



HAL
open science

Productivity and bottom water redox conditions at the Cenomanian-Turonian Oceanic Anoxic Event in the southern Tethyan margin, Tunisia

Mohamed Soua

► **To cite this version:**

Mohamed Soua. Productivity and bottom water redox conditions at the Cenomanian-Turonian Oceanic Anoxic Event in the southern Tethyan margin, Tunisia. *Revue méditerranéenne de l'environnement*, 2011, 4, pp.653-664. hal-00626298

HAL Id: hal-00626298

<https://hal.science/hal-00626298>

Submitted on 25 Sep 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Productivity and bottom water redox conditions at the Cenomanian-Turonian Oceanic Anoxic Event in the southern Tethyan margin, Tunisia

Mohamed SOUA

Entreprise Tunisienne d'Activités Pétrolières, Charguia II, Tunisia. E-mail: soua@etap.com.tn.

Abstract

In Tunisia, five Bahloul spaced sections, Bargou, Jerisa, Guern Halfaya, Kherij and Gafsa were analysed for major and trace elements. These high-resolution chemostratigraphic integrated analyses for the Late Cenomanian–Early Turonian Bahloul Formation provide new insight on the palaeoceanographic evolution of the southern Tethyan margin. Relative low abundance of related terrigenous Ti/Al and K/Al ratios and enrichment of some productivity proxies such as Ba, Cu, and Ni (organic matter related trace elements) suggests that the Bahloul, deposited during a relative short period (400 kyr), was of relatively elevated primary productivity and minimal detrital input. While higher D^* values concurrent with lower Ti/Al ratios are interpreted as caused by enhanced fluvial material contribution, due to more humid climate during the OAE-2. Enhanced humidity triggered probable fluvial influxes, resulted in a sluggish water circulation and consequent anoxic/euxinic conditions favouring the preservation of organic matter at the sea floor. Enrichments in redox-sensitive trace metals U, V, and Mo in the Bahloul Formation deposits and redox indices, such as V/(V+Ni), U/Th, V/Cr, and Ni/Co, indicate that oxygen-restricted conditions prevailed during the Late Cenomanian – earliest Turonian times. High Ba_{xs} values and U_{auth} may indicate anoxic conditions at least at the water–sediment interface during the Bahloul Formation deposition and provide information about low to moderate sulphate-reduction reactions.

Key words: Bahloul Formation, Major and trace elements, Chemostratigraphy, OAE-2.

I. INTRODUCTION

Organic-rich deposits record a global geological event that took place during the Cenomanian-Turonian transition. This event is known by various names, including Oceanic Anoxic Event of the Cenomanian-Turonian boundary (OAE-2), Cenomanian-Turonian Boundary Event (CTBE), Bonarelli Event, Cenomanian Turonian Black Shale Horizon (CTBSH) (e.g. Arthur et al., 1990; Soua and Tribouvillard, 2007). Remarkably, deep basin deposits as well as those of shelf are marked by an enhanced preservation of organic matter (OM).

This OM is related to prevailing hypoxic/anoxic conditions, which occurred simultaneously in different paleogeographic locations (Fig. 1).

During this interval, a worldwide positive carbon isotope ($\delta^{13}C$) excursion was noted and was related to the enhanced burial of OM which is enriched in ^{12}C ; this could be a function of either

enhanced global marine productivity and/or enhanced burial and preservation of OM due to anoxia (Arthur et al., 1990; Calvert and Pedersen, 1993; Luning et al., 2004; Soua and Tribouvillard, 2007). Besides, the OAEs are commonly documented to be associated with active tectonic times and likely elevated carbon dioxide. Some of this excess carbon, buried in the sedimentary rocks was due to enhanced production of OM and/or enhanced preservation of OM. The increase in these parameters is probably due to warm, oxygen-poor deep waters and/or weak ocean ventilation.

In general, the OAE-2 is characterized by: (1) a global transgression (e.g. Maamouri et al., 1994; Abdallah et al., 2000; see Fig. 1) and a rapid sea level rise; (2) a high organic matter content, type II marine origin (e.g. Layeb and Belayouni, 1989; Scopelliti et al., 2006); (3) a short duration: about 0.5 myr (Soua, 2010); (4) an enrichment in trace metals : V, U, Ba, Mo, Cr, Sr (Bechtel et al., 1998); (5) possible radiolarian assemblage bloom (Soua et al., 2006); (6) a benthic faunal scarcity;

(7) a planktonic foraminiferal extinction and turnover, (8) a rapid sea level rise (transgression);

(9) positive $\delta^{13}\text{C}$ and negative $\delta^{18}\text{O}$ excursions (Soua and Tribouvillard, 2007).

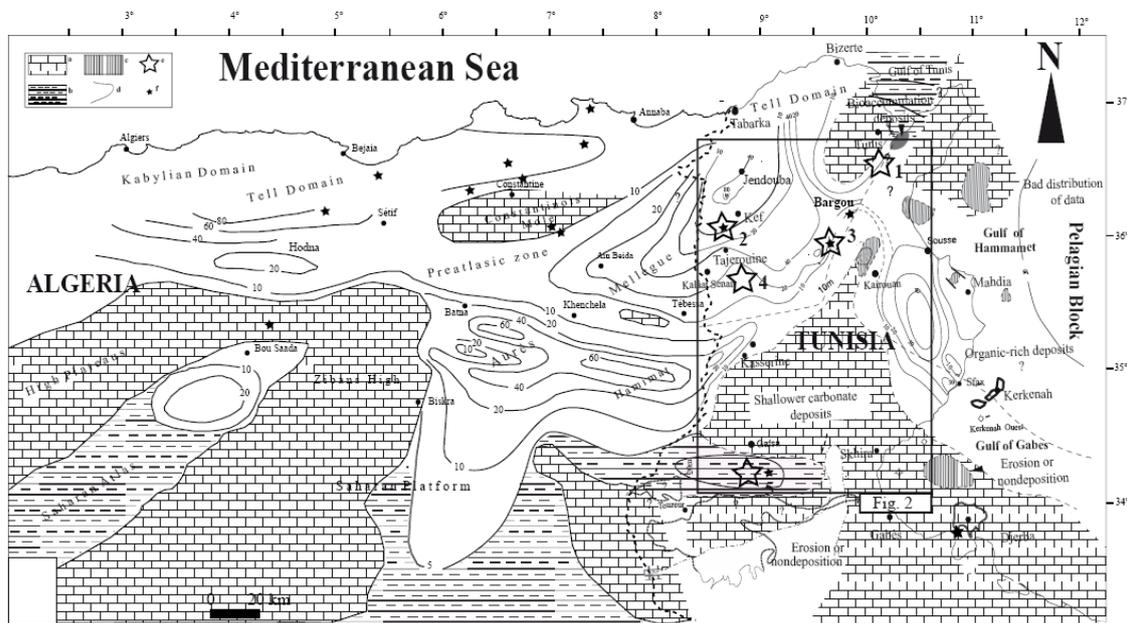


Fig. 1. Facies and thickness of the organic-rich Late Cenomanian-Early Turonian and age of equivalent units in Tunisia and eastern Algeria.

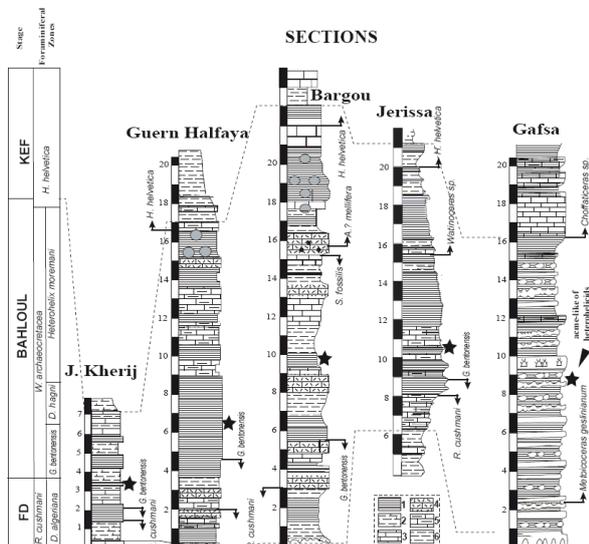


Fig.2. Lithology, foraminiferal biozonation and biostratigraphical correlations between the studied three sections. Lithology legend 1. Black shales, 2. Shaly limestone, 3. Limestone, 4. Siliceous limestone to black shales, 5. Clayey limestone, 6. Shales.

The Late Cenomanian-early Turonian Bahloul Formation is known as black, bituminous laminated marls and limestones, considered as black shales of ~ 20 meter-thick sequence relatively rich in carbonate (shale-limestone facies) (e.g. Buroillet, 1956; Maamouri et al., 1994; Soua and Tribouvillard, 2007; Soua et al., 2009).

It is frequently interpreted as resulting from episodes of increased organic-matter (OM) preservation and burial (e.g., Luning et al., 2004; Soua and Tribouvillard, 2007).

II. GEOLOGICAL SETTING

The Cenomanian-Turonian organic-rich deposits in onshore and offshore Tunisia are mainly found in the North-Central part (Fig.1) of the country and the distribution of the organic content is strongly controlled by halfgraben systems and in some areas by Triassic salt diapiric movements during the Cretaceous (see Soua et al., 2009 for a structural review).

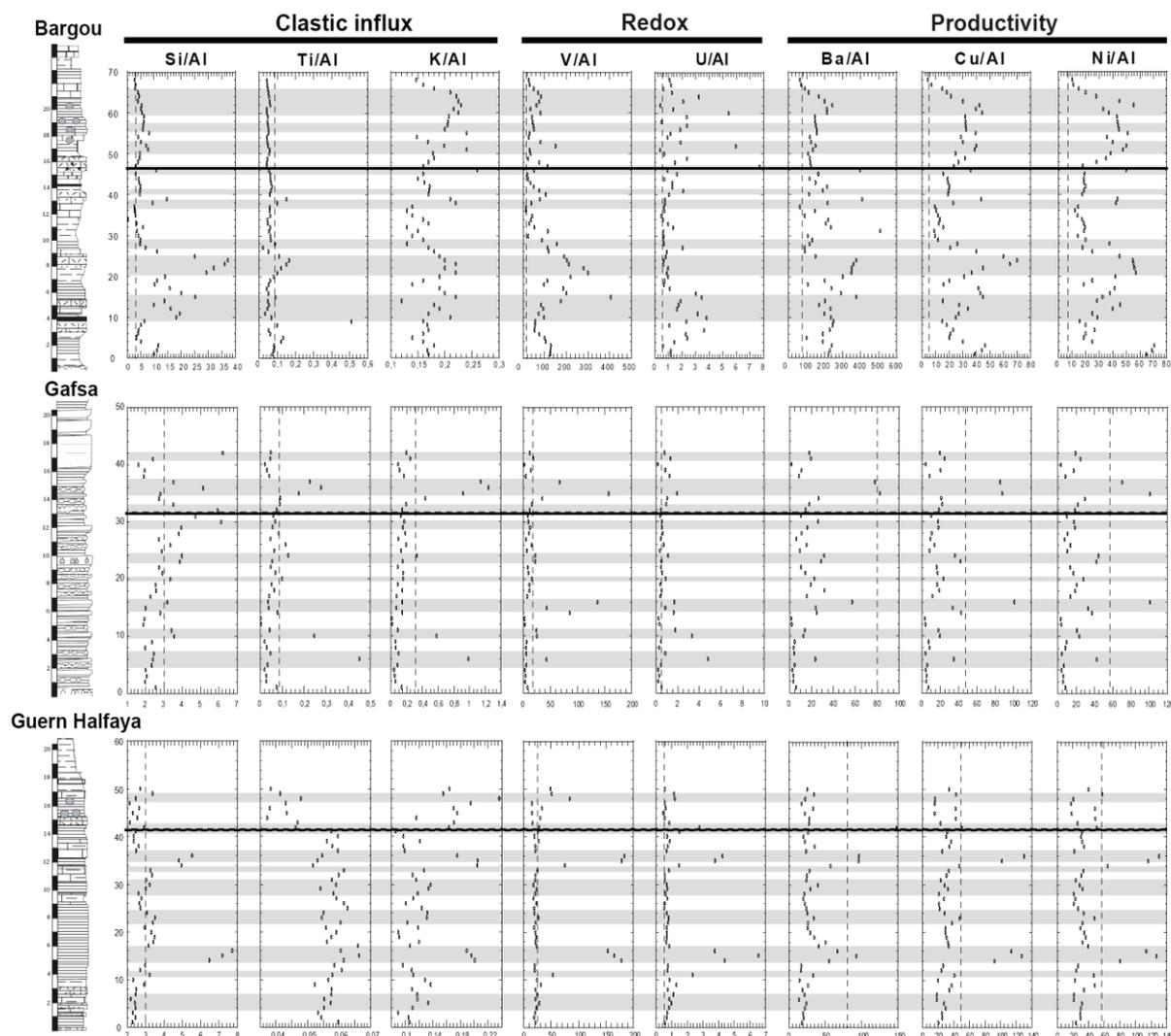


Fig. 3. Evolution of normalized metal concentrations across the Bahloul Formation in the Bargou, Gafsa, Guern Halfaya, Khrii and Jerissa sections.

III. MATERIAL & METHODS

Elemental geochemistry (major and trace element) analyses are performed using ICP-AES and ICP-MS, respectively, at the Laboratory of chemistry (University of Lille1) and Laboratory of analytical chemistry of the “Centre de Recherche et de Développement Pétrolier (CRDP, ETAP)”. From the five studied sections (Fig. 2), a total of 235 samples have been prepared by fusion with LiBO_2 and HNO_3 dissolution. Rock Eval measurements have also been carried out in order to evaluate the Total Organic Carbon in these samples from the Bahloul Formation and to evaluate the U/TOC ratio for four sections (Tab. 1).

Al-normalization of element concentrations in usual marine sediments is the

best and valuable method to estimate element enrichment in relative to reference sediment. Since the reference shales have a diagenetic component, calculation of enrichment factors “EF” may be erroneous. So, the use of EF to evaluate limited enrichment and/or depletion may be delicate. In this paper we calculated the Trace Metal (TM) Enrichment Factor as follows:

$$EF_{\text{TM}} = (\text{TM}/\text{Al})_{\text{sample}} / (\text{TM}/\text{Al})_{\text{average shale}}$$

If EF_{TM} is greater than 1, then TM is enriched relative to average shales and, if EF_{TM} is less than 1, it is depleted (Tribouillard et al., 2006; Brumsack, 2006).

IV. RESULTS

IV.1. Geochemistry

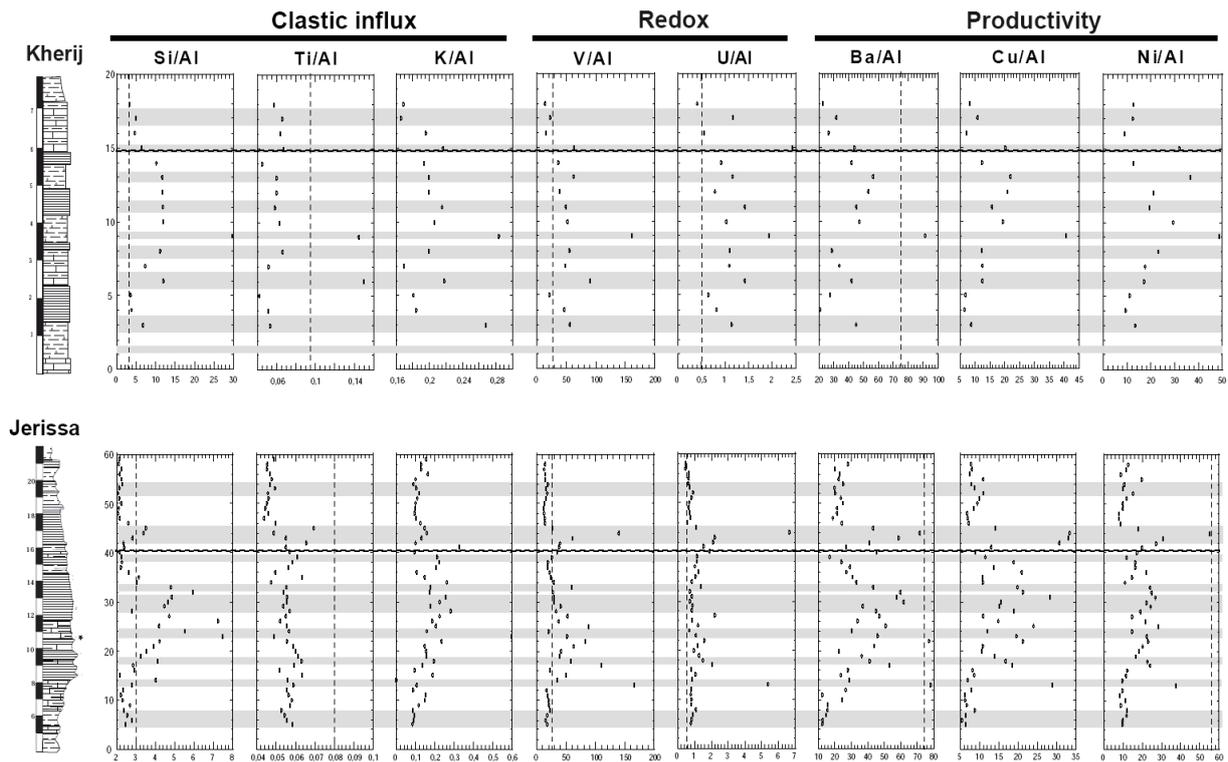


Fig. 4. continued

According to several authors (e.g. Brumsack, 1986, 2006; Scopelliti et al., 2006; Tribouillard et al., 2006), the sedimentary geochemical signal records the influence of three types of fractions.

- A detrital fraction derived from terrigenous sources carried to the sea by rivers and winds, the main proxies of which are Al, Ti, Zr, Th and, to a lesser degree, Cr.
- A biogenic fraction composed of carbonate, silica or organic matter (OM), the main trace-element proxies of which are Ba, Ni and Cu.
- An authigenic fraction mainly composed of sulphides, organo-metallic complexes and insoluble oxyhydroxides, the main proxies of which are Mo, V and U.

Aluminium is used here as a proxy for the land-derived aluminosilicate fraction of the sediments. Most of the major elements (Si, Mg, Na, K and Ti) and some trace elements (Zr, Th and Cr) have a clastic origin and their fluctuations can be related to variations in the nature of the detrital influx. The stratigraphic distribution of some selected elements, which are normalized to Al (element/Al), is illustrated in Fig.3 and 4.

Generally, and consistently with the fact that most elements are strongly tied to Al abundance, the distribution of element/Al ratios are relatively uniform, but some variations are visible within the Bahloul Formation. In all the five studied sections (Fig. 1, Fig. 2), the stratigraphic profiles of all the selected redox-sensitive trace elements (U and V) and palaeoproductivity markers (Ba, Cu, Ni) exhibit moderate to high enrichments in both the lower and upper parts of the Bahloul Formation (Fig. 3), relative to the other parts of the sections, where the samples have element/Al ratios lower or near average shale values (Fig. 3 and 4). Fig. 3 also shows that in all the studied sections, only the interval, near the suggested Cenomanian-Turonian boundary shows enrichment in redox and palaeoproductivity ratios. There are lateral variations in elemental concentrations and it is notable that the redox-sensitive metal/Al ratios in the Bahloul Formation at the Kherij section in northeastern Tunisia and the Gafsa section in southern Tunisia are twice as low as those at the Jerissa and Bargou sections in central Tunisia (Fig. 3 and 4). The Guern Halfaya section (in northern-central Tunisia) shows

intermediate values compared to the other four sections.

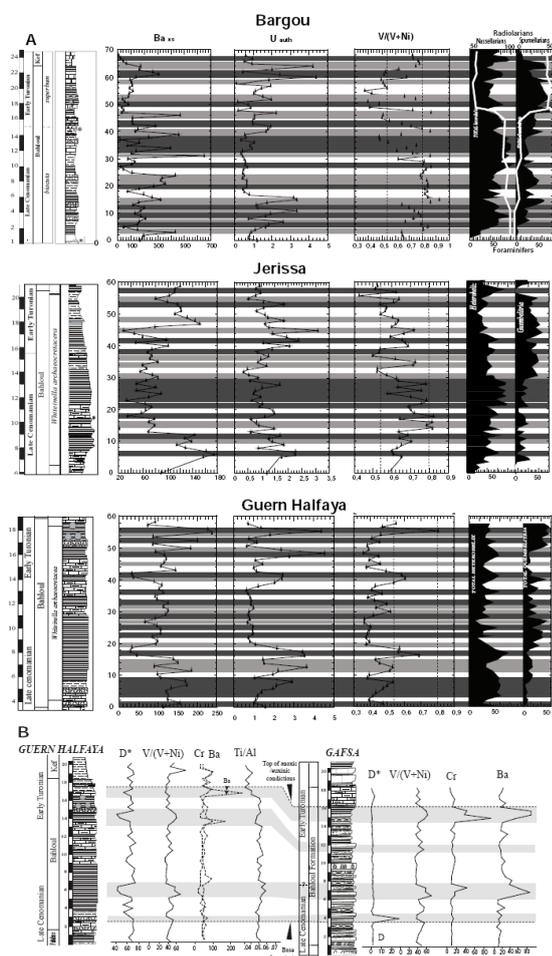


Fig. 5. A. Distribution of Ba_{xs} and U_{auth} at three sections interpreted as indicating anoxic conditions at the water–sediment interface during the Bahloul Fm deposition. B. Distribution and correlation of values of geochemical proxies (D^* , $V/(V+Ni)$, Cr, Ba and Ti/Al) throughout two distant Bahloul sections.

This phenomenon is more accentuated at the Gafsa and Jerissa sections. Among the detrital proxies, Si is the only major element that shows a well-marked positive shift within the lower part of the Bahloul Formation mainly at the Bargou section.

The other major and trace elements have less contrasting fluctuations during the Late Cenomanian–Early Turonian period. Ti and K generally indicate the detrital fraction of sediments. At the five studied sections, uniform related to opaline silica production and radiolaria-bearing sediments. Only the Gafsa section exhibits correlative increased values within the upper part of the Bahloul Formation. Potassium (K) shows similar behaviour within the lower part of the five studied sections, however, the upper part exhibits the opposite pattern (Fig. 3 and 4).

To summarize, in the five sections studied, the geochemical composition of the rocks is strongly influenced by the detrital supply, but some elements show more or less marked enrichment or depletion at several levels within the Bahloul Formation, (depleted in Ti and K, enriched in redox and productivity proxies such as U and V; see Fig. 3, 4 and 5).

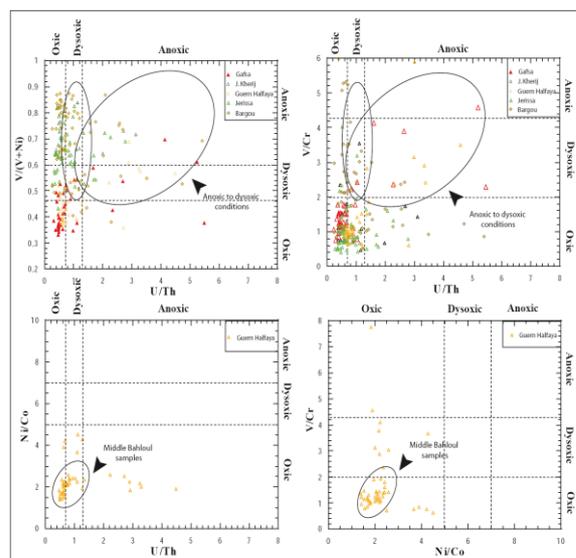


Fig. 6. Crossplots of redox indices. $V/(V+Ni)$ vs. U/Th , V/Cr vs. U/Th , Ni/Co vs. U/Th , and V/Cr vs. Ni/Co .

In addition to element/Al ratios, some redox indices (U/Th , V/Cr , Ni/Co and $V/(V+Ni)$) have been calculated and illustrated as cross-plots in Fig. 6.

Some authors (e.g. Hatch and Leventhal, 1992) suggest that these geochemical indices may be used to give information on the palaeo-oxygen level of the depositional environments. For all four indices, high values are recorded in both the lower and upper parts of the Bahloul Formation (see Fig. 6 and Fig. 7). Nevertheless, the contrast between the samples from the North-Central Tunisian sections and those from southern Tunisia varies according to the considered indices. In each section from North-Central Tunisia, the samples picked in the black shales of the lower and upper part of the Bahloul Formation have mean values of the V/Cr and U/Th ratios above 1.9 and 1.16 respectively (Tab. 1), whereas the samples picked in the middle part of the Bahloul Formation have values that rarely exceed 0.6 and 0.7 respectively. For the V/(V+Ni) most of the Bahloul Formation samples are characterized by $V/(V+Ni) > 0.60$. However, in southern Tunisia (i.e. Gafsa section) a mean reported value of V/(V+Ni) is 0.70 (Tab. 1; Fig. 5). The Ni/Co ratio is calculated only for the Guern Halfaya section and values through the Bahloul Formation black shales do not exceed 4, with a mean value of about 2.2 (Fig. 6).

IV.1.1. Interpretation

Clastic input

In the five sections studied, the uniform stratigraphic distribution of K/Al and Ti/Al (Fig. 3; Fig. 4), suggest a rather homogeneous nature for the detrital supply. However, the Ti/Al and K/Al ratios show their lowest values within the middle part of the Bahloul Formation. Ti is generally enriched in the presence of some accessory minerals that are usually associated with the coarser-grained part of fine-grained siliciclastic sediments (Brumsack, 1986; Calvert and Pedersen, 1996). The relatively low abundance of Ti levels in the Bahloul Formation could thus indicate a decrease in the grain size of the land-derived supply. This grain size reduction might accompany the contemporaneous sea-level rise suggested for the Bahloul Formation (Soua and Tribovillard, 2007).

Alternatively, Machhour et al. (1994) have determined and discussed the D^* geochemical relationship (Tab. 1; Fig. 5B), that is expressed by $Al/(Al + Fe + Mn)$, as a proxy for the detrital

input into the sedimentary basins. At the Guern Halfaya section, the mean D^* value is 0.64 in the lower part of the Bahloul limestones (Fig. 5) and increases through the upper Bahloul exceeding 0.71 (Tab. 1) against 0.55 in typical terrigenous shales (Wedepohl, 1971). In the Gafsa section, increased D^* in the organic-rich interval (a mean value of about 1.94) indicates an enhanced rate of terrigenous supply during Bahloul Formation deposition (Fig. 5). However, as mentioned above, the Ti/Al ratio shows a clear decline through the Bahloul Formation at all sections studied (Fig. 3; Fig. 4 and Fig. 5). These different behaviours can be explained by the fact that D^* is generally related to fluvial influences, while Ti is regarded as a marker for airborne or aeolian detrital supply (Rachold and Brumsack, 2001).

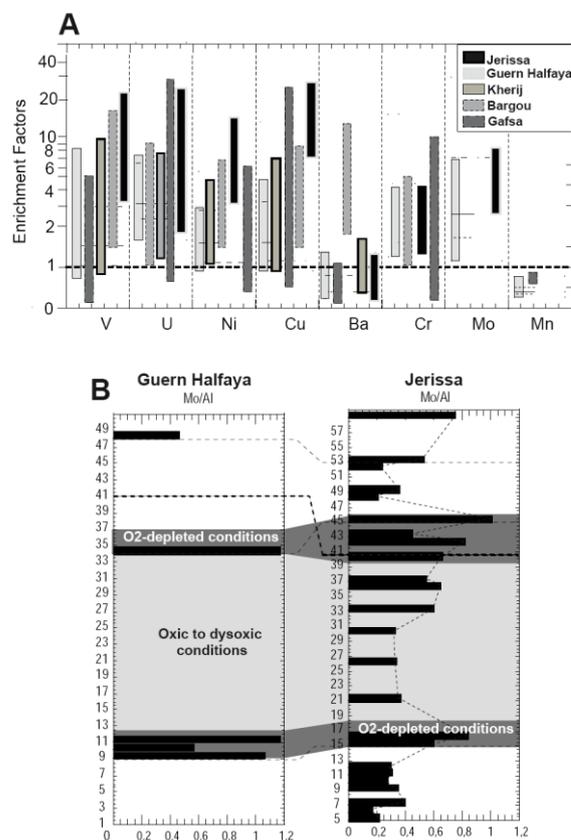


Fig. 7. A. Comparison of enrichment factor of some trace metals (V, U, Cu, Ni, Ba, Cr, Mo and Mn) for the Bahloul Fm of the five studied sections. B. Correlation of the Mo/Al ratio values between Guern Halfaya and Jerissa sections.

The relative low abundance of both D* and Ti could reflect a decrease in eolian supply and probable enhanced fluvial influences during the deposition of the Bahloul Formation (Soua et al., 2008). This second interpretation is plausible but it demands more data about the fluvial material, the dominant current patterns and the location of high-pressure cells potentially affecting global stagnant circulation during the Late Cenomanian - Early Turonian palaeogeography in the eastern Maghreb domain. The Si/Al ratio shows relatively low values within the lower part of the Bahloul Formation at the Guern Halfaya, Gafsa and Jerissa sections. This is consistent with both hypotheses: decreased grain size of the detrital supply, including quartz grains, or a decrease in the airborne quartz silt abundance during the early transgressive interval. However, this Si/Al decrease is not observed at the Kherij section (Fig. 4). In contrast, a strong Si/Al increase is marked in the lower part of the Bahloul Formation at the Bargou section (Tab. 1; Fig. 3). In this case, the increased presence of SiO₂ (see Tab. 1) could be explained by an increase in biogenic SiO₂ (silica-secreting organisms) recorded locally (Soua et al., 2006; see discussion below about the increase in productivity).

Bottom Redox conditions

The Bahloul Formation is enriched in U, V, Cu, Cr, Ba, Ni in all sections, and slightly in Mo (some levels in each section) (Fig. 7). Among these elements U, V and Mo are alleged to be redox sensitive and/or sulphide forming (Dean et al., 1997; Lyons et al., 2003; Tribovillard et al., 2006). The other elements are more indicative of the OM flux to the sediments: Ni and Cu can be fixed in high amounts in sediments under general reducing conditions (Brumsack, 1986; Hatch and Leventhal, 1992; Calvert and Pedersen, 1993; Kolonic et al., 2002; Algeo and Maynard, 2004; Meyers et al., 2005). At all the studied sections, V and U are among the most enriched elements compared to the average shale values (Fig. 7). The enrichment in Mo and U within the black shales of the Bahloul Formation (e.g. Jerissa and Guern Halfaya sections, see Fig. 7B) indicates that the sediments were most likely depleted in O₂ during Bahloul Formation deposition. Of the three redox-sensitive elements (V, U and Mo),

enrichment in U is the highest (Fig. 7), suggesting that accumulation is at least partly mediated by bacterial sulphate reduction reactions (Tribovillard et al., 2006).

In addition, some redox markers, such as U/Th, V/Cr, Ni/Co and V/(V+Ni) (see Fig. 6) were used. According to Jones and Manning (1994) and Hatch and Leventhal (1992), these various ratios cannot be used reliably individually, however, they can be considered collectively. In the present study, these proxies behave consistently and show their highest values in samples coming from the lower part of the Bahloul Formation (Fig. 6). Alternatively, it is observed that oxygen-restricted conditions are recorded from this lower part of the Bahloul Formation (Fig. 7B.). According to the considered ratios, the values suggest dysoxic to oxic (Ni/Co, V/Cr) or anoxic (U/Th) conditions. U/Th and V/(V+Ni) are the most and least discriminating proxies respectively (Fig. 6).

Like V/(V+Ni) ratios, Cr could indicate redox conditions during Bahloul Formation deposition. The V/(V + Ni) values ranging from 0.36 to 0.80 at the Guern Halfaya and Jerissa sections, from 0.37 to 0.93 at the Bargou section and from 0.33 to 0.70 at the Gafsa section (Fig. 5). However, Hatch and Leventhal (1992) assumed that the 0.54–0.80 interval indicates anoxic conditions. Some higher values (> 0.80) suggest euxinic conditions, while values situated beneath 0.54, are interpreted as indicating oxic conditions at the seafloor. In addition, the enrichment of the Cr/Al average in shale indicates an algal source for the organic matter, which concentrates Cr in higher redox potential conditions and the consequent availability of reduced Cr³⁺ to react with organic matter (Hatch and Leventhal, 1992). This is in agreement with rock Eval data recorded from Bahloul Formation samples (Montacer et al., 1986).

In short, through the Bahloul Formation our Al-normalized geochemical data (trace metal abundance and redox ratios) indicate two main pulses of dysoxic to anoxic conditions in the bottom water interrupted by dysoxic to oxic conditions (i.e. through the middle part of the formation).

Primary productivity conditions

According to some authors, barium (Ba) is considered as a primary productivity proxy when it is brought to the sediment as barite (e.g., Dymond et al., 1997; McManus et al., 1998; Tribovillard et al., 2006), whilst McManus et al. (1998) assumed that barite (BaSO_4) may be sensitive to severe sulphate-reducing conditions. In our material, Ba shows slight enrichment in samples from the Bahloul Formation. These levels of enrichment correlate with those of Cu and Ni. These observations suggest some increased productivity at the time of the Bahloul Formation deposition.

Two main Cu/Al and Ni/Al ratio shifts are observed at all the studied sections (Fig. 3 and 4). According to Brumsack (1989) and to Calvert and Pedersen (1993), these elements are usually enriched in reduced sediments. Other authors (e.g. Algeo and Maynard, 2004; Tribovillard et al., 2006) assumed that these elements are mainly brought to the sediment in association with OM and are considered to be reliable markers of OM delivery into the sediment. Thus, the positive excursion of the Ni/Al and Cu/Al ratios recorded here indicate that deposition of the Bahloul Formation is interpreted as corresponding to episodes of increased OM influx and also possibly records increased primary productivity, as confirmed by the abundance of radiolaria, at least at the Bargou section.

This Ba enrichment could indicate barite dissolution and Ba remobilization within moderate reducing conditions below the water/sediment interface. This interpretation is in agreement with the very low Mn enrichment (Fig. 7; Tab. 1), indicating that no oxidizing conditions occurred close to the sediment–water interface. Consequently, the sporadic low Ba concentrations are therefore interpreted as the result of moderate productivity increases. The slight increases in productivity resulted in increased delivery of OM and consequently Ni and Cu. The reducing conditions and sulphide precipitation may have helped in trapping these elements.

In addition, several Si/Al ratio peaks mark the Bahloul Formation at the Bargou, Gafsa and Guern Halfaya sections (Fig. 4), without corresponding peaks in the clastic proxies (Ti and K). In this case, the increased Si abundance must be linked to the echo of local increased biogenic

productivity by silica-secreting organisms (mainly radiolarian and maybe diatoms, consistent with the coeval enrichment in the abundance of the productivity proxies (Ni, Cu and Ba). In general the Bahloul Formation shows moderate to high Ba/Al ratios with an average value between 31 and 41 at the Guern Halfaya, Jerissa, Kherij and Gafsa sections compared to a mean of 193 measured at the Bargou section, located in north central Tunisia (Fig. 3, Tab. 1). Deposition of the Bahloul Formation, i.e. organic-rich sediments coinciding with the oxygen minimum zone “OMZ” (Soua and Tribovillard, 2007), is consistent with results from redox-sensitive elements. This implies a moderate to high degree of barite saturation.

In addition, excess barium (Ba_{xs}) has been interpreted as a palaeoproxy for bio-productivity (Brumsack, 2006; Scopelliti et al., 2006). Dymond et al. (1992) noted that enhanced surface productivity could be predicted by the Ba_{exc} (Tab. 1), while $\text{Ba}_{\text{xs}} = \text{Ba}_{\text{sample}} - [\text{Al}_{\text{sample}} * (\text{Ba}_{\text{shale}} / \text{Al}_{\text{shale}})]$ and while Ba_{shale} and Al_{shale} are as given by Gromet et al. (1984). Ba_{xs} for the Bahloul Formation in the five studied sections shows high values, particularly at the Bargou and Gafsa sections (648.7 ppm and 387.51 ppm respectively), with a mean value of about 150 ppm (Fig. 5A) compared to 70 to 90 ppm in above and below (i.e. in the Fahdene and Kef Formations). Basically, Ba_{xs} indicates genesis of biogenic barite which could be released during phytoplankton necromass decay and could then be precipitated as barite in microenvironments where Ba-sulphate reaches supersaturation (Dehairs et al., 1980; Dymond et al., 1992; Kenison Falkner et al., 1993; McManus et al., 2005; Gingele and Dahmke, 1994; Tribovillard et al., 2006). Such values could indicate some preservation of barite in the Bahloul Formation implying the existence of a moderate rate of sulphate reduction at the water-sediment interface. McManus et al. (1998) have combined Ba_{xs} and U_{auth} in order to evaluate the palaeoredox conditions at the bottom water where $U_{\text{auth}} = U_{\text{total}} - (\text{Th}_{\text{total}}/5)$ (Myers and Wignall, 1987). Basically, uranium is removed from seawater and migrates into organic-rich sediments (Anderson et al., 1989; Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991). According to some authors (e.g. Algeo and Maynard, 2004; McManus et al., 2005;

Tribovillard et al., 2006) U_{auth} enrichment does not occur in the water column, but takes place mainly in the sediment, while U_{auth} may occur by the combination of iron and sulphate reduction (see Tribovillard et al. 2006, for a synthesis).

Elments	Av. Shale	Bargou	G. Halfaya
Si/Al	3.11	9.09	3.06
Ti/Al	0.053	0.07	0.08
Fe/Al	0.55	nd	1.44
Mg/Al	0.18	nd	1.16
Ca/Al	0.18	27.07	20.8
Mn/Al	96	nd	0.31
K/Al	0.34	0.18	0.23
P/Al	0.008	0.13	nd
Ba/Al	66	193.1	31.35
Cr/Al	10.2	32.08	18
Cu/Al	5.1	27.87	39.82
Mo/Al	0.15	nd	nd
Ni/Al	7.7	32.59	40.7
Sr/Al	34	nd	nd
Th/Al		1.75	1.85
U/Al	0.42	92.79	1.8
V/Al	0.2	2.33	48.63

Tab 1. Major and trace elements normalized to Al, average shale calculated from Wedepohl (1971, 1991) and Tribovillard et al. (2006); and their average values.

The Bahloul Formation in all the five studied sections shows a U_{auth} mean value of 1.22 with maxima reaching 4.54, 4.37 ppm and 4.14 at the Guern Halfaya, Bargou and Gafsa sections respectively (Tab. 1). U_{auth} enrichment, when compared to the average shale value of 0.2 ppm (Gromet et al., 1984), may indicate a tendency towards anoxia at the water–sediment interface during Bahloul Formation deposition. However, at the Gafsa section, in southern Tunisia, this enrichment in U_{auth} (up to 4.14 ppm) coincides with that of Ba_{xs} (up to 387.51 ppm). In general, the results obtained for the five sections studied provide information suggesting low to moderate sulphate-reduction reactions at the water–sediment interface.

V. DISCUSSION

V.1. The influence of primary productivity

Based on the geochemical indices used herein, it appears that the conditions during accumulation of the Bahloul Formation were most likely dysoxic to anoxic, inferred from $V/(V+Ni)$ (Fig. 5), with possible intermittent periods of euxinic conditions. In addition, the Bahloul Formation is characterized by periods of relatively increased productivity. Generally, the “productivity” model of Pedersen and Calvert, (1990) can be applied where positive peaks of redox-sensitive (U and V) and productivity (Ba, Cu and Ni) markers are recorded. Increased surface water productivity causes bottom water anoxia by driving benthic oxygen demand to exceed supply through water column mixing. According to Algeo and Lyons (2005), Scopelliti et al. (2006) and Soua et al. (2008), the primary productivity increase may have been induced by enhanced fluvial contribution. Eutrophication would occur in more proximal environments (see discussion in Brumsack, 2006), such as North Africa (see Luning et al., 2004). The relative high concentration of terrigenous material in distal settings should have been enhanced by the marine transgression. Besides, the onset of anoxic conditions, recorded in the lower part of the Bahloul Formation, was not caused by surface productivity. So, it could be predicted that surface water productivity was not only triggering factor for reducing conditions during Bahloul Formation deposition. At Guern Halfaya and Kherij sections, the second productivity peak is recorded before the C/T boundary. Peaks of oxygen depleted conditions (Fig. 7B), inferred from Mo/Al ratio are as significant as those recorded in other sections and are observed a few centimeters above the C/T boundary at Jerissa and a few centimeters below the C/T boundary at Guern Halfaya. For distal and deeper parts of basins, the terrestrial influence is minimal and the concentration of terrigenous nutrients should be low. The source of nutrients has to be autochthonous and thus, most likely results from nutrients released from organic matter decomposition under reducing conditions. The anoxic conditions established during the latest Cenomanian (deposition of the lower part of the Bahloul Formation) would be triggered by a sudden primary productivity increase, coupled with sea-level rise. These anoxic conditions were probably the main cause for the initiation of

reducing conditions and the productivity increase assumed for the remainder of the Bahloul Formation, which would have followed the onset of anoxic conditions in bottom water. Clastic influx proxies (mainly Ti and K) give information on nutrients released from emergent land areas that could be associated with the organic matter (Kolonic et al., 2002; Brumsack, 2006).

V.2. Oxygen depletion

Oxygen depletion in bottom waters, recorded at some levels of the Bahloul Formation, could have been generated by increased productivity and high fluvial input, inducing better organic carbon (C_{org}) preservation, as indicated by high values of the $V/(V + Ni)$ ratio and high Cr/Al values. Oxygen depletion at the water-sediment interface during the deposition of the Bahloul is also indicated by significant values of Mo/Al (Fig. 7B). Alternatively, the occasional occurrences of Oxygen Minimum Zone (OMZ) foraminiferal tracers in the lower and upper parts of the Bahloul Formation are observed within an interval of low $V/(V + Ni)$. In this case, some authors (Algeo and Maynard, 2004; Tribovillard et al., 2006) distinguished redox gradations in some sedimentary systems. Basically, through the Bahloul Formation the U and V enrichment and the absence of any Mo enrichment, cause suboxic/anoxic deposition without free H_2S . On the other hand, sediments exhibiting concurrent enrichment in U, V and Mo reflect euxinic conditions at the sediment–water interface (Tribovillard et al., 2006).

V.3. Variation of detrital flux concentration

Variations in terrigenous material can be inferred from changes in the concentration of detrital flux - sensitive elements. Scopelliti et al. (2006) suggested that lower Ti/Al ratios concurrent with higher D^* values reflect enhanced Ti-depleted fluvial contribution, during which aeolian dust, reflecting Ti-enriched contribution, diminished. In these conditions, enhanced humidity triggered increased fluvial input, induced sluggish circulation and consequently, reduced bottom-water ventilation that promoted a higher preservation rate of organic matter within the Bahloul Formation (Soua et al., 2008).

Using this model, one must point to the high $V/(V + Ni)$, Cr and D^* values with

corresponding low Ti/Al in some levels of the Bahloul Formation (Fig. 5). As a consequence of the suggested circulation model, recycling of nutrients from deeper waters could coincide with enhanced siliceous, carbonate and organic matter production as inferred from relative high Si/Al ratio (mainly in the Bargou section) and $CaCO_3$ content (in the other locations). In addition, lower $V/(V + Ni)$ ratios associated with Cr concentrations may infer an increase in the supply of oxygen to deep waters. This may correspond to times of relatively higher productivity, normal salinity and higher oxygenation. Thus, our results indicate that bottom-water oxygen depletion was periodic rather than continuous during Bahloul Formation deposition.

VI. CONCLUSIONS

Depth profiles of selected geochemical tracers for the Bahloul Formation are presented and interpreted. The following results have been highlighted:

- Geochemical tracers are used in terms of changes in detrital delivery to the sediment, primary productivity and basin-bottom redox conditions during the time of Bahloul Formation deposition.
- Selected crossplots, V/Cr , U/Th , $V/(V+Ni)$ and Ni/Co are used to evaluate the oxic, dysoxic and anoxic levels within the Bahloul. Alternatively, $V/(V+Ni)$ was used to determine the dysoxic, anoxic and even euxinic levels
- Ba_{xs} and U_{auth} may indicate anoxic conditions at the water–sediment interface during the Bahloul Formation deposition and provide information about low to moderate sulphate-reduction reactions at the sediment-water interface,
- Higher D^* values concurrent with lower Ti/Al ratios are interpreted as being caused by enhanced fluvial run off, due to more humid climate during the OAE-2.
- As a consequence of the efficient circulation model, recycling of nutrients from deeper waters could have been more marked and coincide with enhanced biogenic siliceous, carbonate and organic matter production as testified by relatively higher Si/Al in the lower part of the Bahloul Formation in several localities.

- Associated lower V/(V + Ni) ratios and Cr concentrations could reflect an increase in the oxygen supply to deep waters resulting in enhanced sinking organic matter to be oxidized.

Acknowledgemnt : This contribution is part of the author's PhD thesis. MS is indebted to the Journal Editor, Mr Ayed Added, who provided useful suggestions for improvement of the manuscript.

REFERENCES

- ABDALLAH, H., SASSI S., MEISTER C. AND SOUISSI R. 2000. Stratigraphie séquentielle et paléogéographie à la limite Cénomanién–Turonien dans la région de Gafsa–Chotts (Tunisie centrale). *Cretac. Res* 21 (2000), pp. 35–106.
- ALGEO, T.J., LYONS, T.W., 2006. Mo-TOC covariation in modern anoxic marine environments: implication for analysis of paleoredox and hydrographic conditions. *Paleoceanography*, 21, PA1016, doi:10.1029/2004PA001112
- ALGEO, T.J., MAYNARD, J.B., 2004. Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. *Chem. Geol.* 206, 289–318.
- ANDERSON, R.F., FLEISHER, M.Q., LEHURAY, A.P., 1989. Concentration, oxidation state and particulate flux of uranium in the Black Sea. *Geochim. Cosmochim. Acta* 53, 2215–2224.
- ARTHUR, M.A., JENKYN S. H. C. BRUMSACK H. J. AND SCHLANGER S. O., 1990. Stratigraphy, geochemistry, and paleoceanography of organic carbon-rich Cretaceous sequences. *Cretaceous Research, Events and Rhythms*. 75-119.
- BARNES, C.E., COCHRAN, J.K., 1990. Uranium removal in oceanic sediments and the oceanic U balance. *Earth Planet. Sci. Lett.* 97, 94–101.
- BECHTEL, A., PEVAZ, M., PUTTMANN, W., 1998. Role of organic matter and sulphate-reducing bacteria for metal sulphide precipitation in the Bahloul Formation at the Bou Grine Zn/Pb deposit (Tunisia). *Chem. Geol.* 144, 1 – 21.
- BRUMSACK, H.J., 1986. The inorganic geochemistry of Cretaceous black shales (DSDP leg 41) in comparison to modern upwelling sediments from the Gulf of California. In: Summerhayes, C.P., Shackleton, N.J. (Eds.), *North Atlantic Palaeoceanography*. *Geol. Soc. Spec. Publ.*, vol. 21, pp. 447–462.
- BRUMSACK H.-J., 2006 The trace metal content of recent organic carbon-rich sediments: Implications for Cretaceous black shale formation *Palaeogeography, Palaeoclimatology, Palaeoecology*, 232. 344–361
- BUROLLET, P.F., 1956. Contribution à l'étude stratigraphique de la Tunisie Centrale. *Ann. Mines Géol. (Tunis)*, 18, (345 pp.).
- CALVERT, S.E., PEDERSEN, T.F., 1993. Geochemistry of recent oxic and anoxic marine sediments: implications for the geological record. *Mar. Geol.* 113, 67– 88.
- CALVERT, S.E., PEDERSEN, T.F., 1996. Sedimentary geochemistry of manganese: implications for the environment of formation of manganiferous black shales. *Econ. Geol.* 91, 36–47.
- DEAN, W.E., GARDNER, J.V., PIPER, D.Z., 1997. Inorganic geochemical indicators of glacial–interglacial changes in productivity and anoxia on the California continental margin. *Geochim. Cosmochim. Acta*, 61, 4507–4518.
- DEHAIRS, F., CHESSELET, R., JEDWAB, J., 1980. Discrete suspended particles of barite and barium cycle in the open ocean. *Earth Planet. Sci. Lett.*, 49, 528–550.
- DEMAISON, G.J., MOORE, G.T., 1980. Anoxic environments and oil source bed genesis. *Am. Assoc. Pet. Geol. Bull.* 64, 1179–1209.
- DYMOND, J., COLLIER, R., MCMANUS, J., HONJO, S., MANGANINI, S., 1992. Can the aluminium and titanium contents of ocean sediments be used to determine the paleoproductivity of the oceans? *Paleoceanography*, 12, 586–593.
- GINGELE, F., DAHMKE, A., 1994. Discrete barite particles and barium as tracers of paleoproductivity in South Atlantic sediments. *Paleoceanography*, 9, 151–168.
- GROMET, L.P., DYMEK, R.F., HASKIN, L.A., KOROTEV, R.L., 1984. The “North American Shale Composite”: its compilation, major and trace elements characteristics. *Geochim. Cosmochim. Acta*, 48, 2469– 2482
- HATCH, J.R., LEVENTHAL, J.S., 1992. Relationship between inferred redox potential of the depositional environment and geochemistry of the Upper Pennsylvanian (Missourian) Stark Shale Member of the Dennis Limestone, Wabaunsee County, KS, *Geol.* 117, 287–302.
- KENISON FALKNER, K., KLINKHAMMER, G.P., BOWERS, T.S., TODD, J.F., LEWIS, B.L., LANDING, W.M., EDMOND, J.M., 1993. The behavior of barium in anoxic marine waters. *Geochim. Cosmochim. Acta*, 57, 537–554.
- KLINKHAMMER, G.P., PALMER, M.R., 1991. Uranium in the oceans: where it goes and why. *Geochim. Cosmochim. Acta*, 55. 1799–1806.
- KOLONIC, S., SINNINGHE-DAMSTE, J., BÖTTCHER, M.E., KUYPERS, M.M.M., KUHN, W., BECKMANN, B., SCHEEDER, G., WAGNER, T., 2002. Geochemical characterization of

- Cenomanian/Turonian black shales from the Tarfaya Basin (SW Morocco). *J. Pet. Geol. (IN FULL)*, 25, 325–350.
- LAYEB, M. AND BELAYOUNI, H., 1989. La formation Bahloul au Centre et au Nord de la Tunisie: un exemple de bonne Roche mère de pétrole à fort intérêt pétrolier. *Mémoires de l'ETAP*, n°3, Actes des II^{ème} journées de géologie Tunisienne appliquée à la recherche des hydrocarbures, 489-503
- LÜNING S., S., KOLONIC, E., M., BELHAJ, Z., BELHAJ, L., COTA, G., BARIC AND T., WAGNER, 2004. An integrated depositional model for the Cenomanian-Turonian organic-rich strata in North Africa. *ESR*, 64, Issues 1-2, 51-117.
- LYONS, T.W., WERNE, J.P., HOLLANDER, D.J., Murray, R.W., 2003. Contrasting sulfur geochemistry and Fe/Al and Mo/Al ratios across the last oxic-to-anoxic transition in the Cariaco Basin, Venezuela. *Chem. Geol.*, 195, 131–157.
- MAAMOURI, A.L., ZAGHBIB-TURKI, D., MATMATI, M.F., CHIKHAOUI, M., SALAJ, J., 1994. La Formation Bahloul en Tunisie centro-septentrionale: variations latérales, nouvelle datation et nouvelle interprétation en terme de stratigraphie séquentielle. *J. Afr. Earth Sci.*, 18 (1), 37–50.
- MACHHOUR, L., PHILIP, J., OUDIN, J.L., 1994. Formation of laminate deposits in anaerobic – dysaerobic marine environments. *MCG*, 99, 65–82.
- MCMANUS, J., BERELSON, W.M., KLINKHAMMER, G.P., HAMMOND, D.E., HOLM, C., 2005. Authigenic uranium: relationship to oxygen penetration depth and organic carbon rain. *Geochim. Cosmochim. Acta*, 69, 95–108.
- MCMANUS, J., BERELSON, W.M., KLINKHAMMER, G.P., JOHNSON, K.S., COALE, K.H., ANDERSON, R.F., KUMAR, N., BURDIGE, D.J., HAMMOND, D.E., BRUMSACK, H.-J., MCCORKLE, D.C., RUSHDI, A., 1998. Geochemistry of barium in marine sediments: implications for its use as a paleoproxy. *Geochim. Cosmochim. Acta* 62, 3453–3473.
- MEYERS, S.R., SAGEMAN, B.B., LYONS, T.W., 2005. Organic carbon burial rate and the molybdenum proxy: theoretical framework and application to Cenomanian–Turonian oceanic event 2. *Paleoceanography*, 20, PA2002, 1-19.
- MONTACER, M., DISNAR, J.R., ORGEVAL, J.J., 1986. Etude préliminaire de la matière organique de la formation Bahloul dans l'environnement sédimentaire du gisement Zn–Pb de Bou Grine (Tunisie). *BRGM Principal Sci. Tech. Results* 1987, 121.
- MYERS, K.J., WIGNALL, P.B., 1987. Understanding Jurassic organic-rich mudrocks—new concepts using gamma ray spectrometry and palaeoecology: examples from the Kimmeridge Clay of Dorset and the Jet Rock of Yorkshire. In: Legget, J.K., Zuffa, G.G. (Eds.), *Marine Clastic Environments: Concepts and Case Studies*. Graham and Trotman, London, 175–192.
- PEDERSEN, T.F., CALVERT, S.E., 1990. Anoxia vs. productivity: what controls the formation of organic-carbon-rich sediments and sedimentary rocks? *AAPG Bull.*, 74, 454–466.
- RACHOLD, V., BRUMSACK, H.J., 2001. Inorganic geochemistry of Albian sediments from the Lower Saxony Basin NW Germany: paleoenvironmental constraints and orbital cycles. *P3*. 174, 121–143.
- SCOPELLITI, G., BELLANCA, A., COCCIONI, R., LUCIANI, V., NERI, R., BAUDIN, F., CHIARI, M., MARCUCCI, M., 2006. High-resolution geochemical and biotic records of the Tethyan 'Bonarelli Level' (OAE2, latest Cenomanian) from the Calabianca–Guidaloca composite section, northwestern Sicily, Italy. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 208, 293–317.
- SOUA, M., ZAGHBIB-TURKI, D., O'DOGHERTY, L., 2006. Radiolarian biotic responses to the Latest Cenomanian global event across the southern Tethyan margin (Tunisia). *Proceeding of the tenth Exploration and Production Conference, Memoire* 26, 195-216
- SOUA M., 2010 Time series (orbital cycles) analysis of the latest Cenomanian – Early Turonian sequence on the southern Tethyan margin using foraminifera. *Geologica Carpathica*, 61, 2/2010, 111-120
- SOUA, M. AND TRIBOVILLARD, N., 2007. Depositional model at the Cenomanian/Turonian boundary for the Bahloul Formation, Tunisia. *Comptes rendus – Geoscience*, 339 (10), 692-701.
- SOUA M., ZAGHBIB-TURKI D., TRIBOVILLARD N. 2008. Riverine influxes, warm and humid climatic conditions during the latest Cenomanian-early Turonian Bahloul deposition. *Proceedings of the Tenth Exploration and Production Conference, Memoir* 27, 194-200.
- SOUA, M., ECHIHI, O. HERKAT, M., ZAGHBIB-TURKI, D., SMAOUI, J., FAKHFAKH-BEN JEMIA, H., BELGHAJI, H., 2009. Structural context of the palaeogeography of the Cenomanian - Turonian anoxic event in the eastern Atlas basins of the Maghreb. *C. R. Geoscience*, 341, 1029–1037
- TRIBOVILLARD N., ALGEO T. J., LYONS T., ARMELLE RIBOULLEAU 2006 Trace metals as paleoredox and paleoproductivity proxies: An update *Chemical Geology* xx (2006) xxx–xxx
- WEDEPOHL, K.H., 1971. Environmental influences on the chemical composition of shales and clays. In: Ahrens, L.H., Press, F.,