Rivista Italiana di Paleontologia e Stratigrafia	volume 119	no. 1	pp. 19-29	March 2013

PRELIMINARY BIOGEOCHEMICAL DATA ON MICROBIAL CARBONATOGENESIS IN ANCIENT EXTREME ENVIRONMENTS (KESS-KESS MOUNDS, MOROCCO)

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Received: June 22, 2012; accepted: October 30, 2012

Key words: carbonatogenesis; microbialites; extreme environments; mud mounds; Morocco; astrobiology.

Abstract. The Devonian Kess-Kess mounds, cropping out in the Hamar Laghdad Ridge (SE Morocco), provide a useful case-study for understanding the relationships between the microbial metabolic activities and micrite precipitation in an extreme environment. Very fine dark and white wrinkled laminae record microbial activity and the geochemistry of the organic matter allows the characterization of the source organisms.

The biogeochemical characterization of extracted organic matter was performed through the functional group analyses by FT-IR Spectroscopy. FT-IR parameters indicate a marine origin and low thermal evolution for the organic material. The organic matter is characterized by the presence of stretching νC=C vibrations attributable to alkene and/or unsaturated carboxylic acids. Preliminary analysis with GC-MS provides evidence for an autochthonous (<C22) organic matter source for the free carboxylic acids. The origin of short-chain fatty acids that have a marked even over odd C number predominance is attributable to bacteria and/or algae and they are similar to those recorded in recent (Black Sea) and ancient (Late Jurassic to Early Cretaceous) methane-seep microbialites. These biogeochemical signatures of microbial carbonate precipitation in an ancient extreme environment may have implications in astrobiological research considering the recent discovery of carbonate deposits on Mars.

Riassunto. I Kess-Kess mounds del Devoniano che affiorano nell'area di Hamar Laghdad (SE Marocco) costituiscono un laboratorio naturale per lo studio delle relazioni tra le attività metaboliche microbiche e la precipitazione delle micriti in ambienti estremi. La presenza di sottili laminazioni convolute, con la tipica alternanza di lamine chiare e scure, documenta attività microbica in questi sistemi. La materia organica associata a queste microstrutture ha permesso di individuare gli organismi responsabili del processo di biomineralizzazione. La caratterizzazione biogeochimica della materia organica estratta è stata effettuata attraverso l'analisi dei gruppi funzionali in spettroscopia FT-IR. I parametri ottenuti dall'analisi ad infrarossi indicano un'origine marina ed una bassa evoluzione termica dei composti organici. La materia organica è caratterizzata dalla presenza di vibrazioni di stretching di doppi legami di atomi di carbonio (νC=C) attribuibili ad alcheni e/o acidi carbossilici insaturi.

Le analisi preliminari in Gas Cromatografia-Spettrometria di Massa hanno rivelato una sorgente autoctona (<C22) di acidi carbossilici. L'origine degli acidi grassi a catena corta, con forte predominanza di catene con numero pari in atomi di carbonio, è attribuibile a batteri o alghe. Tale presenza è simile a quella registrata in microbialiti depositate in sistemi tipo *methaneseep* sia recenti (Mar Nero) sia fossili (Giurassico Superiore, Cretaceo Inferiore). Questi dati biogeochimici di carbonatogenesi microbica in ambienti estremi possono avere importanti implicazioni nelle ricerche astrobiologiche tenendo conto della recente scoperta di carbonati su Marte.

Introduction

The well-exposed Kess-Kess mounds, cropping out in the Hamar Laghdad Ridge (eastern Anti-Atlas, SE Morocco), preserve their original shape and stratigraphic relationships with the associated strata (Fig. 1). The origin of these carbonate mounds has long been debated. The discovery of seep- and vent-related ecosystems from different geotectonic settings, associated with authigenic carbonate mounds, has allowed the reinterpretation of some mounds as the product of chemosynthetic microbial mediation (Díaz-del-Río et al. 2003; Magalhães et al. 2004; León et al. 2006, 2007; Fernández-Puga et al. 2007; Medialdea et al. 2008). Sound biostratigraphical, sedimentological and palaeontological studies of the Kess-Kess mounds have been performed by Brachert et al. (1992) and Aitken et al. (2002). Nevertheless the origin of these buildups is still under debate and the most consistent hypotheses are related to submarine hydrothermal vents where bacteria

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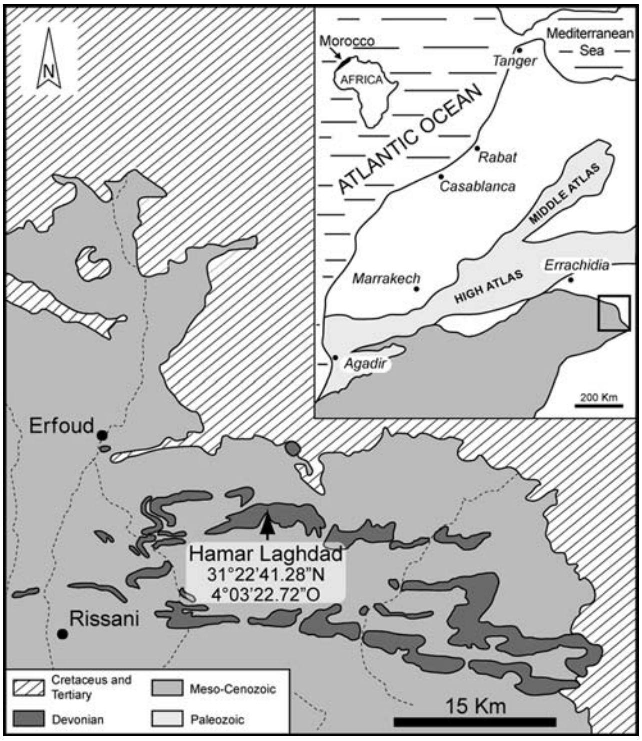


Fig. 1 - Simplified geological map of the Northeastern Anti-Atlas (Morocco) showing the distribution of Devonian rocks and the location of the Hamar Laghdad area, about 18 Km southeast of Erfoud (from Belka 1998, modified).

and/or archaea may have played a prominent role in the carbonate biomineralization (Belka 1998; Mounji et al. 1998; Joachimski et al. 1999).

The proposed hydrothermal model for the origin of the Kess-Kess mounds explains their architecture, setting and isotope geochemistry, but it raises another question, the type of carbonate precipitation control, biotic *vs* abiotic. Micromorphological and fabric characteristics permit to distinguish two types of micrite (Russo et al. 1997). The first type, of autochthonous origin (automicrite) and organic-induced, can be postulated in the case of laminated orclotted peloidal micrite (Tsien 1994; Reitner & Neuweiler 1995). The second type, of detrital origin, can be recognized by the presence of fine graded fabric and/or differences in the particle sizes (Russo et al. 1997).

Bacterially-mediated precipitation of $CaCO_3$ in the Kess-Kess mounds was inferred through micromorphological evidence including the presence of the typical peloidal texture or relics, molds and features that suggest the former presence of bacteria (Guido et al. 2012; Cavalazzi et al. 2007). In this paper, data from UV fluorescence and Fourier Transform Infra-Red (FTIR) Spectroscopy, together with the preliminary results from Gas Chromatography-Mass Spectrometry, were used to reveal and characterize the organic matter. The characterization of organic compounds is necessary to determine which species of bacteria/archaea were responsible for the deposition of $CaCO_3$. The identified biomarkers could indicate the metabolic processes that lead to the syndepositional precipitation of the carbonate minerals.

The studied carbonates are a useful case study for the investigation of ancient biotic activities in extreme environments. Actually, the biosignatures in terrestrial rocks that were deposited in such environments are highly relevant in the search for evidence of life on Mars because the early geological environments of this planet, and Earth, were in many respects similar and, thus, the potential habitats for early life forms were similar (Westall 2008). Moreover, the identification of carbonate deposits on Mars (Pollack et al. 1987; Schaefer 1990; Craddock & Maxwell 1993; Ehlmann et al. 2008) may have very important implications to the search for extinct Martian life, owing to the high potential of carbonates to record traces of biotic activity (Blanco et al. 2011).

Geological setting

The Devonian carbonate mounds in the Hamar Laghdad area (Tafilalt region, Morocco) are located above a volcanic high, where as many as 48 individual mounds were recorded (Brachert et al. 1992). The 100 metre-thick pile of calc-alkaline basalt was emplaced during Lochkovian time (earliest Devonian) above a very thick shale-dominated Ordovician-Silurian succession. The upper surface of the volcanic pile was first colonized by crinoids during Pragian to early Emsian time that left a thick cover (up to 180 m in places) of crinoidal grainstone and rudstone. The mounds and the intermound fine-grained limestones developed on top of the crinoid beds during Emsian time, and were buried by Emsian siliciclastic-rich lime mudstones (Brachert et al. 1992).

Higher in the succession, a second mound event is represented by the Eifelian-Givetian Hollard mound in the eastern part of the Hamar Laghdad area. Together the crinoidal base and the overlying mound and intermound limestones were assigned to the Kess-Kess Formation by Brachert et al. (1992), and the mounds were referred to as the Kess-Kess mounds.

The mounds are cone-shaped, subcircular to subelliptical in cross-section, and commonly reach up to 50 metres in height. Their flanks are steeply dipping, ranging between 35° and 60°, more commonly *circa* 50° (Brachert et al. 1992). The intermound limestones are flat-lying and well-bedded. The internal structure of the mounds is not readily observable since very few mounds are cut (longitudinally or cross-wise) by erosion. Actually the mound architecture prevent the observation of the strata organization, being concentric

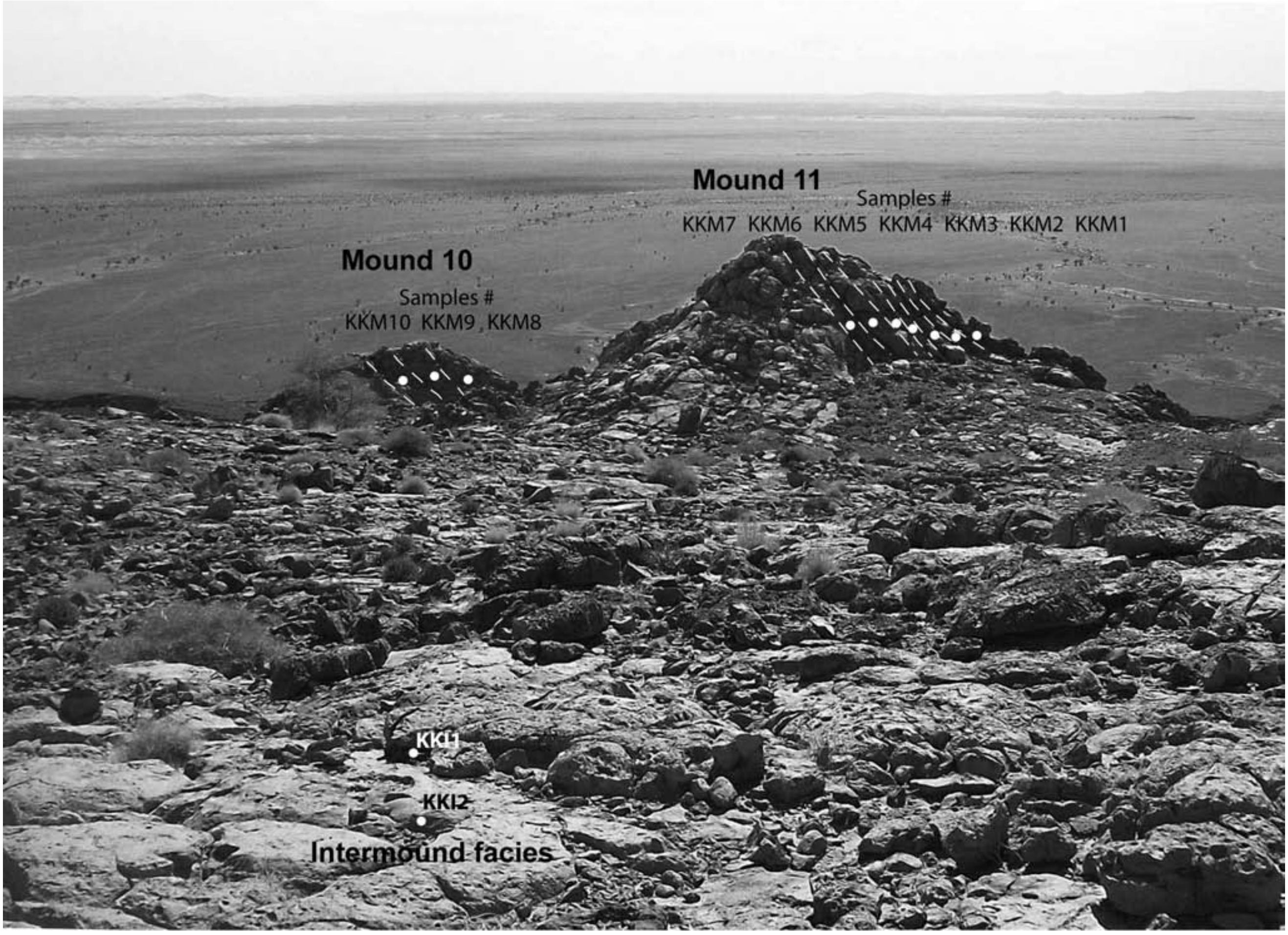


Fig. 2 - The sampled Kess-Kess mounds and intermound facies. White dots represent the location of the samples in mounds 10, 11 and in the intermound facies. The height of the mounds is around 30 m (data from Brachert et al. 1992).

and the most external layer covering all the buildup. The core of the few eroded mound consists of massive limestone, whereas the overlying outer layers are bedded parallel to the flank surface. Bioclasts are randomly dispersed in all the buildup, even if they seem to be less common in the core facies (Brachert et al. 1992; Berkowski 2004, 2006; Belka & Berkowski 2005). The analyzed micrite samples were collected from mounds 10 and 11 (*sensu* Brachert et al. 1992) and from their intermound facies (Fig. 2).

Methods

Thirteen unweathered micrite samples were collected from mounds 10 and 11 as well as from their intermound facies. With mound 11 being partly eroded in the southern flank, 7 samples were collected following the stratal architecture from the core to the peripheral bed. Three samples were collected from mound 10 with the same procedure. Two specimens were taken from the intermound facies between mounds 10 and 11 (Fig. 2).

Of the 13 samples, at meso-scale observation, only 5 revealed well-preserved stromatolitic laminae, sub-centimetric in thickness.

Micro- and nano- morphology of carbonates was characterized by optical and scanning electron microscope (SEM). Chemical composition was determined using energy-dispersive X-ray spectrometer (EDS), FEI-Philips ESEM-FEG Quanta 200F scanning electron microscope linked to an EDAX Genesis 4000 EDS. The samples were polished with 0.25 µm diamond-impregnated surfaces, then etched and carbon coated (about 250 Å). Working conditions and detector constants were as follows: voltage 15 kV, tilt angle 0°, take-off angle 36.01°.

Uncovered thin-sections were examined for fluorescence to reveal the distribution of the organic matter (OM) (Dravies & Yurewicz 1985; Machel et al. 1991; Neuweiler & Reitner 1995; Russo et al. 1997). Fluorescence was induced by a Hg vapour lamp linked to an Axioplan II imaging microscope (Zeiss) equipped with high-performance, wide-bandpass filters (BP 436/10 nm/LP 470 nm for green light; BP 450-490 nm/LP 520 nm for yellow light).

Fluorescence is a form of luminescence and represents the property of a material to emit light when excited by visible or ultraviolet light (Dravies & Yurewicz 1985). The cause of fluorescence is related to residual organic matter preserved in rocks (Dravies & Yurewicz 1985; Machel et al. 1991); however some mineral species fluoresce due to trace element activation (Neuweiler & Reitner 1995).

Fourier Transform – Infrared Spectroscopy was performed in the mid-infrared region (4000-400 cm^{-1}). The spectroscopic analyses were the result of accumulating 256 scans. Several blanks were analysed in order to avoid any atmospheric disturbance and to provide correct measures. Baseline correction was achieved after the acquisition of spectra.

To avoid mineral interference organic compounds were isolated from the carbonate and silicate phases *via* acid separation. The advantage of this technique is the high sensitivity, which allows the detection of many components, even at very low concentrations. Small fragments of carbonate samples showing high fluorescence were hand ground in an agate mortar; three grams of the powder were ultrasonically treated three times with a mixture of dichloromethane/methanol (1:1). Samples were centrifuged after each treatment and the supernatant collected. A few drops of the extract were placed on the crystal of the ATR apparatus and dried under nitrogen flow. The equipment used was a Spectrophotometer Perkin Elmer Spectrum 100 with a Universal ATR (Attenuated Total Reflectance) employed in the following arrangement: a K-Br beamsplitter and a $LiTaO_3$ detector. In this configuration, the resolution was 4 cm^{-1}. Spectral bands were assigned with reference to the literature (Painter et al. 1981; Solomon & Carangelo 1988; Wang & Griffiths 1985; Sobkowiak & Painter 1992).

Biomolecular studies, sample preparations, extractions, and biomarker analyses were performed according to the methods described by Guido et al. (2007).

The organic matter used for biomarker investigation was dried under nitrogen. The acidic fractions were separated from the total extracts by solid phase extraction performed on AminoPropyl Bond Elute© cartridges. Acidic compounds were eluted with ether after acidification of the medium with ether:formic acid (9:1). Fatty acids were esterified using acetyl chloride in anhydrous methanol before the analysis. The identification of molecular compounds was performed by Gas Chromatography-Mass Spectrometry (GC/MS) using a Varian Saturn 2000 equipped with a Varian Factor Four-5MS capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness, cross-linked 5%-diphenyl-95%-dimethyl siloxane). Helium was used as the carrier gas at a linear flow velocity of 1.1 ml/s. The temperature program was as follows: temperature held at 40°C for 1 min, then increased from 40 to 120°C at 30°C·min^{-1}, 120 to 300°C at 5°C·min^{-1} with final isothermal held at 300°C over 20 min. The sample was injected unsplit, with the injector temperature set at 280°C. Squalane was added as internal standard. The MS was operated in the electron impact mode at ion trap temperature of 230°C, emission current of 10 mA.

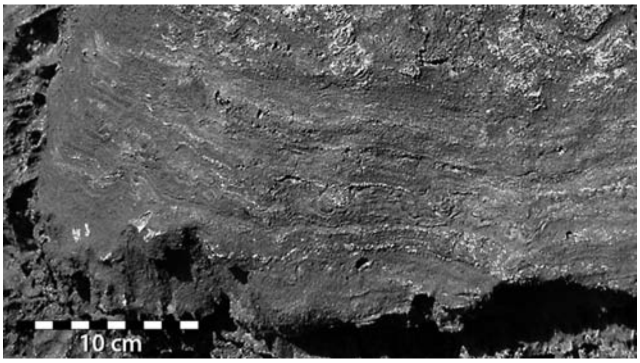


Fig. 3 - Detail of an intermound sample showing stromatolitic fabric. Note the very clear fine laminations.

Micromorphologies and epifluorescence of microbial fabric

The micrite is the dominant component of the Kess-Kess mounds. Laminated microbialites were sampled both in mounds 10 and 11 (*sensu* Brachert et al. 1992) and in their intermound facies (Fig. 3).

These structures are made up of micrometer-sized laminae with irregularly alternating dark and white wrinkled laminae arranged in microcolumnar structures. The very fine wavy-wrinkled laminae, showing antigravity patterns, suggests an organic origin and syn-depositional cementation of this microbialite (Reitner et al. 1995; Russo et al. 1997; Guido et al. 2012).

The dark laminae, in polished bulk samples, observed with incident light appear whitish-pale pink. Epifluorescence observations on these samples provide evidence of the distribution of organic matter remains, concentrated in ill-defined, sub-millimetre-thick layers. Fluorescent layers analyzed in thin-section show microcolumnar structures and the fluorescence follows the micromorphologies of the dark laminae (Fig. 4).

SEM-EDS data showed that the white microbialitic laminae are constituted of low Mg-calcite crystals ranging in size from 5 to 30 μm (Fig. 5). These laminae of variable thicknesses (10 to 40 μm) alternate with thin laminae (from 5 to 15 μm thick) that correspond to the dark laminae. These thin laminae are constituted of small calcite crystals and siliciclastic material (from 1

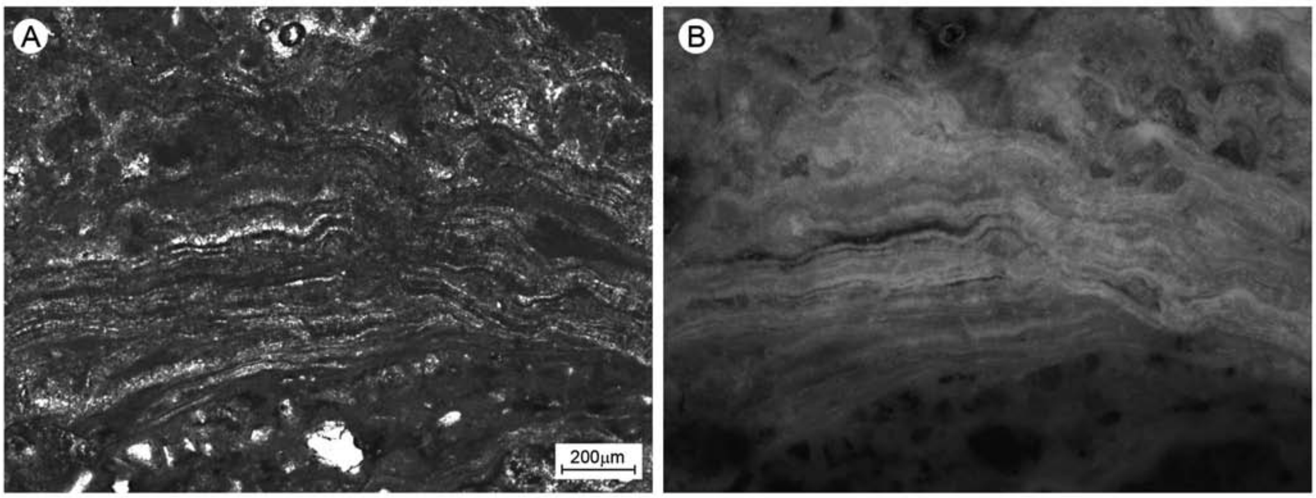


Fig. 4 - Transmitted light (left), and epifluorescence UV (right) microphotographs. The bright fluorescence of the dark laminations reveals an high organic matter content.

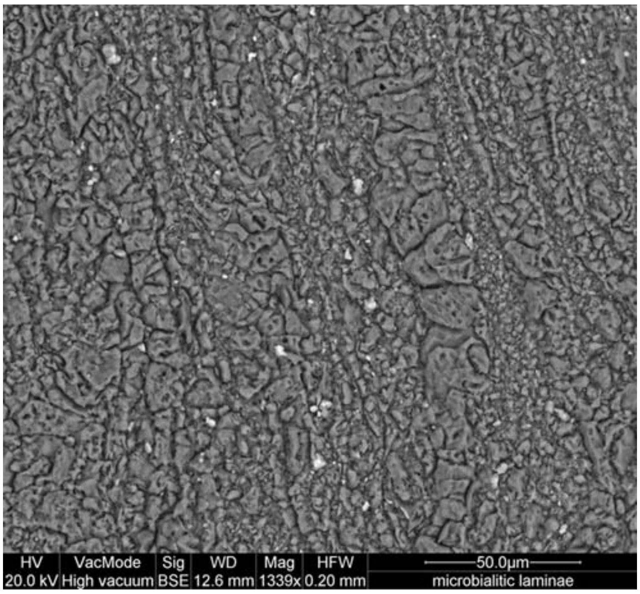


Fig. 5 - Image of microbialite laminations acquired with back scattered electrons (BSE). Note the boundaries between the dark and white laminations as they appear in transmitted light. The white laminations correspond to the area made of large crystals, whereas the dark laminations are made of small crystals.

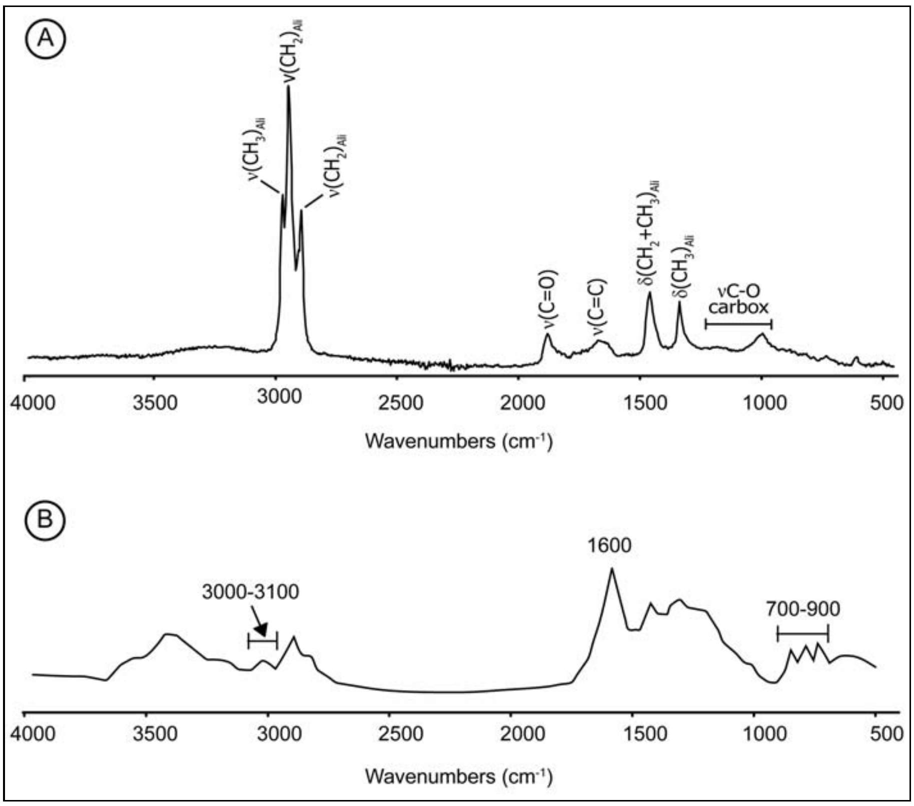
to 5 μm) engulfed by structureless material, locally showing a reticulate network. The presence of siliciclastic grains is demonstrated by the peaks of Si and Al in the EDS spectrum. The structureless material could be attributed to mucilaginous extrapolymeric substance (EPS) remains. In the dark laminae, the EDS spectrum shows carbon peaks higher than those detected in the white laminae, confirming the richness of organic matter in these areas.

Organic matter functional groups

FTIR has been utilised for the characterization of kerogens through measurement of the energy absorbed by the molecules in transition to different vibrational states. Since each functional group tends to absorb infrared radiation in a specific wavelength range, it is possible to detect and discriminate different bond types.

The infrared spectra showed absorption bands between 1000 and 3000 cm^{-1}. They contain stretching aliphatic bands $(\nu CH)_{ali}$ at 2950, 2920 and 2850 cm^{-1}, deformation bands of methyl (δCH_3; 1370 cm^{-1}) and both methyl and methylene [$\delta(CH_2 + CH_3)$; 1460 cm^{-1}] groups (Fig. 6). The spectra also display the band assigned to carbonyl and/or carboxyl groups ($\nu C{=}O$; 1740 cm^{-1}). The $\nu C\text{-}O$ vibration appears between 1300 and 1100 cm^{-1}. The band $\nu C{=}C$, probably related to unsaturated compounds (alkene and/or carboxylic acids), was also recorded. Peaks in the regions between 3000-3100 cm^{-1} and 700-900 cm^{-1} attributable to aromatics groups were detected too (Fig. 6). The band located around 3000 cm^{-1} is attributable to the presence of OH functional groups.

Fig. 6 - A) Infra-red spectra revealing the functional groups of the organic compounds extracted from the laminated microbialite. B) Data from Lis et al. (2005) regarding the thermal maturity of type-II kerogens from Devonian black shales. Note the difference between our spectrum and Lis et al. (2005) data regarding the spectral make-up of the organic compounds with high thermal maturity. Actually, kerogens with increasing maturity exhibit increased aromatic absorption (at 700-900, ~1600, and 3000-3100 cm^{-1}), decreased aliphatic absorption (at 1375, 1450, and 2800-3000 cm^{-1}), and decreased carbonyl and carboxyl absorption (at 1700 cm^{-1}).



Preliminary fatty acid data

Biomarker identifications were based on comparison of GC retention time, interpretation of mass spectrometric fragmentation patterns, and the mass spectra literature. Several blank runs were performed to test the analytical procedure. The absence of measurable recovered bitumen indicated that no detectable laboratory contaminations were introduced into the samples.

The GC traces of the free carboxylic acid fraction, extracted from the laminated micrites, are shown in Fig. 7. Mainly straight-chain, even numbered, saturated carboxylic acids, were detected. They show strong predominance of hexa- and octadecanoic acid (C_{16}, C_{18}) and a small amount of high molecular weight compounds in the region from C_{23} to C_{27}. Iso- and anteiso-fatty acids (C12-C20) were recognized and peak at 14-18 atoms. The GC-MS data confirm the attribution of stretching C=C vibrations (obtained with FT-IR analyses) to fatty acids, which excludes the presence of aromatic compounds.

Discussion

Depositional model

Brachert et al. (1992) maintained the Moroccan mounds are controlled by a self-sustaining interplay of physically induced changes of the environment (currents, storms) and intrinsic biological factors. Belka (1998), using carbon isotopic composition, proposed that the mound-forming carbonate precipitated from brines comprising a mixture of hydrothermal fluids and seawater with a contribution of methane. Belka (1998) maintained that aerobic bacterial oxidation of methane can be considered as the main process driving the carbonate precipitation and rapid lithification of the mounds. Mounji et al. (1998) argued that potential builder organisms were too scarce to have controlled mound accretion, and, contrary to Brachert et al. (1992), suggested that the steep-sided conical mound shape is very difficult to reconcile with a current or wave-driven accumulation of the mud. Mounji et al. (1998) considered therefore that the origin of the conical shape can be related to hydrothermal venting at the sea floor, and the slight asymmetry of the cones may be due to persistent unidirectional currents during venting. Venting system model during mound deposition was corroborated by Berkowski (2004, 2006) and Belka & Berkowski (2005) taking into consideration the presence of a particular "calice-in-calice" growth of monospecific solitary, non-dissepimented rugose corals.

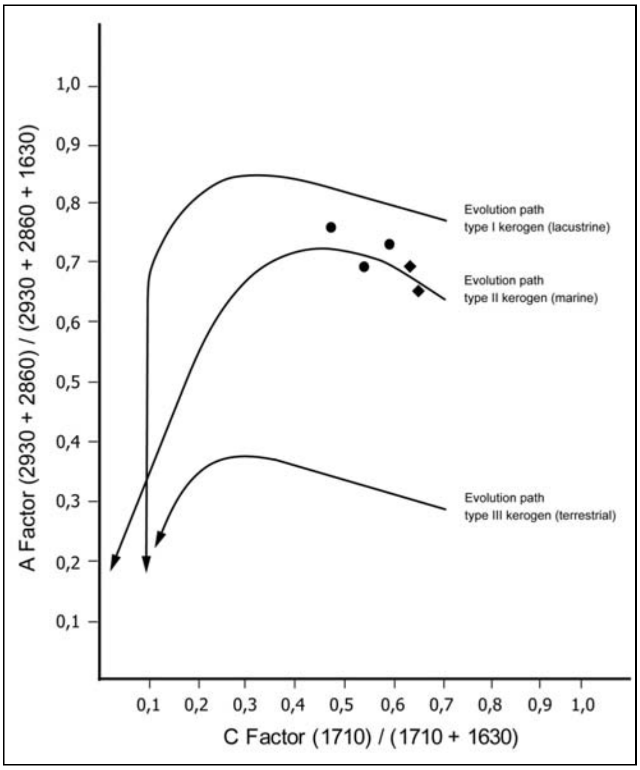


Fig. 7 - Classification of kerogen-type according to A and C Factors (from Ganz and Kalkreuth 1987, modified) obtained from infrared spettroscopy: black circles represent mud-mounds samples, black diamonds intermound facies.

In this research the characterization of lipid fraction with Fourier-Transform Infrared (FTIR) spectroscopy and Gas Chromatography – Mass Spectrometry (GC-MS), together with micromorphological observations of the mineral matrix, allowed the identification of microbial activity involved in micrite deposition of Kess-Kess mounds. The recognized microbial metabolic processes seem to fit with those recorded in recent and ancient methane-seep microbialites in agreement with a hydrocarbon seepage origin for the studied Emsian Moroccan mounds. The proposed hydrocarbon seepage model is based on biomolecular data on autochthonous micrites, while the previous model (hydrothermal vents) was suggested mainly based on isotopic data (Belka, 1998; Mounji et al. 1998) and secondarily on taxonomic and paleoecological considerations on the skeletal component (Belka & Berkowski 2005).

The studied microbialite is made up of millimetre to submillimetre laminae with irregularly alternating wrinkled laminae arranged in columnar structures. The accretionary morphology (very fine wavy-wrinkled laminae), showing anti-gravity patterns, suggests an organic origin and syndepositional cementation of this microbialite (Burne & Moore 1987; Reitner et al. 1995; Russo et al. 1997; Riding 2000; 2008; Planavsky & Ginsburg 2009; Demasi et al. 2011; Guido et al. 2012). Therefore the depositional model, hypothesized for the Kess-Kess mound growth, should take into account the microbial processes inducing the quick hardening of the micrite/skeletal associations. The fast cementation of the mud fraction fully explains the mound depositional geometries with steep flanks, characteristic that seems to be influenced mainly by microbial activity rather than physically induced changes of the environment like currents and storms.

Organic matter thermal evolution

The microbial laminated microfabric analyzed in the present study shows a strong luminescence revealing a rich organic matter content, possibly related to a biological control during deposition.

The evolution of the organic matter, in the stromatolitic samples, is deduced in IR spectra through the presence of peaks in the three aromatic regions: the aromatic C-H stretching region (3000 to 3100 cm^{-1}), the aromatic ring stretching (*ca* 1600 cm^{-1}) and the aromatic C-H out-of-plane deformation bands (700 to 900 cm^{-1}) (Lis et al. 2005). Indeed, with increasing maturity, FT-IR spectra of kerogens exhibit increasing aromatic absorption in the aromatic regions, decreasing aliphatic absorption (at 1375, 1450, and 2800 to 3000 cm^{-1}), and decreasing carbonyl and carboxyl absorption (at 1700 cm^{-1}) (Lis et al. 2005; Guido et al. 2011; Mastandrea et al. 2011). In the studied stromatolitic samples the absence of bands at 700-900 cm^{-1} and 3000-3100 cm^{-1} and the strong absorption of aliphatic, carbonyl and carboxyl functional groups, reveal a low thermal maturity of the organic compounds.

Commonly, microbial signals of modern and ancient seep-deposits can be altered by allochthonous input and/or damaged by biodegradation (Hinrichs et al. 2000; Peckmann et al. 2002). In addition secondary migration of hydrocarbons and progressive alteration

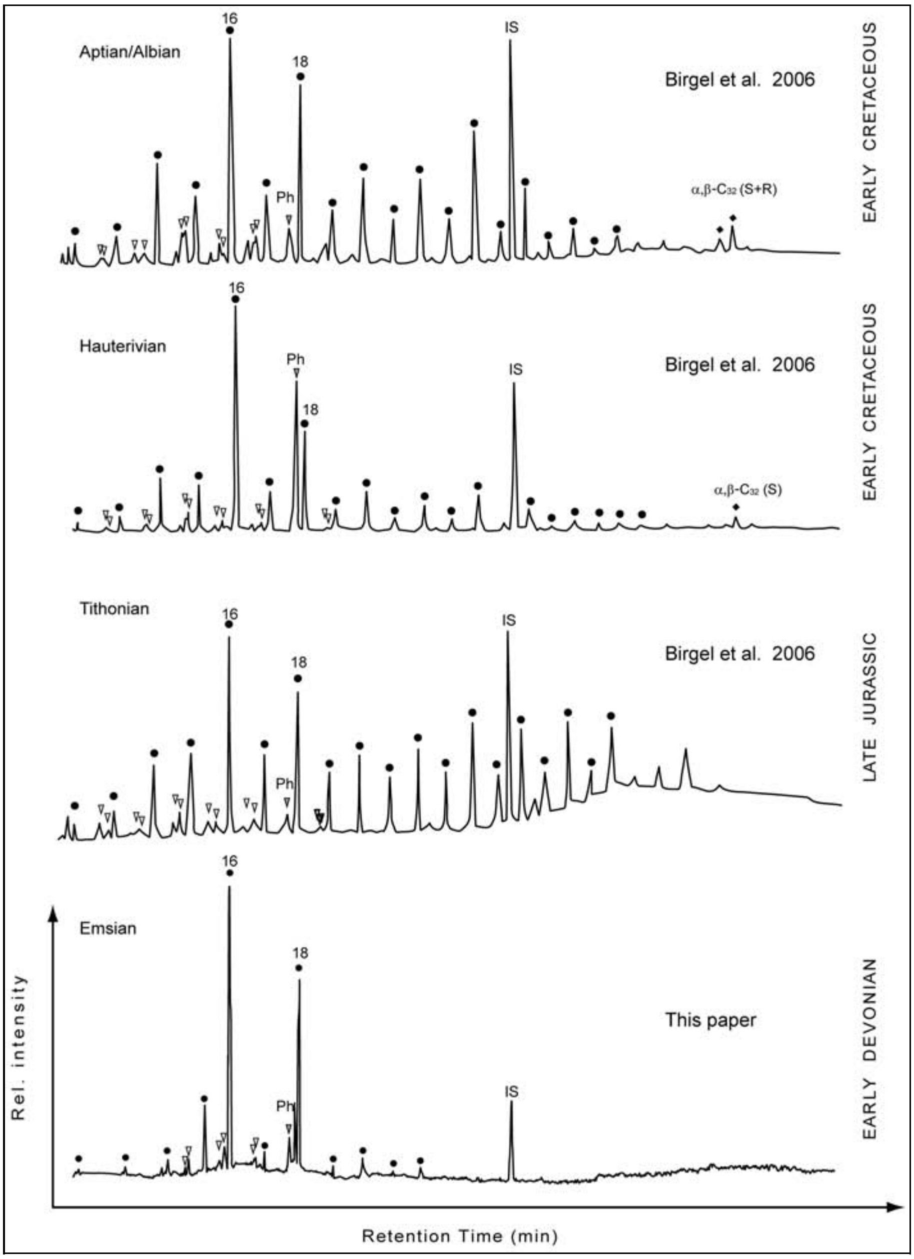


Fig. 8 - Fatty acid fractions from Kess-Kess mounds (this research) and comparison with seep-limestones (from Birgel et al. 2006). Black dots, fatty acids; small white triangles, iso- and anteiso-fatty acids; grey triangles, isoprenoidal acids; black diamonds, hopanoic acids; Ph, phytanoic acid.

through thermal maturation may obscure original signals (Goedert et al. 2003). The low thermal maturation of the organic compounds, recorded in the Devonian mounds of Hamar Lagdhad, can furnish a powerful tool to investigate biomarkers in ancient methane-seep carbonates.

The A Factor (2930+2860 cm^{-1})/(2930+2860 +1630 cm^{-1}) and the C Factor (1710 cm^{-1})/(1710 + 1630 cm^{-1}) were measured for the classification of kerogen types and maturation level of organic compounds (Ganz & Kalkreuth 1987). These factors, used in a similar manner to the traditional H/C – O/C elemental ratios or to Rock-Eval pyrolysis parameters, as Hydrogen Index (HI) – Oxygen Index (OI), are useful to quantify changes in abundances of aliphatic and carbonyl/carboxyl groups and can be utilized to differentiate marine *vs* continental sources. The average values of the Kess-Kess samples is 0.71±0.04 for A factor and 0.62±0.11 for C factor (Fig. 8). These parameters indicate a marine origin for the organic compounds and confirm their low thermal evolution.

The absence of the bands in the 700-900 cm^{-1} and 3000-3100 cm^{-1} regions suggests that the νC=C functional group recorded at 1600 cm^{-1} do not belongs to aromatic compounds. This functional group can be attributed to alkenes and/or unsaturated carboxylic acids, that could be synthesized by microbial communities.

Organic matter source

The distribution of free carboxylic acids in the Kess-Kess mounds provides evidence for an autochthonous (<C22) organic matter source. The origin of short-chain fatty acids, that have a marked even over odd C number predominance, can be attributed to an autochthonous origin, since they are ubiquitously observed in aquatic organisms, such as bacteria or algae (Cranwell 1982). Some fatty acids such as palmitic and stearic acids (16:0 and 18:0 respectively) are ubiquitous. Bacteria are the major source of iso-, ante-iso- and mid-chain branched fatty acids, but they can also be a significant source of palmitoleic (16:1) and cis-vaccenic acids (18:1) (Volkman et al. 1980, 1998; Fulco 1983). Di-unsaturated $C_{18:2}$ acids are also known as typical bacterial components (Kenyon et al. 1972; Cohen & Vonshak 1991; Merrit et al. 1991; Thiel et al. 1997; Peters et al. 2005). The $C_{18:1}$ fatty acid has been found in cultures of several purple sulphur bacteria living in carbonate environments, such as those involved in microbial mat formation (Barbé et al.1990; Grimalt et al.1992; Russell et al. 1997).

The distribution of free carboxylic acids in the Kess-Kess mounds is similar to those recorded in recent (Black Sea, Thiel et al. 2001) and ancient (Late Jurassic to Early Cretaceous, California, Birgel et al. 2006) methane-seep microbialites (Fig. 8). In association to carboxylic acids, these authors record also ^{13}C-depleted archaeal lipid biomarkers such as crocetane and PMI. These biomolecules are commonly used as biomarkers for methanotrophic archaea, which thrive through anaerobic oxidation of methane and may cause carbonate precipitation (Elvert et al. 1999, 2000; Thiel et al. 1999, 2001; Hinrichs et al. 2000; Michaelis et al. 2002; Birgel et al. 2006).

Considering the immaturity of the organic compounds and the strong similarity of the fatty acid distributions between the Kess-Kess mounds and methane-seep microbialites (Fig. 8), further biomolecular analysis through Gas Chromatography-Mass Spectrometry could lead to a model for carbonate precipitation through the activities of archaea-methanotrophs. These data are necessary in order to evaluate the model proposed by several authors (Belka 1998; Mounji et al. 1998; Joachimski & Buggish 1999) that controversially related the origin of the Kess-Kess mounds to submarine hydrothermal vents.

Conclusions

Analysis of organic matter associated to dark and white wrinkled laminae in the Devonian Kess-Kess mounds gives an indication of themicrobial source organisms. This characterization was performed through functional group analyses by FT-IR Spectroscopy and biomolecular characterization by GC-MS. FT-IR parameters indicate a marine origin and low degree of thermal alteration for the organic compounds. The organic matter is characterized by the presence of stretching νC=C vibrations attributable to alkene and/or unsaturated carboxylic acids. Preliminary analysis with GC-MS provides evidence for an autochthonous source (<C22) free carboxylic acidsof the organic matter. The origin of short-chain fatty acids is attributable to bacteria or algae and is similar to those recorded in recent (Black Sea) and ancient (Late Jurassic to Early Cretaceous) methane-seep microbialites. Further investigations on lipid fraction and isotope analyses of high specific biomarkers, like crocetane and PMI, could strengthen the presence of methanotrophic archaea in agreement with a model of microbial carbonate precipitation linked to hydrocarbon seepage environments.

The fast cementation of the mud fraction, induced by microbial activity, agrees with the mound depositional geometries with steep flanks. Therefore the depositional model hypothesized for the growth of the Kess-Kess mounds should take into account the microbial processes inducing the quick hardening of the micrite/skeletal associations rather than the physical changes of the environment or the doubtful palaeocological indication deriving from metazoan associations.

The biogeochemical signature of microbial carbonate precipitation in ancient extreme environments may have implications in astrobiological research considering the recent discovery of carbonate deposits on Mars.

Acknowledgements. We are indebted to the reviewers for their suggestions that greatly improved the manuscript. This research has been funded by Regional Operative Program (ROP) Calabria ESF 2007/2013 - IV Axis Human Capital - Operative Objective M2-Action d.5 (Post-Doctoral Fellowship - Adriano Guido) and grants MIUR (Project PRIN 2008_Prot.2008JCZSJS_004).

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