Available online at www.sciencedirect.com
ScienceDirect
Applied Geochemistry 22 (2007) 1311–1328
Applied Geochemistry
www.elsevier.com/locate/apgeochem

# Cementation of kerogen-rich marls by alkaline fluids released during weathering of thermally metamorphosed marly sediments. Part II: Organic matter evolution, magnetic susceptibility and metals (Ti, Cr, Fe) at the Khushaym Matruk natural analogue (Central Jordan)

Marcel Elie [a,*], Isabelle Techer [b], Laurent Trotignon [c], Hani Khoury [d], Elias Salameh [d], Didier Vandamme [e], Philippe Boulvais [f], Serge Fourcade [f]

[a] G2R, Nancy-Université, CNRS, BP 239, 54506, Vandoeuvre les Nancy, France
[b] UMR CNRS 6635-CEREGE, Université d'Aix-Marseille 3, 150 rue Georges Besse, 30035 Nîmes, France
[c] CEA Cadarache DTN/SMTM/LMTE, Bât. 307, 13108 St. Paul lez Durance, France
[d] Department of Geology, University of Jordan, P.O. Box 17167, Amman 11942, Jordan
[e] UMR CNRS 6635-CEREGE, Université d'Aix-Marseille 3, BP 80, 13545 Aix-En-Provence Cedex 4, France
[f] UMR CNRS 6118-Géosciences Rennes, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes, France

Received 12 October 2005; accepted 14 February 2007
Editorial handling by M. Gascoyne
Available online 30 March 2007

**Abstract**

Spontaneous combustion, less than 1 Ma ago, affected a 60-m thick sediment pile of biomicrite at the Khushaym Matruck site (Jordan). The present study shows that three retrograde alteration stages occurred: weathering, thermal stress and oxidative alkaline perturbation. μ-FT-i.r. spectra of isolated kerogens and oxygen index of whole rocks indicate that oxidation of organic matter occurred down to ~10 m beneath the metamorphosed zone at Khushaym Matruck. The occurrence of the oxidative weathering bacterially mediated, as suggested by the mass chromatograms of saturated hydrocarbons, can explain high Rock-Eval $T_{max}$ values and low petroliferous potential measured along the sedimentary pile. On the other hand, the thermal extent of combustion events was limited to the first 2 m from the contact. The mean reflectance of 0.20–0.24% and porosity of ca. 50% of the grey clayey biomicrites indicate that organic matter was very immature and sediments were unconsolidated at the time of the combustion event. Using mineralogy, microscopic analyses of vegetable debris and magnetic susceptibility, a suite of characteristic points corresponding to the thermal imprint can be assessed: (i) $x = 0m$, $T \sim 1000$ °C, (ii) $x = 1$ m, $T \sim 350$ °C, (iii) $x = 2$ m, $T \sim 150$ °C and (iv) $x > \sim 8$ m, $T \sim 30$ °C. Paleocirculation of meteoric groundwater in the 'cement-marbles' generated high-pH fluids that have circulated via fractures and through the matrix porosity of the underlying biomicrites but have also induced alkaline hydrolysis and oxidative attack of the organic matter. The polysaccharide/lignin ratio derived from μ-FT-i.r. analyses shows that the delignification of vegetable debris and degradation of polysaccharides progressively decline in the indurated zone, which indicates a decrease in the pH of

* Corresponding author.
*E-mail address:* marcel.elie@g2r.uhp-nancy.fr (M. Elie).

0883-2927/$ - see front matter 
doi:10.1016/j.apgeochem.2007.02.013

migrating solutions. The latter also severely oxidized organic matter at 2.10 and 3.05 m as revealed by the oxygen index and induced the generation of bitumen. The spatial correlation between the oxidation levels of organic matter and the metal contents (Fe, Ti and Cr) suggests that redox reactions were responsible for the immobilization of metals in the indurated biomicrites. The intensity of these reactions is attributed to changes in the fluid flow regime within the sedimentary column.


## 1. Introduction

At the Khushaym Matruck site (Central Jordan), a biomicritic formation (Upper Cretaceous –Upper Palaeocene Muwaqqar Formation) is overlain by around 60 m of natural cements and marbles formed by spontaneous combustion of the organic matter from the sediment (Alexander and Smellie, 1998; Rassineux et al., 2001; Techer et al., 2006). Temperatures reached in the bituminous formation during the thermal event must have been in the range from 1000 to 1100 °C as minerals such as spurrite were formed (Fourcade et al., 2007). Paleocirculation of meteoric groundwater in these 'cement-marbles' has generated alkaline fluids that are suspected to have percolated through the underlying sedimentary formation (Techer et al., 2006; Fourcade et al., 2007). Organic matter is a very sensitive environmental marker that has likely recorded the effects of thermal stress due to combustion events, those of weathering and those induced by alkaline fluids. These alteration processes must have been superimposed, making discrimination between them difficult because (i) they can induce similar physico-chemical transformations of the organic matter, (ii) the earlier alterations can be modified and obscured by younger events, or (iii) the degree of alteration induced by the earlier events can have been too strong, precluding the record of further events.

Changes occurring in organic matter in response to natural high heating rates are well-known through the studies of geological formations intruded by sills or dykes (Simoneit et al., 1981; Clayton and Bostick, 1986; Bishop and Abbott, 1995). Because temperature horizons adjacent to a dyke range from 400 °C to 150 °C and the heating durations from a few hours to several days, these geological environments have been considered as intermediates between heating experiments and progressive sedimentary maturation (Bishop and Abbott, 1993). An effective oil window, corresponding to vitrinite reflectance values ranging from 0.60% to ca. 1.7%, has been defined by Bishop and Abbott (1995) in such environments. Trends in molecular and structural parameters were found to be consistent with thermal maturation when approaching the intrusions. The heating effects of intrusions strongly depend on the physico-chemical properties of the intruded rock and on the maturity level of organic matter prior to intrusion (Raymond and Murchison, 1988, 1991; Bishop and Abbott, 1995). No or thin thermal aureoles were formed when unconsolidated sediments, containing large porewater volumes, were intruded by sills or dykes soon after sedimentation (Einsele et al., 1980; Rullkötter et al., 1982; Simoneit and Philp, 1982; Raymond and Murchison, 1991; George, 1992). On the other hand, the thermal effect could operate up to a distance corresponding to 75% of the dyke thickness when a well-compacted sediment is intruded in dry conditions (Clayton and Bostick, 1986; George, 1992; Bishop and Abbott, 1993, 1995; Farrimond et al., 1996).

The influence of weathering on organic matter has also been investigated. Weathering can be bacterially mediated or not. Whatever its nature, weathering induces a whole series of complex reactions with drastic changes in the molecular and structural characteristics of organic matter (Leythaeuser, 1973; Clayton and Swetland, 1978; Rowland and Maxwell, 1984; Petsch et al., 2000). Both elemental composition and infrared spectroscopy showed the incorporation of O and loss of H in kerogen without any significant variation in its N content (Petsch et al., 2000). Copard et al. (2002) have drawn attention to possible erroneous interpretations when attempting to infer the maturity level of weathered coals by considering Rock-Eval parameters alone. Although there is no consensus, the reflectance of vitrinite appears unaffected by both weathering and artificial oxidation (Chandra, 1958; Ingram and Rimstidt, 1984). The gas chromatography–mass spectrometry traces of oils highly biodegraded show a hump of unresolved complex mixture where *n*-alk-

anes are absent. Artificial oxidation of sediments with low-organic content in a ventilated oven induced an increase in the amounts of low molecular weight compounds with increasing oxidation times. Although these experiments do not perfectly simulate weathering, it has been demonstrated that oxidation in a ventilated oven satisfactorily duplicates the oxidative alteration of organic matter stored for a long time under uncontrolled atmosphere (Elie et al., 2000).

Effects of alkaline solutions on sedimentary organic matter are much less documented. The increasing interest put on these effects is related to the concepts of geological disposal for nuclear waste, which plans to use concrete and cement-bearing materials as building structures or as waste containment packages. Schäefer et al. (2003) showed that organic matter can play a role in the stabilization of clay minerals under alkaline conditions. Previous studies on the water-extractable fraction showed that hydrophilic organic compounds are highly mobilized by high-pH fluids (Claret et al., 2003, 2005). Alkaline leaching combined with an oxidizing alteration in a ventilated oven drastically increases the amount of organic compounds released from sediments with low-organic content (Elie et al., 2004). All these studies speculated on the ability of hydrophilic organic compounds to mobilize inorganic species, including radionuclides, at high-pH, unfortunately without comparing experimental data with geological systems. Alkaline hydrolysis has been much more

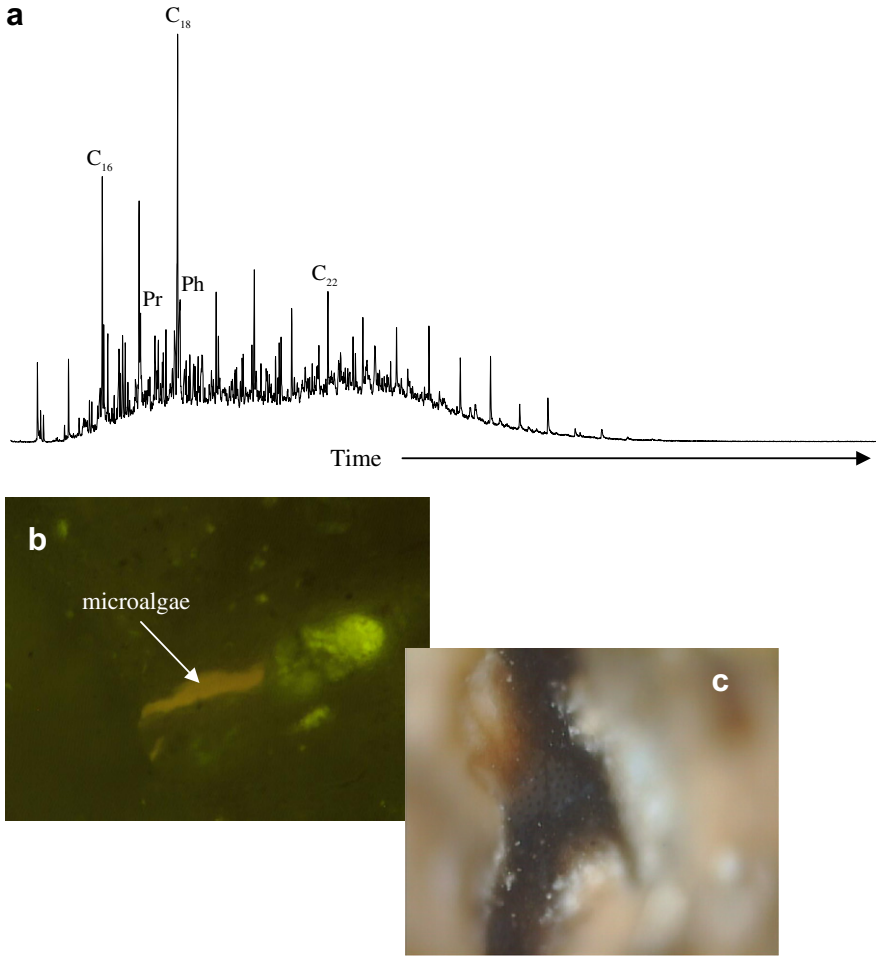


Fig. 1. Analysis of an 'unaltered' sample from the Khushaym Matruk site. (a) GC–MS trace of the saturated hydrocarbons fraction, (b) optical microscopy of isolated kerogen under fluorescence showing the presence of microalgae and (c) optical microscopy of the whole rock under reflected white light showing a well-preserved lignocellulosic porosity.

studied in industrial sectors including paper pulp manufacturing, agricultural and food industries. One of the delignification treatments, which consists in decomposing lignocelluloses into polysaccharides and lignin, is performed with high-pH solutions from room temperature up to 150 °C with short reaction times (Playne, 1984; Karr and Holtzapple, 2000; Chang et al., 2001, and references therein). The effects of alkaline fluids depend on the nature of dissolved ions. Oxidation methods by alkaline permanganate have shown that kerogen is susceptible to oxidative attack, alkaline hydrolysis or both (Djuricic et al., 1971; Machihara and Ishiwatari, 1983).

The sediments from Khushaym Matruck site are rich in organic matter. Although they contain more than 5% organic matter, the content is lower than those measured for sediments from the Maqarin site, another pyrometamorphic site in the same sedimentary kerogen-rich formation also located in Jordan (Khoury et al., 1992 ; Alexander et al., 1992). The gas chromatography–mass spectrometry traces of the saturated hydrocarbon fractions from unaltered sediments are dominated by low molecular weight *n*-alkanes, which is indicative of a major contribution of marine organic matter (Fig. 1a). Some lamalginite-type microalgae with an orange colour and high H contents were identified under fluorescence, which suggests an immature stage (early diagenesis) of organic matter (Fig. 1b). Petrographic analyses of the whole rocks also show the presence of well-preserved lignocellulosic structures that are typical of very immature organic matter (Fig. 1c). The aim of the present study is to determine how far a percolating alkaline fluid may alter organic matter in geological conditions. Analytical techniques based on molecular analyses, gross and spectroscopy geochemical characterizations as well as microscopic examinations were used to study the organic matter along a vertical profile at Khushaym Matruck site. The reliability and specificity of geochemical indicators used to estimate the thermal impact of combustion events, low-temperature weathering and alkaline hydrolysis are important prerequisites for deciphering the multiple processes involved. Geochemical signals obtained on altered organic matter were compared with metal contents along the same profile. Attention has been focused on three metals, namely Cr, Fe and Ti because of their potential relevance to the behaviour of other transition elements. Magnetic susceptibility was measured to estimate the maximum temperatures reached by the biomicrites underlying the metamorphic unit.

## 2. Materials and methods

### 2.1. Sampling

The geological setting has been described in detail by Techer et al. (2006). Seven samples were collected in the baked biomicrites crosscut by numerous micro-cracks between 0.25 and 3.05 m from the contact zone and six other samples in the grey clayey biomicrites crosscut by sub-vertical centimeter-wide cracks mainly filled with gypsum (Techer et al., 2006). The samples are referenced in Fourcade et al. (2007). Organic matter present in gypsum was not analysed in the present study.

### 2.2. Examination of organic matter

Rocks were analysed for organic matter less than two years after their sampling, thus avoiding possible photo-oxidation of the organic matter due to storage (Elie et al., 2000). Pyrolyses were carried out on whole-rock samples using a Vinci Rock-Eval 6 instrument at ISTO (Orléans, France) to determine total organic C (TOC) and maturity level of organic matter. Polished blocks of whole rocks collected at 2 m and 8 m below the interface with the cement-marbles were analysed under reflected white light using a MPV-Combi Leitz microscope fitted with oil immersion objective at magnification ×50 at INCAR (Oviedo, Spain). The analytical procedure and reflectance measurements were performed in accordance with the ISO 7404-3 and ISO 7404-5 methods. Around 20 g of ground and dried whole-rock samples were extracted using a Dionex ASE 200 accelerated solvent extraction system at 100 bar and 80 °C with dichloromethane as solvent. The extractable organic matter was concentrated in a rotary evaporator and weighed after complete dichloromethane removal under a $N_2$ stream. The organic extracts were separated into saturated and aromatic hydrocarbons and into polars by liquid chromatography (LC) on silica microcolumns. The recovered fractions were dried under a $N_2$ stream and mass balances were calculated.

Kerogens were isolated from whole rock powders using the standard HCl/HF procedure, washed with distilled water and freeze-dried at Baseline DGSI (Texas, USA). The recovered amounts of isolated

kerogens from baked biomicrites were not enough for a heavy liquid separation. Rock-Eval runs were carried out on the isolated kerogens since the reliability of Rock-Eval data from whole-rock samples can be questionable on account of their low H contents (HI < 6 mg HC/g TOC). Rock-Eval pyrolyses of isolated kerogens were performed at Baselines (Texas, USA). The isolated kerogens were also analysed by FT-i.r. microscopy in the near IR region (wave numbers: 4000–600 $cm^{-1}$). An aliquot was placed between the two diamond cells (Spectra-Tech int.). After compression by screwing, FT-i.r. spectra were recorded on the organic matrix and lignocellulosic debris using a Brucker IFS-88 equinox spectrometer coupled to a Brucker multipurpose infrared microscope at LEM (Vandoeuvre, France). Emission Scanning Electron Microscope (S2500 Hitachi LaB6) equipped with an Energy Dispersive X-ray Spectrometer (Spectro EDS System Vantage manufactured by Thermo Electron Corporation) of the University of Nancy (France) was used to determine the elemental composition of the lignocellulosic debris in the isolated kerogens mounted on an In pellet.

### 2.3. Magnetic characterizations

Magnetic characterizations were conducted on whole rocks or separated fractions. The specific magnetic susceptibility $\chi$ ($m^3\,kg^{-1}$) was measured using a Kappabridge KLY2 – CS2 susceptometer. Ambient temperature measurements were done by placing a fragment (~10–30 g) of sample in the specimen holder. Temperature measurements, were done on powdered samples put in quartz tubes from −196 °C to 700 °C. Temperature corrections and measurement protocols are described in Mathé (1996).

For selected samples, the magnetic minerals were separated and concentrated using first a chemical treatment which consisted of a dilute acetic acid attack over 6–10 h followed by dispersion of the clay fraction using Na hexametaphosphate. The chemical treatment was combined with magnetic separation. X-ray diffraction of the separated phases was then performed with a Philips 1729 diffractometer (Co anticathode).

### 2.4. Chemical analyses of metals (Fe, Cr, Ti)

Bulk samples of the biomicrites collected along the trench profile were ground in an agate mortar and then attacked using classical techniques (alkaline fusion, acid dissolution). Analyses of the solutes were performed with a Jobin-Yvon ICP-AES spectrometer. The relative error on Fe, Ti and Cr concentrations is estimated at less than 10%.

## 3. Results

### 3.1. Rock-Eval analysis

The isolated kerogens from the unaltered biomicrites have 485–510 °C $T_{max}$, whereas those from baked biomicrites have 510–551 °C $T_{max}$ (Table 1). These high $T_{max}$ values suggest that organic matter has reached an overmature stage. TOC of whole rocks does not show any significant evolution with the distance from the cement-marbles, and ranged between 5.24% and 7.27% (Table 1). With the exception of one sample (at 2.10 m), the high $T_{max}$ values confirm the strong alteration of organic matter throughout the whole profile. The H content of the whole rocks is lower than 10 mg HC/g TOC (Table 1). Fig. 2 shows that organic matter from the Khushaym Matruk site has been strongly oxidized up to ~10 m beneath the contact. The oxidation level differs along the profile with maximum values of oxygen index (OI, mg $CO_2$/g TOC) observed at 2.10, 3.05 and 8.20 m from the contact (Fig. 1).

Table 1
TOC (% of rock), hydrogen index (HI in mg HC/g TOC) and $T_{max}$ (°C) for whole rocks and isolated kerogens along the sedimentary profile

| Distance to contact (m) | Whole rock | | | Isolated kerogen |
|---|---|---|---|---|
| | TOC (%) | HI (mg HC/g TOC) | $T_{max}$ (°C) | $T_{max}$ (°C) |
| 0.25 | – | – | – | 543 |
| 0.50 | – | – | – | – |
| 1.00 | 5.25 | 1.0 | 551 | 542 |
| 2.00 | 7.27 | 0.0 | 544 | 550 |
| 2.10 | 6.59 | 2.0 | 551 | 551 |
| 2.10 | 5.65 | 1.0 | 317 | – |
| 2.20 | 7.19 | 1.0 | 535 | 543 |
| 2.60 | 5.24 | 1.0 | 617 | 540 |
| 3.05 | 5.79 | 1.0 | 526 | 510 |
| 6.00 | 6.32 | 1.0 | 513 | – |
| 6.00 | 5.81 | 2.0 | 517 | 485 |
| 7.85 | 6.61 | 2.0 | 512 | 485 |
| 7.95 | 5.55 | 2.0 | 525 | 485 |
| 8.00 | 6.63 | 1.0 | 513 | 510 |
| 8.20 | 5.82 | 6.0 | 508 | 492 |

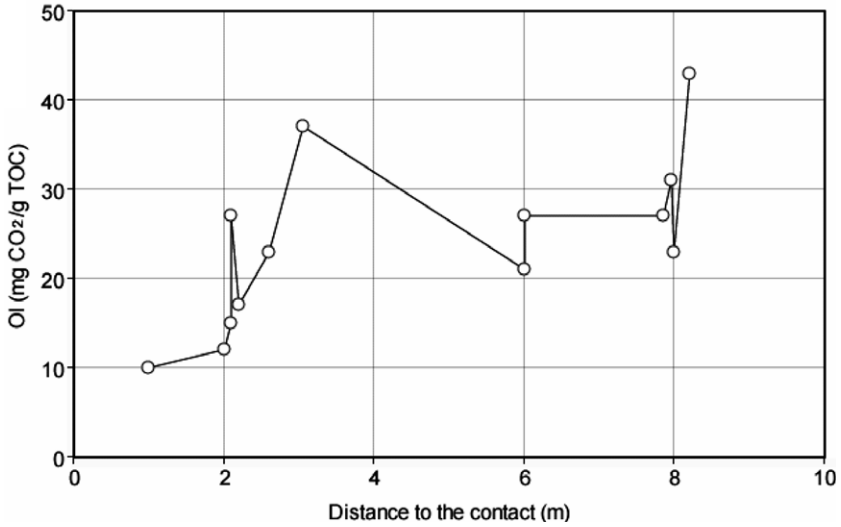


Fig. 2. Evolution of the Oxygen Index (OI in mg $CO_2$/g TOC) of the whole rocks vs. distance from the metamorphic unit.

### 3.2. Micro-infrared spectroscopy of isolated kerogen

FT-i.r. spectra recorded on the organic matrix (Fig. 3a) show high concentrations of oxygen functionalities in the macromolecular structure as usually observed in strongly oxidized organic material (Rhoads et al., 1983). The broad absorption band in the 3700–2400 $cm^{-1}$ region indicates the presence of OH groups that can be attributed to alcohols, phenols or carboxyl groups (Starsinic et al., 1984). An absorption band at ca. 1712 $cm^{-1}$, which is commonly attributed to the C=O stretch in oxidized side-chains, is observed. The absorption band centred at approximately 1450 $cm^{-1}$ cannot be assigned to asymmetrical C–H bending in $CH_3$ and $–CH_2–$ on account of the absence of a CH stretching band at 2920 $cm^{-1}$. It can be associated with H bonded to O, like OH groups in carboxylic acids. The increase in the broad band centred at ca. 1250 $cm^{-1}$ and its broadening into the 950 $cm^{-1}$ region also suggest the presence of carboxylic acids. Ether bonds cannot be excluded since they may contribute to the broad band at ca. 1250 $cm^{-1}$ (Cookes et al., 1986). The assignment of the band at ca.1620 $cm^{-1}$ is more uncertain because it can be caused by aromatic C=C bonds and by O-containing structures such as carboxylates, phenolic groups and highly conjugated carbonyl groups such as diaryl ketones or quinones (Painter et al., 1980). The weakness or absence of the bands between 2970 and 2840 $cm^{-1}$, assigned to symmetrical and asymmetrical stretching of $CH_3$ and $CH_2$ groups leads to the conclusion that the aliphatic content of these organic matrices is very low or nil. The aromatic H concentration also appears negligible because no absorption bands were observed at ca. 3040 $cm^{-1}$ and in the 900–700 $cm^{-1}$ region arising from aromatic CH stretching and out-of-plane bending, respectively.

FT-i.r. spectra recorded in lignocellulosic debris show major changes along the profile (Fig. 3b). In samples far from the contact (grey biomicrite), the broad band centred at 3350 $cm^{-1}$ can be identified as corresponding to OH bonds in phenols, alcohols, carboxylic acids or water. The absorption band observed at 3000–2800 $cm^{-1}$ is caused by methyl and methylene group stretching vibrations. The low discrimination of methyl and methylene groups could result from a highly cross-linked structure. In the baked biomicrites (0–3.05 m from the contact), the adsorption band attributed to the H vibrations of OH bonds in alcohol, phenol, carboxyl or water is broadened. The aliphatic band in the 3000–2800 $cm^{-1}$ is better resolved, suggesting a lower cross-linking degree of alkyl chains. The spectral features in the 2000–800 $cm^{-1}$ region of debris from grey biomicrite closely match those of unaltered lignocelluloses (Given et al., 1984). In the carboxyl/carbonyl region, samples display a shoulder at 1720 $cm^{-1}$, originating from stretching of C=O bonds unconjugated to aromatic rings, and an absorption band at 1655 $cm^{-1}$ that can be assigned to C=O stretching vibrations conjugated to aromatic rings and/or in amides (I) (Table 2). The relative abundance of this latter band decreases with proximity to the cement-marbles. The adsorption

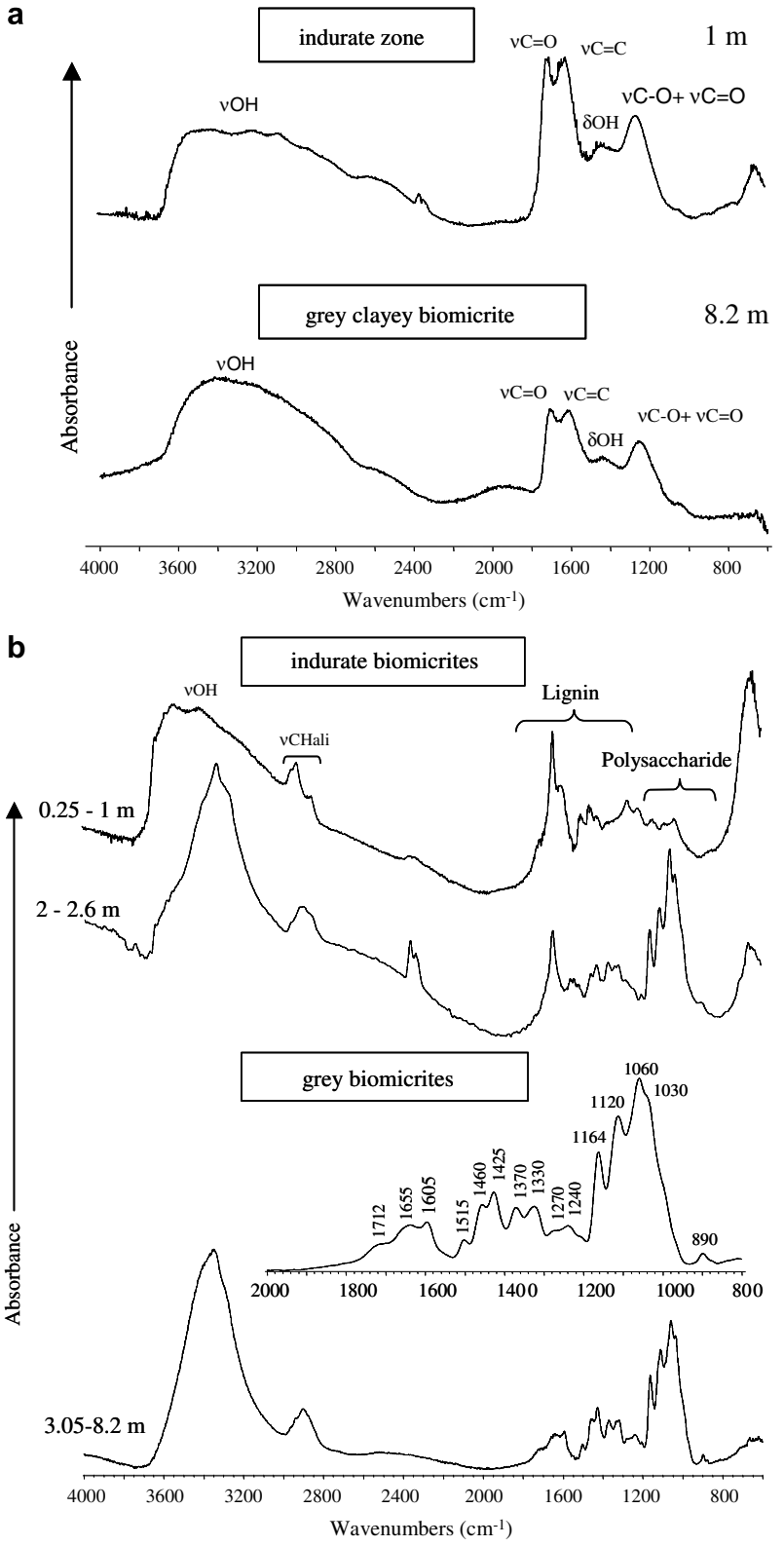


Fig. 3. FT-i.r. spectra of isolated kerogen recorded in (a) the organic matrix, and (b) the lignocellulosic debris.

Table 2
Main assignments of lignin, polysaccharides and protein FT-i.r. bands (Ibarra et al., 2004)

| | |
|---|---|
| *Lignin* | |
| 1714–1725 $cm^{-1}$ | Stretching of C=O unconjugated to aromatic rings |
| 1655 $cm^{-1}$ | Stretching of C=O conjugated to aromatic rings |
| 1594–1609 $cm^{-1}$ | Aromatic ring vibrations and C=O stretching |
| 1504–1515 $cm^{-1}$ | Aromatic ring vibrations |
| 1421–1424 $cm^{-1}$ | Asymmetric C–H bending (in $CH_3$ and $–CH_2–$) |
| 1329–1330 $cm^{-1}$ | Aromatic ring breathing |
| 1270 $cm^{-1}$ (shoulder) | Aromatic ring breathing |
| 1216–1225 $cm^{-1}$ | C–C, C–O and C=O stretching |
| 1114–1125 $cm^{-1}$ | Aromatic in-plane C–H bending |
| 1030–1033 $cm^{-1}$ | Aromatic in-plane C–H bending |
| 913–929 $cm^{-1}$ | Out-of-plane aromatic C–H bending |
| 833–834 $cm^{-1}$ | Out-of-plane C–H bending |
| *Polysaccharide* | |
| 1613 $cm^{-1}$ | Water |
| 1370 $cm^{-1}$ | Symmetric bending of aliphatic C–H |
| 1030–1170 $cm^{-1}$ | C–O stretching in alcohols |
| *Protein* | |
| 1655–1658 $cm^{-1}$ | C=O Stretching in amides (I) |
| 1516 $cm^{-1}$ | C=O Stretching in amides (II) |

bands at 1605, 1515 and 1430 $cm^{-1}$, attributed to aromatic skeleton vibrations, are more intense in backed biomicrite samples than in the grey unaltered biomicrites. The absorption bands at 1515 $cm^{-1}$, attributed to C=O stretching in amides (II), at 1462 $cm^{-1}$ to asymmetrical C–H bending in $CH_3$ and $–CH_2–$, and at 1370 $cm^{-1}$ to symmetrical bending of aliphatic C–H in polysaccharides are observed in all the samples (Table 2). Lignocellulosic debris from grey unaltered biomicrites exhibit intense bands in the 1170–1037 $cm^{-1}$ region that are attributed to C–O stretching vibration of alcohol functions in polysaccharides (Ibarra et al., 2004). Fig. 3b indicates that the samples closest to the cement-marbles (metre mark <1 m) have a much weaker C–O stretching band. The polysaccharide/lignin ratio has been calculated by integrating the spectra regions 1200–860 $cm^{-1}$ and 1910–200 $cm^{-1}$ that are attributed to lignin and polysaccharide bands, respectively (Fig. 4). The abundance of polysaccharides relative to lignin displays a smooth upward decrease in the grey clayey biomicrites followed by a drastic drop from 3.05 m when approaching the contact with the metamorphic unit (Fig. 4).

### 3.3. Optical microscopy and SEM-EDX of isolated kerogen

Petrographic observations show that the lignocellulosic debris are very rare, oxidized, rounded and small (~5 μm) in the baked biomicrites collected in the first 2 m beneath the metamorphic zone. Mean vitrinite reflectance values of 1.5% and 0.6% are measured at 1 and 2.00 m, respectively. The organic particles in the grey biomicrites are present as gels and/or huminite. Mean reflectance values range from 0.20% to 0.24%.

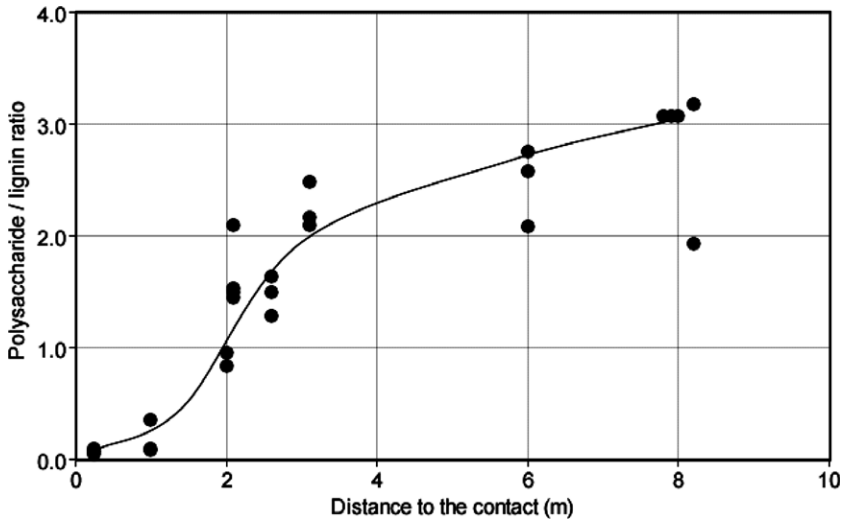


Fig. 4. Trends in the polysaccharide/lignin ratio deduced from FT-i.r. spectra of lignocellulosic debris *vs.* distance to the metamorphic unit.

SEM-EDX results show that plant debris in the grey clayey biomicrite are dominated by O. Higher C contents are observed in lignocellulosic debris from the baked biomicrites, and N is absent in the samples that are the closest to the cement-marbles. Three main sections are identified from trends in the elemental composition of lignocellulosic debris: (i) a first section between 8.20 and 8.00 m that is characterized by a slight decrease in O content, (ii) in the second stage, for samples between 8.00 m and 2.10 m below the contact, the atomic C/N ratio increases upward and (iii) in the third section the proximal vegetal debris (1.00–0.25 m) are free of N and progressively enriched in C when the metamorphosed zone is approached (Fig. 5).

### 3.4. Extractable organic matter

Fig. 6a shows that the solvent-extractable organic matter yields are very low. The highest amounts are recovered in the baked biomicrites where two production peaks are observed at 2.10 and 2.60 m. Except at 1.00 m from the contact, the polars yield follows an evolutionary pathway similar to that of extractable organic matter in the baked biomicrites and at the bottom of the profile (Fig. 6a). The amounts of saturate and aromatic hydrocarbons are lower with two concentration peaks at 2.20 and 3.05 m from the contact (Fig. 6b).

### 3.5. Magnetic investigations

At distances greater than 3 m from the contact, the magnetic susceptibility of the biomicrite remains in the range from $1\times10^{-8}$ to $3\times10^{-8}$ $m^3\,kg^{-1}$ which characterizes very weakly susceptible sediments. At distances less than 3 m, a strong increase of the susceptibility is observed with a first secondary maximum noted at 2.5 m ($\sim1.1\times10^{-7}$ $m^3\,kg^{-1}$) followed by the main peak at 1 m from the contact ($3.6\times10^{-6}$ $m^3\,kg^{-1}$) (Fig. 7).

Variations of the magnetic susceptibility with temperature were studied for the samples that are the closest to the metamorphic unit (A3-5, LA3-4, A3-6) under air and Ar atmospheres. Curie temperatures of 580 °C (A3-5) and 620 °C (LA-3-4 and A3-6) were recorded. X-ray diffraction on separated fractions of sample LA3-4 showed the presence of haematite and maghemite.

### 3.6. Bulk chemical analysis of metals (Fe, Cr, Ti) in selected samples

Iron, Cr and Ti concentrations display strong variations along the profile (Table 3; Fig. 8). Far

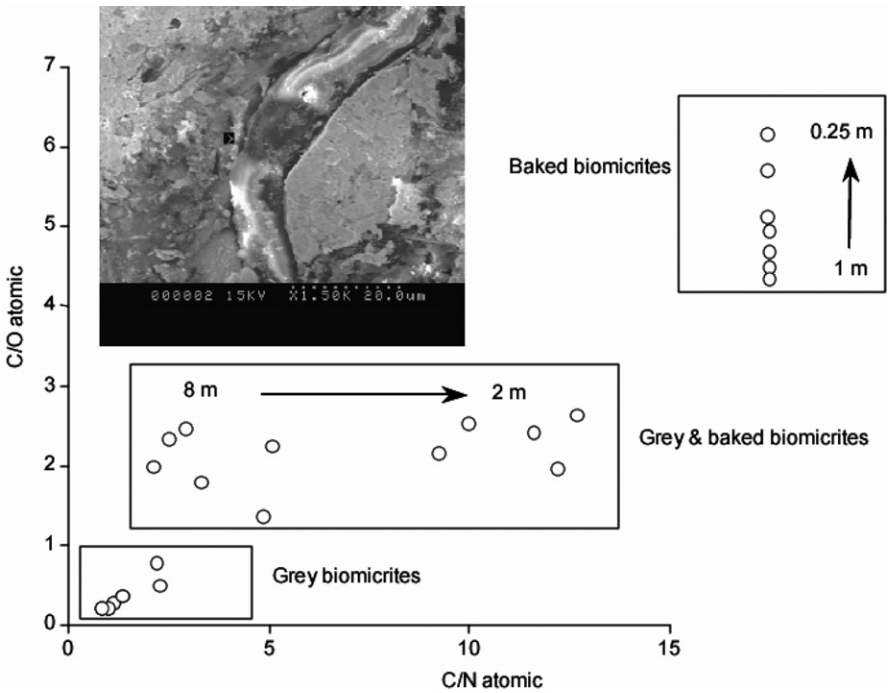


Fig. 5. Correlation plot of $C/O_{at}$ *vs.* $C/N_{at}$ ratios derived from SEM-EDX analysis of the lignocellulosic debris.

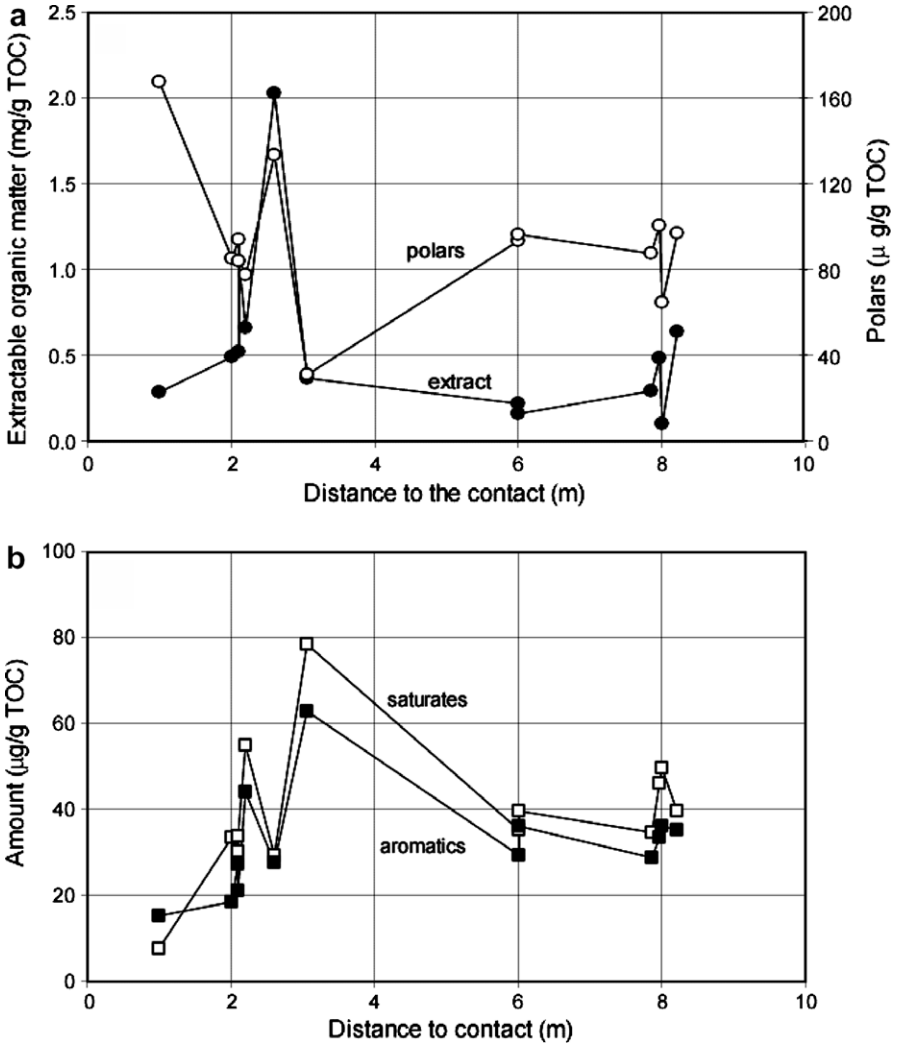


Fig. 6. Evolution of (a) amounts of extractable organic matter (in mg/g TOC) and polar compounds (in μg/g TOC), and (b) aliphatic and aromatic hydrocarbons (in μg/g TOC) with the distance to the metamorphic unit.

from the contact, Fe concentrations are in the range of 8000–9500 ppm. A major concentration peak (~15000 ppm) is found at 2.5 m and a secondary concentration peak (~8600 ppm) at 1 m from the contact. Profiles for Ti and Cr exhibit a third concentration peak (~1200 ppm for Ti, 9400 ppm for Cr) that is observed at about 3 m from the contact.

## 4. Discussion

### *4.1. Spatial and temporal evidence of alkaline perturbation, thermal stress and weathering effects*

The spontaneous combustion of organic matter in biomicrites at Khushaym Matruck has certainly affected the underlying sediments, not only thermally, but also indirectly by the chemical action of the percolating alkaline fluids derived from hydrolysed 'cement-marbles'. Mineralogical and isotopic data are compatible with a progressive pH buffering of the migrating fluids beneath the first 3 m of baked biomicrites, which is attributed to the reactive clay component of biomicrites and to $CO_2$ uptake (Fourcade et al., 2007). The original aspect of the present study concerns the fate of organic matter under the effects of weathering, heating and leaching by high-pH fluids. Did the organic matter record these distinct alteration processes? If so, does it provide information to discriminate each of them and to estimate their extent in the geological environment?

Care must be exercised when using some geochemical parameters like organic matter-maturity

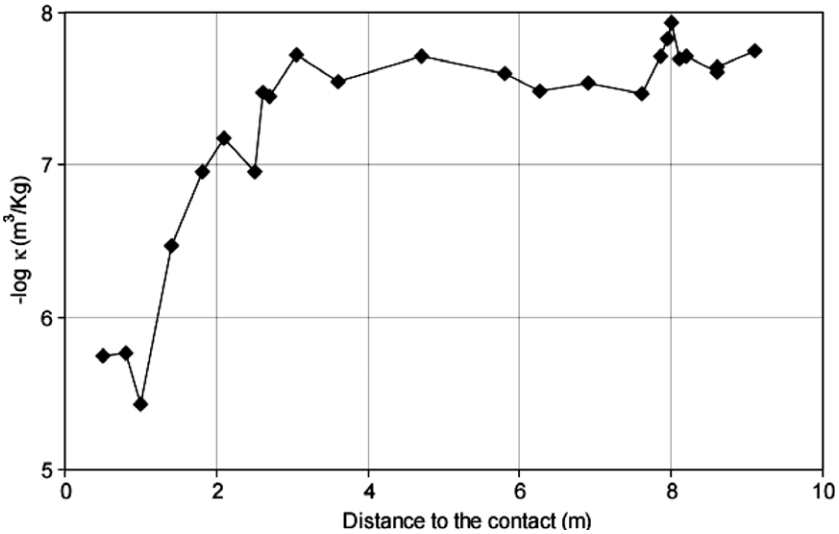


Fig. 7. Trends in the logarithm of specific magnetic susceptibility *vs.* the distance to the metamorphic unit.

Table 3
Contents in Cr, Fe and Ti along the sedimentary profile

| Distance to contact (m) | Cr (ppm) | Fe (ppm) | Ti (ppm) |
|---|---|---|---|
| 0.5 | 780 | 6785 | 675 |
| 0.8 | 1475 | 6695 | 1045 |
| 1 | 2590 | 8620 | 755 |
| 1.4 | 2010 | 7625 | 760 |
| 1.8 | 2225 | 8120 | 695 |
| 2.1 | 9840 | 15315 | 1425 |
| 2.5 | 7157 | 10,425 | 1045 |
| 2.7 | 5295 | 7820 | 595 |
| 3 | 9415 | 6822 | 1205 |
| 6.15 | 1950 | 7345 | 875 |
| 9.1 | 1280 | 9430 | 1010 |

indicators in geological environments which are affected by oxidative processes. It has been demonstrated that weathering and artificial oxidation can alter the thermostability of kerogen and induce a drastic increase in the Rock-Eval $T_{max}$ values (Landais et al., 1984; Copard et al., 2002). These alteration processes tend to destroy the aliphatic chains and to incorporate O into the kerogen structure (Petsch et al., 2000). They are also responsible for decreasing petroliferous potential (Elie et al., 2004). The oxidation effects on vitrinite reflectance have been examined both naturally and under controlled laboratory conditions. No overall consensus exists concerning the influence of weathering on the petrographic characteristics of organic matter and the mechanisms involved still need to be understood. Measurements of the vitrinite reflectance of coals that have been oxidized by an exposure to air provide anomalously high values relative to those obtained from equivalent fresh samples (Othman and Ward, 2002). Conversely, studies of weathered seam coals clearly showed a decrease in vitrinite reflectance with weathering (Ganz et al., 1990). In addition, it has been experimentally demonstrated that the vitrinite reflectance was unaffected by low-temperature oxidation (Chandra, 1958). Ingram and Rimstidt (1984) claimed that weathering effects did not significantly alter the reflectivity of organic particles, and concluded that the vitrinite reflectance may be regarded as the most reliable maturity indicator in geological environments perturbed by oxidizing percolating fluids.

The organic extract yields are very low despite the high organic C content of sediments from the Khushaym Matruk site. Organic matter also shows negligible petroleum potential (<10 mg HC/g TOC for the whole rocks) and so high $T_{max}$ values suggest that it probably reached the dry gas generation window in the grey biomicrite. This is at variance with the petrographical analyses of unaltered rocks showing that the organic matter has experienced a very limited diagenetic history. FT-i.r. spectra of the bulk kerogen, characterized by the absence of aliphatic bands and the predominance of O functionalities, are very similar to those of the refractory organic matter in soils (Quénéa et al., 2005). In addition, high oxygen index values show that all the sedimentary profile has been altered. Oxidative weathering or artificial oxidation in a ventilated oven lead to the formation of a refractory organic

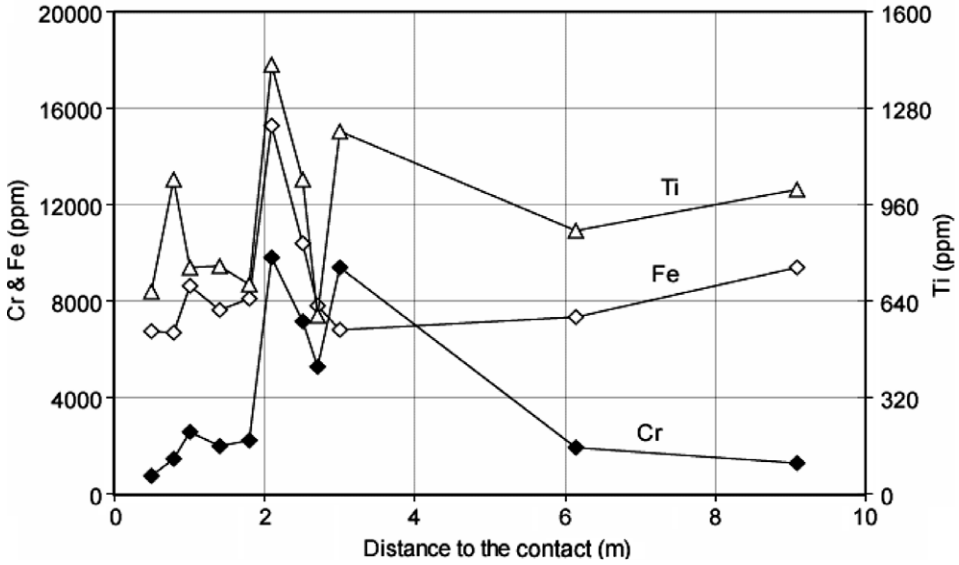


Fig. 8. Evolutions of concentrations in Ti, Fe, Cr (in ppm) *vs.* the distance to the metamorphic unit.

matter having a very low petroleum potential. The organic extract yield also decreases with increasing oxidation time in a ventilated oven (Landais et al., 1991). Oxidative weathering likely occurred at low-temperatures at Khushaym Matruk. The GCMS traces of saturated hydrocarbon fractions are shifted toward low molecular weight species and show the presence of a hump of unresolved compounds, suggesting that organic matter has experienced both abiotic and biotic oxidizing conditions (Fig. 9).

The thermal impact related to the combustion process seems restricted to the first 2.0 m beneath the contact with the metamorphic unit. The high atomic C/O ratios of plant debris, characteristic of the lignin-vitrinite stage in the peatification-coalification diagram of vegetal components (Tissot and Welte, 1984), may be due to the thermal effect. A mean vitrinite reflectance of 0.6% indicates that organic matter has only reached the onset of petroleum generation at 2.00 m from the contact. Such a maturity level corresponds to temperatures much lower than 100 °C in a sedimentary basin and around 150 °C for a sedimentary formation intruded by dykes or sills (Simoneit et al., 1981; Bishop and Abbott, 1995; Galushkin, 1997). The maximum of thermal stress that it has been possible to determine by means of optic microscopy analyses was at 1.00 m from the contact where the measured value of 1.5% suggests that the dry gas zone has

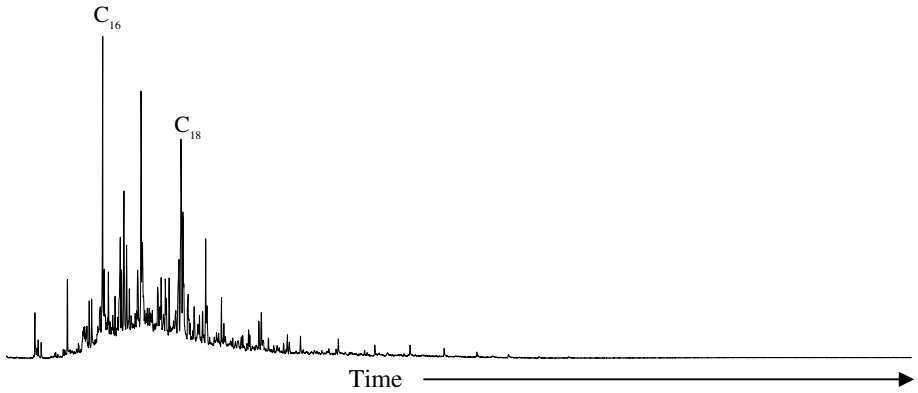


Fig. 9. GC–MS trace of saturated hydrocarbon fraction from sample altered by both abiotic and biotic oxidation.

been reached. In the present case of an *in situ* combustion process the time scale is intermediate between those of laboratory experiments (dry gas temperature threshold >400 °C) and of organic matter evolution in a sedimentary basin (dry gas temperature ~200 °C), the inferred temperature likely ranges between 300 and 400 °C. This range is consistent with magnetic investigations that show a very strong susceptibility anomaly at meter mark 1 m (Fig. 7). Previous investigations on other sites where similar combustion processes occurred, namely the Mottled Zone in Israel (Ron and Kolodny, 1992) and the site of Maqarin in Jordan (Vandamme et al., 2003), showed that upon heating, pyrite framboïds initially present in fossil tests of the sediment are pseudomorphosed into magnetic minerals (magnetite, maghemite). Transformation of pyrite into magnetite occurs at relatively low-temperature (from 150 °C to 350 °C) in heated clay-bearing sediments (Schill et al., 2002; Moreau et al., 2005). In the case of the Khushaym Matruk site, the combustion process was probably a strongly oxidative event since S is mostly present in the $SO_4$ form in the cement-marbles and the measured Curie temperatures are best consistent with maghemite-type products (Trotignon et al., 2005b). In Maqarin, a redox zonation was identified showing two adjacent magnetic anomalies related to maghemite and magnetite, respectively (Vandamme et al., 2003). A plausible temperature range of about 350 °C is thus proposed at a distance of 1 m in the profile, based on the vitrinite reflectance and on the location of the main magnetic anomaly. This major magnetic anomaly is also associated with a peak in Fe, Cr and Ti concentrations across the profile (Fig. 8). Analyses of magnetic minerals observed in Maqarin in the same sedimentary formation showed indeed traces of Cr and Ti in the observed maghemite and magnetite grains (Vandamme et al., 2003). The weaker magnetic anomaly observed in the profile at 2.6 m distance is well correlated with the maximum concentration of Cr-bearing clay minerals reported by Rassineux (2001) and with the second Fe, Cr, Ti concentration peak (Fig. 8). In contrast, the metamorphic events did not have any major impact on organic matter from the bottom of the baked zone (2.10–3.05 m) down to the undisturbed grey clayey biomicrites. The mean vitrinite reflectances are similar to those found in well-preserved plant debris, indicating that the Upper Cretaceous-Lower Paleocene sediments from Khushaym Matruck have been neither deeply buried nor thermally altered by metamorphic events. The low maturity level of organic matter is strengthened by the atomic C/O ratio values of lignocellulosic debris that vary from those of the cellulose stage to those of the huminite stage (Tissot and Welte, 1984) when approaching the contact. The presence of polysaccharides, unexpected for plant debris in sediments of Upper Cretaceous-Lower Paleocene age, also argues for a low thermal stress as far as sedimentary burial or metamorphic processes are considered. The limited influence of thermal stress inferred from organic matter study is consistent with the low magnetic susceptibility values measured at distances greater than 3 m away from the contact.

Mineralogical examinations and thermodynamic calculations suggest that hydrothermal alteration occurred in the metamorphic unit at temperatures lower than 100 °C with $pH_{fluid}$ values between 10.5 and 12 (Fourcade et al., 2007). Paleocirculation of meteoric groundwater in these cement-marbles has generated alkaline fluids that have percolated through the underlying sedimentary formation. Actually, little is known about the behaviour of sedimentary organic matter submitted to alkaline perturbation, and this question has recently been addressed with the concepts of geological disposal for nuclear wastes. Microscopic analyses show the presence of vegetable debris in the sediments from Khushaym Matruk site that have certainly been altered by the migrating alkaline fluids. As a matter of fact, delignification alkaline treatments of lignocellulosic materials are used in industry including paper pulp manufacturing, agricultural and food industries. Lignocellulose is mainly formed of three closely associated components, hemicellulose, cellulose and lignin. Basically, covalent crosslinkages have been suggested to occur between lignin and carbohydrates (cellulose, hemicellulose) in the form of ester and ether functionalities. One of the delignification reactions occurring at lower temperatures (room temperature to 150 °C) include saponification of intermolecular ester bonds using Ca hydroxide as alkali reagent (Playne, 1984; Chang et al., 2001; Karr and Holtzapple, 2000). In the Khushaym Matruk case study, major variations have been observed in the chemical composition of lignocellulosic debris with distance from the marble-cements. Spectral features in the 2000–800 $cm^{-1}$ region and polysaccharide/lignin ratios of microorganic particles from grey biomicrite samples closely match those of unaltered lignocelluloses (Given et al., 1984; Ibarra et al., 2004). The abundance of

polysaccharides relative to lignin drastically decreases with proximity to the metamorphic zone and this is attributed to the alkaline perturbation. By comparing with industrial delignification processes, high-pH hydrolysis appears to represent the most probable cause of the alteration of lignocellulosic debris. The subsequent degradation of polysaccharides is likely related to the same event since temperature alone would have been too low to induce such a transformation (Glaus et al., 1999; Knill and Kennedy, 2003, and references therein). The observed trends suggest a progressive pH buffering of the migrating fluids from 2.00 to 3.05 m, a fading of their effects further than 3.05 m from the contact and a more or less total absence of such effects at the bottom of the grey clayey biomicrites. It is noteworthy that all these tendencies are consistent with mineralogical and isotopic data (Fourcade et al., 2007).

In summary, both the thermal impact of combustion events, the weathering and the alkaline perturbation affected the first 2 m of biomicrite below the contact. Using mineralogy, organic matter and magnetic susceptibility, a suite of characteristic points can be assessed, depicting the thermal imprint of combustion events: contact ($x = 0$ m, $T \sim 1000$ °C), ($x = 1$ m, $T \sim 350$ °C), ($x = 2$ m, $T \sim 150$ °C) and ($x > \sim 8$ m, $T \sim 30$ °C undisturbed rock). The combined effects of alkaline perturbation and weathering processes are recognizable between 2.0 and 3.05 m below the contact. The influence of the alkaline perturbation drastically declines in the grey clayey biomicrites, especially down from 6.0 m where oxidative weathering appears to be the main effect. Chronologically, the low extract yields obtained in the baked biomicrites, despite the temperature deduced from magnetic susceptibility, suggest that organic matter firstly experienced weathering before the impact of combustion events and was finally altered by the high-pH fluids.

### *4.2. Bearing of the KM site on deep storage: relative migration and trapping of Cr, Ti, Fe*

An important issue for assessing the performance of a repository for the deep disposal of radioactive wastes is the confining capacity of the host rock under high-pH conditions. Organic matter in sediments could contribute to the immobilization of elements during the migration of alkaline fluids. The behaviour of Cr, Ti and Fe was studied because of their potential relevance to the behaviour of other transition elements. The genetic relationship between Ti and organic materials is not fully understood in the rare U deposits where they are associated (Theis, 1979; Smits, 1984). Some studies call for the formation of complexes of Ti with carbonate ions and specific organic ligands to explain its mobility under low-temperature conditions (Hayes et al., 1996). Parnell (2004) interpreted the occurrence of Cr inclusions in vein-hosted bitumen as a result of the mobilization of Cr by bitumen followed by the crystallization of minerals from a solidifying metal-rich hydrocarbon fluid. Chromium is frequently found in hexavalent and trivalent states under natural environmental conditions. Oxidation of Cr(III) to Cr(VI), very slow in the natural systems, is possible under high temperature and pH conditions as those used in the high-lime chromite ore processing plants (Eary and Rai, 1988; Farmer et al., 2002; Geelhoed et al., 2002). The mobility of Cr(VI) strongly depends on the anionic environment, pH and redox conditions (Brigatti et al., 2000; Zachara et al., 2004). Reduction of Cr(VI) to Cr(III), which can be induced by Fe(II) (Eary and Rai, 1989; Fendorf and Li, 1996; Buerge and Hug, 1997, 1999; Peterson et al., 1997; Pettine et al., 1998), organic matter (Wittbrodt and Palmer, 1995; Banks et al., 2006) or microorganisms (Chen and Hao, 1996), is an effective mechanism for immobilizing the chromate ions.

The mineral composition of the cement-marbles unit suggests that the temperature reached in the metamorphic zone was around 1050–1100 °C (Fourcade et al., 2007). Cr(VI)-containing solid phases could be formed under such conditions. Unfortunately, metal speciation was not carried out on the cement-marbles or the biomicrites in the present study. Mineralogical and petrographical examinations of sediments from the Khushaym Matruck site showed dissolution of biomicrite-forming detrital silicates like quartz, feldspars, mica and of diagenetic phyllosilicates, and the dissolution-precipitation of secondary phases, including amorphous silica, zeolites and Cr phyllosilicates also occurred in the zone strongly disturbed by high-pH solutions (Rassineux, 2001). Chromium is structurally bound to the smectites in this zone whereas it is present as an oxide at the bottom of the baked zone and in the grey clayey biomicrites (Rassineux, 2001). Incorporation of Cr in the smectites is made possible by Cr(III)/Al substitutions (Khoury et al., 1984). Investigations conducted on samples collected at the Maqarin site, which has

experienced combustion events similar to those of Khushaym Matruk, have shown that the Cr present in the initial biomicrite and unaltered cements is in the +III oxidation state (Rose et al., 2002 ; Trotignon et al., 2005a). The Cr(VI)/Cr(III) ratio in cements at Maqarin increases significantly with the alteration grade and several Cr(VI)-bearing solid phases (gypsum, ettringite, barite, hashemite) have been observed in the altered cementitious horizons at the Maqarin site (Milodowski et al., 1992; Trotignon et al., 2005a). Hyperalkaline groundwaters sampled in Maqarin contain 0.5–5 mg/L dissolved Cr as Cr(VI) (Clark et al., 1992), which gives evidence for the export of this metal after oxidation. Observations of cements in Khushaym-Matruk (see Fourcade et al., 2007) revealed the presence of Ba($(1-x)$ $SO_4$, $x$ $CrO_4$) among the alteration products in fractures. A similar transfer process of Cr is therefore, strongly suggested at the Khushaym Matruk site. Paleocirculation of meteoric groundwater in the cement-marbles has generated alkaline fluids containing metals that have not only undergone transportation but also redox reactions. Organic matter in the underlying biomicrites can be one of the reactants involved in these redox reactions, reducing Cr(VI) to Cr(III) and affecting the mobility of Cr in the sedimentary column (Wittbrodt and Palmer, 1995; Banks et al., 2006). Metal contents are higher at the bottom than at the top of the baked biomicrites, indicating that the pH conditions also influenced metal uptake. It is worth noting that the metal patterns in Fig. 7 show two peaks at 2.10 and 3.05 m that coincide with higher oxidation levels of organic matter (Fig. 1) and higher yields of hydrocarbons (Fig. 6b). This could be interpreted in terms of changes in the transportation regime of the alkaline fluids moving via microcracks or by diffusion through open porosity.

## 5. Conclusions

FT-i.r. microscopy and oxygen index data showed that organic matter from the Khushaym Matruk site has been highly oxidized up to a distance of ~10 m beneath the metamorphic zone. The oxidative weathering induced the formation of refractory organic matter having very low petroleum potentialities and high Rock-Eval $T_{max}$ values. The GC–MS traces of saturated hydrocarbons suggest that weathering was both abiotic and mediated by microorganisms. The occurrence of marbles at Khushaym Matruk site is explained by the spontaneous combustion of biomicrites. Its related thermal impact seems restricted to the first 2.0 m away from the contact. Using mineralogy, microscopic analyses of microorganic particles and magnetic susceptibility, a suite of characteristic temperature–distance coordinates can be assessed for this thermal impact: ($x = 0$ m, $T \sim 1000$ °C), ($x = 1$ m, $T \sim 350$ °C), ($x = 2$ m, $T \sim 150$ °C) to the undisturbed rock ($x > \sim 8$ m, $T \sim 30$ °C).

Paleocirculation of meteoric groundwater in the cement-marble formation has induced alteration and hydration of minerals in this unit. Alkaline fluids were generated that way and percolated through the underlying sedimentary formation. One of the significant contributions of the present study is to highlight the ability of lignocellulosic debris to track changes in the physico-chemical properties of alkaline fluids. In the baked biomicrites, the polysaccharide/lignin ratio progressively increases with distance to the contact. The authors think that this trend reflects a decline of delignification reactions and a subsequent degradation of polysaccharides due to a progressive decrease in the pH of migrating fluids rather than the thermal impact of combustion events.

The other major contribution concerns the role of the organic matter and regime of fluid transfer through a sedimentary column in the immobilization of transition metals such as Cr, Ti and Fe. Data from the Maqarin site showed that solid phases containing Cr(VI) are formed in the altered cement-marbles due to high-pH alteration conditions by air-rich waters. Solid phases similar to those observed at the Maqarin site are found in the altered cement-marbles in Khushaym Matruk. Subsequently, solid phases were dissolved by the meteoric water and oxidized elements like Cr(VI) were transported by the migrating fluids through the sedimentary column. Bulk chemical analysis of metals showed that Fe, Ti and Cr contents are higher at the top than at the bottom of the baked biomicrites suggesting that pH buffering has played a role in their trapping. These elements have not only undergone migration but also reactions. The coincidence between metal content, oxygen index and hydrocarbon yield patterns in the baked biomicrites suggests that kerogen was involved in redox reactions and influenced the mobility of metals. Further investigations are needed to decipher the relationship between the alteration level of organic matter and the speciation of metals. The baked biomicrites are crosscut by numerous micro-cracks such that the

alkaline solutions could have migrated via fractures and by diffusion through the open porosity. It is thought that the reactivity between the components of the host rock and the migrating fluids are strongly dependant on the fluid flow regime. Thus, in addition to the anionic environment, pH and redox conditions, the regime of fluid transfer through a sedimentary column seems to be a major factor controlling the uptake of metals.

## Acknowledgements

This study is part of the Maqarin Phase IV Project that was supported by Andra, CEA, JNC, Nagra, Nirex, SKB and the University of Jordan (Prof. H. Khoury). The Centre National de la Recherche Scientifique (CNRS) and Agence Nationale pour la Gestion des Déchets Radioactives (ANDRA) are thanked for providing the financial support *via* GdR FORPRO (action FORPRO 2001.VII) for this research. Thanks are due to I.D. Clark and to an anonymous reviewer for reviewing an earlier version. M.A. Kohler is thanked for his technical assistance in scanning electron microscopy.

## References

Alexander, W.R., Smellie, J.A.T., 1998. Maqarin natural analogue project: ANDRA, CEA, NAGRA, NIREX and SKB synthesis report on phases I, II and III, Nagra Report NPB 98-08, Nagra, Wettingen, Switzerland.

Alexander, W.R., Dayal, R., Eagleson, K., Eikenberg, J., Hamilton, E., Linklater, C.M., McKinley, I.G., Tweed, C.J., 1992. A natural analogue of high pH cement pore waters from the Maqarin area of northern Jordan II: results of predictive geochemical calculations. J. Geochem. Explor. 46, 133–146.

Banks, M.K., Schwab, A.P., Henderson, C., 2006. Leaching and reduction of chromium in soil as affected by soil organic content and plants. Chemosphere 62, 255–264.

Bishop, A.N., Abbott, G.D., 1993. The interrelationship of biological marker maturity parameters and molecular yields during contact metamorphism. Geochim. Cosmochim. Acta 57, 3661–3668.

Bishop, A.N., Abbott, G.D., 1995. Vitrinite reflectance and molecular geochemistry of Jurassic sediments: the influence of heating by Tertiary dykes (northwest Scotland). Org. Geochem. 22, 165–177.

Brigatti, M.F., Franchini, G., Lugli, C., Medici, L., Poppi, L., Turci, E., 2000. Interaction between aqueous chromium solutions and layer silicates. Appl. Geochem. 15, 1307–1316.

Buerge, I.J., Hug, S.J., 1997. Kinetics and pH dependence of chromium(VI) reduction by iron(II). Environ. Sci. Technol. 31, 1426–1432.

Buerge, I.J., Hug, S.J., 1999. Influence of mineral surfaces on chromium(VI) reduction by iron(II). Environ. Sci. Technol. 33, 4285–4291.

Chandra, D., 1958. Reflectance of oxidized coals. Economic Geol. 53, 102–108.

Chang, V.S., Nagwani, M., Kim, C.H., Holtzapple, M.T., 2001. Oxidative lime pretreatment of high-lignin biomass. Appl. Biochem. Biotechnol. 94, 1–28.

Chen, J.M., Hao, O.J., 1996. Environmental factors and modeling in microbial chromium(VI) reduction. Water Environ. Res. 68, 1156–1164.

Claret, F., Schäfer, T., Bauer, A., Buckau, G., 2003. Generation of humic and fulvic acid from Callovo-Oxfordian clay under high alkaline conditions. Sci. Total Environ. 317, 189–200.

Claret, F., Schäfer, T., Rabung, T., Wolf, M., Bauer, A., Buckau, G., 2005. Differences in properties and Cm(III) complexation behavior of isolated humic and fulvic acid derived from Opalinus clay and Callovo-Oxfordian argillite. Appl. Geochem. 20, 1158–1168.

Clark, I.D., Fritz, P., Milodowski, A.E., Khoury, H.N., 1992. Sampling and analytical methods in: A natural analogue study of the Maqarin hyperalkaline groundwaters. Nagra Technical Report 91-10, Wettingen, Switzerland, pp. 19–40.

Clayton, J.L., Bostick, N.H., 1986. Temperature effects on kerogen and molecular and isotopic composition of organic matter in Pierre Shale near an igneous dike. Org. Geochem. 10, 135–143.

Clayton, J.L., Swetland, P.J., 1978. Subaerial weathering of sedimentary organic matter. Geochim. Cosmochim. Acta 42, 305–312.

Cookes, N.E., Fuller, O.M., Gaikwad, R.P., 1986. FT-i.r. spectroscopic analysis of coals and coal extracts. Fuel 65, 1254–1260.

Copard, Y., Disnar, J.R., Becq-Giraudon, J.F., 2002. Erroneous maturity assessment given by $T_{max}$ and HI Rock-Eval parameters on highly mature weathered coals. Int. J. Coal Geol. 49, 57–65.

Djuricic, M., Murphy, R.C., Vitorovic, D., Biemann, K., 1971. acids obtained by alkaline permanganate oxidation of kerogen from the Green River (Colorado) shale. Geochim. Cosmochim. Acta 35, 1201–1207.

Eary, L.E., Rai, D., 1988. Chromate removal from aqueous wastes by reduction with ferrous ion. Environ. Sci. Technol. 22, 972–977.

Eary, L.E., Rai, D., 1989. Kinetics of chromate reduction by ferrous ions derived from hematite and biotite at 25 °C. Am. J. Sci. 289, 180–213.

Einsele, G., Gieskes, J.M., Curray, J., Moore, D.M., Aguayo, E., Aubry, M.-P., Fornari, D., Guerrero, J., Kastner, M., Kelts, K., Lyle, M., Matoba, Y., Molina-cruz, A., Niemitz, J., Rueda, J., Saunders, A., Schrader, H., Simoneit, B., Vacquier, V., 1980. Intrusion of basaltic sills into highly porous sediments, and resulting hydrothermal activity. Nature 283, 441–445.

Elie, M., Faure, P., Michels, R., Landais, P., Griffault, L., 2000. Natural and laboratory oxidation of low-organic-carbon-content sediments: comparison of chemical changes in hydrocarbons. Energ. Fuel. 14, 854–861.

Elie, M., Faure, P., Michels, R., Landais, P., Griffault, L., Mansuy, L., Martinez, L., 2004. Effects of water-cement solutions on the composition of organic compounds leached from oxidized Callovo-Oxfordian argillaceous sediment. Appl. Clay Sci. 26, 309–323.

Farmer, J.G., Thomas, R.P., Graham, M.C., Geelhoed, J.S., Lumsdon, D.G., Paterson, E., 2002. Chromium speciation and fractionation in ground and surface waters in the vicinity

of chromite ore processing residue disposal sites. J. Environ. Monitor. 4, 235–243.
Farrimond, P., Bevan, J.C., Bishop, A.N., 1996. Hopanoid hydrocarbon maturation by an igneous intrusion. Org. Geochem. 25, 149–164.
Fendorf, S.E., Li, G., 1996. Kinetics of chromate reduction by ferrous iron. Environ. Sci. Technol. 30, 1614–1617.
Fourcade, S., Trotignon, L., Boulvais, P., Techer, I., Elie, M., Vandamme, D., Salameh, E., Khoury, H., 2007. Cementation of kerogen-rich marls by alkaline fluids released during weathering of thermally metamorphosed marly sediments. Part I: Isotopic (C,O) study of the Khushaym Matruk natural analogue (central Jordan). Appl. Geochem. 22, 1293–1310.
Galushkin, Y.I., 1997. Thermal effects of igneous intrusions on maturity of organic matter: a possible mechanism of intrusion. Org. Geochem. 26, 645–658.
Ganz, H.H., Kalkreuth, W., Ganz, S.N., Öner, F., Pearson, M.J., Wehner, H., 1990. Infrared analysis – State of art. Berliner Geowiss. Abh. A, 1011–1026.
Geelhoed, J.S., Meeussen, J.C.L., Hillier, S., Lumsdon, D.G., Thomas, R.P., Farmer, J.G., Paterson, E., 2002. Identification and geochemical modeling of processes controlling leaching of Cr(VI) and other major elements from chromite ore processing residue. Geochim. Cosmochim. Acta 66, 3927–3942.
George, S.C., 1992. Effect of igneous intrusion on the organic geochemistry of a siltstone and a oil shale horizon in the Midland Valley of Scotland. Org. Geochem. 18, 705–723.
Given, P.H., Spackman, W., Painter, P.C., Rhoads, C.A., Ryan, N.J., 1984. The fate of cellulose and lignin in peats: an exploratory study of the input to coalification. Org. Geochem. 6, 399–407.
Glaus, M.A., Van Loon, L.R., Achatz, S., Chodura, A., Fischer, K., 1999. Degradation of cellulosic materials under the alkaline conditions of a cementitious repository for low and intermediate level radioactive waste. Part I: Identification of degradation products. Anal. Chim. Acta 398, 111–122.
Hayes, P.D., Walling, S.D., Tieh, T.T., 1996. Organic and authigenic mineral geochemistry of the Permian Delaware Mountain Group, West Texas: implications for the chemical evolution of pore fluids. SEPM Spec. Publication 55, 163–186.
Ibarra, D., del Río, J.C., Gutiérrez, A., Rodríguez, I.M., Romero, J., Martínez, M.J., Martínez, A.T., 2004. Isolation of high-purity residual lignins from eucalypt paper pulps by cellulase and proteinase treatments followed by solvent extraction. Enzyme Microb. Technol. 35, 173–181.
Ingram, G.R., Rimstidt, J.D., 1984. Natural weathering of coal. Fuel 63, 292–296.
Karr, W.E., Holtzapple, T., 2000. Using lime pretreatment to facilitate the enzymatic hydrolysis of corn stover. Biomass Bioenerg. 18, 189–199.
Khoury, H.N., Mackenzie, R.C., Russell, J.D., Tait, J.M., 1984. An iron-free volkonskoïte. Clay Min. 19, 43–57.
Khoury, H.N., Salameh, E., Clark, I.D., Fritz, P., Bajjali, W., Milodowski, A.E., Cave, M.R., Alexander, W.R., 1992. A natural analogue of high pH cement pore waters from the Maqarin area of northern Jordan I: introduction to the site. J. Geochem. Explor. 46, 117–132.
Knill, C.J., Kennedy, J.F., 2003. Degradation of cellulose under alkaline conditions. Carbohyd. Polym. 51, 281–300.
Landais, P., Monthioux, M., Meunier, J.D., 1984. Importance of the oxidation/maturation pair in the evolution of humic coals. Org. Geochem. 7, 249–260.
Landais, P., Michels, R., Kister, J., Dereppe, J.-M., Benkhedda, Z., 1991. Behavior of oxidized type II kerogen during artificial maturation. Energ. Fuel. 5, 860–866.
Leythaeuser, D., 1973. Effects of weathering on organic matter in shales. Geochim. Cosmochim. Acta 37, 113–120.
Machihara, T., Ishiwatari, R., 1983. Evaluation of alkaline permanganate oxidation method for the characterization of young kerogen. Org. Geochem. 5, 111–119.
Mathé, P.E., 1996. Application du paléomagnétisme et du magnétisme des roches à l'étude des processus d'altération supergène – Thèse de 3e Cycle Univ. Aix-Marseille III.
Milodowski, A.E., Khoury, H.N., Pearce, J.M., Hyslop, E.K., 1992. Results: source/sink terms in: A natural analogue study of the Maqarin hyperalkaline groundwaters. Nagra Technical Report 91-10, Wettingen, Switzerland, pp. 41–83.
Moreau, M.G., Ader, M., Enkin, R.J., 2005. The magnetization of clay-rich rocks in sedimentary basins: low-temperature experimental formation of magnetic carriers in natural samples. Earth Planet. Sci. Lett. 230, 193–210.
Othman, R., Ward, C.R., 2002. Thermal maturation pattern in the southern Bowen, northern Gunnedah and Surat Basins, northern New South Wales. Int. J. Coal Geol. 51, 145–167.
Painter, P.C., Snyder, R.W., Pearson, D.E., Kwong, J., 1980. Fourier transform infrared study of the variation in the oxidation of a coking coal. Fuel 59, 282–285.
Parnell, J., 2004. Titanium mobilization by hydrocarbon fluids related to sill intrusion in a sedimentary sequence, Scotland. Ore Geol. Rev. 24, 155–167.
Peterson, M.L., Brown Jr., G.E., Parks, G.A., Stein, C.L., 1997. Differential redox and sorption of Cr(III/VI) on natural silicate and oxide minerals: EXAFS and XANES results. Geochim. Cosmochim. Acta 61, 3399–3412.
Petsch, S.T., Berner, R.A., Eglinton, T.I., 2000. A field of the chemical weathering of ancient sedimentary organic matter. Org. Geochem. 31, 475–487.
Pettine, M., d'Ottone, L., Campanella, L., Millero, F.J., Passino, R., 1998. The reduction of chromium (VI) by iron (II) in aqueous solutions. Geochim. Cosmochim. Acta 62, 1509–1519.
Playne, M.J., 1984. Increased digestibility of bagasse by pretreatment with alkalis and steam explosion. Biotechnol. Bioeng. 26, 426–433.
Quénéa, K., Derenne, S., Largeau, C., Rumpel, C., Mariotti, A., 2005. Spectroscopic and pyrolytic features and abundance of the macromolecular refractory fraction in a sandy acid forest soil (Landes de Gascogne, France). Org. Geochem. 36, 349–362.
Rassineux, F., 2001. Project Maqarin: phase IV. Contribution à l'identification des transformations minéralogiques de la biomicrite au contact d solutions alcalines sur le site de Khushaym Matruk. Rapport Final. D RP 0ERM 01–019.
Rassineux, F., Griffault, L., Smellie, J., Trotignon, L., Raynal, J., Khoury, H., Mercier, F., 2001. Mineralogical evolution of clay-bearing rock during alkaline alteration (Khushaym Matruk, Central Jordan). In: Cidu, R. (Ed.), Proceedings of the 10th International Symposium Water Rock Interaction (WRI-10), Villasimius Italy, pp. 1363–1366.

Raymond, A.C., Murchison, D.G., 1988. Development of organic maturation in the thermal aureoles of sills and its relation to sediment compaction. Fuel 67, 1599–1608.

Raymond, A.C., Murchison, D.G., 1991. The relationship between organic maturation, the widths of thermal aureoles and the thickness of sills in the Midland valley of Scotland and Northern England. J. Geol. Soc. Lond. 148, 215–218.

Rhoads, C.A., Senftle, J.T., Coleman, M.M., Davis, A., Painter, P.C., 1983. Further studies of coal oxidation. Fuel 62, 1387–1392.

Ron, H., Kolodny, Y., 1992. Paleomagnetic and rock magnetic study of combustion metamorphic rocks in Israël. J. Geophys. Res. 97 (B5), 6927–6939.

Rose, J., Crouzet, N., Trotignon, L., Susini, J., Khoury, H., Salameh, E., Milodowski, A., Mercier, F., 2002. Effect of leaching on the crystallographic sites of trace metals associated with natural cements (site of Maqarin, Jordan): case of Cr. J. Phys. IV France 104, 447–450.

Rowland, S.J., Maxwell, J.R., 1984. Reworked triterpenoids and steroid hydrocarbons in a recent sediment. Geochim. Cosmochim. Acta 48, 617–624.

Rullkötter, J., von der Dick, H., Welte, D.H., 1982. Organic petrography and extractable hydrocarbons of sediment from the Gulf of California, Deep Sea Drilling Project Leg 64. In: Curray, J.R., Moore, D.G., Aguayo, J.E., Aubry, M.-P., Einsele, G., Fornari, D., Gieskes, J., Guerrero-Garcia, J., Kastner, M., Kelts, K., Lyle, M., Matoba, Y., Molina-Cruz, A., Niemitz, J., Rueda-Gaxiola, J., Saunders, A., Schrader, H., Simoneit, B.R.T., Vacquier, V. (Eds.), Initial Reports of the Deep Sea Drilling Project 64, pp. 837–853.

Schäefer, T., Claret, F., Bauer, A., Griffault, L., Ferrage, E., Lanson, B., 2003. Natural organic matter (NOM)–clay association and impact on Callovo-Oxfordian clay stability in high alkaline solution: spectromicroscopic evidence. J. Phys. IV 104, 413–416.

Schill, E., Appel, E., Gautam, P., 2002. Towards purrhotite/magnetite geothermometry in low-grade metamorphic carbonates of the Thethyan Himalayas (Shiar Khola, Central Nepal). J. Asian Earth Sci. 20, 195–201.

Simoneit, B.R.T., Philp, R.P., 1982. Organic geochemistry of lipids and kerogen and the effects of basalt intrusions on unconsolidated oceanic sediments: sites 477, 478 and 481, Guaymas Basin, Gulf of California. In: Curray, J.R., Moore, D.G., Aguayo, J.E., Aubry, M.-P., Einsele, G., Fornari, D., Gieskes, J., Guerrero-Garcia, J., Kastner, M., Kelts, K., Lyle, M., Matoba, Y., Molina-Cruz, A., Niemitz, J., Rueda-Gaxiola, J., Saunders, A., Schrader, H., Simoneit, B.R.T., Vacquier, V. (Eds.), Initial Reports of the Deep Sea Drilling Project 64, pp. 883–904.

Simoneit, B.R.T., Brenner, S., Peters, K.E., Kaplan, I.R., 1981. Thermal alteration of Cretaceous black shale by diabase intrusions in the Eastern Atlantic-II. Effects on bitumen and kerogen. Geochim. Cosmochim. Acta 45, 1581–1602.

Smits, G., 1984. Some aspects of the uranium minerals in Witwatersrand sediments of the early Proterozoic. Precambrian Res. 25, 37–59.

Starsinic, M., Otake, Y., Walker, P.L., Painter, P.C., 1984. Application of FT-i.r. spectroscopy to the determination of COOH groups in coal. Fuel 63, 1002–1007.

Techer, I., Khoury, H.N., Salameh, E., Rassineux, F., Claude, C., Clauer, N., Pagel, M., Lancelot, J., Hamelin, B., Jacquot, E., 2006. Propagation of high-alkaline fluids in an argillaceous formation: case study of the Khushaym Matruk natural analogue (Central Jordan). J. Geochem. Explor. 90, 53–67.

Theis, N.J., 1979. Uranium-bearing and associated minerals in their geochemical and sedimentary context, Elliot Lake, Ontario. Geol. Surv. Can. Bull. 304, 1–50.

Tissot, B.P., Welte, D.H., 1984. Petroleum Formation and Occurrence. Springer-Verlag, Berlin.

Trotignon, L., Rose, J., Khoury, H., Mercier, F., Barré, N., Provitina, O., Cook, J., Milodowski, A., Susini, J., Bienvenu, P., Raimbault, L., Trocellier, P., Bulle, C., Crouzet, N., Arnal, N., Adam, F., Michaud, V., 2005a. Investigations sur le comportement et la migration des éléments Re, Cr, Mo et Se sur le site de Maqarin (Jordanie septentrionale) Technical Note CEA/DTN/SMTM/LMTE 2005-04, CEA Cadarache, France (in English).

Trotignon, L., Vandamme, D., Fontanini, L, Raynal, J., Khoury, H., Milodowski, A. Bienvenu, P., 2005b. Investigations sur les propriétés magnétiques et géochimiques d'échantillons de roches prélevés sur le site de Maqarin (Jordanie septentrionale). Technical Note CEA/DEN/DTN/SMTM 05-002 (in English).

Vandamme, D., Fontanini, L., Trotignon, L., Raynal, J., Khoury, H., Milodowski, A., Rassineux, F., Mäder, U., Bienvenu, P., 2003. Investigations on the combustion metamorphism halo of bituminous micrites (Maqarin site – Northern Jordan) (presentation EUG April 2003, Nice, France).

Wittbrodt, P.R., Palmer, C.D., 1995. Reduction of Cr(VI) in the presence of excess soil fulvic acids. Environ. Sci. Technol. 29, 255–263.

Zachara, J.M., Ainsworth, C.C., Brown Jr., G.E., Catalano, J.G., Mckinley, J.P., Qafoku, O., Smith, S.C., Szecsody, J.E., Traina, S.J., Warner, J.A., 2004. Chromium speciation and mobility in a high level nuclear waste vadose zone plume. Geochim. Cosmochim. Acta 68, 13–30.