Characterization of organic matter deposited in the oriental zone from Moknine hypersaline environment, oriental Tunisia

Raja CHAIRI* and Zohra EL ASMI DJELLOULI
Laboratoire de Ressources Minerales et Environnement
Faculté des Sciences de Tunis 2092 Univ. Tunis El Manar
Tunisie

Abstract The geochemistry data show that the total organic carbon (TOC) contents are high in the surface sediments in the eastern part of the Moknine's Sebkha. Low decreasing of organic matter (OM) with increasing depth indicates the good preservation of OM in modern sediments. "Lignite levels" inserted in the sand sequence and deposited at the edge and in the intermediate zone are considered as lithologic and organic markers. It is characterized by high TOC and poor hydrogen index (HI), indicating a higher plant origin and good preservation of OM in thin beds under anoxic condition.

In all samples low values of HI are typical for strong terrigenous input in the Sebkha. Gas chromatography (GC) of saturate fraction showed that OM in the border zone is provided from plants but in the central zone OM is a mixture of terrestrial fraction and little fraction from microalgae. The study of free lipids indicated that this environment was influenced by intense bacterial and microbial activities, as evidenced by the abundance of n-alkanes and nC_{18}-nC_{22}.

Key words evaporate system; modern sediment; diagenetic OM; anoxic environment

1 Introduction

Till up to now, only a few detailed geochemical studies of organic matter (OM) have been performed in modern sediments of evaporitic systems. This environment is characterized by high biomass production (Busson, 1979; Rouchy, 1982; Warren, 1986, Baranger et al., 1988; Kenig et al., 1995). Microbial sulfate reduction is a major mineralization process of organic matter in the anoxic environment (Sorokin, 1962, Jorgensen, 1982; Lallier-Vergès et al., 1993). The anaerobic process will degrade sedimentary OM with the same efficiency as aerobic degradation (Henrichs and Reeburgh, 1987). However, Hite and Anders (1991) showed that the degradation of OM by methanogenic bacteria is inhibited in the evaporate system, which promotes OM accumulation and preservation in sediments. Geochemical differences among various evaporitic settings are more obvious (Kenig et al., 1995). However, the well-established organic indicators of highly saline depositional environments are low pristane/phytane ratio (ten Haven et al., 1988) and predominance of even numbered over odd numbered n-alkanes (Welte and Waples, 1973).

The purpose of this work is to constrain the origin of OM in the eastern part of Moknine Sebkha where the factors controlling the distribution of OM in modern sediments and its diagenetic alteration and evolution under hypersaline conditions are also considered in this study.

2 Geological setting

The Sebkha of Moknine is located in the eastern part of Tunisia, southeast of Moknine and northwest of Mahdia (Fig. 1). A littoral barrier, 4 km in length, separates the Sebkha from the Mediterranean Sea and it belongs to the group (Fig. 1) of Sebkha with lozenge morphology (Amari and Bedir, 1988).

3 Methods

Six cores (SM1, SM2, SM3, SM4, SM5 and SM6) were obtained from the eastern part of the Moknine's Sebkha (Fig. 1). Sampling was performed by means of a PVC tube (75 mm in diameter). Before analysis, sediments were dried at 40°C.

Rock-Eval pyrolysis and TOC determination were carried out under standard conditions on a Girdel Oil-Show-Analyzer (Espitalié et al., 1977). Total lipids were extracted with $CHCl_3$ in a Soxshlet apparatus (12 h). The origin and composition of free lipids were de-

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* Corresponding author: Chairi_ra@yahoo.fr

termined by chromatography with a silica gel column (Behar and Leblond, 1984) and gas chromatography using a Carlo Erba HRGCC 5300 Mega series (SP 2100 capillary column: 30 m × 0.25 mm, programmed from 80 to 300 °C at 4°C/min). All the analyses were made on the lutitique fraction (< 63 μm).

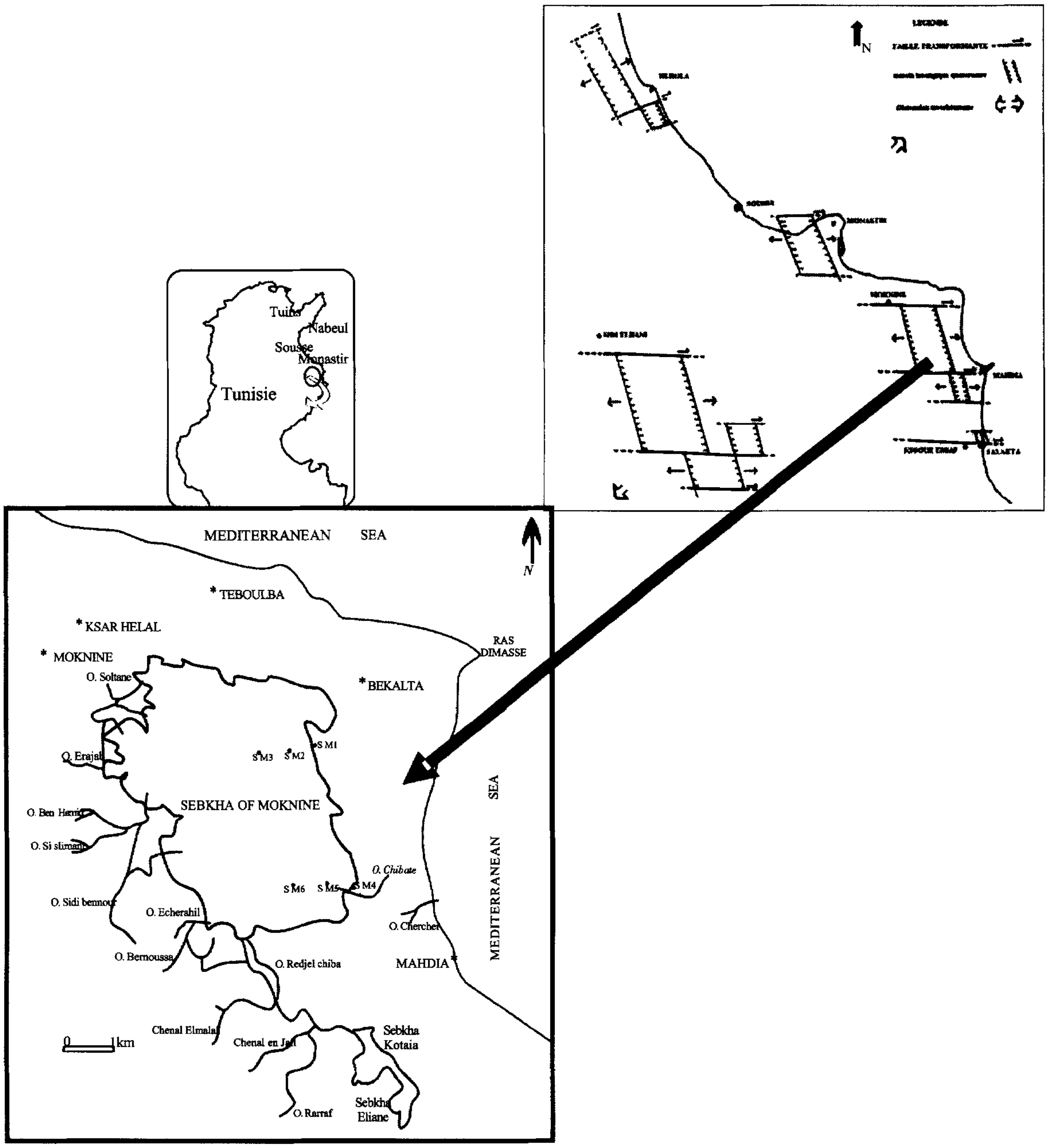

Fig. 1. Moknine's evaporitic system and core location.

4 Results and discussion

4.1 Lithology

Lateral distribution is very dissymmetric in this Sebkha (Chairi and Bélayouni, 2001): sand was deposited at the periphery, espetially on the western side, mixed facies (sandy-clay, clayey-sand) were deposited in the intermediate zone and the center of the Sebkha is occupied by clayey facies.

The cores sampled at the periphery (SM1 and SM4) are composed of sand intercalated with clay and thin lignite levels. In the intermediate zone cores (SM2 and SM5), a mixed facies with thin lignite levels is observed. The center of the Sebkha is occupied by homogeneous facies composed of clay and silto-clay (Fig. 2).

Lignite level is the result of destruction of higher plants at the periphery during flood, which is simultaneously covered by sand sequences (Photo 1).

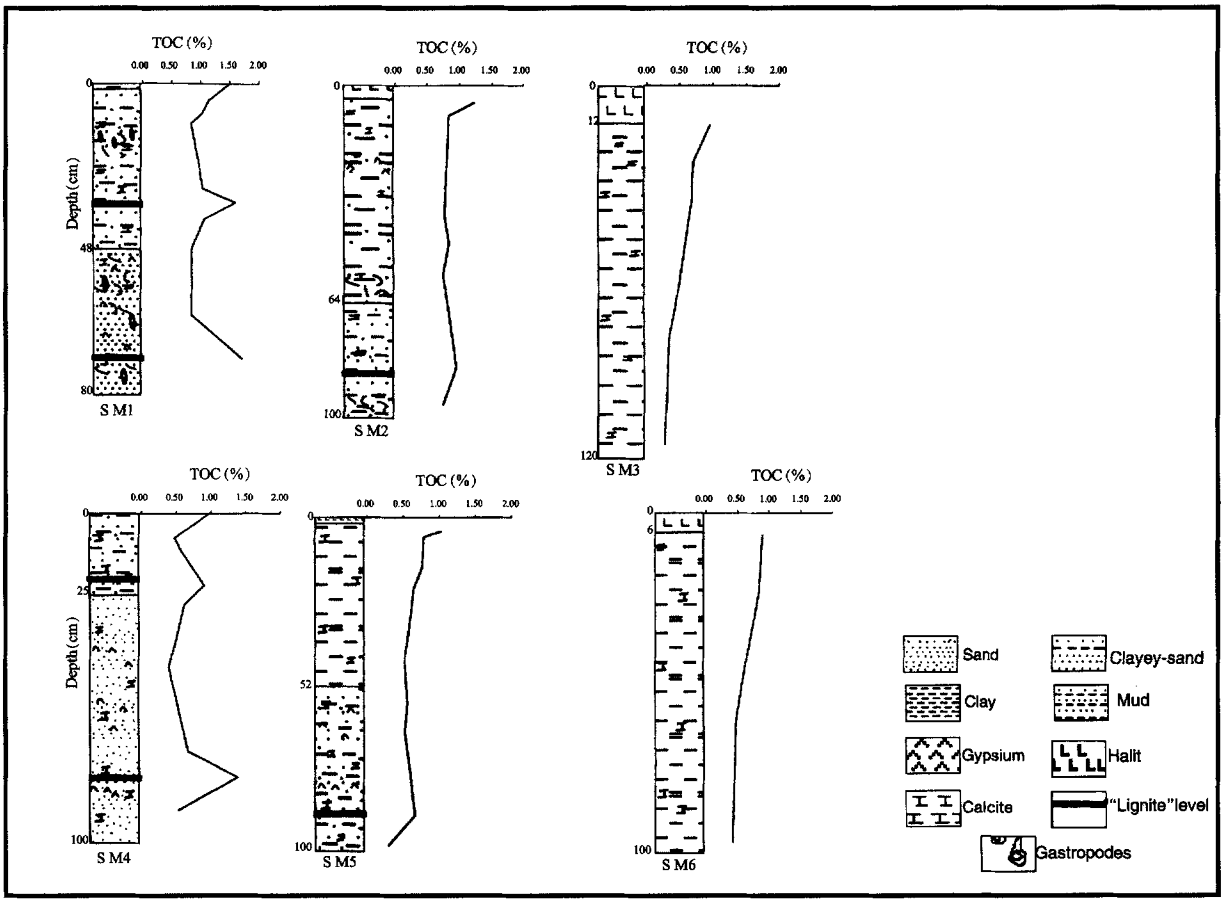

Fig. 2. Variation of TOC with depth in peripeheral cores (SM1 and SM4) and intermediate cores (SM2 and SM5) and central cores (SM3 and SM6) from the Moknine's Sebkha.

The evaporates formed in the Moknine Sebkha are gypsum and halite. Gypsum crystals dispersed in the periphery and intermediate core sediments resulted from interstitial water evaporation. Halite was precipitated at higher levels of evaporation in the central part. The carbonates are composed of calcite which was derived from chemically precipitated, detrital and biogenic fractions (Chairi and Belayouni, 2001; Chairi, 2004).

4.2 Geochemistry data

4.2.1 TOC

The total organic carbon (TOC) varies between 0.65% and 1.55% in core SM1, 0.48% and 1.35% in core SM4, 0.78% and 1.26% in core SM2, 0.33% and 1.04% in core SM5. Variations in TOC in the peripheral and intermediate cores are related to lithology (Fig. 2). OM distribution is influenced both by lithofacies heterogeneity and by the occurrence of thin beds of "lignite", which were formed by *in-situ* destruction of higher plants (*Zygophylum album*, *Atriplex inflata*, *Legium aspartum and Salicornia arabica*) which grew in this zone by sand during flood.

In the central part TOC varies between 0.23% and 0.87% in core SM3 and 0.38% and 0.79% in core SM6. OM is better preserved in upper centimeter level than at depth.

The decrease of TOC values with increasing depth is progressive, illustrating the preservation of OM in the Moknine's Sebkha. In hypersaline systems sulfates and halite are deposited at extremely high sedimentation rates and may be one of the factors controlling OM preservation. Lateral distribution of organic carbon has testified that not only lithology affects organic enrichment, even the sources of OM and the preservation conditions intervene.

4.2.2 Hydrocarbon compounds

Free and potential hydrocarbons (S1 and S2) obtained by Rock Eval pyrolyses are less abundant in the sediments sampled in the eastern part of the Sebkha (S1 and S2 <0.5 mg HC · g^{-1} · sed), showing the values are typical of modern sediments. Hydrocarbons in S1 and S2 decrease with increasing depth. The progressive evolution of hydrocarbons could indicate the preservation of OM in the modern sediments of the Moknine's Sebkha. Hydrocarbons have the same origin, for which S1 positively correlates (R^2: 0.95) with S2 (Fig. 3). The low total hydrocarbon (S1 + S2 < 1 mg HC · g^{-1} · sed) contents in all samples and in "lignite" levels are typical of the type III (continental OM). Finally, the values of hydrogen index (HI) are generally low (Fig. 4) due to the major contribution of continental OM (Huc et al., 1992).

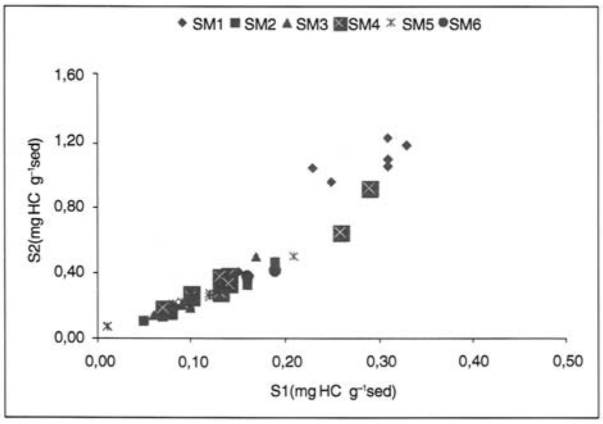

Fig. 3. Free hydrocarbon (S1) vs. potential hydrocarbon (S2).

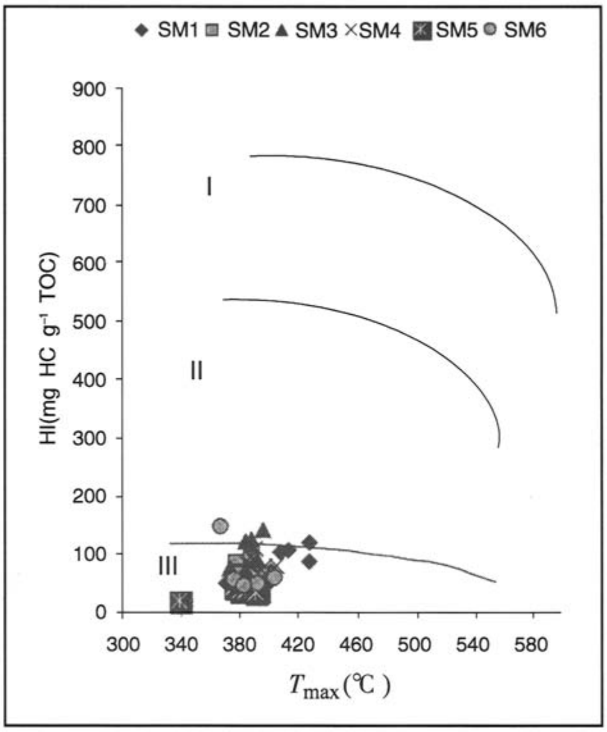

Fig. 4. HI/T_{max} diagram.

4.2.3 Studies of the lipidic fraction

The contents of extractable organic matter (EOM) vary between 65 μg/g and 465 μg/g at the periphery, 25 μg/g and 535 μg/g in the intermediate zone and 95 μg/g and 500 μg/g in the central part. These low contents of free bitumen indicate the biological origin of the extracts. The main components of the EOM are NSO compounds (40% – 90%), which is in agreement with the biological origin of the lipidic fraction analyzed in the sediments sampled in the eastern part of Moknine's Sebkha and the immaturity of the OM (Tissot and Welte, 1978; Espitaliè et al., 1977, 1985; Curial, 1987; Moretto, 1987). A bimodal distribution of n-alkanes is observed for the saturated hydrocarbons (Fig. 5). This pattern of distribution reflects a mixed lacustrine and terrestrial origin for the OM (Blumer et al., 1971; Tissot and Welte, 1978; Baranger and Disnar, 1988). The first mode is centered on nC_{10}-nC_{22} with the maxima at nC_{18} and nC_{22} and the predominance of even n-alkanes that represent microalgal sources. This has been confirmed by the abundance of docosane (nC_{22}), attributed to microalgae of evaporatic systems (Meyers and Ishiwatari, 1993; ten Haven et al., 1985; Schreiber et al., 2001; Chairi, 2005). A similar result was also obtained for the sediments of the Quero and Tirez lakes in Spain (Schreiber et al., 2001).

The second mode ranges from C_{25} to C_{33} with a maximum at C_{25} and a predominance of odd n-alkanes typical of terrestrial OM. The Carbon Preference Index (CPI) ranges from 1.16 to 5.72, reflecting a high detrital continental contribution to OM in the Sebkha.

In the lignite level the distribution of n-alkanes shows an odd carbon number predominance with a mode in nC_{25}-nC_{31} and represents higher plant input (Fig. 5).

The predominance of odd or even (nC_{18}, nC_{22}) n-alkanes in all samples confirms the immaturity of OM (Jonathan et al., 1976). The "humps" at the bases of saturate is due to the presence of unresolved complex mixture (UCM). This indicates that the OM has un-

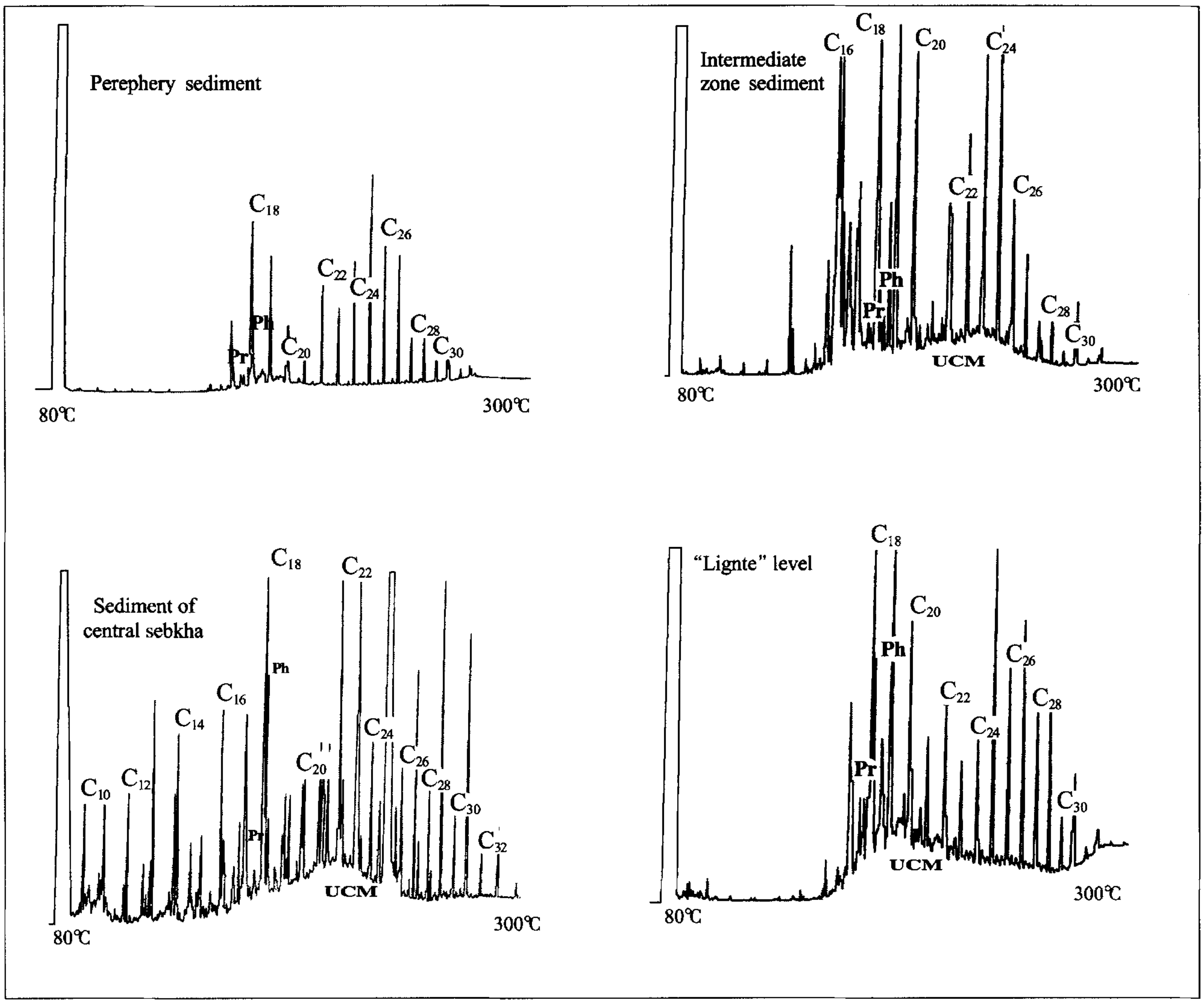

Fig. 5. Gas chromatogram of saturate fraction. Pr. Prystane; Ph. phytane; UCM. Unresolved complex mixture.

dergone biodegradation (Peter and Moldowan, 1993). Pr/Ph ratios range from 0.20 to 1.10. These ratio values are usually typical of sediments deposited under hypersaline conditions (ten Haven et al., 1988) and can result from reducing conditions (ten Haven et al., 1985, 1988; Peter and Moldowan, 1993). Phytols from which the pristane and phytane are supposed to be chiefly derived can originate cyanobacteria, eukaryote algae, higher plants and sulphur bacteria (Kenig et al., 1995). Reducing conditions prevailing in modern sediments are well illustrated in Waples diagram (Fig. 6), where all samples are concentrated in the anoxic domain.

5 Conclusions

High quantities of NSO compounds and low T_{max} and a predominance of odd n-alkanes indicate the immature nature of OM deposited in modern sediments of the Moknine's Sebkha. Reducing conditions in the Sebkha and rapid deposition of the salt protect OM from oxidation and ensure its good preservation.

The Sebkha provides three principal sources of sedimentary OM: microalgae, terrestrial organic debris and high halophyte growing plants at the margin. An important contribution of higher plants characterizes the border of the Sebkha. It is composed of debris of higher land plants that were fluvially transported into the Sebkha and higher halophyte plants which grew at the edge. In the central zone, OM has a mixed lacustrine/terrestrial origin with important quantities of terrigenous material. Little fraction from autochthonous material was derived from microalgae and indicated both by the mode of distribution of n-alkanes and by the presence of docosane nC_{22}, which is abundant in all samples.

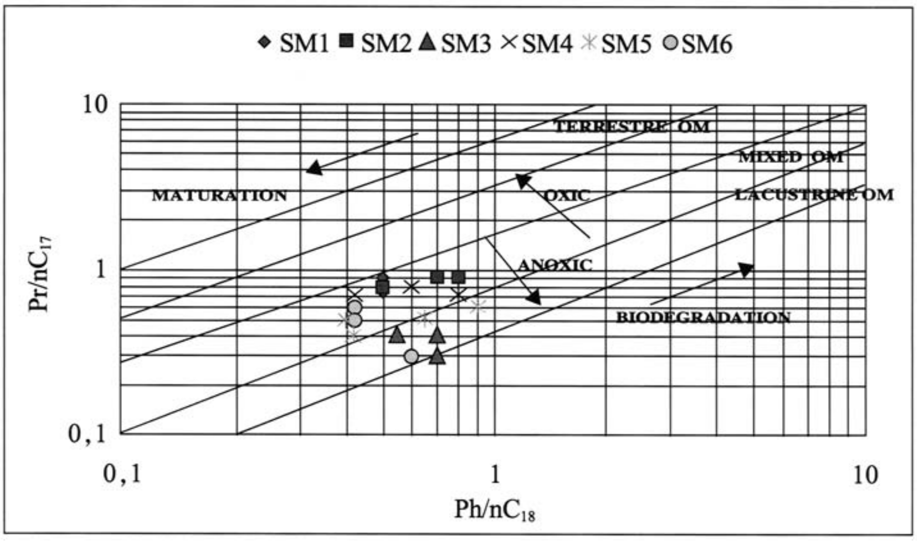

Fig. 6. Waples diagram: organic matter type, environment and maturity degree.

The series of cores sampled in the eastern part of the Sebkha showed that the lateral sedimentological variations are accompanied by changes in OM distribution. Higher OM abundance in the marginal part than in the central part is explained by the different origins of OM inputs. Vegetation growth on the border of the Sebkha and low topography allow the accumulation of organic matter at the edge, while OM deposited in the central part originated from the western part where rivers are abundant. The bulk organic and mineral materials of the Sebkha originated from the west (Chairi, 2004).

OM is, however, generally hydrogen-poor (HI values less than 110 mg HC · g^{-1} TOC) and mainly of terrigenous origin. The greater HI values in the central zone are the result of better OM preservation and microalgal contribution. In this zone, OM preservation is related to rapid sedimentation under hypersaline conditions and little degradation before and after deposition. However, OM originating from microalgae is dominated by a massive contribution of terrigenous OM.

Paleoenvirenment reconstruction of the evaporitic system of Moknine indicates that the presence of these beds rich in OM ("lignite" level) within the sandy sequences is the consequence of successive periods of flood in the Sebkha. "Lignite" levels are characterized by high TOC and poor IH and long chain of n-alkanes which indicate higher plant origin and good preservation in thin level under anoxic condition. These levels are interpreted as lithologic and organic "markers".

The sedimentary cycle starts with the destruction of higher plants developed at the border of the Sebkha during flood and covered by a sequence of sand. The sedimentation cycle is stopped by plant proliferation. Such a situation will remain unchanged until the next flood of the Sebkha, which will result in the second sequence of deposits of the same type.

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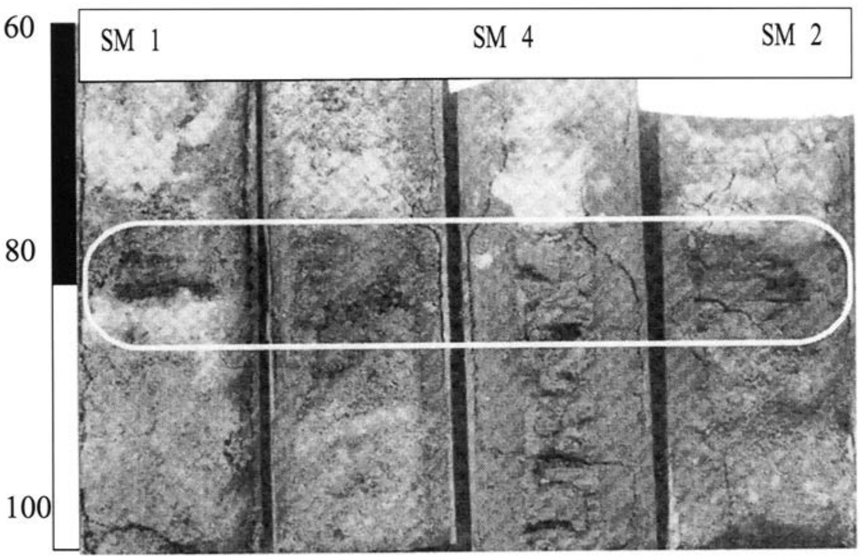

Photo 1. "Lignite" levels in the periphery and intermediate cores.