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STUDY OF THERMAL BEHAVIOUR OF ORGANIC MATTER FROM NATURAL PHOSPHATES (YOUSSOUFIA – MOROCCO)

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Abstract

Thermogravimetry (TG), differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) were used to study the thermal behaviour of the organic matter in the natural phosphate and its concentrate kerogen from the Moroccan deposit. The TG analysis showed that both the investigated samples exhibited a one-step thermal oxidation in the main mass loss area, between 160 and 540°C, attributed to the hydrocarbon material. When DSC analyses of oxidation as well as pyrolysis yielded two evolutionary stages of the hydrocarbon in this temperature range : the first one at 160–360°C and the second one above 360°C. Pyrolytic kerogen decomposition was monitored by measuring changes in the principal FTIR organic bands. The results showed, in the first stage, the progressive decrease of signals due to CH_2 and CH_3 vibrations as well as the carbonyl and carboxylic bands, and their subsequent disappearance at 300°C. In the second stage above 400°C, the signal due to the aromatic components (1600 cm^{-1}) appeared but decreased with increasing temperature up to 540°C.

Keywords: DSC, FTIR, kerogen, natural phosphate, oxidation, pyrolysis, TG, X-ray diffraction, X-ray photoelectron

Introduction

Kerogen represents the main form of the sedimentary organic matter that occurs on Earth [1]. Understanding the chemical structure of kerogen provides information on the nature and the origin of the organic matter, accumulation and transformation processes and oil genesis [2]. Due to the heterogeneity and complexity of kerogens, several analytical techniques have been used to correlate and predict the properties of their structure. Particularly, Fourier transform infrared spectroscopy (FTIR) has been one the most widely used methods for routine molecular characterization [3, 4], qualitative typing of kerogen [5, 6]

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and for yielding interesting information about the evolution and the chemical nature of functional groups during the oxidation and pyrolysis processes [7–10]. This paper is aimed to describe the further use of FTIR, combined with the differential scanning calorimeter (DSC), to study the compositional features and the thermal behaviour of the natural phosphate and concentrate kerogen extracted from it.

Experimental procedure

Samples

Phosphate samples were obtained from a mine at Youssoufia (Morocco). Rock phosphates in this site cover an area of about 700 km^2 extending over 50 km in length. The phosphates bed has a maximum depth of 15 m and is divided into layers I and II–III deposited during the Montien and Maestrichien period, respectively. Our samples are from layer I where the organic matter is trapped in the framework of the rocks. Favourable physical conditions allowed the conversion of this matter to bituminous compounds, responsible for the grey colour of the phosphate. The origin and composition of this matter are probably similar to those of all fossil fuels, which have not undergone complete decay [11]. The total organic matter constitutes around 5% of the rocks dry mass. In the case of phosphates, and contrary to other sediments such as bituminous shales, this value indicates that the rock is relatively rich in organic matter [12].

Preparation of kerogen

The phosphate sample was demineralized by a modified version of the methods used for the isolation of kerogen from natural phosphate as indicated in previous study [13]. 100 g of dried natural phosphate were treated with chloroform to extract the bitumens until the solvent in the soxhlet arm becomes colourless. The bitumen-free (BFP) phosphate was then dried and weighed. It is subsequently attacked with HCl until no further carbon dioxide evolved. The residue was washed with hot distilled water until the silver nitrate test for chlorides was negative. The hydrochloric attack was repeated twice to eliminate all calcium products. The decarbonated phosphate (CFP) was dried, washed with concentrated HCl and treated with concentrated HF (5 mL g^{-1} decarbonated phosphate) at 60°C under a nitrogen atmosphere for 8 h. The silicate-free phosphate obtained in this step was then washed with hot distilled water and the HF treatment step was repeated. After drying the SF phosphate, a saturated boric acid solution was added and the sample was stirred for 30 min. Finally, the remaining brown solid was treated with 6 N HCl and the kerogen was washed with hot distilled water to remove chlorides and dried overnight at 60°C. It should be noted that pyrite is known to be the major mineral component remaining after HCl/HF treatment [14]. The yields of the demineralization procedure of the natural phosphate are shown in Table 1.

Table 1 The composition of natural phosphate

Component	Mass/%
Bitumen	0.40±0.03
Apatite, carbonates[a]	86.6±0.2
Silicates	7.9±0.1
Pyrite	0.30±0.01
Kerogen	4.8±0.1

[a] Includes sulphides, sulphates, oxides and hydroxides

Sample characterization

XPS analyses of the samples were carried out with a Riber Mac 2 semi-imaging analyser and were recorded by means of a 300 W AlK_α radiation (1486.6 eV).

The X-ray diffractograms were obtained with a Philips spectrometer using the CuK_α radiation produced at 32 kV and 20 mA by a Philips PW 1043 X-ray tube.

FTIR spectra were obtained with a Perkin Elmer-1725 spectrometer. Spectra of natural, demineralized and thermally treated phosphate products were obtained at a resolution of 2 cm^{-1}.

Thermal analyses

The processes of pyrolysis and oxidation were followed using a Shimadzu Model-50 Series TG analyser as well as Perkin Elmer DSC-7. The samples were heated under nitrogen or oxidant atmosphere from 25 to 540°C at 10°C min^{-1} heating rate.

Results and discussion

Sample characterization

The chemical analysis by the X-ray photoelectron (XPS) of the products at various stages of the demineralization process of natural phosphate are shown in Fig. 1. The natural phosphate studied are characterized by relatively high phosphorus, calcium and silicium contents. This may be attributed to the presence of fluorcarbonate-apatite, carbonates and silicate minerals originally present in the phosphate (Figs 1a and 1b). This component materials are absent in spectrum of kerogen (Fig. 1c) which conformed complete demineralization of natural phosphate.

From the results of X-ray analysis, the phosphate is represented as fluorcarbonateapatite (Fig. 2), the main accompanying minerals are dolomite, calcite and α-quartz. There are also some amounts of kaolinite and pyrite.

Demineralization procedure results

In order to obtain kerogen concentrate, the removal of mineral matters from the natural phosphate was checked by FTIR analysis after each step of extraction. The results

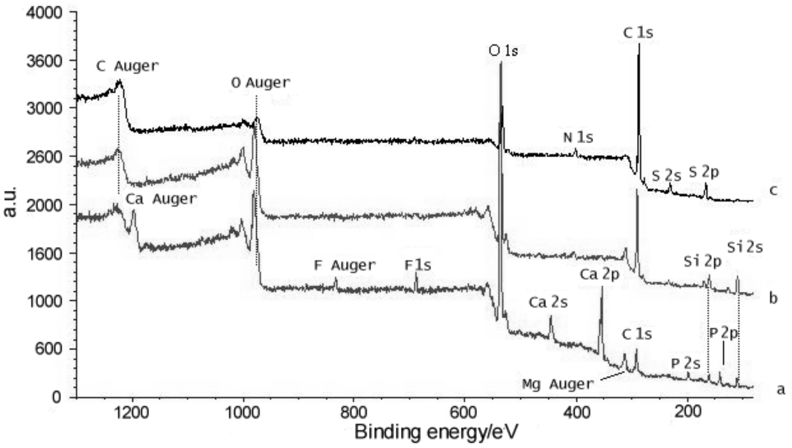

Fig. 1 XPS spectra of a – natural phosphate, b – carbonate-free phosphate and c – kerogen

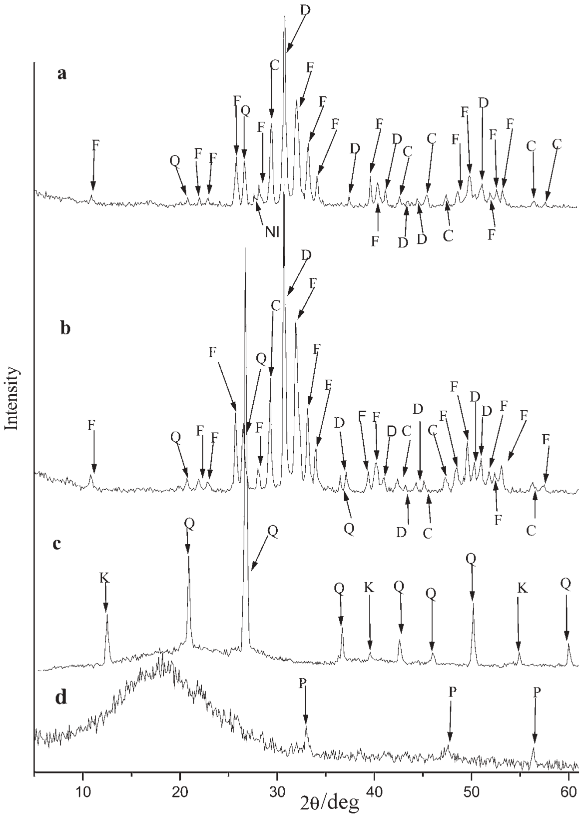

Fig. 2 X-ray diffractogram of a – natural phosphate, b – bitumen-free phosphate, c – carbonate-free phosphate and d – kerogen
F: fluorcarbonateapatite; D: dolomite; C: calcite; Q: quartz; K: kaolinite; P: pyrite

are given in Fig. 3. Chloroform treatment was performed to extract bitumens of natural phosphate. FTIR spectra of the original phosphate and bitumen-free phosphate (BFP) showed no difference (Figs 3a and 3b). The removal of fluorcarbonateapatite and carbonate minerals by extraction with HCl was evident by the difference between the spectra of BFP and carbonate-free phosphate (CFP). Their bands were no longer evident in the CFP spectrum (Fig. 3c); a strong band in the range of 900–1100 cm^{-1} centred at 1045 cm^{-1}, medium intensity bands at 576 and at 606 cm^{-1}, and the doublet of the structural carbonate bands at 1429 and 1455 cm^{-1} attributed to CO_3^{2-} ions replaced PO_4^{3-} ions (fluorcarbonateapatite) [15, 16]; sharp band at 865 and a relatively less sharp band at 714 cm^{-1} (calcite) and the bands at 725 and at 875 cm^{-1} (dolomite) [17]. Further extraction with a HF/HCl mixture showed, as expected, the loss of main silicate minerals bands (α-quartz and kaolinite) in the 1100–900 and 550–450 cm^{-1} ranges [18]. By contrast, hydrochloric acid and hydrofluoric acid treatments did not affect pyrite; a broad band at 422 cm^{-1} attributed to residual pyrite [19] in the FTIR spectrum of kerogen (Fig. 3d).

Relatively to the internal standard most organic bands common to the four FTIR spectra seemed to be more intense in the case of the kerogen. The FTIR spectrum of kerogen concentrate (Fig. 3d) displayed stretching aliphatic bands (CH_3+CH_2) at 2923 and 2852 cm^{-1} and the deformation bands of methyl (1368 cm^{-1}) and both methyl and methylene groups (CH_3+CH_2; 1456 cm^{-1}). FTIR spectrum also showed

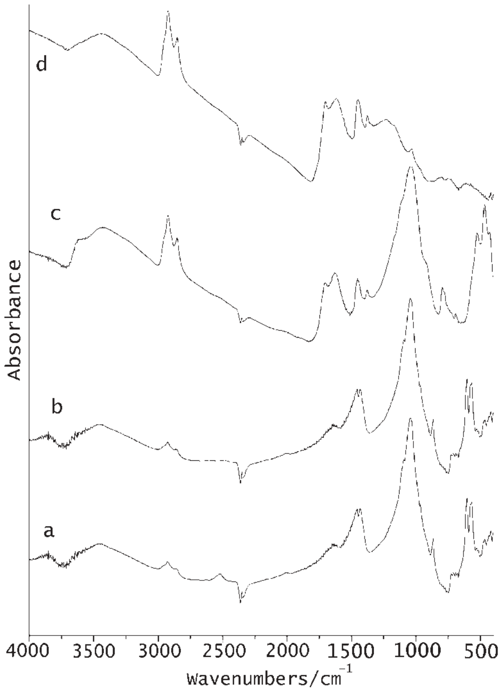

Fig. 3 FTIR spectra of a – natural phosphate, b – bitumen-free phosphate, c – carbonate-free phosphate and d – kerogen

distinct bands assigned to the carbonyl and or carboxyl groups (C=O; 1704 cm^{-1}), and to the stretching vibration of aromatic carbons (C=C; 1622 cm^{-1}) [20]. In the region 1000–1200 cm^{-1}, various bands appeared assigned to aliphatic alcohol, ester and ether C–O bonds [4, 8, 19, 21]. In addition, the bands assigned to the out of plane deformation vibration of one isolated aromatic C–H bond (Char_1; 870 cm^{-1}), two or three adjacent aromatic C–H bonds (CHar_{2-3}; 814 cm^{-1}) and four adjacent aromatic C–H bonds (CHar_4; 750 cm^{-1}) [20–22].

Thermogravimertic analyses

TG analyses were carried out in order to examine the trend of organic matter decomposition by heating. The TG curves (normalized to unit mass) of natural phosphate and kerogen concentrate at a heating rate of 5°C min^{-1} in air atmosphere are shown in Fig. 4. This latter clearly shows that there were two stages of mass loss profile up to 540°C. The low temperature phase, below 160°C, corresponds to the loss of moisture water. Haddadin and Tawarah [23] also attributed the lower temperature mass loss to physical change in the kerogen, molecular rearrangement accompanied by the gas release. The loss of hydrocarbon materials took place during the second stage of decomposition. It is evident that the natural phosphate and its kerogen concentrate which exhibited one stage evolution of hydrocarbon materials within the temperature range of 160 to 540°C. Moreover, the extractable organic contents were approximately 5 and 90% of the original sample mass for natural phosphate and its kerogen concentrate, respectively. The medium temperature portion of the thermal curves might represent thermal decomposition identical to that observed in a previous study in an inert atmosphere [13]. This singular step thermal decomposition of natural phosphate is similar to those observed for various solid fuels such as those from Colorado [24] Jordan [25] Ohio, West, Virginia, and North Carolina [26], all in the USA, Aleksinac and Knjazevac in Yugoslavia [27], Beypazari in Turkey [29], and Kark, Dharanji and Malgeen in Pakistan [29].

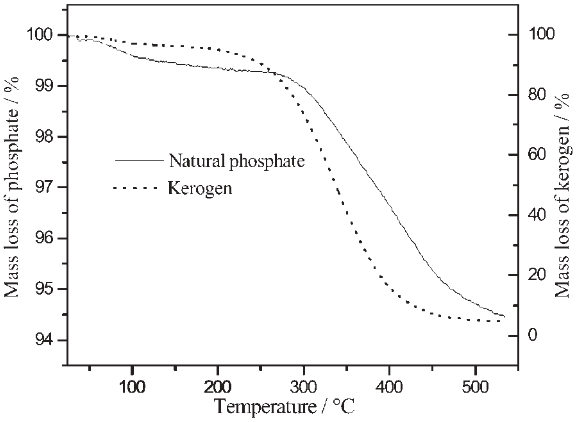

Fig. 4 Non-isothermal TG curves at 5°C min^{-1} in air for a – natural phosphate and b – kerogen

Differential scanning calorimetry

DSC enabled us to follow the heat changes during the reactions. The DSC traces of natural phosphate and kerogen, at a heating rate of 5°C min^{-1} in air atmosphere up to 540°C, are represented in Fig. 5. This figure indicates that natural phosphate exhibits two exothermic peaks at 325 and 420°C as the temperature was increased. As they occurred in the DSC curve of kerogen concentrate, these peaks were the result of the oxidation of only the organic matter in the original phosphate. Moreover, the two peaks were also observed in inert atmosphere (Fig. 6). Similar results were obtained by other workers using DTA and DSC to investigate the oxidation of oil shales and coals [18, 22, 30, 31]. In this regard, Stuart and Levy [32] showed that main temperature oxidation of kerogen is a complex two-stage phenomenon. They found that the first step involves a progressive disappearance of aliphatic and carbonyl group

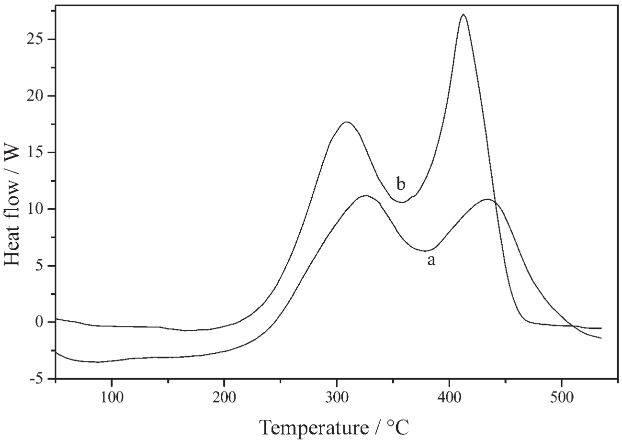

Fig. 5 DSC curves at heating rate of 5°C min^{-1} in air for a – natural phosphate and b – kerogen

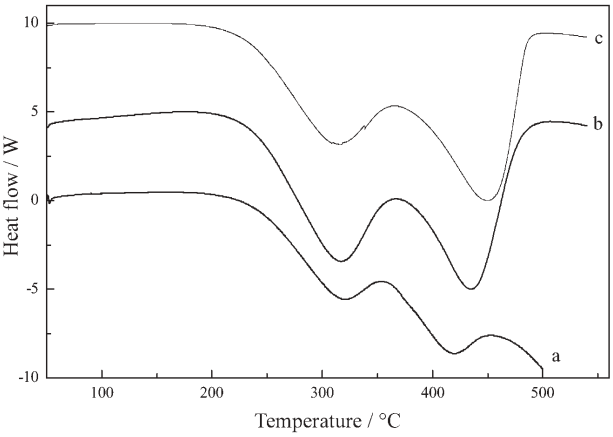

Fig. 6 DSC curves at heating rate of 5°C min^{-1} in nitrogen for a – natural phosphate, b – decarbonated phosphate and c – kerogen

whereas stage 2 is the pyrolysis of an aromatic residue. While Cetinkaya and Yürüm [18] suggested that these peaks result to the chain oxidation reactions of organic matter. In addition, it has been demonstrated [33–35] that kerogen, when heated, first decomposes to a soluble organic material, pyrobitumen, which then decomposes to form the final products of oil, gas and coke.

Effect of temperature on natural phosphate and kerogen decomposition

Thermal transformation of the natural phosphate

Because of the strong emission bands from minerals, it is difficult to clearly assign changes in the FTIR spectrum of the raw phosphate in the region 400–2000 cm^{-1}. It is well known that in some cases overtone and combination bands of minerals can appear enhanced in emission [36] and these mostly occur in the 1200–1800 cm^{-1} region. Nevertheless, some information can be obtained from the aliphatic C–H stretch which is free from interference.

The sequence of FTIR spectra in Fig. 7 outlines the principal thermochemical changes during the pyrolytic stage of the natural phosphate. These spectra are domi-

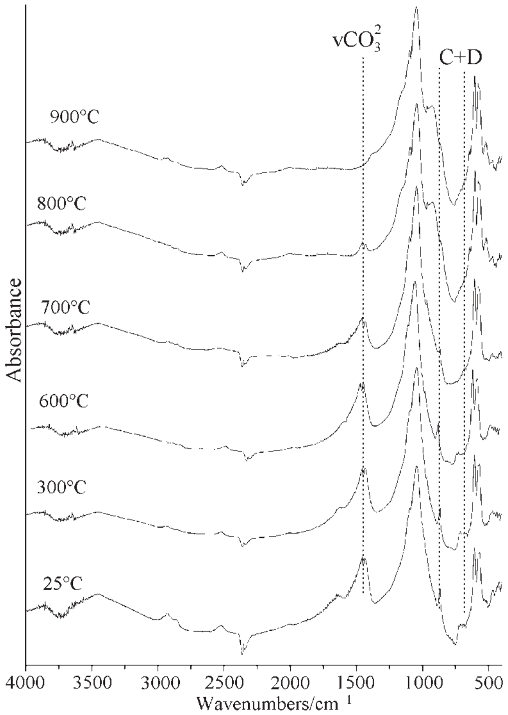

Fig. 7 FTIR spectra for sequential pyrolysis of the natural phosphate D: dolomite ; C: calcite

nated by fluorcarbonateapatite. But there is no change in the spectra up to 300°C except for a disappearance of intensity of the aliphatic C–H stretch band in the 2700–3000 cm^{-1} region. By 600°C, almost all emission bands due to organic materials in the range 1500–2000 cm^{-1} were lost. Between 600 and 700°C, the carbonate band at 1440 cm^{-1} lost intensity and disappeared completely by 800°C in accordance with the expected decomposition. The remaining features at 800°C are related to the apatite mineral.

Thermal transformation of kerogen concentrate

The FTIR spectra of kerogen concentrate obtained after heating at the temperature range of 25 to 600°C are shown in Fig. 8. As expected, almost all emission bands due to the minerals are absent. A general sequence transformation can be seen. Firstly, a progressive decrease in aliphatic C–H bands (3000–2800; 1368; 1456 cm^{-1}); carboxyl bands C=O (1704 cm^{-1}) and the C–O band (1200–1000 cm^{-1}) were observed. That is, in the initial stages of pyrolysis, decarboxylation is the primary process, accompanied by the removal of ester and alkanone groups. As the kerogen decomposes, the progressive removal of aliphatic functional groups can be further observed until the aliphatic features finally disappear at 300°C. At pyrolysis levels higher than this, the stretching vibration of aromatic carbons (C=C; 1622 cm^{-1}) is still prominent and a residual band at 900–1300 cm^{-1} can also be observable, indicating the presence of substituted aromatic ring of heteroaromatic entities. At 600°C, the aromatic residue decomposes, as shown by the gradual diminution of the 1622 cm^{-1} band and for the fully pyrolysed spent kerogen concentrate, no bands attributable to the organic functional groups remain, indicating that the residual material is the elementally carbon.

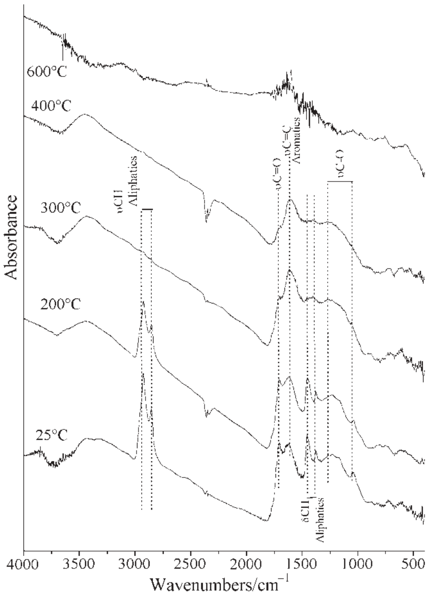

Fig. 8 FTIR spectra for sequential pyrolysis of the kerogen

The FTIR spectral changes that occur in the residues after each stage of pyrolysis confirm previous results that the two major DSC peaks pyrolysis (oxidation) at 260 and 420°C denoting two-stage pyrolysis (combustion) of the kerogen component; stage 1 involves the complete decomposition of aliphatic constituents whereas stage 2 is the pyrolysis of an aromatic residue.

Conclusions

In this research, an experimental study on the thermal behaviour of organic matter in phosphate from Moroccan deposit (Youssoufia – Morocco) was presented. The following results were obtained from the research conducted:

- The oxidation process of natural phosphate and its kerogen concentrate showed a singular step of thermal oxidation accompanied by mass loss between 160 and 540°C attributed to hydrocarbons.
- DSC analyses of oxidation as well as pyrolysis exhibited two stages of thermal evolution of hydrocarbon materials. In the first stage, the progressive decrease aliphatic and carbonyl groups, and their subsequent disappearance at 300°C. In the second stage above 400°C, the aromatic components appeared but decreased with increasing temperature up to 540°C.

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