

## INTERACTION OF KEROGEN AND MINERAL MATRIX OF AN OIL SHALE IN AN OXIDATIVE ATMOSPHERE

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### ABSTRACT

The effects of the inorganic matrix of the oil shale on the oxidation of the kerogen at temperatures up to 1000°C in an air atmosphere were investigated. Kerogen was isolated by successive HCl, HF and LiAlH<sub>4</sub> treatments. The initial shale and each product of every demineralization process were oxidized in a thermogravimetric system in an air atmosphere. The oxidation products were analyzed by Fourier transform infrared spectroscopy. Changes in the chemical structure of the organic material of the shale were correlated with the separated constituents of the inorganic matrix. Oxidation of the kerogen occurred in two stages. The first stage was complete at about 400°C. The oxidized product after the first stage contained a char of an aromatic ring system substituted with some aliphatic material and carbonyl groups. Calcium minerals increased the reactivity of the aromatic part of the organic material towards the oxidation reactions. Where calcium minerals were absent, mainly the aliphatic and the carbonyl groups decomposed. Silicates and pyrites did not affect the reactivity of the organic material in oxidation reactions.

### INTRODUCTION

Oil shales consist of complex sapropelic organic material of high molecular weight (kerogen) which is finely distributed in an inorganic matrix. The inorganic constituent of the oil shales affect the reactions of the organic matter both physically and chemically. The interaction between kerogen and the inorganic matrix during reactions is not well understood. It is the aim of this report to investigate the effects of the inorganic material of the oil shale on the oxidation of the kerogen at temperatures up to 1000°C in an air atmosphere.

Oxidation studies of the oil shales using thermal analysis techniques indicated that high-temperature oxidation of the kerogen is a complex two-stage phenomena [1–3]. Recently, it was found [4] that the high-temperature oxidation of kerogen in a number of Australian shales occurred in two

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stages. The first stage involved the oxidation of aliphatic material to give a char containing aromatic moieties while the second stage of the oxidation was merely the combustion of the char produced.

In the present study the kerogen of an Israeli shale was isolated by successive HCl and HF demineralization procedures. Every product of each demineralization step was oxidized in a thermogravimetric system under a dynamic atmosphere of air. The oxidation products were analysed by Fourier transform infrared spectroscopy. Changes in chemical structure of the organic material of the shale were correlated with the separated constituents of the inorganic matrix. This provided information on the high-temperature oxidation mechanism of the kerogen and the effects of the inorganic matrix on oxidation reactions.

## EXPERIMENTAL

Samples of oil shale used in this work were from the Zefa Efe oil shale deposit. This deposit is situated 40 km southeast of Beer Sheva. The kerogen was isolated according to the method described recently [5,6]. Dried oil shale (100 g) was extracted with benzene/methanol (7:3; 4 ml g<sup>-1</sup> shale) to extract the bitumens until the solvent in the arm of the Soxhlet was colourless. The bitumen-free (BF) shale was washed with methanol, dried and weighed. Bitumen-free shale was stirred at room temperature with aqueous HCl solution (conc. HCl 1:6; 5 ml g<sup>-1</sup> BF shale) until no further carbon dioxide evolved. The shale was washed with water until the silver nitrate test for chloride in the washings was negative. The HCl treatment was repeated twice. The carbonate-free (CF) shale was dried and used in the next step to eliminate silicates. The carbonate-free shale was wetted with concentrated HCl and stirred with concentrated HF (5 ml g<sup>-1</sup> CF shale) at 60°C for 1 h. Stirring was continued for an additional hour to evaporate the volatile silicon products. The silicate-free (SF) shale was washed with water, the HF-treatment step was repeated and the product was dried. Pyrite in the silicate-free shale was removed by LiAlH<sub>4</sub> treatment. Silicate-free shale was stirred with LiAlH<sub>4</sub>/THF (5 g LiAlH<sub>4</sub>/g SF shale) solution at 60°C for 1 h. After the reaction, the LiAlH<sub>4</sub> was decomposed with propanol and the kerogen was first washed with dilute HCl solution and then with water and dried. Sufficient amounts of all the products of each demineralization step were saved for TG and FTIR analyses. Elemental analyses of the oil shale and kerogen are presented in Table 1.

Thermogravimetric data were obtained using a Mettler TA 3000 system equipped with a TG 50 thermobalance interfaced with a TC 10 TA processor via a Mettler 03 data interface. Temperature was measured with a Pt 100 temperature sensor. Powdered samples (5–10 mg) in alumina crucibles of 0.07 ml volume were oxidized in a dynamic air atmosphere. The samples were heated from 35 to 980°C at 10°C min<sup>-1</sup>.

TABLE 1  
Elemental analyses of Zefa Efe oil shale and kerogen

	% (dry ash-free basis)				
	C	H	N	S	O(diff)
Oil shale	62.2	6.9	2.4	10.6	17.9
Kerogen	62.8	7.8	2.6	9.0	17.9

Infrared spectra were obtained with a Nicolet MX-1 FTIR spectrometer. KBr pellets were prepared by grinding 2.5 mg, 150  $\mu\text{m}$  particle size, raw shale (or demineralization product) with 200 mg KBr in a grinder for 20 min. Pellets, 13 mm in diameter, were pressed in an evacuated die from about a 60 mg mixture of KBr and sample, and dried at 110°C for 72 h under a nitrogen atmosphere to remove water. Spectra were obtained at a resolution of 2  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

Derivative thermogravimetric (DTG) oxidative profiles of the shale and its demineralization products are presented in Fig. 1. Figure 1a is the DTG curve for the initial oil shale. In this figure we can differentiate four groups of peaks corresponding to the oxidation of different chemical structures in the shale. The first group of peaks within the temperature range 50–115°C is due to the loss of moisture. The second peak, which was observed only in the DTG curve of initial shale situated between 115 and 200°C, indicated a peak temperature at 135°C and constituted 2.1% of the whole shale. The consecutive demineralization product, the bitumen-free shale (BF shale), did not contain this peak. Therefore, the peak within the 115–200°C temperature range was most probably due to the oxidation of bitumens that were extracted with the benzene/methanol mixture to obtain the BF shale.

The third group of peaks observed in the DTG curves of shale and all of its demineralization products was positioned at a wider range which depended on the type of material was due to the organic matter (kerogen) of the shale. As it was also observed recently [3,4], the high-temperature oxidation of the organic material of the shale occurred in two stages. The temperatures of the peaks due to the oxidation of the organic material are given in Table 2. The peak temperatures of kerogen oxidation both in shale and BF shale were at about the same position, near 370 and 465–470°C. Extraction of the bitumens did not displace the peak temperatures.

As the severity of the treatment for demineralization increased, the position of the first oxidation peak shifted towards lower temperatures and the second oxidation peak moved to higher temperatures. HCl treatment to decompose carbonate minerals shifted the first oxidation peak from 370 to 350°C, and HF treatment lowered it further to 300°C. The  $\text{LiAlH}_4$  treat-

TABLE 2

Oxidation temperatures of the organic material and amount of the organic material remaining unoxidized in experiments run up to valley temperature

	Temperature at the start of oxidation (°C)	Peak oxidation temperatures (°C)		Valley temperature (°C)	Organic matter remaining unoxidized in experiments run up to valley temperature (%)
		$T_1$	$T_2$		
Shale	200	370	470	420	57.9
BF shale	200	370	465	420	59.2
CF shale	180	350	485	380	69.7
SF shale	150	300	520	380	73.0
Kerogen	130	300	540	400	70.4

ment did not affect the temperature of the first oxidation peak. On the other hand, the second oxidation peak shifted towards higher temperatures in all of the demineralization products. The shift of the first oxidation stage towards lower temperatures was probably due to the removal of inorganic material which prevented the proper contact of oxygen and organic material. Prior to the removal of the inorganic matrix, the heat supplied was used to supply the necessary activation energy for the initiation of oxidation reactions. Therefore, upon the elimination of the inorganic matrix the organic material became more susceptible for oxidation reactions; these reactions probably started at lower temperatures, as shown in Table 2. Temperatures at which the oxidation reactions started decreased steadily from initial shale to kerogen from 200 to 130°C.

The amount of organic matter which remained unoxidized at the end of the first oxidation stage (temperature of the valley between the first and second oxidation stages) increased from shale to carbonate-free shales (CF shale) and stayed constant up to kerogen. This was due to the catalytic effect of the carbonate minerals upon the oxidation of organic material. Recently, we characterized the carbonate minerals in the shale used in the present study as calcite [6] by an X-ray diffraction study. Higher reactivities of the lignite chars in the oxidation reactions were attributed to the presence of a high calcium content [7]. It was also found that removal of calcium by demineralization reduced the reactivity of the coals in oxidation reactions [8,9]. With the removal of calcite minerals in the present study the percentage of the organic material which remained unoxidized increased by about 10%. This result is in accord with the findings of the Walker and co-workers [7-9] concerning the catalytic effect of calcium in the oxidation of coals. The removal of silicates and pyrite with HF and  $\text{LiAlH}_4$ , respectively, did not affect the amount of unoxidized organic material remaining.

Fourier transform infrared (FTIR) spectroscopy was utilized in order to

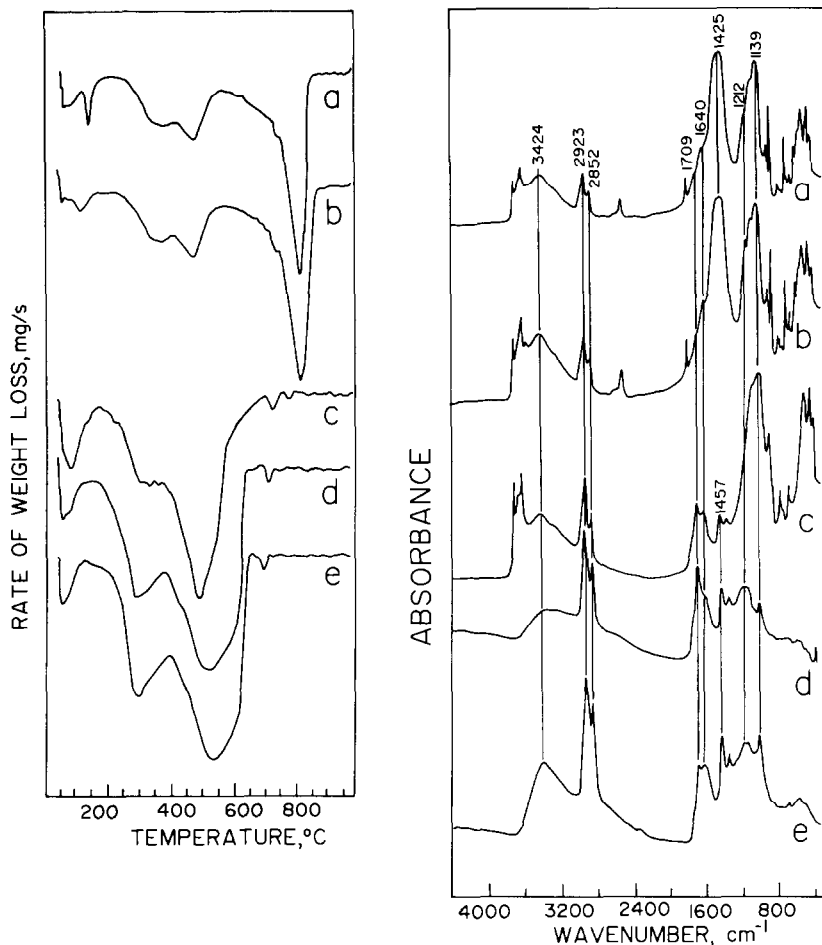


Fig. 1. DTG oxidative profiles of (a) initial shale, (b) BF shale, (c) CF shale, (d) SF shale and (e) kerogen.

Fig. 2. FTIR spectra of (a) initial shale, (b) BF shale, (c) CF shale, (d) SF shale and (e) kerogen.

follow the oxidation reactions of the organic material in the shale and its demineralized products. FTIR spectra of the initial shale, its demineralization products and of the residual material from experiments run until the end of the first oxidation stage (valley temperature) were measured. The FTIR subtraction technique was used to determine the material absent in the FTIR spectra of the material remaining after the first oxidation stage.

The infrared spectra of the shale and its demineralization products are given in Fig. 2. Table 3 lists the principal inorganic and organic group frequencies as well as their assignments observed in shale and demineralization products. In a recent FTIR investigation we reported [6] the effects of the demineralization processes on the organic material of the shale used in

TABLE 3

Principal inorganic and organic group frequencies encountered in the oil shale

Wavenumber ( $\text{cm}^{-1}$ )	Assignment
1425, 875, 711	Calcium carbonate (calcite) [10]
1100–900, 550–450	Silicates [11]
3700–3600	Kaolinite [11]
425–350	Pyrite [12]
3424	OH stretching [10,13]
2923	Asymmetric CH stretching of methylene groups [10,13]
2852	Symmetric CH stretching of methylene groups [10,13]
1709	C=O stretching [10,13]
1640	Aromatic ring stretching [10,13]
1457	Asymmetric $\text{CH}_2$ and $\text{CH}_3$ bending [10,13]
1379	Symmetric $\text{CH}_3$ bending [10,13]

the present study. It was concluded that hydrochloric acid and hydrofluoric acid treatments did not alter the chemical composition of the organic matter. The organic matter was neither hydrolysed nor oxidized. Lithium aluminium hydride treatment, while removing the pyrite remaining in the SF shale, reduced part of the carbonyl groups to newly formed hydroxyl groups. There were no other major chemical changes in the structure of kerogen due to demineralization processes.

Figure 3 shows the Fourier transform infrared spectra of the residual matter of oxidized shale and its demineralization products which were obtained in experiments run until the end of the first oxidation stage. The major difference between the original spectra (Fig. 2) and the spectra in Fig. 3 is that the spectra of the oxidized material contained diminished, organic group absorption bands. The intensity of the phenolic hydroxyl bands near  $3400 \text{ cm}^{-1}$  greatly decreased. This indicated loss of hydroxyl functionalities during the first stage of oxidation. Levy and Stuart [4] did not observe aliphatic groups after the first oxidation stage of several shales. We found that the aliphatic groups survived the oxidative conditions of the experiments. The presence of absorption bands at 2929 and  $2852 \text{ cm}^{-1}$  due to asymmetric and symmetric stretching of CH in methylene groups, respectively, and the presence of a weak absorption due to asymmetric  $\text{CH}_2$  and  $\text{CH}_3$  bending confirmed the presence of aliphatic structures in the residual matter after the first stage of oxidation. The pattern of the groups of absorption bands within the region  $3000\text{--}2800 \text{ cm}^{-1}$  suggest the presence of cycloparaffins in the oxidized material [13]. In the FTIR spectra of the oxidized material from shale and BF shale the absorptions due to aromatic ring stretching at  $1629 \text{ cm}^{-1}$  and carbonyl stretching are not well resolved;

they are indicated as shoulders. These bands were overlapped by the strong absorption of the carbonate minerals at  $1427\text{ cm}^{-1}$ . In the FTIR spectra of oxidized material free of carbonate minerals (Fig. 3c, d, e), bands due to absorptions of carbonyl and aromatic stretching can be identified. This indicated that oxidation of the kerogen up to the end of the first oxidation stage produced aromatic material containing carbonyl functionalities and some aliphatic substitution.

The FTIR spectra of the material that was oxidized during the first oxidation stage are presented in Fig. 4. Figure 4 is the result of the subtraction of the spectra in Fig. 3 from those in Fig. 2. The resultant spectra in Fig. 4 indicated the material extracted from the initial shale and its demineralization products due to oxidation. These spectra suggested that oxidation until the end of the first stage affected both the organic material and the inorganic matrix of the shale. It appeared that a great deal of aliphatic structures were lost during the first oxidation stage. In addition to this, oxidation also caused losses in the aromatic structure of the organic material.

The presence of high-intensity carbonyl absorption bands in the difference spectra indicated the destruction of these functionalities during oxidation reactions. As stated above, the phenolic hydroxyl groups also decreased due to oxidation. The greatest effect related to the loss of hydroxyl groups can be observed in the difference spectra of kerogen and oxidized kerogen (Fig. 4d). The strong absorption at the  $3400\text{ cm}^{-1}$  in Fig. 4d confirms the lack of this band in the FTIR spectrum of the oxidized kerogen in Fig. 3e.

According to the spectra in Fig. 4 most of the silicate minerals which were originally present in the unoxidized shale and demineralization products decomposed during the first oxidation stage. Pyrites were also oxidized; the presence of a  $427\text{ cm}^{-1}$  absorption specific for pyrite groups in the difference spectra indicated the decomposition of pyrites into iron oxides in the first stage.

Our results indicated that the first oxidation stage involved the oxidation of aliphatic and aromatic structures, decomposition of phenolic hydroxyl and carbonyl groups. In addition to the oxidation of organic material, the inorganic matrix of the shale also decomposed partially during the oxidation reactions. It seemed that the material left after the first stage of oxidation contained aromatic material with carboxylic groups and considerable amounts of aliphatic substitution. Although most of the aliphatic groups were oxidized during the first stage of oxidation, some aliphatic material remained in all of the residual matter produced in the first stage of oxidation. Our findings suggested that the second stage of the oxidation of shales was the oxidation of the char which constituted aromatic structures with aliphatic and carbonyl substitution.

The presence of a strong absorption at  $1638\text{ cm}^{-1}$  in Fig. 4a indicated that in the whole shale and BF shale the oxidized portion of the material was

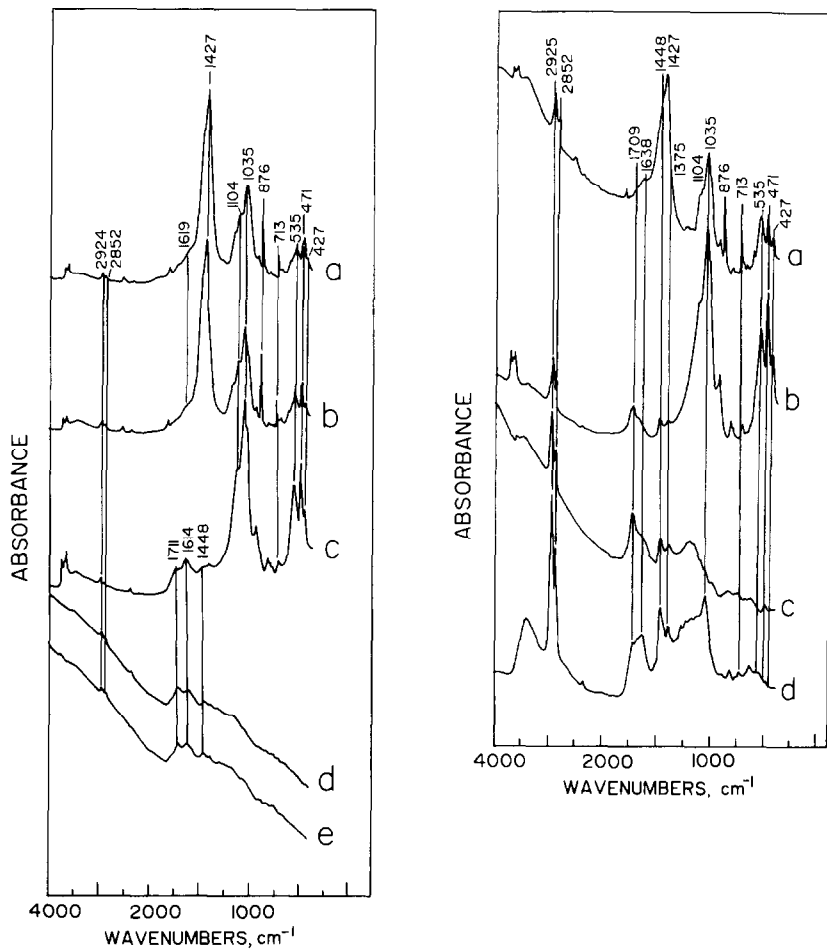


Fig. 3. FTIR spectra of oxidized products of (a) initial shale, (b) BF shale, (c) CF shale, (d) SF shale and (e) kerogen.

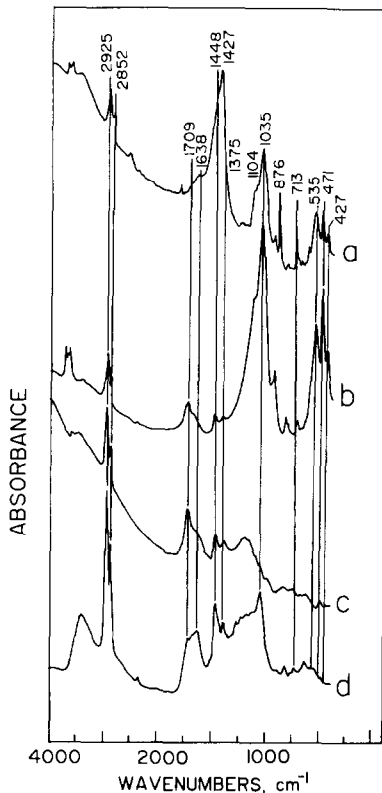


Fig. 4. FTIR difference spectra of (originals)-(oxidized products) (a) initial shale, (b) CF shale, (c) SF shale and (d) kerogen.

composed of aromatic structures substituted with aliphatic material and some carbonyl groups. It appeared that calcium carbonate catalyzed the oxidation of the aromatic moieties. On the other hand, in the demineralization products, which were free of calcium carbonate, the absorption of the aromatic band at  $1638\text{ cm}^{-1}$  was weak but the aliphatic and carbonyl absorptions were dominant. This indicated that aliphatic and carbonyl groups were more susceptible to oxidation than the aromatic ring system of the organic material in the cases where calcium minerals were absent. Silicates and pyrites had no effect on the oxidation reactions.



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