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Biogeochemical signals of unfossilizable organisms in terrestrial problematic carbonates: relevance to carbonatogenesis and astrobiology

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Abstract. The origin of "Kess-Kess" mounds of the Hamar Laghdad Ridge, SE Morocco, is still under debate. The biogenicity of these structures seems to be related to submarine hydrocarbon seapage or, less probably, to hydrothermal vents in which bacteria and/or archaea play a prominent role in the carbonate biomineralization.
To investigate the traces of prokaryotic metabolic activity, which possibly caused the laminated microbialite precipitation, the research was focused on micro-nanomorphology of the very fine dark and white wrinkled laminations and biogeochemical analyses of their organic remains. The geochemical 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 compounds. The organic matter, inside the laminated micrite, is characterized by the presence of stretching νC=C vibrations attributable to alkene and/or unsatured carboxylic acids. These organic compounds are likely to be synthesized by bacteria and/or archaea communities via methanotrophic metabolism.
This approach permit to detect biosignatures of microorganisms belonging to communities which flourished in methanotrophic extreme environments, like those that could have characterized the early Earth and Mars.

Key words. problematic carbonates – organic matter – methane – Morocco – Devonian

1. Introduction

Mud mounds are often enigmatic buildups: the factors controlling their growth and depositional geometries cannot be observed in modern environments. The carbonate mounds, informally called "Kess-Kess", cropping out in the Hamar Laghdad Ridge (eastern Anti-Atlas, SE Morocco) are the most spectacularly exposed carbonate buildups of the world and, due to differential erosion, they show the original shape and the relationships with associated strata (Fig. 1). The origin of these carbon-

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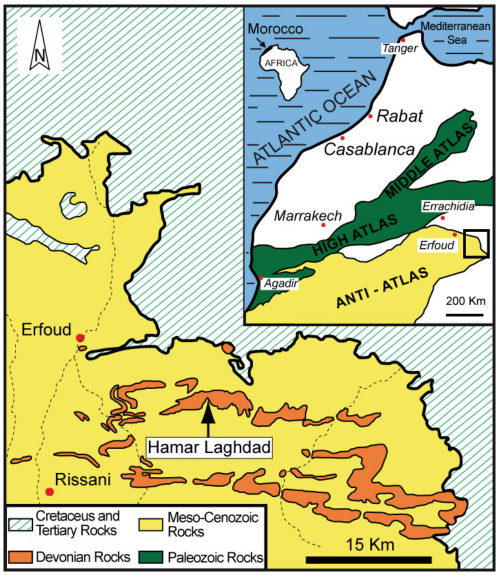

Fig. 1. Simplified geological map of the study area.

ate mounds has long been debated. The discovery of seep- and vent-related ecosystems from different geotectonic settings, associated to autigenic carbonate mounds, allowed the reinterpretation of some mounds as the product of chemosynthetic microbial mediation.

Biostratigraphical, sedimentological and paleontological studies of the Kess-Kess mounds have been performed by Brachert et al. (1992), Peckmann et al. (1999, 2005), 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 or hydrocarbon seapage (Mounji et al. 1996, 1998). In both bacteria and/or archaea may have played a prominent role in the carbonate biomineralization (Belka, 1994, 1995, 1997, 1998).

Belka (1998), Mounji et al. (1998) and Peckmann et al. (1999) proposed that the mound-forming carbonate precipitated from brines comprising a mixture of hydrothermal fluids and seawater with a contribution of thermogenic methane. Belka (1998) maintained that methane aerobic bacterial oxidation can be considered as the main process driving the carbonate precipitation and the rapid lithification of the mounds.

Bacterially-mediated precipitation of $CaCO_3$ in the kess-kess mounds was inferred through micromorphological evidence like the presence of the typical pelletoidal texture or relics, molds, or forms that can suggest former bacteria (Peckmann et al., 1999; Cavalazzi et al., 2007).

In this paper we used a methodology to reveal and characterize the organic matter. This procedure, preserving the original biotic signature, furnish a reliable approach to rule out if the bacterial metabolic activity is the main process driving carbonate precipitation and its lithification. Considering the presence of methane and carbonate deposits on Mars (Pollack et al., 1987; Schaefer, 1990; Craddock and Maxwell, 1993) our approach may be extremely important for the implications on the search for extinct Martian life.

2. Methodology

The 20 analyzed micrite samples were collected from the mounds 10 and 11 (*sensu* Brachert et al., 1992) and in their intermound facies (Fig. 2). Micro and nanomorphology 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.

Fourier Transform - Infrared Spectroscopy was performed in the mid-infrared area (4000-400 cm^{-1}). The equipment used was a Spectrophotometer Perkin Elmer Spectrum 100 with a Universal ATR (Attenued Total Reflectance) employed in the following arrangement: a K-Br beamsplitter and an $LiTaO_3$ detector. In this configuration, the resolution was 4 cm^{-1}.

3. Micrites

The studied laminated microbialites are made up of micrometer sized laminations with irregularly alternating dark and white wrinkled laminae arranged in microcolumnar structures (Fig. 3a). The accretionary morphology

Fig. 2. Panoramic view of Hamar Laghdad massif with the kess-kess mounds.

(very fine wavy-wrinkled laminations), showing antigravity patterns, suggests an organic origin and a syndepositional cementation of this microbialite (Reitner et al.,1995; Russo et al., 1997).

The dark laminae, in polished bulk samples, observed with incident light appear whitish-pale pink. Epifluorescence observations on these samples put in evidence the distribution of organic matter remains, concentrated in ill-defined, submillimeter sized, layers. Fluorescent layers analyzed in thin section show microcolumnar structures and is possible to note that fluorescence follows the micromorphologies of the dark laminae (Fig. 3b).

SEM-EDS data showed that the white microbialitic laminae are constituted of low Mg-calcite crystals ranging in sizes from 5 to 30 μm. These laminae of variable thicknesses (10 to 40 μm) alternate with thin laminations (from 5 to 15 μm thick) that correspond to dark laminae (Fig. 4). These thin laminations are constituted of small calcite crystals and siliciclastic material (from 1 to 5 μm) is engulfed by structureless material sometime showing a reticule network. The presence of siliciclastic grains is demonstrated by the peaks of Si and Al in the EDS spectrum (Fig. 4).

4. Fourier Transform Infrared analysis (FT-IR)

The infrared spectra showed bands between 1000 and 3000 cm^{-1}. They contain stretching aliphatic bands (νCH)ali at 2950, 2920 and 2850 cm^{-1}, and deformation bands of methyl (δCH_3; 1370 cm^{-1}) and both methyl and methylene [(CH_2 + CH_3); 1460 cm^{-1}] groups (Fig. 5). The spectra also display the band assigned to carbonyl and/or carboxyl groups (νC=O; 1740 cm^{-1}). The νC-O vibration appears between 1300 and 1100 cm^{-1}. We recorded also the band νC=C probably related to unsatured compounds (alkene and/or carboxylic acids). We did not record peaks in the regions between 3000-3100 cm^{-1} and 700-900 cm^{-1} attributable to aromatics groups (Fig. 5).

5. Discussion And Conclusions

The organic induced deposition of the micrite has been testified by its micromorphology. Actually the accretionary growth type (very fine wavy-wrinkled laminations), showing antigravity patterns, suggests an organic origin and syndepositional cementation of the micrite. Microbialite laminae show a bright epifluorescence revealing a rich organic matter content, possibly related to the biological control during their deposition.

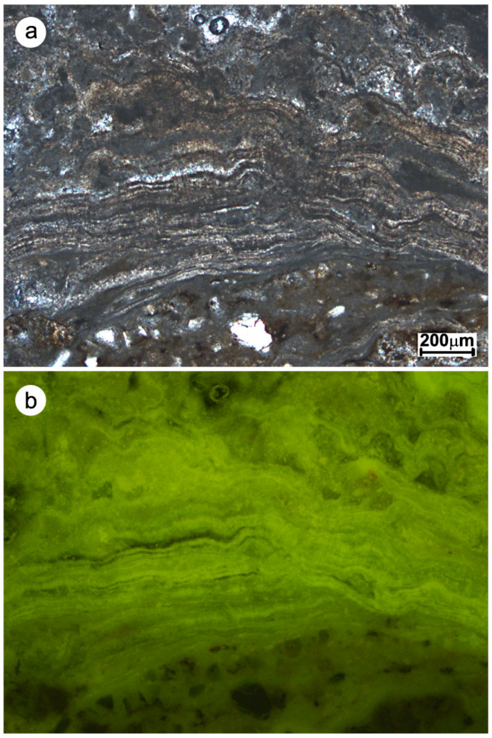

Fig. 3. Microphotographs with petrographic microscope: transmitted light (a), and epifluorescence UV (b). The bright fluorescence of the dark laminations reveals a high organic matter content.

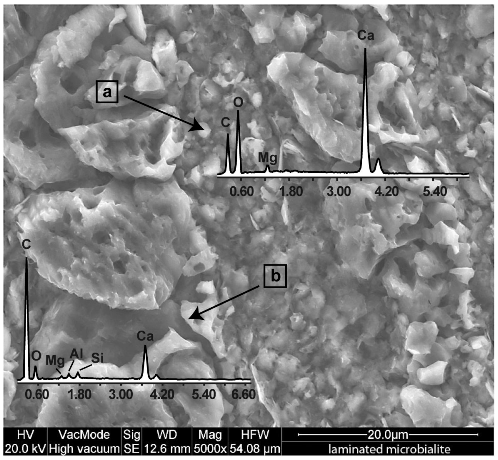

Fig. 4. Micromorphology of the laminated microbialite observed with secondary electrons (SE). Note the difference between the area made of large crystals (white laminations) and the area made of small crystals (dark laminations). The EDS spectra reveal laminae are made up of low Mg-calcite, in additions the laminations with smaller crystals contain also siliciclastic elements (Si and Al). Furthermore the high carbon peak in the spectrum taken inside these laminae can be attributable to a higher amount of organic matter remains (EPS).

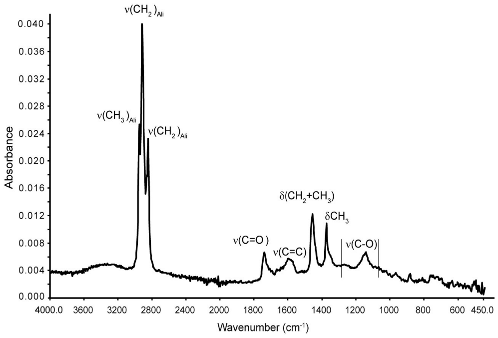

Fig. 5. Infrared spectra reveal the functional groups of the organic compounds extracted from the laminated microbialite.

FT-IR spectra show an high prevalence of aliphatic functional groups respect to those of carboxyl acids. The absence of the bands in the 700-900 cm^{-1} and 3000-3100 cm^{-1} regions allow to exclude that the *ν*C=C functional group recorded at 1600 cm^{-1} belongs to the aromatic compounds. We attribute this functional group to alkene and/or unsatured carboxylic acids, synthesized by bacteria and/or archaea communities, which triggered the precipitation of the micrite through their metabolic activities.

The organic matter evolution has been deduced 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, FT-IR spectra of kerogens, with increasing maturity, 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., 2010). In the studied mound 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.

The A Factor (2930+2860 cm^{-1})/(2930+2860+1630 cm^{-1}) and the C Factor (1710 cm^{-1})/(1710 + 1630 cm^{-1}) were used in order to quantify changes in abundances of aliphatic and carbonyl/carboxyl groups. These factors can be 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), for the classification of kerogen types and maturation level of organic compounds (Ganz and Kalkreuth, 1987). In the Kess-Kess samples the average of A factor is 0.7 while those of the C factor is 0.6. These parameters indicate a marine origin for the organic compounds and confirm their low thermal evolution.

Secondary migration of hydrocarbons and progressive alteration through thermal maturation may obscure original signals of organic matter. 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. Further analyses in Gas Chromatography-Mass Spectrometry could confirm the presence of specific bacterial/archaeal biomarkers.

Finally this approach permit to detect biosignatures of microorganisms belonging to communities which flourished in methanotrophic extreme environments like those that could have characterized the early Earth and Mars.

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