

## Mineralogical characterization and preliminary assessment of the hydrocarbon potential of organic-rich sedimentary rock from the western part of Central Kongo

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**Abstract:** In this work, the mineralogical characteristics and the assessment of the petroleum potential of organic carbon-rich sedimentary rock (CK sample) originating from the western part of the Central Kongo were the subject of a preliminary analysis and the results were compared with those of Moroccan oil shales. The mineralogical characterization was carried out using X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Fourier Transform Infra-Red (FTIR) spectroscopy, Thermal Gravimetry/Differential Thermal Analysis (TG/DTA) and Scanning Electronic Microscopy (SEM-EDX). The results show that the examined sedimentary rock contain a significant part of minerals, about 80%, consisting of quartz, clays and pyrite, similar to those frequently found in oil shales. The pyrolysis also indicates the presence of volatile matter between 250 and 580°C, attributed to the Organic Matter (OM) disseminated within the sedimentary rock as was shown in several carbon-rich materials. The detection of pyrite in the CK sample reveals the existence of a reducing environment during the preservation period of OM in the source rock. The assessment of the petroleum potential using the basic Rock-Eval method associated with the elemental analysis and <sup>13</sup>C Cross Polarization/Magic Angle Spinning Nuclear Magnetic Resonance (<sup>13</sup>C CP/MAS NMR) spectroscopy indicated a very good organic richness (TOC=10.77%), very good petroleum potential (S<sub>2</sub>=80.4 mgHC/g rock) with the sapropelic OM described as type I kerogen (H/C molar ratio of 1.71) characterized by high hydrogen index (HI=746 mgHC/g TOC) and low oxygen index (OI=13 mgCO<sub>2</sub>/g TOC) values. The Rock-Eval results were confirmed by <sup>13</sup>C CP/MAS NMR spectroscopy which shows the exclusive presence of aliphatics. The mineralogical and petroleum characteristics of CK sample show a great resemblance with those of known oil shales such as Moroccan oil shales and its kerogen is probably related to a marine or lacustrine environment which formed in anoxic sedimentary rocks and with a thermal evolution that has just reached the early stage of the oil window.

**Keywords:** Mineralogy, Thermal analysis, Source rock evaluation, Rock-Eval analysis, Kerogen.

### Introduction

Nowadays, the demand for energy is constantly growing due to global population growth and industrial development, particularly for emerging countries. Energy from conventional resources such as oil and natural gas cannot fully meet global economic development in the near future, as its availability and reserves are gradually regressing. Another aspect of energy exploration, currently in progress and of interest to both researchers and governments is the ability to convert unconventional resources such as organic-rich sedimentary rocks containing solid fuels. Indeed, investigation on sedimentary rocks capable of producing new hydrocarbons with the appearance similar to

conventional crude oils has intensified in recent years because of the great potential of global reserves that is available. Some countries have already taken steps to develop their own mining industries such as United States of America (USA), Canada, Estonia, China and Brazil<sup>1,2</sup>. Others are in the process of being set up such as Morocco which ranks seventh in the world's reserves<sup>3</sup> or, in the geochemical exploration stage like the Democratic Republic of the Congo which possess the largest potential estimation on the African continent<sup>4</sup>.

Carbon-rich sedimentary rocks refer to all mineral rocks containing solid OM in the form of kerogen like coal, oil shale and tar sand. This OM can be converted by pyrolysis into synthetic fuel, valuable chemical products via various processes or burned

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directly for electricity production<sup>5-7</sup>. The kerogen is consisting of complex organic polymers having 3D structure and which is insoluble in common solvents<sup>8</sup>. Its type and nature are depending on its environment during accumulations and preservation conditions in the sediment and also to maturational changes during diagenesis<sup>9-11</sup>. The determination of these factors through the basic Rock-Eval method is fundamental for the grade classification of OM-rich rocks. Therefore, several analytical methods have developed specific criteria to assess the generative potential of the source rock such as reported by Peter and Cassa<sup>12</sup> and Hunt<sup>13</sup>. These criteria are based on evaluation of OM content illustrated by Total Organic Carbon (TOC) measurements. Van Krevelen<sup>14</sup> and Tissot and Welt<sup>15</sup> have classified the OM into four main types named I, II, III and IV according to the molar ratio of the elements carbon, hydrogen and oxygen.

Several regions of the African continent have significant potential for organic-rich sedimentary rocks capable of producing alternative crude oil but so far, no real industry has been established and there is a great delay in this area due to the high cost of necessary investments and the unstable tendency of conventional oil prices that faces such development. According to World Energy Council in its recent report of 2010, the largest reserves of energetic sedimentary rocks in Africa are located in the Democratic Republic of the Congo and consist mainly of oil shale with total oil evaluated at 100 billion barrels in place. This value is practically twice the proven reserves of oil shale in Morocco<sup>3</sup>.

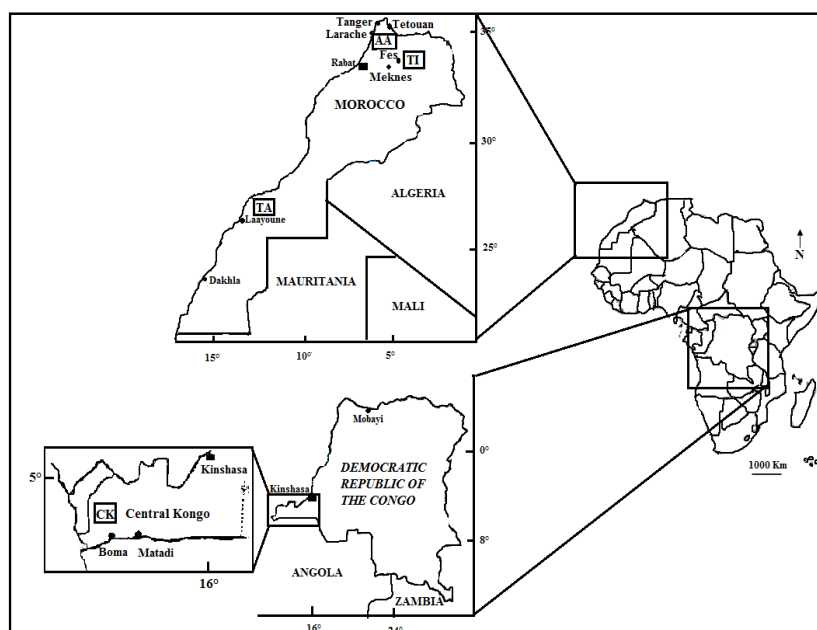
In the present study, the mineralogical and Rock-Eval analyses were conducted on sedimentary rock from western Central Kongo formation of the

Democratic Republic of the Congo. In fact, few geological studies were carried out on this part<sup>16,17</sup> but to our knowledge; the geochemical investigations of the Central Kongo are very scarce compared with other areas of the country. Our objective is to examine the nature and type of the western Central Kongo sedimentary rock and to evaluate their oil-generating potential. A comparison of source rock characterization with the known Moroccan oil shales was also made and discussed.

### Geological location

The west Central Kongo region is part of the Neoproterozoic PanAfrican-Brasiliano Orogenic Belts that contain two N-S-trending orogens<sup>16</sup>. It takes the core of the Central African shield and can be determined as an assembly of archaic fragments, including the Kasai, Mbomou, and the Chaillu-Gabon cratons, which were once overtaken with the Sao Francisco (Brazil) craton, to form the amalgamated Central African landmass at the time of Gondwana assembly<sup>18</sup>. The turning on of the South Atlantic Ocean and the break-up of Gondwana resulted in an elevated Rift shoulder forming the present western boundary of the Congo. While separation of South America from Southern Africa got started during the earliest Cretaceous and kept on well into the middle Cretaceous and was coming after by a major Santonian compressional event across Central African and the development of the Cenozoic East African Rift system<sup>18,19</sup>.

The study site represents the Central Kongo region of the Democratic Republic of the Congo, at Kakongo (Mavuma) which is located about 60 kilometers North-West of the Boma City (Fig. 1).



**Figure 1.** Location map of the studied sites: Sedimentary rock of the western Central Kongo (CK), Timahdit (TI), Tarfaya (TA) and Arbaa Ayacha (AA)

The source rocks of Timahdit (TI), Tarfaya (TA) and Arbaa Ayacha (AA) have been the subject of huge previous researches<sup>20-23</sup>. The site of Timahdit is situated in the region of Fes-Meknes at 1800 m altitude of the Middle Atlas. It is 30 km south of the town of Azrou on the N13 National road and, The Tarfaya site is located in the Laayoune-Sakia El Hamra region of southern Morocco and 890 km southwest of the capital of Morocco, Rabat. Arbaa Ayacha region is about 63 km SW of the city of Tetouan (about 70 km to the North-East of the city of Larache) on the road Tetouan - Larache (Fig. 1).

## Experimental

### Experimental Materials

Collection of sedimentary rock samples was carried out by our partners from the Center of Geological and Mining Research (CGMR) of Kinshasa, Democratic Republic of the Congo. Sampling was conducted in an area where there is a great similarity of rock deposits. Only the unexposed layers to air that are involved in order to avoid the effects of weathering. The collected samples were firstly washed repeatedly with distilled water, dried in an oven at 80°C overnight, then crushed, homogenized and subsequently sieved to less than 180 µm (80 mesh), according to the American Society for Testing Materials (ASTM); standard (E11), and the International Confederation for Thermal Analysis and Calorimetry (ICTAC) committee recommendations for thermal measurements<sup>24,25</sup>. Finally, the samples obtained were stored in a vacuum desiccator for further use.

### Mineralogical analysis

X-Ray Diffraction (XRD) is an analytical technique generally used to identify minerals and other crystalline phases in a wide range of materials, including sedimentary rocks. In this study, the powder XRD patterns were performed using X-ray diffractometer (Siemens D 500) equipped with a copper anticathode ( $\lambda_{\text{CuK}\alpha} = 1.541838 \text{ \AA}$ ) with scanning speed of  $0.04 \text{ }^\circ\text{s}^{-1}$ , from 5 to 60 ( $^\circ 2\theta$ ) and at a tube voltage of 35 kV and a current of 30 mA. Identification of minerals in the samples was achieved using the database software of International Centre for Diffraction Data (ICDD) as source of reference diffraction patterns (JCPDS files).

X-Ray Fluorescence (XRF) analyses were carried out to quantify the mineral content in the samples, by using FX Axios PW4400 spectrometer system. The proportions of the major elements in the samples, expressed as oxides, were calculated using the instrument software.

Scanning Electron Microscopy coupled with Energy Dispersive X-Ray micro analyzer (SEM-EDX) was used to characterize the morphology and distribution of minerals and, the identification of OM in the sedimentary rock. SEM-EDX data were collected using a Jeol model JSM-5400 equipped

with an Oxford ISIS model EDX spectroscopy module for local chemical analysis. Semi-quantitative analyses were made with an accelerating voltage of 20 kV and working distance (WD) of 18.6 mm. The sample was imaged at a range of magnifications to obtain high resolution micrographs and to achieve better contrast between the pore and solid phases.

Fourier Transform Infra-Red in conjunction with Attenuated Total Reflectance (FTIR-ATR) spectroscopy was performed to identify qualitatively organic, polymeric and inorganic materials by observing their characteristic absorption bands. The spectra were recorded using a Jasco FT/IR 4600 spectrometer provided with ATR (Pro One) module. The samples were scanned in transmission with  $4 \text{ cm}^{-1}$  resolution at the range  $4000\text{-}400 \text{ cm}^{-1}$ .

The simultaneous thermal analysis provides valuable information on structural changes and help to estimate the volatile species of the samples as a function of the temperature. The TG/DTG/DTA experiments were conducted on a Labsys<sup>TM</sup> Evo Setaram apparatus from ambient to 1000°C by using the ICTAC recommendations for collecting and performing the experimental data. A powdered mass of about 10 mg was subjected to a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  under air or nitrogen gaseous flow of  $45 \text{ mL min}^{-1}$ .

### Source rock evaluation

The Rock-Eval pyrolysis has been widely recognized by the petroleum industry as a useful technique for rapid assessment of the potential of hydrocarbons generation of the source rock and can provide valuable information on the type and thermal maturity of the associated OM of numerous sedimentary rocks. The method was firstly developed at "Institut Francais de Pétrole" (IFP)<sup>26</sup> and later modified by Lafargue and Behar<sup>27,28</sup>. The Rock-Eval analysis was performed using Rock-Eval 6 instrument equipped with a Flame Ionization Detector (FID) and Thermal Conductivity Detector (TCD) to measure the content of organic compounds and CO<sub>2</sub> respectively. A thermocouple is used to measure the temperature of evolved chemical reactions. The powdered sample was paralyzed at temperature program sequences, from 300 to 650°C, in helium flow. The amounts of hydrocarbons generated during the pyrolysis process were quantified to determine the main parameters used in source rock evaluation. The main parameters measured during pyrolysis include the presence of free hydrocarbons S1 (mgHC/g rock) at 300°C, the hydrocarbon generation potential of the rock, S2 (mgHC/g rock) at 300-650°C, the amount of carbon dioxide CO<sub>2</sub> obtained after oxidation program (850°C), S3 (mgCO<sub>2</sub>/g rock), temperature at which the maximum rate of S2 hydrocarbon evolution takes place, Tmax (°C), and the Total Organic Carbon content, TOC (wt. %). Some other parameters including Hydrogen Index (HI) corresponding to the

amount of pyrolyzable hydrocarbons relative to the TOC in the sample ( $S2/TOC \cdot 100$ ), Oxygen Index (OI), which corresponds to the amount of carbon dioxide released from pyrolyzable organic compounds relative to the TOC of  $((S3/TOC) \cdot 100)$ , and Production Index (PI), which is defined as the ratio  $(S1/(S1+S2))$ , were calculated from the above-measured values.

The chemical composition of OM contained in raw sample; expressed as weight percentage (wt.%) of C, H, N and S elements was conducted on Flash 2000 EA 1112, Thermo Fisher Scientific Elemental Analyzer, according to ASTM D5373 requirements (Official Method).

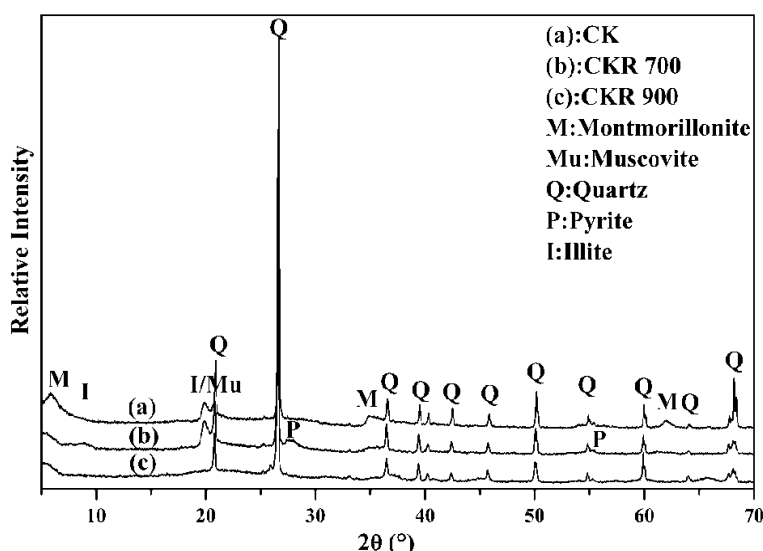
The solid-state  $^{13}C$  CP/MAS NMR were carried out on a 600 MHz Bruker NMR spectrometer at the resonance frequency of 150 MHz, with a contact time of 2 ms and relaxation delay of 5 s. The spectra were obtained at 93K averaging over 250 scans. The chemical shifts were referenced to the DMSO using adamantane as an external standard. All organic chemical analysis experiments were performed at the

National Office of Hydrocarbons and Mines (ONHYM) and the laboratories of CNRST-UATRS, Rabat, Morocco.

## Results and Discussion

### XRD analysis

Fig. 2 displays the XRD analysis of the western Central Kongo sedimentary rock (CK) and the subsequent residues obtained after treatment in air for 3 hours at 700 °C (CKR 700) and at 900 °C (CKR 900). The XRD pattern of CK sample (Fig. 2. a) shows that the quartz is the dominant mineral composition with the observed diffraction peaks corresponding to JCPDS Card file No. 01-079-1910. In addition, a small amount of clay minerals is present as montmorillonite, illite and muscovite. The appearance of the diffraction peak at  $2\theta = 8.5^\circ$  (10 Å) probably indicates the presence of interstratified illite/montmorillonite, which is recognized as the most abundant mixed-layer clay minerals in sedimentary rocks and soils<sup>29</sup>.



**Figure 2.** XRD diagrams of the western Central Kongo sedimentary rock: Raw sample (CK), treated at 700°C (CKR 700) and treated at 900°C (CKR 900)

Indeed, clay minerals play an important role in fundamental geological research and oil industry and, their association with OM in sedimentary rocks can predict the quality of organic-rich source rock, hydrocarbon generation and expulsion processes<sup>30,31</sup>. Several studies suggest that there is a close relationship between hydrocarbon reservoirs and the presence of expanded clay minerals such as montmorillonite<sup>32,33</sup>. Thus, the source rock presents a great potential for hydrocarbon generation due to the stable pore water that holds in montmorillonite clay by comparing with the non-expanded ones<sup>34</sup>. In addition, the presence of expanded clays in sedimentary rocks has some catalytic effects on oil generation process as can be seen for oil shales<sup>35</sup>.

The absence of carbonate minerals in the CK sample, commonly observed in several sedimentary rocks implies that the rock examined is predominantly siliceous and probably deposited in a marine environment<sup>36</sup>. On the other hand, the sample calcined in air atmosphere at 700°C (CKR 700) (Fig. 2.b) shows slight changes. The clay structure of montmorillonite is collapsed leading to the major oxides of  $SiO_2$  and  $Al_2O_3$  while the structure of illite and muscovite remain unaltered at this temperature. However, we note the presence of a low content of pyrite which is consistent of JCPDS Card No. 42-1340. The treatment at 900°C (CKR 900) (Fig. 2.c) leads to the appearance of quartz and pyrite. Table 1

displays the semi-quantitative XRD analysis of the CK and CKR samples.

**Table 1.** Semi-Quantitative XRD analysis.

Samples	quartz	montmorillonite	pyrite	illite/muscovite
Raw CK	+++	++	No visible	+
Residue CKR 700	++++	Destroyed	+	+
Residue CKR 900	+++++	-----	+	Destroyed

+: Trace; ++: Small; +++: Moderate; ++++: Large; +++++: Dominant

### Mineralogical analysis

The mineral composition of the raw sample (CK) and its treated form at 900°C (CKR 900), determined by XRF analysis and expressed as the relevant oxides, are presented in Table 2. From XRF results, the loss on ignition (L.O.I.) of CK sample was found to be 28.3%; this is attributed to weight loss of H<sub>2</sub>O, OH types issued from the moisture and the decomposition of clay minerals, in addition to the important percentage of volatile organic species associated with the mineral matrix. Similar results were also obtained on oil shales and attributed to the existence of OM<sup>37</sup>. This OM is the most important component of sedimentary rocks<sup>38</sup> and it cannot be detected by XRD analysis due to the amorphous nature and complex structure of organic carbon. It is also worth noting the domination of quartz component (48.3 %) followed by alumina (15.9 %) and iron oxide (1.23 %) reflecting the presence of clay minerals. The concomitant existence of iron and

sulfur elements suggests the presence of pyrite in CK sample and indicates anoxic condition of the depositional environment of the source rock. The existence of a reduction environment provides good conditions for preservation of volatile matter such as OM and is thermodynamically less efficient due to oxygen deficiency<sup>7,39</sup>. The small percentage content of Mg and Ca shows the almost total absence of carbonate species such as dolomite and calcite as it is confirmed by XRD analysis. The existence of sodium, potassium and magnesium shows the contribution of clay minerals in the chemical composition of the CK sample. As for the treated sample at 900°C (CKR 900), the percentage of minerals increased under the temperature effect notably for major oxides due to the removal of OM and water molecules. Other chemical elements with very low contents are also found in the investigated samples (Table 2).

**Table 2.** Mineralogical composition (wt.%) of Raw CK and Residue (CKR 900).

Elements	Raw CK	Residue (CKR 900)
SiO <sub>2</sub>	48.3	67.2
Al <sub>2</sub> O <sub>3</sub>	15.9	22.1
Fe <sub>2</sub> O <sub>3</sub>	1.23	1.47
MgO	2.68	3.60
CaO	0.13	0.21
Na <sub>2</sub> O	0.11	0.18
K <sub>2</sub> O	0.18	0.22
SO <sub>3</sub>	2.27	0.44
TiO <sub>2</sub>	0.63	0.72
P <sub>2</sub> O <sub>5</sub>	0.11	0.14
Others	0.16	0.29
Loss Of Ignition (L.O.I.)	28.30	3.43

**Others:** ZrO<sub>2</sub>, CuO, ZnO, SrO, NiO, Nb<sub>2</sub>O<sub>5</sub>, Y<sub>2</sub>O<sub>3</sub>, I, Ac, Rb.

### Scanning electron microscopy (SEM-EDX)

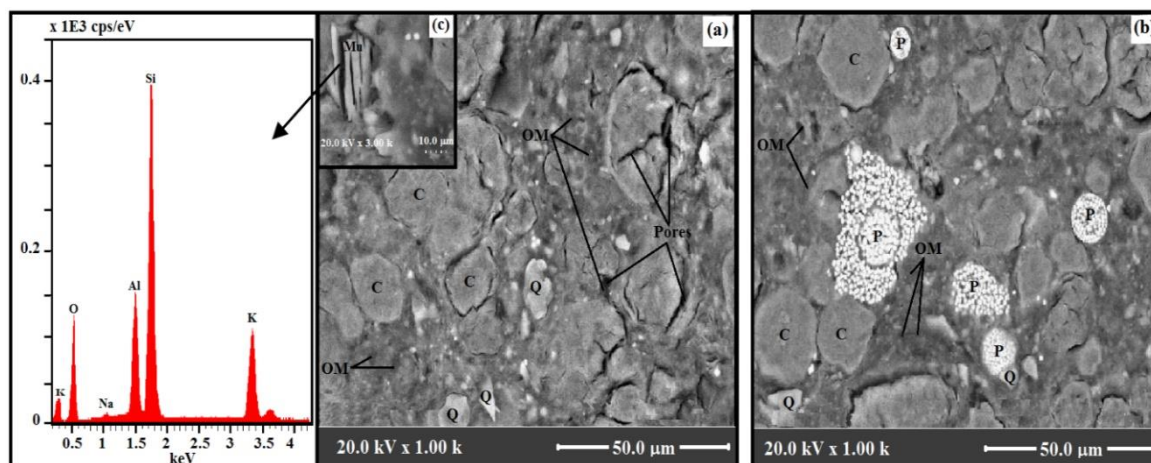
The microstructure examination of the raw CK sample is illustrated in micrographs of Fig. 3(a, b, c). This microstructure is characterized by an irregular distribution of the chemical components and grain sizes as can be shown in Fig. 3(a, b). The microanalysis EDX reveals that quartz and clay minerals are the major mineral phases in accordance with the XRD and XRF results. The muscovite clay is recognized by the observation of a phyllosilicate

framework consisting of sheet structure made of layers (Fig. 3(c)). It is also noted the presence of two populations of pyrite (Fig. 3(b)), identified as single or aggregate framboids dispersed non-uniformly and developing an approximately spherical external shape as shown in many carbon-rich sedimentary rocks<sup>40,41</sup>. The formation of pyrite framboid is closely related to the geochemical composition of the sedimentary rock studied and its occurrence provides evidence of the reducing environment during the

deposition process which promotes the preservation conditions of OM<sup>42</sup>.

The existence of many pore types with various sizes was observed in the Fig. 3(a). Some of them contain a dark grey matter, which is identified as OM, while others are apparently empty. These pores and their connectivity are important for the storage

and flow of hydrocarbons that could be generated by the conversion of OM. Presence of the OM has been observed in many parts of the surface and located predominantly in the pores and slits, between the phyllosilicate sheets (muscovite). The microstructural characteristics observed in the CK sample are very similar to those reported for several oil shales accommodating a good quality of OM<sup>43,44</sup>.



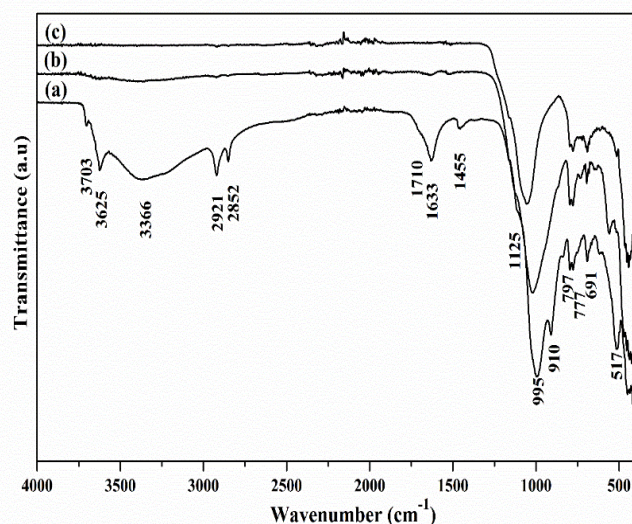
**Figure 3.** SEM-EDX analysis of the raw CK sample  
(Quartz: Q, Muscovite: Mu, Pyrite: P, Clays: C and Organic Matter: OM)

#### FTIR-ATR spectroscopy

Fig. 4 shows the FTIR-ATR spectra of (CK), (CKR 700) and (CKR 900) samples. As can be seen, the IR spectrum of the CK sample (Fig. 4(a)) reveals a complex signature represented by a multitude of vibrational bands belonging to both the mineral matrix and the disseminated organic component. Some organic bands are partially overlapped by the strong absorption region of mineral phases (1200-700  $\text{cm}^{-1}$ ). Thus, the bands observed beyond 3500  $\text{cm}^{-1}$ , at 3703 and 3625  $\text{cm}^{-1}$  were attributed to OH associated to Si and Al of clay minerals present in the CK sample (Si-OH, Al-OH)<sup>45,46</sup>. The flared band between 3500-3200  $\text{cm}^{-1}$ , giving a maximum at around 3366  $\text{cm}^{-1}$  is due to moisture and OH stretching bands of internal water molecules belonging to clay mineral structures<sup>46</sup>. This band is usually associated to another at 1633  $\text{cm}^{-1}$ , which is related to the bending modes of water molecules. In this region of absorption, it is not excluded the presence of organic OH due to OM<sup>47</sup>. The doublet appearing in the range of 2930 and 2800  $\text{cm}^{-1}$  is assigned to asymmetric and symmetric stretches of alkyl  $\text{CH}_2$  groups, respectively. The broadening type of the  $\text{CH}_2$  bands indicates that methyl groups ( $\text{CH}_3$ ) also exist in this absorption region<sup>48,49</sup>. These bands present an additional vibration at 1455  $\text{cm}^{-1}$ , due to asymmetric bending of  $\text{CH}_2$  and  $\text{CH}_3$  groups<sup>50</sup>. Another shoulder observed at 1715  $\text{cm}^{-1}$  may arise from the carbonyl stretching mode of ketones, aldehydes and carboxylic acids<sup>49</sup>. However, the

nature of the shoulder band and its higher absorption value is rather related to the presence of esters and not to other functional groups<sup>51,52</sup>. The contribution at 691  $\text{cm}^{-1}$  is ascribed to the vibration of the skeletal  $\text{CH}_2$  of linear chains with more than four  $\text{CH}_2$  groups<sup>37</sup>. The appearance of bands due to CH groups is a clear indication of the presence of OM in the CK sample, in accordance with the results previously shown in XRF and SEM-EDX analyses.

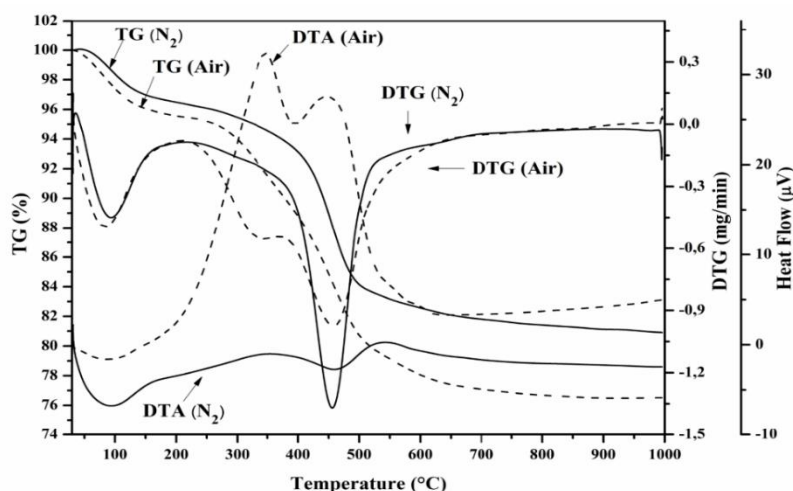
The main absorption characteristic of the mineral component of CK sample is shown in the range of 1200-900  $\text{cm}^{-1}$ , with a maximum observed at 995  $\text{cm}^{-1}$ . This absorption area is assigned to the asymmetric stretching vibration of Si-O groups of clay minerals and quartz. The band located at 910  $\text{cm}^{-1}$  is due to stretch of Si-OH. The symmetric stretches at 797 and 777  $\text{cm}^{-1}$ , and the symmetric and asymmetric Si-O bending mode appear at 692, 517 and 450  $\text{cm}^{-1}$ , respectively<sup>54</sup>. The absence of carbonate absorption bands ( $\text{CO}_3^{2-}$ ), which normally appears at 1400  $\text{cm}^{-1}$  confirms our previous XRD results and chemical analyses. On the other hand, the samples obtained after heat treatment (CKR 700) (Fig. 4(b)) and (CKR 900) (Fig. 4(c)) show the disappearance of bands due to OM with a slight shift of the spectrum toward the high frequencies. This is certainly due to the structural arrangement of silica and alumina imposed after the thermal degradation of OM and complete dehydroxylation of clay minerals.



**Figure 4.** FTIR-ATR spectra of the western Central Kongo sedimentary rock: Raw sample (a), treated at 700°C (CKR 700) (b) and 900°C (CKR 900) (c)

### Thermal analysis

Fig. 5 displays the thermal behavior of the CK sample under nitrogen and air atmospheres at heating rate of 10 °C min<sup>-1</sup>.



**Figure 5.** Thermal analysis of the CK sample under air and nitrogen atmospheres

Two main regions can be distinguished in thermal diagrams (Fig. 5), the first is observed at temperatures of less than 200°C and corresponding to mass loss of 3-4%. It is attributed to evaporation of moisture and water molecules associated with quartz and clay minerals. The second region which appeared between 250-550°C characterizes the nature and the structure of carbon and, represents the conversion of OM included in the CK sample, as was already reported by several thermal studies of oil shales<sup>55,56</sup>. In this temperature region, the oxidation reaction shows two independent effects with total mass loss of 14.8%. It corresponds to the oxidation of different carbon structures into CO<sub>2</sub> and H<sub>2</sub>O. The first exothermic peak in DTA curve appears more intense than the second; this behavior indicates that the aliphatic carbons represented by long chains are predominant species in OM of the examined sedimentary rock. Similar behavior has also been

observed in the thermal oxidation of Moroccan Timahdit oil shale<sup>57</sup>. A third exothermic peak appearing beyond 550°C in thermal oxidation with a low mass loss (< 2%) is assigned to the oxidation of pyrite<sup>7,57</sup>. In the pyrolysis, the reaction presents a mass loss of 11.5% and probably leads to formation of oil and gas by thermal cracking of OM. This reaction is accompanied by an endothermic effect in DTA curve.

### Rock-Eval analysis

The Total Organic Carbon (TOC) combined with the Rock-Eval parameters can be determined to evaluate the generative potential; type of OM and thermal maturity of the source rock of the CK sample. The results are shown in Table 3 and compared with those obtained from known Moroccan oil shales: Timahdit (TI), Tarfaya (TA) and Arbaa Ayacha (AA), in order to identify the

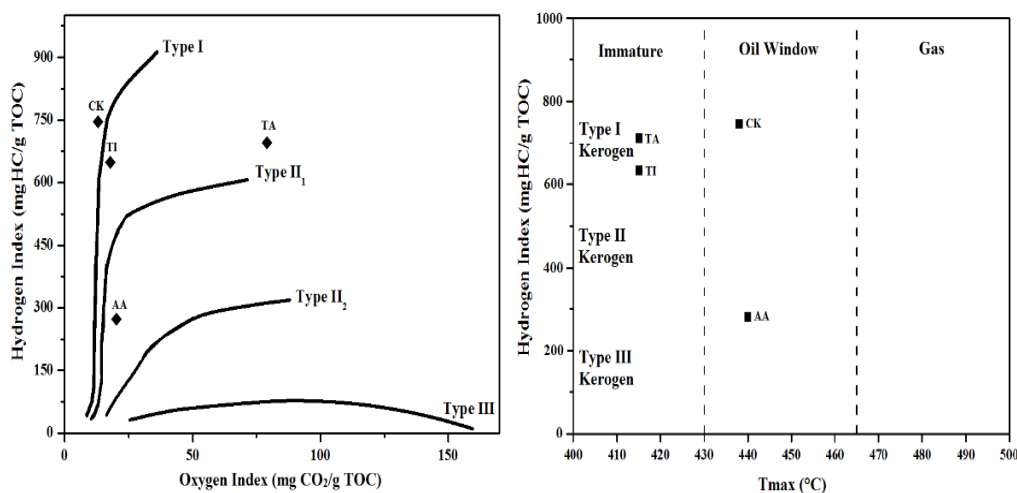
main features of the CK sample from the western Central Kongo which has great petrographic similarity with oil shales.

The quantity of OM in the sedimentary rock is indicated by the TOC content and S1 and S2 parameters. The TOC content of the CK sample is 10.77% and it is found to be comparable to TI oil shale but it is considerably higher than the values obtained on TA and AA oil shales. The high value of TOC reflects the organic matter-rich rock nature which is assigned to favorable production and conservation environments of the OM and which has a strong tendency to hydrocarbons generation<sup>37,58</sup>. In contrast, the value of S1 parameter which is 2.7 mgHC/g rock indicates the less volatile OM referred to as free or sorbed hydrocarbons (bitumen) because the CK sample is in low maturity level, as discussed later. In addition, the S2 value which is an indicative of hydrogen-rich kerogen and a key measurement in term of petroleum potential of source rock presents a value of 80.4 mgHC/g rock. The high S2 value of the CK sample is higher than that of the Moroccan oil shales and indicates an excellent potential for producing hydrocarbons from the source rock at the maximum pyrolysis temperature (Tmax) of 438°C. Regarding the S3 parameter, it corresponds to 1.41 mgCO<sub>2</sub>/g rock and refers to the CO<sub>2</sub> formed during the pyrolysis of the CK sample up to 390°C.

According to Peters and Cassa<sup>12</sup>, high hydrogen index (HI) and low oxygen index (OI) values indicate that OM of the source rock has a sapropelic type I kerogen. The analysis results in Table 3 show an HI of CK sample equal to 746 mgHC/g TOC, higher than those obtained on Moroccan oil shales and low OI (13 mgCO<sub>2</sub>/g TOC) reflecting the type I kerogen nature of OM (Fig. 6(a)). High HI value may predict the oil richness of the source rock and hence its quality. These results were confirmed by elemental analysis of the CK sample (Table 4). In fact, the molar ratio H/C = 1.71 indicates that the kerogen contained in OM is of type I and can thus provide a better oil yield<sup>8</sup>. As a reminder, the type I kerogen shows a great tendency to produce liquid hydrocarbons and it occurs mainly from marine environments and forms only under anoxic conditions<sup>28, 37</sup>. The obtained value Tmax of 438°C suggests that the OM of CK sample is in an immature stage evolution or has just reached the beginning of the oil window stage. The HI vs. Tmax diagram (Fig. 6(b)) confirms the above results and classifies OM of the CK sample as type I kerogen as has been shown in elemental analysis. The presence of sulfur associated with OM (Table 4) is related to the reducing depositional environment and early diagenetic processes that occurred either in marine or lacustrine sediments<sup>59</sup>.

**Table 3.** Rock-Eval parameters of the CK sample and Moroccan oil shales.

Parameters	CK	TI	TA	AA
TOC (wt.%)	10.77	10.86	7.03	4.30
S1 (mgHC/g rock)	2.70	3.51	4.11	0.96
S2 (mgHC/g rock)	80.40	68.93	50.06	12.14
S3 (mgCO <sub>2</sub> /g rock)	1.41	1.88	6.07	0.97
HI (mgHC/gTOC)	746	634	712	282
OI (mgCO <sub>2</sub> /gTOC)	13	17	86	23
Tmax (°C)	438	415	415	440
PI	0.032	0.040	0.070	0.073
S2/S3	57.43	36.66	8.33	12.51
GP	83.10	72.44	54.17	13.10
References	This study	60	61	23





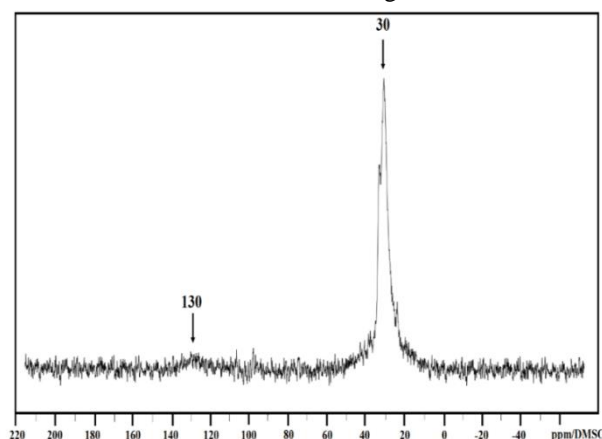
**Figure 6.** HI vs. OI diagram (a) and HI vs. Tmax diagram (b)**Table 4.** Organic elemental analysis (wt. %) of the CK sample.

C	H	N	S
10.86	1.55	0.25	0.69

**13C CP/MAS NMR analysis**

Fig. 7 displays the solid state  $^{13}\text{C}$  CP/MAS NMR analysis of the powder CK sample at 93K. The spectrum shows a narrow resonance signal centered at 30 ppm, as has been observed in numerous oil shales<sup>62,63</sup>. This signal was attributed to carbon ( $\text{sp}^3$ , hybridized) inferring that almost all the carbon species are in aliphatic forms, (Methylene groups,  $-\text{CH}_2-$ ). As reported by Mann et al.<sup>64</sup>, the signal width, in the high field region, which is of about 10 ppm, for CK sample indicates homogeneity of aliphatic species consistent with relatively large aliphatic polycyclic and/or chain structure. It should

be noted that the shoulders observed at 23 ppm and 33 ppm are probably related to the presence of methyl ( $-\text{CH}_3$ ) at the end of the aliphatic chains and alicyclic groups respectively<sup>65</sup>. These types of carbon are hydrogen rich and are largely responsible for oil that could be generated upon pyrolysis, in accordance with the results of Rock-Eval analysis. The  $^{13}\text{C}$  CP/MAS spectra of Moroccan oil shales present both aliphatic and aromatic carbons, due to the structural kerogen type of the source rock. For comparison with the CK sample, Table 5 displays the chemical shifts of principle carbon types in the kerogen of Moroccan oil shales.

**Figure 7.**  $^{13}\text{C}$  CP/MAS NMR of the CK sample**Table 5.** Chemical shifts of Raw CK sample and Moroccan oil shales.

Samples	Aliphatic $\delta_{\text{ppm}}$	Aromatic $\delta_{\text{ppm}}$	O-Alkyl $\delta_{\text{ppm}}$	Carboxyl $\delta_{\text{ppm}}$	Type kerogen	References
Raw CK	30.1	traces	-----	-----	I	This study
Kerogen-(TI)	30.1	134.7	78.7	177.3	I-II	66
Kerogen-(TA)	30	130	-----	-----	I-II	61

**Conclusion**

The mineralogical and the oil-generating potential of western Central Kongo sedimentary rock (CK) were investigated using different analytical techniques. The mineral part of the CK sample is mainly constituted of Quartz and clays, like components found in oil shales. The SEM observations confirm the XRD and XRF analysis results. It was also noteworthy the presence of Pyrite as framboid shape and some pores which are filled by carbonaceous OM. The thermal analysis (TG/DTA) and FTIR results showed that the CK sample contains a sufficient amount of volatile OM with high similarity to kerogen in oil shales. The Rock-Eval analysis associated with organic chemistry elemental results indicated that the OM

content of the CK sample is in the same order of magnitude as a typical oil shale. The TOC content (10.77%) was found similar to TI Moroccan oil shale and higher than TA and AA Moroccan oil shales reflecting that the CK sample is an organic matter-rich rock capable of generating oil upon heating. The Tmax parameter value of 438°C indicated that the OM is in an immature stage evolution or has just reached the beginning of the oil window stage. The high HI and low OI values imply that the OM is dominated by type I kerogen and deposited in anoxic marine or lacustrine environment. This geological environment constitutes good conditions for preserving OM. Type I kerogen was also confirmed by  $^{13}\text{C}$  CP/MAS NMR spectroscopy result which indicates a strict dominance of aliphatic species. The CK sedimentary rock studied here presents the same

qualities as an oil shale and has a great potential for generating oil with appearance similar to crude oil.

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