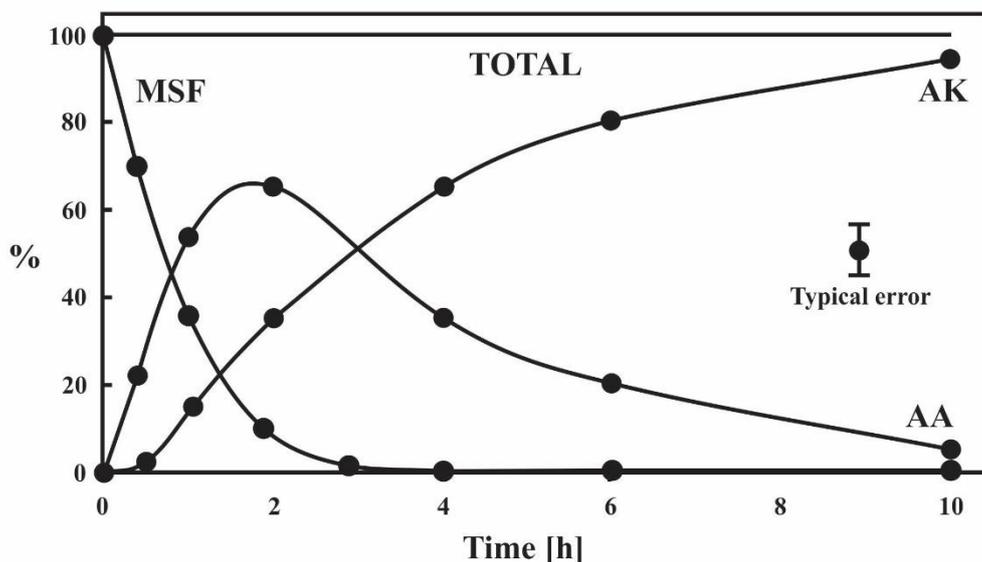


Figure 2. Amounts (%) of MSF, AA and AK after heating of MSF at 200 °C in the presence of air O<sub>2</sub> for 0.5 h to 10 h.

**Fourier transform infrared (FTIR) spectroscopy.** FTIR spectra of the QM kerogens, the asphaltenes/MSF's of the DMO/DM crudes, and AA's/AK's were obtained using KBr discs, employing a Perkin-Elmer 1600 FTIR spectrometer. Band assignments have been made according to the literature, for example [8 - 10].

**Micro-FTIR spectroscopy.** Micro-FTIR spectroscopic analyses of the DMO-118 crude components were performed using a Bruker IFS66 Fourier transform infrared spectrometer equipped with a mercury cadmium telluride detector cooled by liquid nitrogen. The AA and AK samples were placed on potassium bromide plates. Interferograms were acquired in the transmission mode within the range 4000–900  $\text{cm}^{-1}$  by accumulating 256 scans at a spectral resolution of 4  $\text{cm}^{-1}$ . Spectral bands were assigned with reference to the literature, for example [8 - 10].

**Electron spin resonance.** The electron spin resonance (ESR) spectra measurements were carried out of the selected organochemical samples, which were placed in pure silica tubes (Suprasil grade). Spectra were recorded on a Bruker ER-200 series ESR spectrometer with a Bruker ER-044 X-band (9.4 GHz) bridge, using standard 100 kHz field modulation and a rectangular TE cavity. Frequency was measured using a Hewlett-Packard frequency meter. Calibration of magnetic field (H) was performed with the DPPH standard  $g = 2.0037 \pm 0.0005$  [11].

## Results and discussion

**Heating experiments.** As we pointed out above, heating experiments at 200 °C in the presence of air  $\text{O}_2$  have been carried out on the MSF samples evenly distributed over glass plates. The choice of these conditions was justified by the experimental facilities they entail, although it is realized that they represent a poor imitation of the natural habitat of asphaltic crudes.

The results of the heating experiments of MSF-118 are listed in Table 4 and are shown in Fig. 2. These results show that the percentage of MSF-118 during the laboratory heating ( $t = 0.5, 1, 2, 4, 6$  and  $10$  h);  $[\text{MSF}] = 100\%$  when heating time  $t = 0$ . The experiments reveal marked changes in the composition of a MSF-118 upon exposure to different periods of heating. In the early stages (up to about 2.5 h) thermal asphaltization/kerogenization of this MSF is dominated by AA. The amount of AA reaches the maximum value at 2 hours and decreases gradually from 2 h up to 10h when it reaches a minimum ( $<5\%$ ), Fig. 2. During the advanced stages (about 2.5 h -10 h) of heating, a gradual increase in the formation of AK at the expense of both MSF-118 and AA took place. The amount of AK reaches its maximum value of ca. 95 % at 10 h. Thus, most of MSF-118 is converted into kerogen-like, insoluble material. For this reason, we view AA as an intermediate in the conversion of MSF-118 into AK. Thus, kerogenization of MS-118 entails two successive steps and the generation of AA seems to precede the formation of AK. The latter would mostly result from successive reactions in which AA acts as intermediate products. Similar results were obtained for other selected DMO/DM crudes.

**The FTIR and micro-FTIR spectra and their analyses.** The FTIR spectra of MSF-118 (a) and its AK (b) and AA (c), the DMO-118 asphaltenes (d) and polar fraction (e), and the QM-3 kerogen (f), are shown in Fig. 3. The spectra have been normalized by a multiplication procedure so that they appear to derive from an equivalent sample size.

In general, the FTIR spectra indicate that all materials studied contain predominantly long aliphatic chains (or macromolecules) characterized by the bands at 2930, 2850  $\text{cm}^{-1}$  and 1450  $\text{cm}^{-1}$ . Their inflections near 2960  $\text{cm}^{-1}$  and 1370  $\text{cm}^{-1}$  indicate that in all these chains are present numerous  $\text{CH}_3$  groups. The highly aromatic structures are also present but much less than aliphatic chains since the aromatic bands at 3050, 870, 820 and 780  $\text{cm}^{-1}$  have much

lower intensities. The broad band at 1700-1600  $\text{cm}^{-1}$  in these spectra with a maximum near 1700  $\text{cm}^{-1}$  corresponds to the stretching vibration of the C=O group.

The FTIR spectra of MSF-118 (Fig. 3a), AA (Fig. 3b) and AK (Fig. 3c) are generally similar to those spectra of the DMO-118 asphaltenes (Fig. 3d), DMO-118 polar fraction (Fig. 3e) and the QM-3 kerogen (Fig. 3f). Comparison of the FTIR spectra of AA/AK obtained through oxygenic transformation of MSF-118 with that from non-heated MSF reveals some essential differences. There is a marked reduction in the aliphatic C-H stretching bands (around 2800  $\text{cm}^{-1}$  to 2950  $\text{cm}^{-1}$ ) and CH bending bands (around 1450  $\text{cm}^{-1}$ ) with increasing kerogenization of MSF-118. These absorption bands have essentially disappeared for AK. Aromatic C-H absorption bands near 3050  $\text{cm}^{-1}$  vary little, if at all, with kerogenization. There is a marked

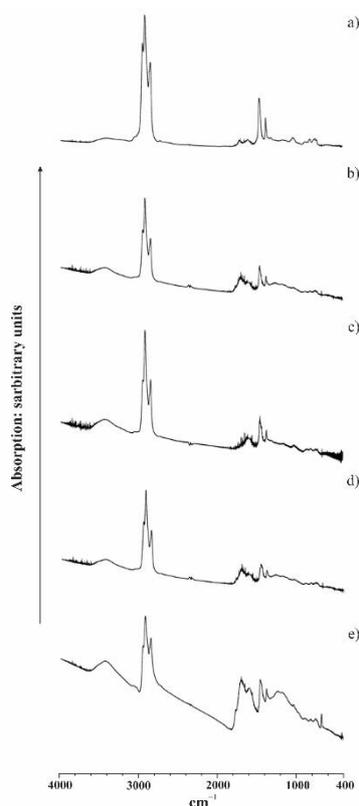


Figure 3. The FTIR spectra of: a) MSF-118, b) AA, c) asphaltenes of DMO-118, d) QM-3 kerogen, and e) AK.

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cm<sup>-1</sup> to 2950 cm<sup>-1</sup>) and CH bending bands (around 1450 cm<sup>-1</sup>) with increasing kerogenization of MSF-118. These absorption bands have essentially disappeared for AK. Aromatic C-H absorption bands near 3050 cm<sup>-1</sup> vary little, if at all, with kerogenization. There is a marked increase in the absorption bands in the carbonyl region around 1700 cm<sup>-1</sup>. This infers the presence of various types of carbonyl moieties in the long and highly aliphatic macromolecules of AK. In general, the FTIR spectrum of AA is similar to the spectrum of asphaltenes extracted from the Dead Sea asphalt [3]. Further discussion of the FTIR spectra of these materials would go beyond the scope of this paper.

Several changes due to asphaltenization/kerogenization of MSF-118 are observed. The most significant changes are the enhanced carbonyl absorptions in the 1700 cm<sup>-1</sup> region and a decrease in the aliphatic C-H absorptions in the 2850-2950 cm<sup>-1</sup> (CH stretching) and 1450 cm<sup>-1</sup> (CH, bending) regions. These changes are quite discernible in the difference spectra. Minor changes are observed in the aromatic CH vibrations in the 750 - 850 cm<sup>-1</sup> region as well. Similar FTIR findings are obtained for other MSF's.

The micro-FTIR spectra of AA/AK of MSF-118 revealed the presence of aliphatic C-H, aromatic C-H and various oxygenated functional groups, including carbonyl (C=O), C-O-C and C-OH groups. Functional group concentrations were found to be ordered as follows: [aliphatic C-H]>[C-O] >[C=O]. Aliphatic C-H was found to exist in significant quantities. These results confirm the above FTIR and finding: a significant amount of aliphatic chains is present in AA/AK.

**Vanadyl porphyrins and AK.** In several works from this Laboratory vanadyl porphyrins (VOP), one of the most of the most prominent groups of molecular fossils, are identified in the asphaltic crudes, as well as in their asphaltenes/polar fractions and the source rock kerogens, employing mainly ESR [12–19 and references therein]. Figs. 4a and 4b show typical ESR spectra of VOP of the QM-3 kerogen and AK, respectively. Similar spectra were recorded for AA (not shown), numerous DMO/DM asphaltenes and QM kerogens [12-19]. These findings indicate a way by which a VOP (mainly simple alkyl VOP) associated with the MSF can become a part of asphaltenes/kerogen during catagenesis. For further discussion, see the reference [18].

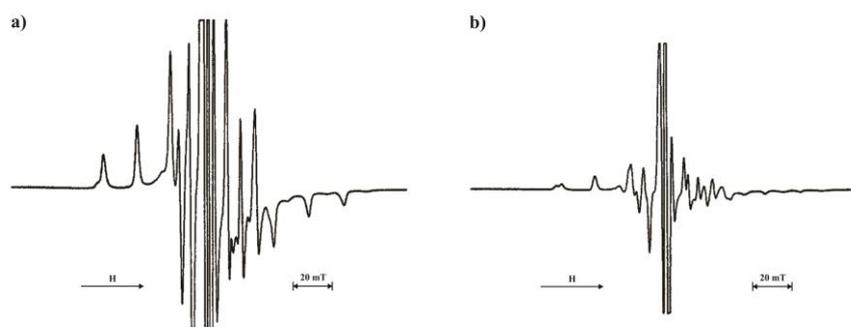


Figure 4. First derivative, room temperature, anisotropic ESR spectrum of VOP: a) QM-3 and b) AK.

**Kinetics of thermal asphaltenization/kerogenization.** A general model can, then, be stated to describe the mechanism of MSF transformation into artificial asphaltenes/kerogen:



MSF is transformed into AA with rate constants  $k_{AA}$ . The latter are, in turn, transformed into AK with rate constant  $k_{AK}$ .

It is evident from the aforementioned results that MSF-118 generates (in the first stage on laboratory heating in the presence of air  $O_2$ ) instantly, geologically speaking, AA resembling the DM asphaltenes. This asphaltene-like product (an intermediate) in the later stage of heating was converted (also instantly, geologically speaking) into AK which is similar to the QM kerogens.

The asphaltenization/kerogenization of MSF-118 (in units of percentage by mass) can be described by a first-order reaction equation:

$$-\ln [\text{MSF}] = kt - \ln 100$$

where  $k$  is an overall rate constant and in units of  $h^{-1}$ . Thus, the reaction behaves as a typical system of first-order consecutive reactions, for all practical purposes. Therefore, a plot of  $\ln[\text{MSF}]$  vs.  $t$  should give a straight line with a slope =  $k$ . Although experimental values are limited, a straight line can be roughly approximated at temperatures 190 °C, 200 °C and 210 °C, Fig. 5. Rate constants  $k$  (calculated from the slope of the lines in Fig. 5) are plotted vs. temperature,  $1/T \times 10^5$  [ $K^{-1}$ ] in Fig. 6. This plot can be well-fitted by the following first-order reaction equation:

$$-\ln k = 0.5 E_a / T - 43$$

In the derivation of the equation, we assumed that the process is governed by the Arrhenius law  $k = A \exp(-E_a/RT)$ , which relates  $A$ , frequency factor and the activation energy  $E_a$ , the universal gas constant  $R$  and the absolute temperature  $T$  and  $E_a$  are properties of MSF-118,  $O_2$  and AA/AK. The activation energy  $E_a$  (the energy of the overall reaction about the generation of AA and AK) is estimated to be ca. 40 kcal  $mol^{-1}$ .

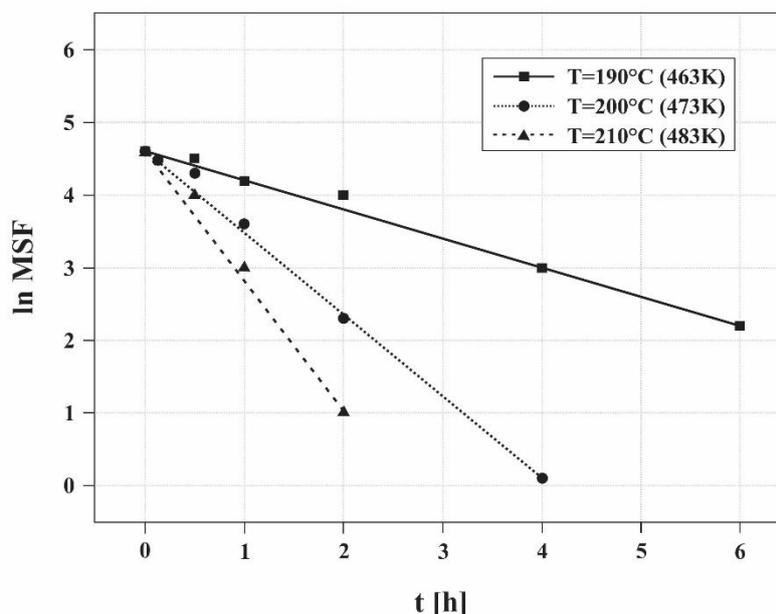


Figure 5. Rate of asphaltenization/kerogenization of MSF-118 in the presence of air  $O_2$  at 190 °C, 200 °C and 210 °C according to first-order reaction kinetics (see text).

We roughly estimate using the above experimental data that the half-life,  $t_{1/2}$  (that is, the time in which 50 % of MSF-118 is converted into AA/AK) is about 45 min. For comparison,  $t_{1/2}$  of the Dead Sea asphaltenes is about 145 min under the same experimental conditions. These values, roughly speaking, infer that macromolecules of the MSF-118 and the Dead Sea asphaltenes are involved in similar chemical transformations during the oxygenic kerogenization. This conclusion is reasonable since they have similar chemical structures elucidated from their FTIR spectra: compare the MSF spectrum in Fig. 3a with the Dead Sea asphaltene spectrum [3]. It is important to note that a simple calculation shows that at a temperature of 60 °C  $t_{1/2}$  of MSF-118 would be roughly about 250 years.

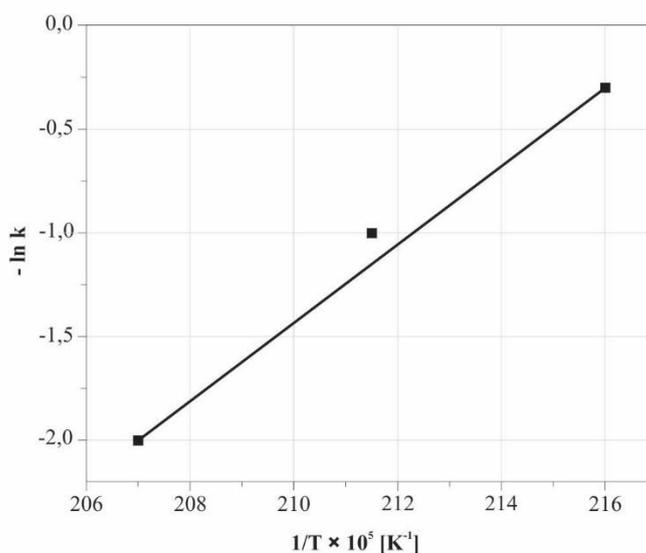


Figure 6. “Arrhenius plot” (see text) showing decreasing rates of MSF-118 conversion.

In the above kinetic estimation of experimental data, we assumed that the AA/AK formation is a first-order reaction, i.e., the rate of this process is only proportional to the concentration of MSF-118 ( $[\text{MSF}]$ ) at any time,  $d[\text{MSF}]/dt = -k[\text{MSF}]$ . This is an oversimplification because it implies that the only quantity required in modeling the AA/AK formation is the initial concentration of MSF-118 ( $[\text{MSF}]$ ) not considering the influx of  $\text{O}_2$  from the atmosphere, i.e., partial pressure of  $\text{O}_2$  within the MSF sample:  $p(\text{O}_2)$ . Then we assume that the rate constant  $k$  of this (pseudo-) first-order reaction is governed by the Arrhenius law. In other words, we hypothesize that the single activation energy ( $E_a$ ) in the Arrhenius equation could describe bulk oxygenic asphaltenization/kerogenization of MSF-118, AA/AK generation. This assumption is another oversimplification of the real process which involves a large variety of complex parallel/consecutive reactions with widely different  $E_a$ 's and  $A$ 's. A knowledge of these kinetic parameters is crucial in our attempt to kinetically model asphaltenization/kerogenization of MSF. Such a requirement is, however, well beyond our current analytical/computational capabilities. Crude geochemists face similar difficulties in the evaluation of the results of their kinetic studies of crude formation/maturation.

Our present findings, however, allow us to assume that, in the first approximation, the overall process of AA/AK formation from MSF-118 can be described as reasonably satisfactory by the first-order model based on the Arrhenius equation.

The most intriguing result of this study is that almost the entire MSF is completely kerogenizable under suitable laboratory conditions, i.e. it is possible to convert MSF completely into AK during laboratory heating under relatively mild thermal conditions in an air O<sub>2</sub> atmosphere. On the other hand, kinetic data shows that for a sufficiently long time, the asphaltization/kerogenization of MSF in an asphaltic crude could be effectively fast especially at the subsurface under natural oxygenic conditions (i.e. if atmospheric O<sub>2</sub> is present in unlimited supply) even if it was subjected to common subsurficial temperatures ( $\leq 60^{\circ}\text{C}$ ) [2]. Of course, these experiments are not able to simulate the natural process, as there are probably important factors (e.g. host rock and its components, groundwaters and its O<sub>2</sub> content, etc.) other than temperature/time that may affect this process. In general, there is an obvious enrichment in asphaltenes from the non-asphaltic (light) crude at great depth (say,  $\geq 2000$  m) to the asphaltic (heavy) near-surface [20, 21 and the references therein].

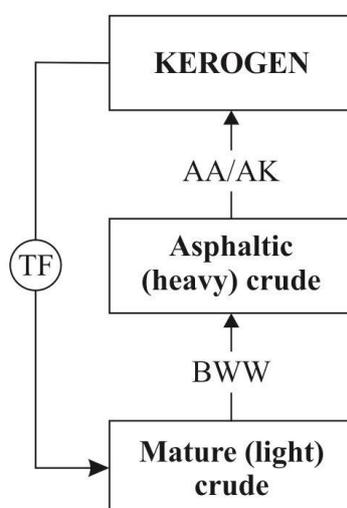


Figure 7. Speculative model for the oxygenic asphaltization/kerogenization of primary (light) crude in a natural environment.

Fig. 7 shows an oversimplified speculative model of the oxygenic asphaltization/kerogenization of initial primary (mainly light) mature crude into kerogen. This process could occur in the subsurface region of a natural environment, Fig. 7. According to this model, primary (light) crude *via* the alternation processes (AP) such as biodegradation/water-washing/evaporation/oxidation is transformed into an asphaltic (heavy) crude which undergoes to further transformation into kerogen through oxygenic asphaltization/kerogenization (AA/AK) in the near-surface region. We may speculate that this natural AK can then be pushed deeper into the Earth's subsurface by tectonic forces (TF), with increasing burial depth/ temperature, natural AK may progressively crack (catagenesis) to "secondary" light or directly to heavy crude. **The light crude may then rise to near the surface, where it can be transformed by AP into heavy oil. Then any of these two heavy oils may react with atmospheric O<sub>2</sub> generating "secondary" natural AK. This may be a form of the geological carbon cycle.**

**The mechanisms of asphaltization/kerogenization of MSF.** The mechanism(s) by which MSF is converted to AK through AA (as an intermediate) cannot be deduced from the data alone. At the moment, we may suggest that AA is the result of a series of consecutive/random repolymerization/polycondensation reactions of the saturated/aromatic hydrocarbons by the action of atmospheric O<sub>2</sub>. Such newly formed AA molecules then may continuously undergo to further chemical transformations (through oxygenic kerogenization) by which they become

increasingly condensed/insoluble giving rise to the AK molecules. The changes that occur during oxygenic asphaltization/kerogenization of MSF are complex and involve not only the modification of the carbon structures of the saturated/aromatic hydrocarbon molecules but also alterations of the composition of the heteroatomic groups attached to their carbon skeletons. It is reasonable to speculate that free radicals play an essential role in this process. Indeed, combustion and many natural and laboratory organic polymerization reactions involve free radicals. As a result, many organic polymers are formed through radical polymerization. For instance, drying vegetable oils harden due to radical crosslinking by O<sub>2</sub> from the atmosphere.

### Concluding remarks

It may be concluded that laboratory heating of MSF at a relatively low temperature of 200 °C in the presence of air O<sub>2</sub> produces asphaltene-like/kerogen-like materials. A similar process may occur under much milder ( $\leq 60$  °C) natural thermal subsurficial oxygenated conditions.

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