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Signatures of Hydrocarbon Venting in a Middle Devonian Carbonate Mound (Hollard Mound) at the Hamar Laghdad (Antiatlas, Morocco)

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SUMMARY

The Middle Devonian Hollard Mud Mound is situated in the eastern Hamar Laghdad, which is a small mountain range in the Tafilalt in SE Morocco. In contrast to the well known Lower Devonian Kess-Kess mounds, the Hollard Mound is of Middle Devonian age. The facies in the core of this mud mound differs from that of the other parts of the mound, and exhibits signatures of ancient hydrocarbon venting. The carbonate phases of the core facies are derived from the oxidation of vent fluids and consist of clotted micrite, a cryptocrystalline carbonate associated with spheres of uncertain origin, and a calcitic rim cement (rim cement B). These vent carbonates show $\delta^{13}C$ values in the range of -11 to -20‰ PDB indicating that some of their carbon is derived from isotopically light hydrocarbons. Fossiliferous micrite has been affected by hydrocarbon venting in the proximity of the vent site, which is indicated by intermediate $\delta^{13}C$ values between vent carbonates and not affected sediments. Bivalves occur in dense populations within the core facies. They form autochthonous shell accumulations and are almost exclusively articulated. It is likely that these bivalves were dependent on chemosynthesis similar to their counterparts at modern vents. The vent deposits also exhibit an unusual prasinophyte assemblage, which might have been linked to the specific nutrient availability at the vent site.

The ancient vent site is characterized by an enhanced carbonate precipitation and rapid lithification. The latter is corroborated by the three-dimensional preservation of phytoplankton (prasinophytes and acritarchs) and the occurrence of stromatactoid pores. An early phase of carbonate corrosion predating the formation of vent carbonates affected the fossiliferous micrite of the core facies and is thought to be related to a phase of H_2S-rich venting.

1 INTRODUCTION

After the discovery of hydrothermal vents at oceanic spreading centers (LONSDALE, 1977, CORLISS et al., 1979) cold methane seeps have been described. Methane seeps occur at convergent plate margins (KULM et al., 1986, SIBUET et al., 1988) and passive continental margins (PAULL et al., 1984, DANDO et al., 1991). Chemosynthetic bivalves and tube worms that live at hot and cold vents are dependent on bacteria oxidizing the reduced venting fluids. These bivalves and tube worms harbour chemolithotrophic or methanotrophic bacteria in their tissues. By oxidizing reduced sulfur compounds, methane or higher hydrocarbons, endosymbiontic and free living bacteria are the basis of the foodweb at vent sites (RAU & HEDGES, 1979, ARP & CHILDRESS, 1981, FELBECK et al., 1981, CAVANAUGH, 1983, CHILDRESS et al., 1986, CAVANAUGH et al., 1987, FISHER, 1990).

Carbonate precipitation is one of the most significant processes associated with methane seeping from the seafloor. Recent occurrences of vent-related carbonates have been reported from the Gulf of Mexico (PAULL et al., 1984, ROBERTS et al., 1993, ROBERTS & AHARON, 1994), from the Washington/Oregon accretionary prism (KULM et al., 1986, RITGER et al., 1987, KULM & SUESS, 1990), off California (BARRY et al., 1996), off Barbados (JOLLIVET et al., 1990, LEPICHON et al., 1990), from the North Sea (HOVLAND et al., 1987), and off Pakistan (VON RAD et al., 1996). Some of the carbonate carbon of these precipitates is derived from the oxidation of isotopically light methane which results in an extreme ^{13}C depletion of cold seep carbonates. In addition to seep related biota and petrographical evidence the stable isotopes of carbon are an important tool to recognize ancient seep carbonates.

Tertiary methane-derived carbonates have been reported from Washington State (GOEDERT & SQUIRES, 1990, CAMPBELL, 1992) and from the Apennine chain of the Italian peninsula (CLARI et al., 1994, TERZI et al., 1994). The Late Cretaceous

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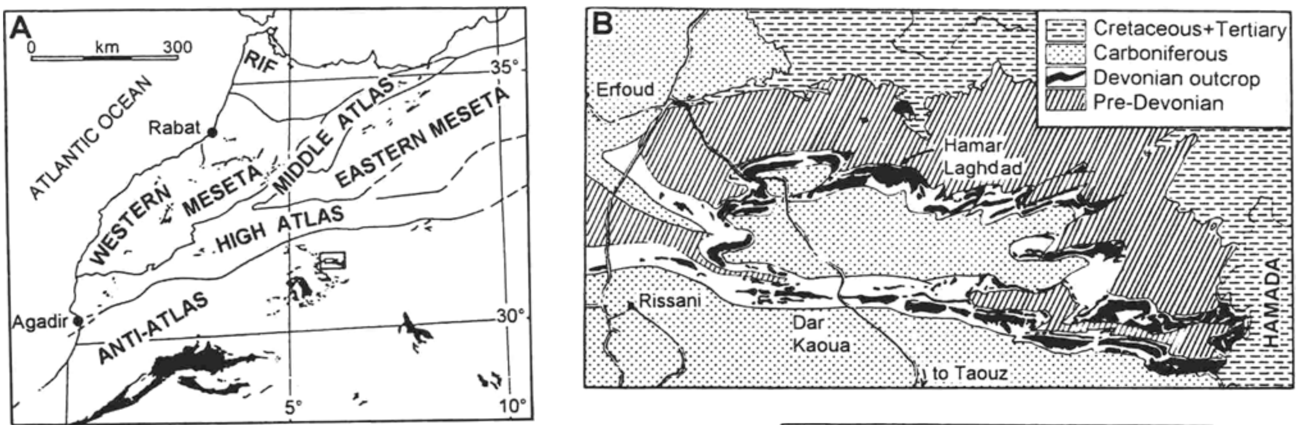


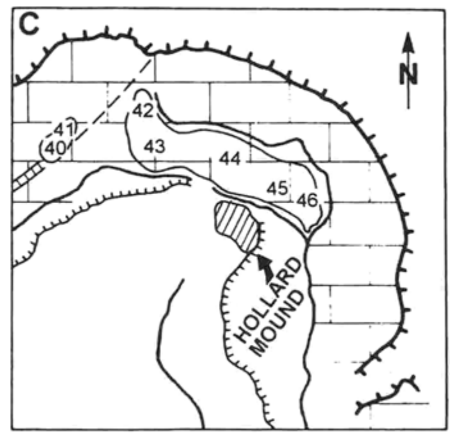


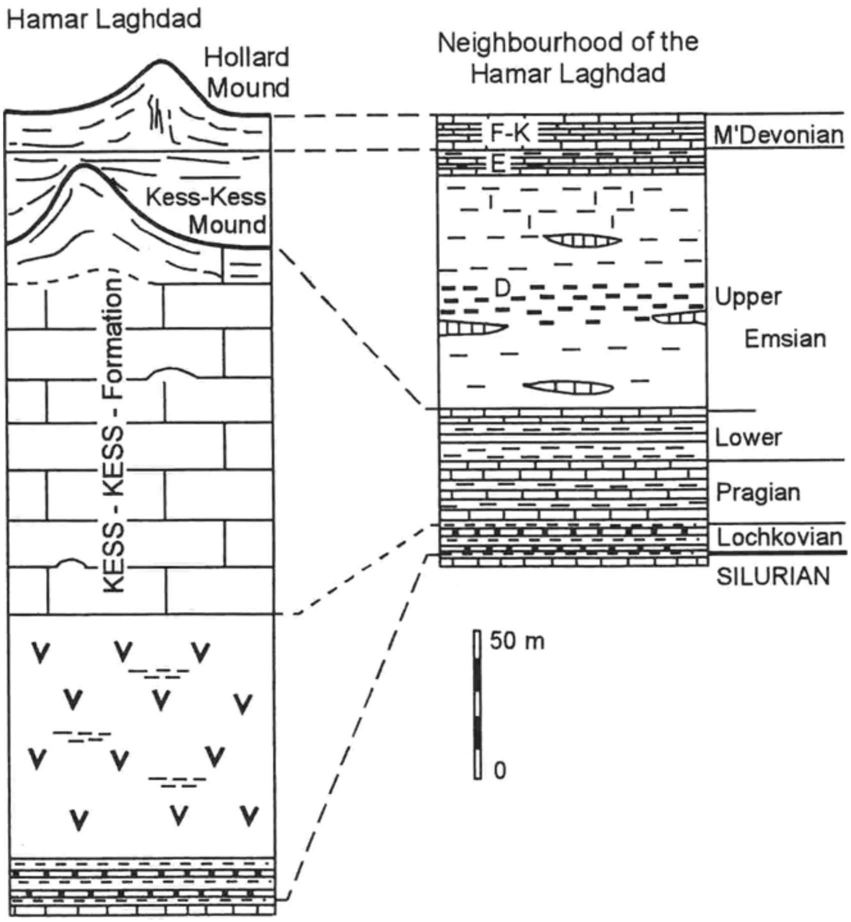
Fig. 1. Position of the Hollard Mound at the eastern part of the Hamar Laghdad (C), northern Tafilalt (B), SE-Moroccan Antiatlas. Block signature in 1C indicates the Emsian Kess-Kess Formation; nos. 40-46 correspond to the numbering of Lower Devonian mud mounds in BRACHERT et al. (1992). Black spots in A: Devonian outcrop.

(Campanian) Tepee Buttes in Colorado (KAUFFMAN et al., 1996) and Aptian/Albian carbonate mounds of the Canadian Arctic (BEAUCHAMP et al., 1989, BEAUCHAMP & SAVARD, 1992, SAVARD et al., 1996) have been interpreted to be related to methane seeps. Fossil cold seep limestones ranging in age from Tithonian to Albian occur within deep-water turbidites of the Great Valley Group (Jurassic-Cretaceous) in California (CAMPBELL et al., 1993). Jurassic cold seep carbonates have been reported from Antarctica (KELLY et al., 1995) and from the Oxfordian black shales of southeastern France (GAILLARD et al., 1992). VON BITTER et al. (1990 and 1992) suggested that the Carboniferous (Visean) Bryozoan/Microbial Mounds in Newfoundland were formed by chemosynthetic processes at marine vents. LITTLE et al. (1997) reported on a Silurian hydrothermal-vent related community from the southern Urals in Russia. Middle Ordovician mounds and washout depressions of the Ottawa Valley (Canada) exhibit a similar appearance as modern seepage-related seabed features in the North Sea (HOVLAND, 1989). Due to this similarity and the occurrence of dense fossil accumulations on the Ordovician mounds and in the depressions a seepage origin of these structures is proposed (HOVLAND, 1989). LAVOIE (1997) reported Lower Ordovician ophicalcites in the southern Quebec Appalachians (Canada) and suggested that carbonate precipitation was mediated by microbial communities at a venting system similar to modern white smokers.

The Lower Emsian Kess-Kess mounds of the eastern Antiatlas (Morocco) from the Hamar Laghdad area have been interpreted to be related to venting hydrothermal waters (MOUNJI et al. 1996, 1997, 1998) or to the bacterial oxidation of thermogenic methane derived from underlying basaltic intrusives (BELKA, 1994, 1995, 1997, 1998a, b). BELKA's interpretation is based on samples from Frasnian neptunian dikes, i.e. from dikes much younger than the Emsian mounds, but also from the mound and intermound facies itself. Unfortunately nothing is mentioned with respect to the exact position of those samples from the mound facies that yield strongly negative $\delta^{13}C$ values. Thus it can not be controlled if some of the samples derive from the Hollard Mound, subject of our investigation. BELKA (1998b, Fig. 9) figured the Hollard Mound as "the mud ridge exposed in the eastern Hamar Laghdad". It can be deduced from BELKA's text (p. 369) and his Fig. 4, that the "mud ridge in the eastern part of the Hamar Laghdad" is identical with the Kess-Kess complex 42-46 in BRACHERT et al. (1992), which is of Lower Devonian, Emsian age (Lower and lowermost Upper Emsian). However, the Hollard Mound does not belong to this complex, but is situated immediately south of it (Fig. 1C), and is of Middle Devonian age. Here we report only on that Middle Devonian mud mound that was introduced to the literature by HOLLARD (1967) and named 'Hollard Mound' by WALLISER (1991). The emphasis is placed on the core facies of this mound where dense clusters of articulated bivalves occur. The aim of this paper is to present this autochthonous assemblage and to discuss the conditions that sustained the bivalves and the formation of the core facies carbonates.

2 GEOLOGICAL SETTING AND STRATIGRAPHY

The Hamar Laghdad (Hamer-el-Khdad, Ahmar-el-Khdad, Hamar Larhdad) is a small mountain range in the



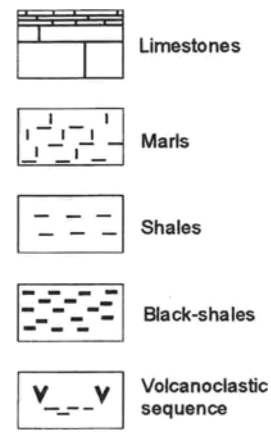


Fig. 2. Comparison of the exceptional sequence at Hamar Laghdad and the sequence in the adjacent areas (schematic; D-K: indices for the stratigraphic unitsaccording to Fig. 4, D and E : Upper Emsian; F-K: Middle Devonian).

Tafilalt (Tafilalet), 18 km ESE of Erfoud in SE Morocco. This area is about 75 km S of the northern border of the African craton (Fig. 1). In most cases, the Palaeozoic sediments of this region are slightly tilted due to the weak effect of the Variscan orogeny on the epicratonic sediments of late Precambrian and Palaeozoic ages.

In the Tafilalt, the Devonian sequences show features characteristic of a differentiated, relatively shallow, but vast epicontinental sea with prevailing hemipelagic to pelagic faunas and facies, respectively. The sequences are condensed, except within the deeper basinal parts in the SW. Gaps in sedimentation may occur, especially within the interval from late Givetian to late Famennian. Sequences with predominately pelitic sediments alternate with limestone sequences and correspond well with the global transgression-regression cycles.

When compared with that general pattern of the Tafilalt Devonian, the Hamar Laghdad shows an exceptional feature resulting from volcanic activity during the middle and late Lochkovian (Fig. 2): Effusiva and a few sedimentary intercalations built a presumably N-S striking submarine ridge, at the Hamar Laghdad about 5.2 km wide and, after partial denudation, up to 100 m high.

The volcanoclastic rise became settled by crinoids which produced up to 180 m of crinoidal limestone during the Pragian and Lower Emsian (Zlichovian). In the uppermost part of this so-called Kess-Kess Formation (Brachert et al., 1992), mud mounds developed. Among them the cone-shaped mounds with their steep flanks, called Kess-Kess, are especially spectacular and have, therefore, been the subject of numerous investigations. The upper part of the Kess-Kess Formation is equivalent to the *Mimagoniatites* Limestone, a widely distributed hemipelagic to pelagic facies equivalent. At the very beginning of the basal Upper Emsian (Dalejan) *Nowakia cancellata* Zone, both the Kess-Kess Formation and the *Mimagoniatites* Limestone were followed by pelitic sediments. Corresponding facies changes are recognized worldwide and referred to the global Middle Emsian Event (M'Em Event, *cancellata* Event, Daleje Event; see Fig. 3, and compilation in Walliser, 1996).

The Hollard Mud Mound is situated near the eastern extent of the Hamar Laghdad immediately S of Kess-Kess 45 in Brachert et al. (1992: Fig. 4). The Hollard Mound is clearly younger than the Kess-Kess mounds. According to our calculation, it started to develop about 3 million years later, at the very beginning of the Eifelian (Fig. 3). This basal Middle Devonian time-level is also characterized by a global event, i.e. the Emsian-Eifelian Boundary Event (Em/Ei Event, *Pinacites* Event, Chotec Event). The formation of the mud mound continued up to the uppermost Givetian and ended at the globally transgressive Givetian-Frasnian Boundary Event (Gi/Fr Event, *asymmetricus* Event, Ense Event).

Many of the Eifelian and Givetian horizons can be traced continuously within a few hundred meters from the

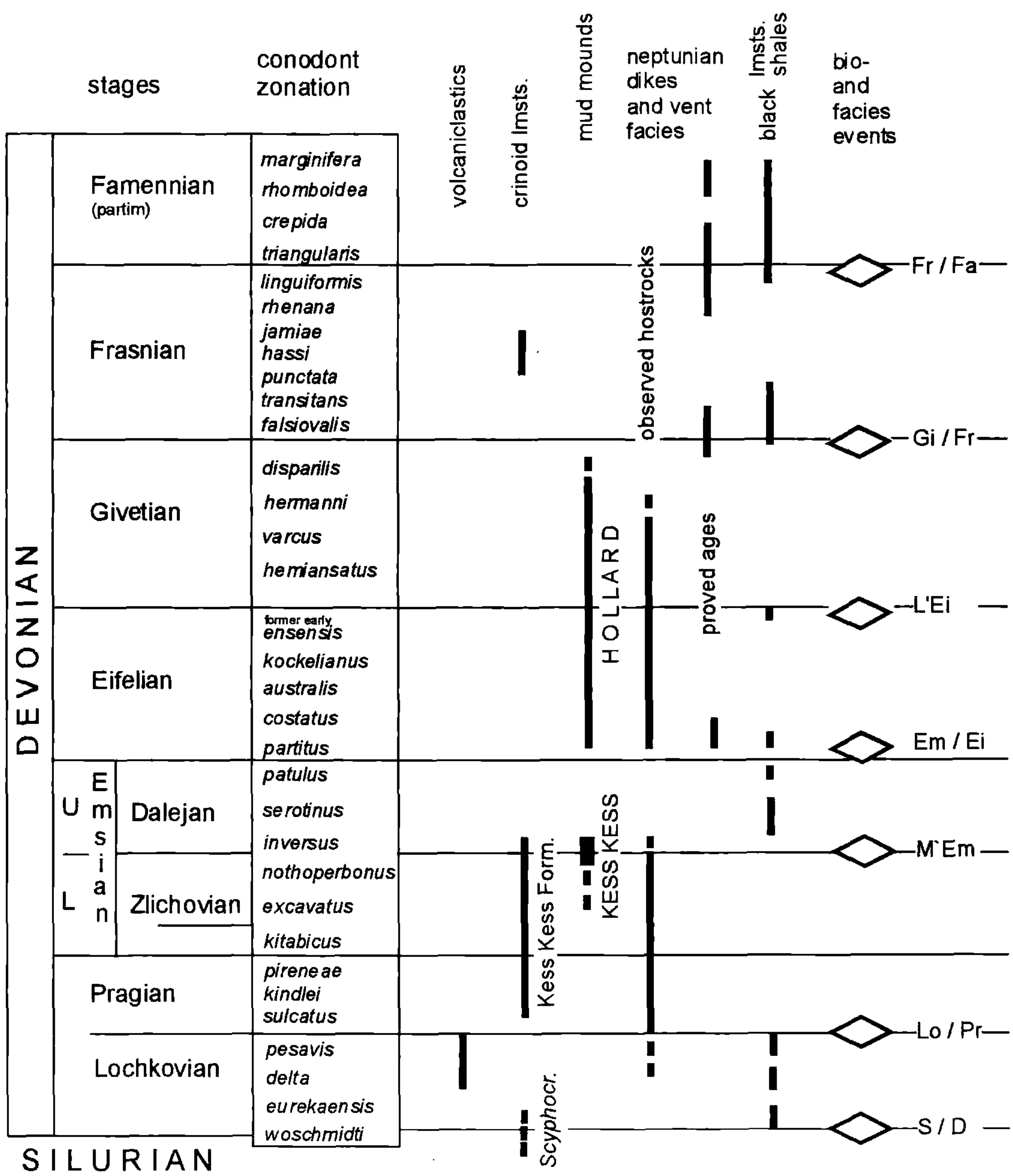


Fig. 3. Stratigraphic range of important features at the Hamar Laghdad (from BRACHERT et al., 1992, Fig. 6; updated and revised). L: Lower, M': middle, U: Upper, L': late

mud mound into hemipelagic facies (Fig. 4; Pl. 47/1). This has been the subject of a facies analysis by TÖNEBÖHN (1991). He pointed out that the episodic development of the mud mound was controlled by sea-level changes: transgressions are growth-promoting, regressive tendencies are growth-inhibiting.

At many places within the Hamar Laghdad neptunian dikes are exposed. They exclusively penetrate the intermound facies of the Kess-Kess Formation as well as younger sequences, but it has not been observed that they end just below or within the Emsian mud mounds. According to these circumstances, it seems that the dikes are younger than the Kess-Kess mounds. Thus, the assumption of other authors that there is a causal connection between the formation of the Kess-Kess mounds and the neptunian dikes can neither be verified nor falsified.

At the Hollard Mound a special situation exists with respect to neptunian dikes. In the core, from the base up to the top of the mound, a zone is exposed several meters wide consisting of dike fillings, vent deposits, and vent-influenced sediments as described below. This carbonate complex will be termed the core facies (Fig. 4), in contrast to the off-mound sediments and the portions of the mound which are not vent-influenced.

In the north-eastern part of the Hollard Mound, near its base, *Polygnathus partitus* was found in two different sites, in vent deposits including bivalves, but also in the immediately adjacent sediments with abundant bivalves, thus confirming the synchronous formation of both facies. The mentioned conodont species characterizes the lowermost Eifelian which is closely connected with the global Em/Ei Event, respectively. However, further investiga-

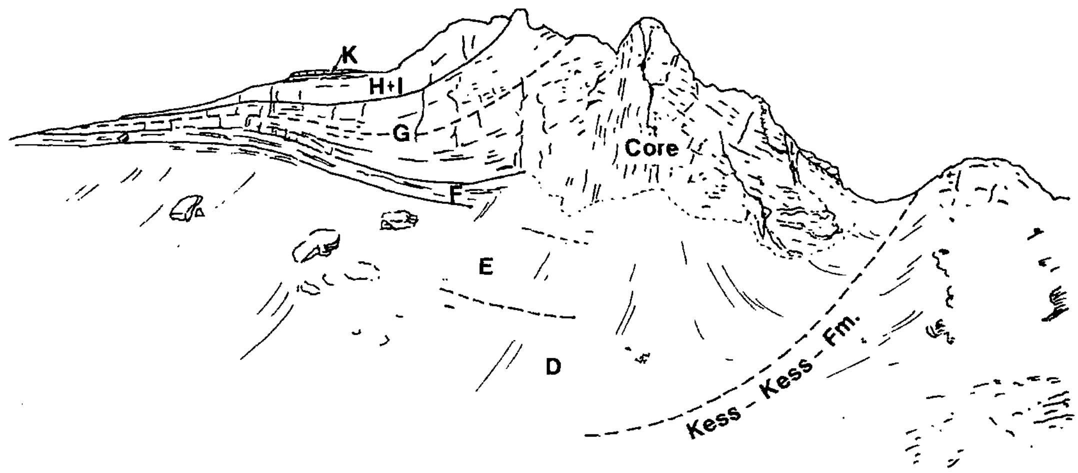


Fig. 4. The Hollard Mound, seen from E (same viewpoint as Pl. 47/1). Letters indicate stratigraphic units, of which the Givetian ones significantly increase in thickness towards the core of the mound (D + E: Upper Emsian; F: basal Eifelian *Pinacites* Limestone; F-H: Eifelian; I+K: Givetian, with *Pharciceras* Limestone at the top). Dotted lines: supposed positions of boundaries between stratigraphic units where boundaries are covered by debris.

tions are necessary to determine the relations in age and development between the core facies and host rocks in all parts of the Hollard Mound.

3 METHODS

Thin sections (15 x 10 cm) used for petrographical studies were partly stained with combined potassium ferricyanide and alizarin red, dissolved in 0.1 % HCl solution. Polished thin sections (48 x 28 mm) were additionally studied with cathodoluminescence technique using a Citl CCL 8200 Mk3A. Samples for carbon and oxygen stable isotope ratios were taken from polished slabs using a hand held microdrill. CO_2 was liberated by the standard phosphoric acid technique (McCrea, 1950) at 75°C. Isotope measurements were made with a Finnigan Mat 252 mass spectrometer using a Carbo-Kiel carbonate preparation-technique at the University of Erlangen. The $\delta^{13}C$ and $\delta^{18}O$ values are reported relative to the PDB standard and appropriate correction factors were applied. The precision of the measurements ranges for both carbon and oxygen from 0.01 to 0.05 ‰. A correction factor for $\delta^{18}O$ values of -0.8‰ (Sharma & Clayton, 1965) was added to the $\delta^{18}O$ ratios of dolomitic samples.

4 PALAEONTOLOGY AND PALYNOLOGY

The limestone immediately adjacent to the central core yields the following rich micro-fauna (sample IMGP Göttingen, 91-3752): Conodonts: *Polygnathus partitus*, *Po.* sp., *Belodella* sp., *Neopanderodus* sp.; fragments of Articulata and 1 ostracode; numerous scolecodonts; numerous ammodiscid and irregular (free and attached) foraminifera; steinkerns of endolithic organisms.

The macrofauna is dominated by phacopid trilobites and bivalves. Small gastropods are frequent, whereas only a few orthocone cephalopods, dacryoconarids and ostracodes are present. The large bivalves included in the core facies and the immediately adjacent sediments represent at least two different taxa. Cross sections indicate that they most probably do not belong to *Modiomorpha* as Tönebohn (1991) assumed, but rather to taxa of the Anomalodesmata, presumably to the Pholadomyoida. The bivalves of the core facies are almost exclusively articulated and represent an autochthonous assemblage. Bivalves of the adjacent sediments are disarticulated.

Six samples have been selected to test their potential for palynological evidence. Carbonates and silicates were removed by hydrochloric and hydrofluoric acid treatment but screening and oxidation procedures were omitted in order to avoid loss of small and fragile palynomorphs. Very fine-grained material was the dominant type of organic matter in all samples. Only one sample (HOS 97/14) yielded a reasonably diverse but somewhat unusual phytoplankton assemblage consisting mainly of rare polygonomorph and acanthomorph acritarchs and more abundant prasinophytes. Noteworthy features of this assemblage are the three-dimensional preservation of the spinose acritarchs, which is apparently due to the very early lithification of the limestone, and the relative abundance of exceptionally small forms, which are here considered to represent prasinophytes. Among the latter only those exhibiting a more conspicuous morphology can be attributed to known taxa.

The following taxa have been registered during a preliminary survey:

Acritarchs:

Multiplicisphaeridium ramusculosum (Deflandre) Lister 1970
Palacanthus ledanoisii (Deunff) Playford 1977
Polyedrixium cf. *embudum* Cramer 1964
Polyedrixium pharaonis Deunff 1961
Veryhachium europaeum Stockmans & Willière 1960
Veryhachium pannuceum Wicander & Loeblich 1977
Veryhachium sp.

Veryhachium cf. trispininflatum CRAMER 1964
Veryhachium trispinosum (EISENACK) DEUNFF 1954
Prasinophytes:
Cymatiosphaera pastilla HASHEMI & PLAYFORD 1998
Cymatiosphaera cf. *pavimenta* (DEFLANDRE) DEFLANDRE 1954 *sensu* PLAYFORD 1977
Cymatiosphaera sp.
Dictyotidium sp.
Leiosphaeridia spp.
Lophosphaeridium cf. *deminutum* PLAYFORD in PLAYFORD & DRING 1981
Lophosphaeridium sp.

All these taxa are reported from Lower to Middle Devonian, respectively Frasnian strata of Laurussia and Peri-Gondwana terranes but are long-ranging and do not provide any more specific stratigraphic information beyond the conodont evidence.

The diversity of small prasinophytes is definitely greater than apparent from the above list of taxa. They are rarely presented in the literature and probably disregarded in most Palaeozoic phytoplankton studies. The significance of their spatial and temporal distribution therefore is virtually unknown. HABIB & KNAPP (1982) report abundant small "acritarchs", respectively prasinophytes, from Lower Cretaceous sediments in the deep western North Atlantic where dinoflagellate cysts and normal acritarchs are rare. They attribute this distribution to the selective long distance transport of the small forms. STAPLIN (1961) notes that in Devonian reefs of Alberta, Canada, simple phytoplankton morphologies are associated with reef facies while more complex forms increase off-reef. A more common association with exceptional environments such as presented here, however, should be considered and tested.

It is widely accepted that prasinophytes often form phytoplankton blooms under conditions of exceptional salinity and nutrient supply (TAPPAN, 1980). PRAUSS & RIEGEL (1989) suggested a connection with salinity stratification and resulting black shale formation. Similarly a suitable habitat may be provided at vent sites by chemoclines in the water column and the associated nutrient availability.

5 PETROGRAPHY OF THE CORE FACIES

In the core facies of the Hollard Mound deposition and precipitation of carbonate occurred in several phases. Dark-grey fossiliferous micrite represents the sediment of the normal marine Eifelian depositional environment and is the phase formed first. The phases which are postdating the formation of this micrite are a clotted micrite, a calcitic rim cement (rim cement B), an inclusion-rich calcitic cement (rim cement I), rhombohedral calcite and dolomite (listed in chronological order).

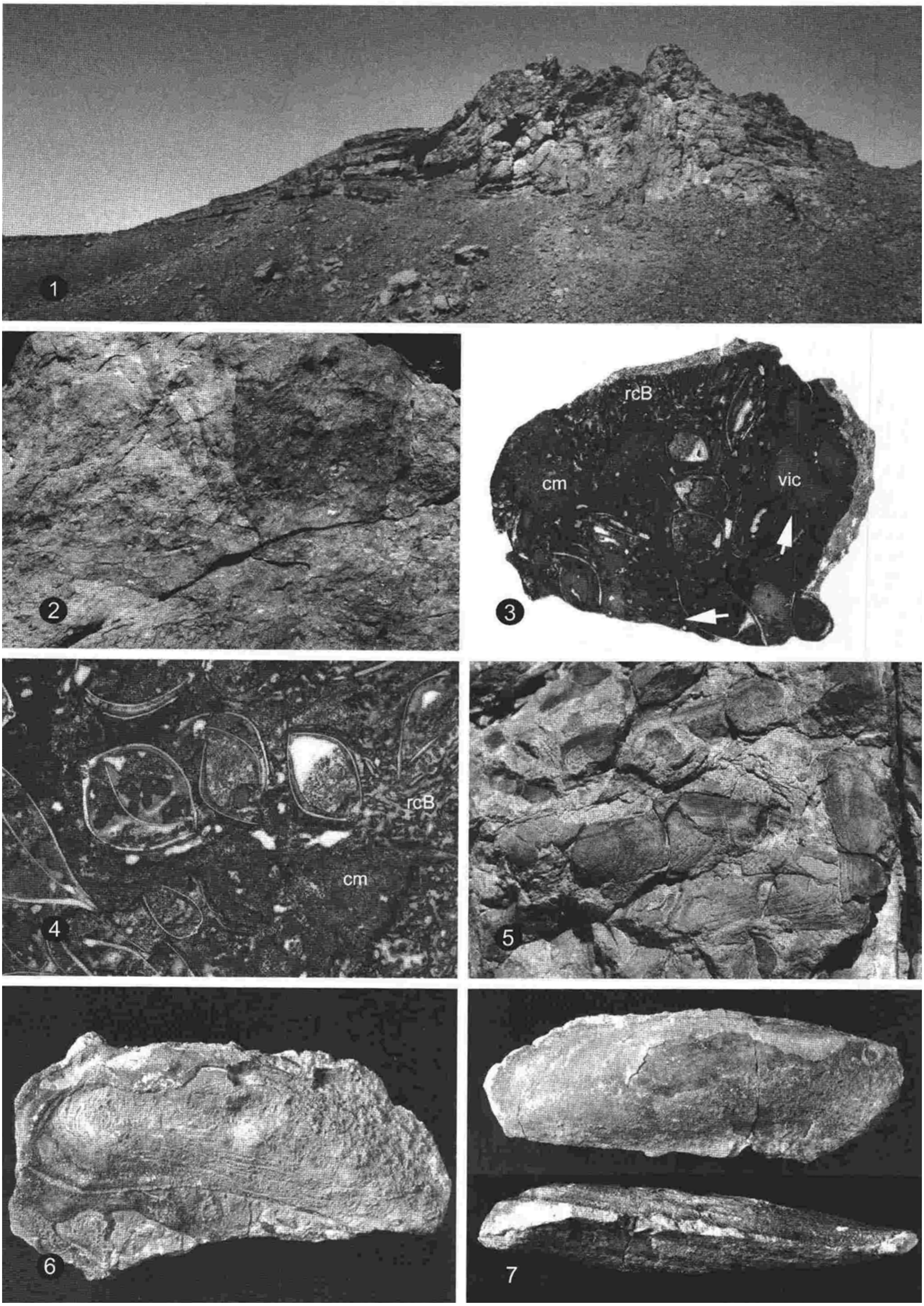
The dark-grey uniform fossiliferous micrite is packed with the remains of different, mostly benthic, organisms forming a wackestone. It is preferentially affected by neomorphism, with the micrite altered to microspar with crystal size ranging from 10 to 20 µm. Under cathodoluminescence the micrite gives an intense, uniform reddish response, whereas neomorphic zones have a dull luminescence (Pl. 48/1).

Clotted micrite is the most conspicuous phase under plane-polarized light. It consists of dark-brown to black, cloudy, micritic aggregates surrounded by bright-grey micrite or calcitic spar (Pl. 48/2). Framboidal pyrite is common in this phase and especially abundant at the transition between the fossiliferous micrite and the rim cement B (B: banding). Occasionally that micrite exhibits a stromatolitic fabric. The transition to the uniform fossiliferous micrite is sharp, whereas the transition to the rim cement B may either be sharp or gradational (Pl. 48/5). In case of a gradational transition a facies with hollow microspheres is frequently found between the clotted micrite and the rim cement B (Pl. 48/3). These spheres range in diameter from 50 to 200 µm and their walls appear to be made of an organic-rich material. The thickness of the walls is irregular. The spheres are embedded in a cryptocrystalline authigenic carbonate. Under cathodoluminescence the spheres show a dull to moderate orange luminescence and the carbonate which surrounds them emits an intense orange luminescence (Pl. 48/4).

The rim cement B appears to be banded due to growth-zone boundaries defined by changes in colour and by single sheets of inclusions. The bands vary from light- to dark-brown in colour, with the darker bands containing

Plate 47 Hollard Mound; vent carbonates and associated bivalves (Middle Devonian, Hamar Lagdad, Morocco).

Fig. 1. The Hollard Mound with its core facies on the lower right side of the mound (compare Fig. 4.).
Fig. 2. Sedimentary dikes within the core facies. The width of the figure is approximately 60 cm.
Fig. 3. Polished slab of the core facies carbonates with vent influenced carbonate (vic), clotted micrite (cm) and the rim cement B (rcB). The arrows point to corrosion surfaces on fossiliferous micrite. The width of the figure is 23 cm.
Fig. 4. Articulated bivalves embedded in vent carbonates (scanned thin section from the slab shown in Fig. 4.). The width of the figure is 11 cm.
Fig. 5. Bivalves within vent-influenced sediments. The width of the figure is 17 cm.
Fig. 6, 7. Two different bivalve species characteristic for the core facies. The widths of the figures are 10 cm (Fig. 6.) and 11 cm (Fig. 7.).


1
2
rcB
cm
vic
3
rcB
cm
4
5
6
7

greater amounts of inclusions (Pl. 48/8). The average thickness of these successions is 5 mm. Framboidal pyrite is frequent in this phase. Splays of radial-fibrous calcite cement are a variety of this phase of carbonate precipitation and occur contemporaneously to the banded cement (Pl. 48/6). In places the rim cement B together with the clotted micrite makes up more than 90% of the rock volume. The banded cement shows a dull reddish respectively intense orange luminescence (Pl. 48/7). A relation between the Cl-colour of the bands and the amount of inclusions is not obvious. Nearby the transition with the rim cement I the banded cement exhibits very intense orange luminescence (Pl. 49/2)

The rim cement I (I: inclusion-rich) has a medium thickness of about 1 mm. It consists of a calcite rich in inclusions and uniform in appearance (Pl. 48/8 and 49/1). Under plane-polarized light, no crystal boundaries are recognizable within the crust, but under crossed nicols stubby, irregular crystals can be recognized. The diameter of the dark, blistery inclusions ranges from 5 to 20 µm. Under cathodoluminescence it becomes evident, that the rim cement I grew in several phases. Two growth zones which show an heterogeneous dull or moderate orange to orange fluorescence are separated by a narrow seam of intense orange luminescence (Pl. 49/2). The two zones, which are about 0.2 mm and 0.8 mm wide, are subdivided by even narrower seams into three zones regarding the first main zone and into five zones regarding the second main zone (Pl. 49/3).

Rhombohedral, ferroan calcite represents the last phase of calcium carbonate formation (Pl. 49/1). Macroscopically it appears whitish. The average diameter of crystals is 4 mm, but crystals up to 2 cm may occur. Its rhombohedral cleavage is obvious due to the high amount of fissures within crystals. The iron content increases towards the centers of the cavities. This calcite shows a moderate orange to dull luminescence under cathodoluminescence. Three types of dolomite occur in the core facies limestones. Isolated, rhomb-shaped crystals of dolomite are scattered in the calcitic matrix (Pl. 49/4). This is a neomorphic fabric. The matrix surrounding the dolomitic crystals may either be micritic or transformed to pseudospar. The zoned dolomite crystals exhibit an average crystal size of 100 µm. Under plane-polarized light two phases of dolomite growth are observed. Inclusions of iron oxides are common and are enriched in the inner zone or at the transition from the inner to the outer zone. The second type of dolomite is represented by vein-filling sub- to euhedral crystals with a medium crystal size of 80 µm. The veins are reddish-brown due to a high content of iron oxide inclusions within the dolomites. Both matrix and vein-filling dolomites exhibit and homogenous dull luminescence under cathodoluminescence. The third type of dolomite occurs in some of the stromatactoid cavities were it is surrounded by rhombohedral calcite. The sub- to euhedral rhombs exhibit an average crystal size of 60 µm. These zoned dolomites are of similar appearance like the matrix dolomites, but show an orange luminescence under cathodoluminescence at the transition from the inner to the outer zone were inclusions of iron oxides cause a brownish colour.

Fossiliferous micrite is affected by corrosion, which is obvious from the frequent irregular surfaces, which are truncating the micrite (Pl. 47/3). Pyrite is often enriched on these surfaces (Pl. 48/5). The precipitation of clotted micrite postdates corrosion.

Stromatactoid pores are a common feature of the core facies deposits. These cement-filled cavities have a smooth lower surface and a vaulted, irregular upper surface. They are of centimeter scale and occur in the fossiliferous but not in the clotted micrite. Two types, occasionally three types of cements fill the cavities. The earlier type is rim cement B, the later phase is the ferroan calcite filling up the center of the cavity. The intermediate rim cement I is rare, but occurs in some larger pores. Internal skeletal parts are rare. Occasionally internal sediments consisting of carbonate mud are deposited at the bottom of the cavities. Shelter cavities are also common and show a skeletal support of the roof (auloporoid corals and trilobite skeletons).

Plate 48 Carbonate phases of the core facies (Hollard Mound, Eifelian, Hamar Laghdad, Morocco).

Fig. 1. Vent influenced carbonate (orange, vic) and neomorphic fabric (dull, nf), cathodoluminescence pattern. x 86

Fig. 2. Clotted micrite, plane-polarized light. x 69

Fig. 3. Carbonate associated with spheres, plane-polarized light. x 66

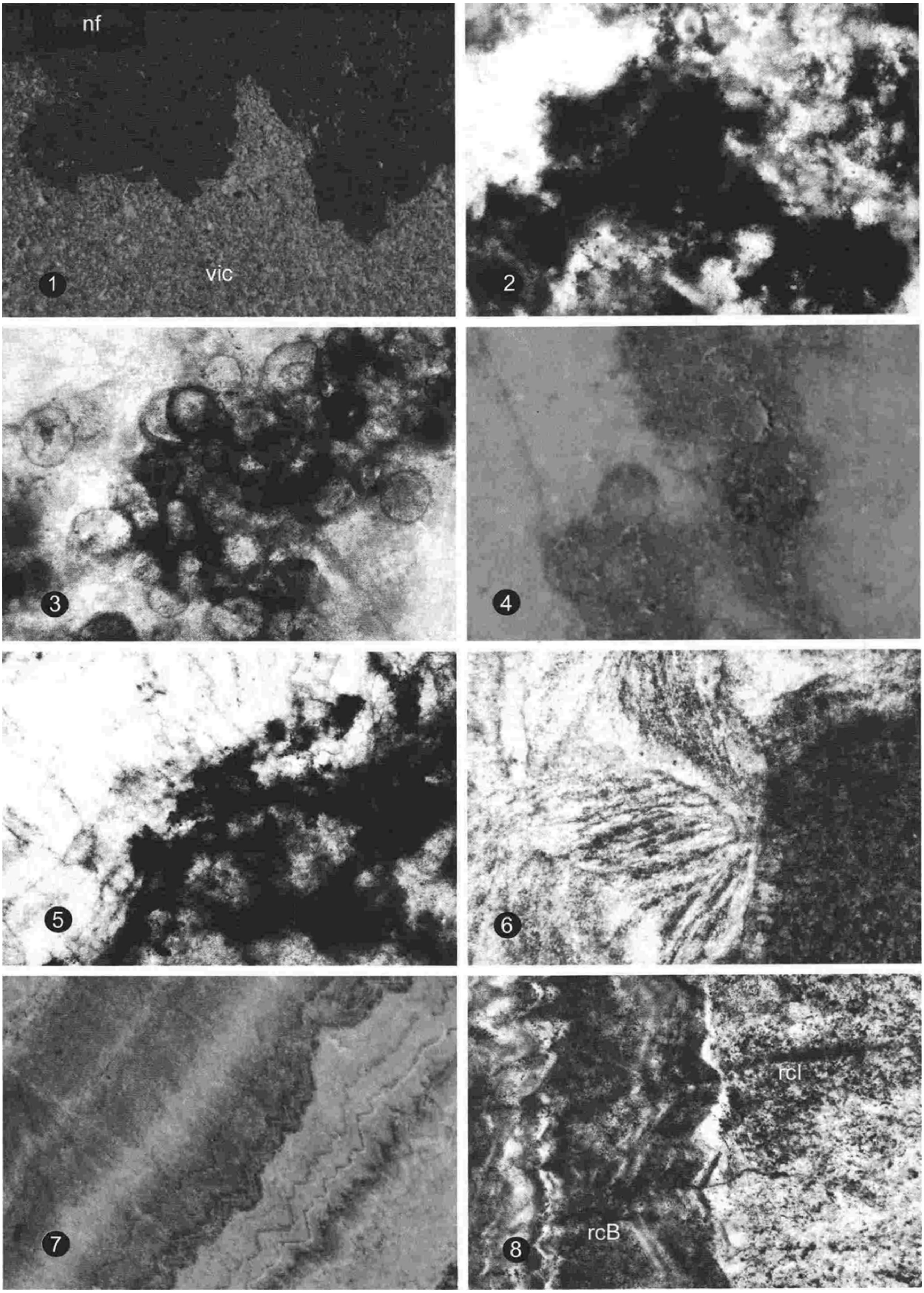
Fig. 4. Carbonate (orange) associated with spheres (dull to moderate orange), cathodoluminescence pattern. x 70

Fig. 5. Transition from micrite (down right) to the rim cement B with framboidal pyrite, plane-polarized light. x 72

Fig. 6. Calcitic splay, variety of the rim cement B, plane-polarized light. x 72

Fig. 7. The rim cement B in its common, banded appearance, cathodoluminescence pattern. x 40

Fig. 8. The transition from the rim cement B (rcB) to the inclusion-rich rim cement I (rcI), stained thin section, plane-polarized light. x 66


nf
vic
1
2
3
4
5
6
rcl
7
rcB
8

6 STABLE ISOTOPES

Fossiliferous micrite formed prior to the other carbonate phases is ^{13}C-depleted with $\delta^{13}C$ values ranging from -2.02 to -10.92‰ PDB (Fig. 5). The carbonate of a bivalve mold, which was sampled in the periphery of the core facies, yielded a $\delta^{13}C$ of -13.81‰. Clotted micrite, carbonate associated with spheres, and rim cement B are strongly depleted in ^{13}C. $\delta^{13}C$ values of these phases range from -10.88 to -20.00‰ PDB. Among these phases clotted micrite ranges from -10.88 to -19.49‰, carbonate associated with spheres from -15.80 to -18.49‰, and the rim cement B from -16.53 to -20.00‰. Analyses of the rim cement I, which postdates the formation of these ^{13}C-depleted carbonates, yielded $\delta^{13}C$ values which cluster between +2.32 and -3.64‰. Late diagenetic rhombohedral, ferroan calcite again exhibits a trend towards lighter $\delta^{13}C$ values (-7.47 to -11.04‰), whereas dolomites range from -4.05 to -4.58‰. The analysis of an early sedimentary infilling from a stromatactoid cavity yielded a $\delta^{13}C$ value of +2.07‰. A sample of mound sediment exposed laterally to the core facies yielded a $\delta^{13}C$ value of +1.19‰.

$\delta^{18}O$-values of the fossiliferous micrite range from -9.16 to -11.44‰ PDB. Clotted micrite (-2.09 to -10.36‰), carbonate associated with spheres (-6.96 to -9.15‰), rim cement B (-3.46 to -4.23‰), rim cement I (-1.72 to -6,75‰), ferroan calcite (-3.31 to -12.32‰), and dolomite (-1.72 to -12.32‰) exhibit a wide range of $\delta^{18}O$ values. The $\delta^{18}O$ value of the sedimentary filling of -11.00‰ is in the range of the $\delta^{18}O$ values of the fossiliferous micrite and the sample of the mound sediment analysed is just slightly less depleted (-8.51‰).

7 DISCUSSION

7.1 Hydrocarbon-derived carbonates

$\delta^{13}C$ as low as -25‰ PDB are typical for carbonates formed in the sedimentary zone of bacterial sulfate reduction (Irwin et al., 1977). If the carbonate carbon is completely derived from organic substrates oxidized by sulfate reducing or other bacteria the carbonates will reflect the carbon isotope composition of these organic compounds. However, precipitation of carbonates with carbon completely derived from organic matter are an exception. Most commonly the stable isotope composition reflects a mixing of two different sources: marine bicarbonate with an $\delta^{13}C$ value of about 0‰ and organic compounds with a light carbon-isotope composition. Carbonates precipitated at cold methane seeps typically exhibit $\delta^{13}C$ values in the range of -30 to almost -70‰ (Ritger et al., 1987). These extremely light values are caused by the microbial oxidation of methane followed by the incorporation of the resulting CO_2 into the authigenic carbonate minerals. Methane is the isotopically lightest compound known in nature (-60 to -110‰ for biogenic and -50‰ for thermogenic methane; Whiticar et al., 1986). Roberts & Aharon (1994) report $\delta^{13}C$ values of modern hydrocarbon-derived carbonates in the range of -18 to -55‰ from the northern Gulf of Mexico, at which less negative values averaging -25‰ were related to crude oil seeps. Cold seep carbonates of the Lower Oxfordian from Beauvoisin (southern France) exhibit $\delta^{13}C$ values in the range of -10 to -25‰ (Gaillard et al., 1992). These Jurassic carbonates were found to contain high amounts of mid-chain n-alkanes typical for crude oils in its intracrystalline matrix, indicat-

Plate 49 Carbonate phases of the core facies and palynological inventory (Hollard Mound, Eifelian, Hamar Laghdad, Morocco).

Fig. 1. The transition from the inclusion-rich rim cement I (rcI) to the rhombohedral calcite (rC), stained thin section, plane-polarized light. x 69

Fig. 2. Rim cement B, rim cement I and rhombohedral calcite (from left to right). Two main growth zones within the rim cement I are evident, cathodoluminescence pattern. x 43

Fig. 3. Growth zones within the rim cement I (rcB: rim cement B; rC: rhombohedral calcite), cathodoluminescence pattern. x 50

Fig. 4. Rhomb-shaped crystals of dolomite scattered in a pseudosparitic matrix, stained thin section, plane-polarized light. x 66

Fig. 5, 6. *Multiplicisphaeridium ramusculosum* (Deflandre) Lister, slide HOS 97/14-10. x 750

Fig.7. *Veryhachium* sp., slide Hos 97/14-5. x 750

Fig. 8, 9. *Polyedrixium pharaonis* Deunff, slide HOS 97/16-6. x 750

Fig. 10. *Veryhachium europaeum*, slide HOS 97/14-3. x 750

Fig. 11. *Veryhachium* cf. *trispininflatum* Cramer, slide HOS 97/14-9. x 900

Fig. 12. *Veryhachium pannuceum* Wicander & Loeblich, slide HOS 97/14-5. x 750

Fig. 13, 14. *Palacanthus ledanoisii* (Deunff) Playford, slide HOS 97/14-10. x 900

Fig. 15, 16. *Lophosphaeridium* sp., slide HOS 97/14-9. x 900

Fig. 17. *Lophospaeridium* cf. *deminutum* Playford, slide HOS 97/14-6. x 1400

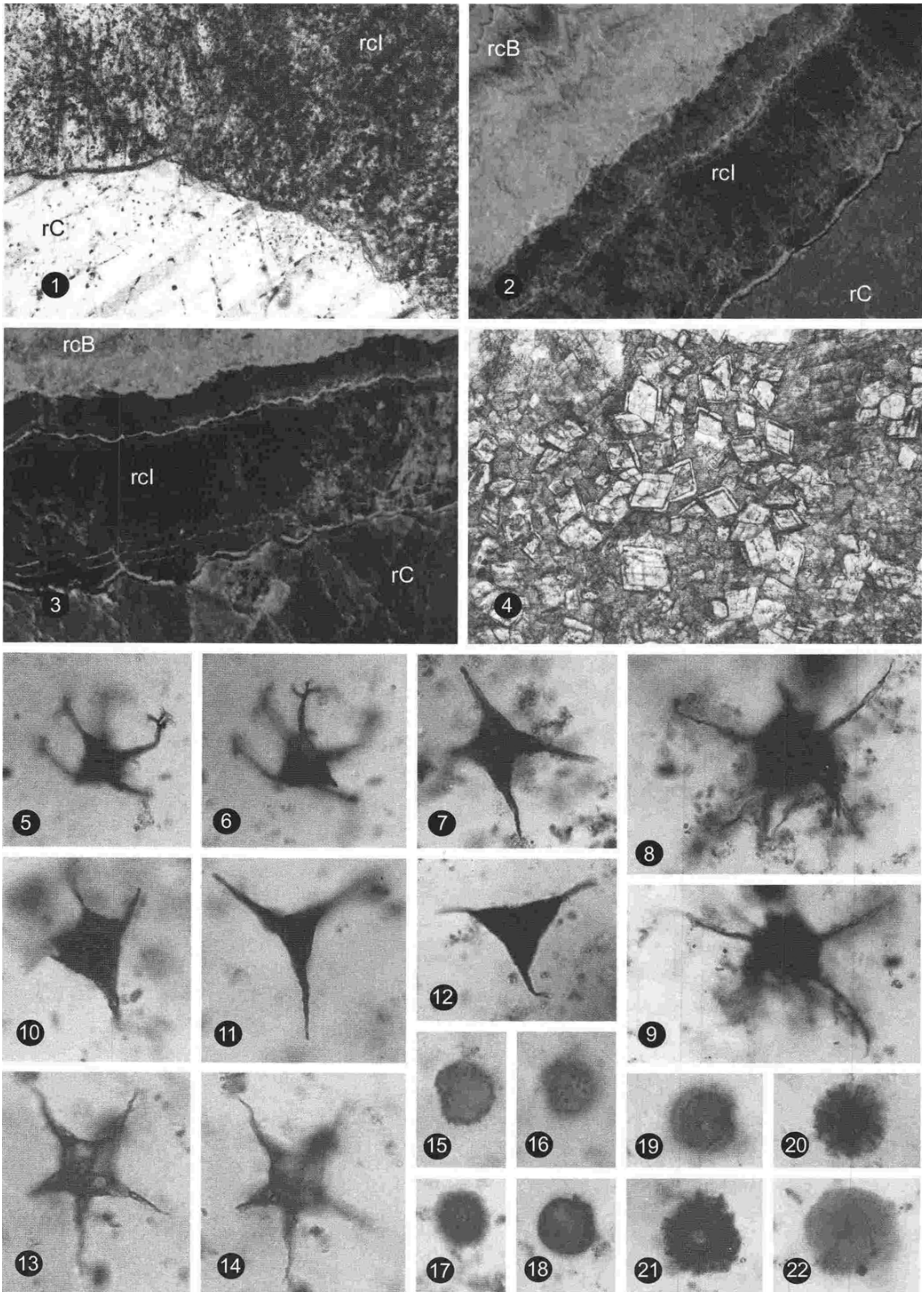
Fig. 18. *Dictyotidium* sp., slide HOS 97/14-9. x 900

Fig. 19. *Cymatiosphaera* sp., slide HOS 97/14-9. x 750

Fig. 20. *Cymatiosphaera pastilla* Hashemi & Playford, slide HOS 97/14-9. x 900

Fig. 21. *Cymatiosphaera* sp., HOS 97/14-5. x 750

Fig. 22. Bacterial colony(?), slide HOS 97/14-9. x 750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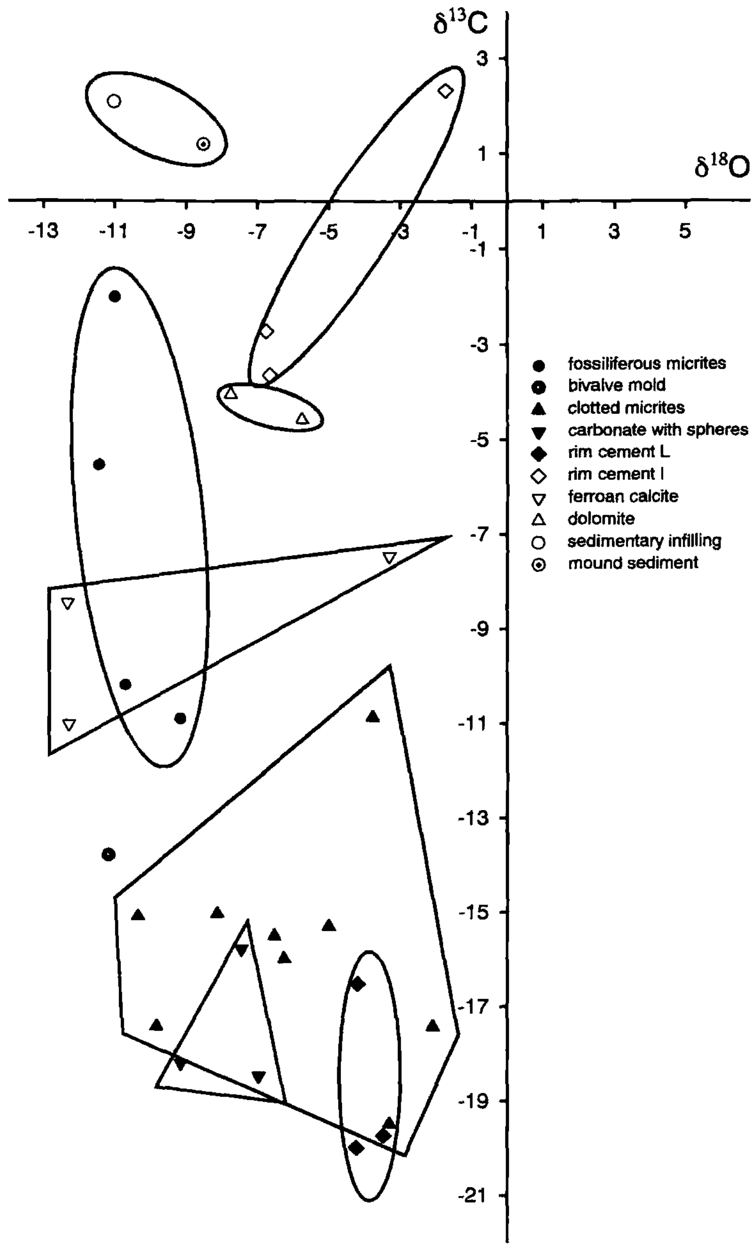

Fig. 5. $\delta^{13}C$ and $\delta^{18}O$ plot of carbonate phases in the Hollard Mound

ing a petroleum composition of the ancient seepage fluids (PECKMANN et al., 1997).

The clotted micrite, the cryptocrystalline carbonate associated with spheres, and the banded rim cement B from the core facies of the Hollard Mound exhibit light $\delta^{13}C$ values, which account for a seepage origin of these carbonate phases. These values are not depleted enough to evidence that the carbonate precipitated exclusively from a methane-rich fluid source. In case of the Kess-Kess mounds, which are also situated at the Hamar Laghdad, BELKA (1998b) suggests a contribution of thermogenic methane derived from the underlying basaltic intrusives. This may be also valid for the Hollard Mound. However, with the present data an evaluation of the hydrocarbon composition of the seepage fluid is not possible due to the uncertainty regarding the extent of mixing with marine bicarbonate.

A trend towards lighter $\delta^{13}C$ values from the fossiliferous micrite to the clotted micrite and the rim cement B is obvious. The fossiliferous micrite had been affected to a lesser extent by hydrocarbon venting than the clotted micrite and the rim cement B. This results in an intermediate stable isotope composition between not affected marine sediments and vent carbonates. Carbonates which have not been affected by the hydrocarbon venting are represented by a sedimentary infilling of carbonate mud within a cavity of the core facies ($\delta^{13}C$: +2.07‰) and by a sample of micritic mound sediment adjacent to the core facies (+1.19‰).

The precipitation of the rim cement I, with its $\delta^{13}C$ composition ranging from +2.32 to -3.64‰, marks the ceasing of the seepage. This abrupt change probably reflects an incomplete record due to an interruption of carbonate precipitation. Ferroan calcite and the dolomites are late diagenetic phases. They document a shift towards lighter $\delta^{13}C$ values due to abiotic reactions like the decarboxylation of the buried organic residues in the zone IV described by IRWIN et al. (1977).

The $\delta^{18}O$ values from the carbonate of the Hollard Mound are exclusively negative and not compatible with precipitation in a normal marine environment as it is indicated by the associated fauna. Based on low $\delta^{18}O$ values, the Lower Devonian Kess-Kess mounds have been interpreted to be related to hydrothermal venting (BELKA, 1998, MOUNJI et al., 1998). This interpretation is supported by REE signatures (BELKA, 1998) and by $^{87}Sr/^{86}Sr$ values (MOUNJI et al., 1998). The $\delta^{18}O$ values of fossiliferous micrite from the core facies of the Hollard Mound are in the range of values obtained from neptunian dike microspar (BELKA, 1998) and microspar and internally sedimented mud from the Kess-Kess mounds (MOUNJI et al., 1998). This may account for a relation to hydrothermal processes involved in the formation of fossiliferous micrite. If the indistinct trend towards heavier values from the fossiliferous micrite to clotted micrite and the rim cement B (mean -10.7 vs. -6.0‰) will be supported by additional data, a decrease of temperature is indicated. This trend towards heavier $\delta^{18}O$ values corresponds with a trend towards lighter $\delta^{13}C$ values which may be explained by a shift from hydrothermal venting to hydrocarbon venting at lower temperatures.

The vent carbonates of the core facies are developed in three modes, as clotted micrite, as cryptocrystalline authigenic carbonate associated with spheres, and as banded cement. Clotted micrites or peloidal micrites have been reported from several ancient and modern vent-related carbonates (BEAUCHAMP & SAVARD, 1992; CAMPBELL et al.,

1993; FRIEDMAN, 1991; ROBERTS & AHARON, 1994). Clotted microfabrics are common in many microbial carbonates like, for example, in thrombolites, which have an internal mesostructure (mesoclots) often formed by submillimeter-size clotted, peloidal microstructures (KENNARD & JAMES, 1986). However, its clotted fabric is a vague criterion to establish a microbial mediation in the precipitation of this carbonate phase from the Hollard Mound. But in addition to the evident microbial oxidation of hydrocarbons ($\delta^{13}C$ values) linked to carbonate precipitation, the clotted fabric may account for the crucial role of bacteria in rock formation.

The origin of the spheres embedded in authigenic vent carbonate is dubious. Considering the vent setting the formation of these microspheres due to escaping fluids offers an attractive explanation. Fluid bubbles in a viscose medium could have attracted organic compounds which were adsorbed to the surface of the bubbles. Self-organization of organic compounds on specific inorganic interfaces, like mineral grains, is a well known process (COLLINS et al., 1995). The arrangement of hollow microspheres in clusters, could be explained by a conglomeration of the coated gas bubbles caused by cohesion.

Banded cement (rim cement B) is the last carbonate phase of the core facies which formed due to hydrocarbon venting. Laminated fabrics are reported from other ancient vent carbonates. Within the Gateway Pass Limestone Bed in Antarctica laminated calcitic cement crusts are present as substrate-parallel layers or as botryoidal linings in cavities (KELLY et al., 1995). CAMPBELL et al. (1993) report on layered cement fabrics in cold seep carbonates in the Jurassic-Cretaceous Great Valley Group in California and CLARI et al. (1994) mention cement fringes in Miocene methane-derived carbonates from the northern Apennines. The banded cement of the Hollard Mound and its radial-fibrous variety formed in voids, which were probably generated by escaping seep fluids. During burial diagenesis these voids were filled by ferroan calcite.

7.2 Ancient hydrocarbon vent-site

Bivalves are the most conspicuous faunal element of the core facies and of the adjacent sediments. The articulated individuals are arranged in clusters similar to the high abundance faunas of modern hydrocarbon-vents (cf. KULM et al., 1986). On the basis of the petrographic characteristics of the core facies deposits and the occurrence of the dense bivalve aggregation analog to Mesozoic, Cenozoic and modern vent populations, we propose that the Devonian bivalves at the Hollard Mound core facies are chemosynthetic counterparts to the post-Palaeozoic vent bivalves. Today, chemosynthesis occurs in different bivalve families (Vesicomyidae, Mytilidae, Solemyidae, Thyasiridae and Lucinidae), indicating that this ability is not restricted to singular taxa. The bivalves of the Hollard Mound are important as they extend the record of inferred chemosymbiosis in bivalves to the Middle Devonian instead of the Late Jurassic (cf. CAMPBELL & BOTTJER, 1995).

An episode of carbonate corrosion is evident from the effect on fossiliferous micrite. Other carbonate phases have not been affected, indicating that this episode occurred prior to the precipitation of hydrocarbon-derived carbonates. H_2S-rich fluids are held responsible for corrosive effects at vent sites (BEAUCHAMP & SAVARD, 1992). The frequent concentration of framboidal pyrite at the truncation surfaces points to this mechanism. This implies that the fluid composition changed from a H_2S-rich early phase to an hydrocarbon-rich, H_2S-poor phase during vent activity.

Stromatactis is a common feature of Palaeozoic mud mounds and some Mesozoic bioherms (BECHSTÄDT, 1974, BATHURST 1980, REITNER, 1986). The Late Cretaceous Tepee Buttes in Colorado, which have been demonstrated to be related to methane venting, exhibit structures similar to Palaeozoic stromatactis (KAUFFMAN et al., 1996). This is, to the best of our knowledge, the only report of stromatactoid pores in ancient hydrocarbon-related carbonates. In case of the Hollard Mound the early cemented fossiliferous micrite of the core facies is crucial for the formation of cavities. The micrite and the early cements within the stromatactoid cavities are vent-related. Sedimentary infillings are derived from a facies unaffected by hydrocarbon venting from the periphery of the ancient vent site and late cements were formed during burial diagenesis. We propose that vent fluids triggered cement formation, which might have been mediated by organic films (lamination). It is supposed that the fluids that moved through the stromatactis pore system controlled the nutrient supply in this cryptic environment.

8 CONCLUSIONS

1. The core facies of the Hollard Mound exhibits signatures of ancient hydrocarbon venting. $\delta^{13}C$ values of carbonates, carbonate phases similar to those reported from other vent sites, and dense clusters of articulated bivalves associated with these carbonate phases account for a vent origin of this facies.
2. The carbonate phases which have been found to be related to hydrocarbon venting are clotted micrite, cryptocrystalline carbonate associated with spheres, and the rim cement B. These vent carbonates show $\delta^{13}C$ values in the range of -11 to -20‰ PDB. At the periphery of the vent site fossiliferous micrite of the surrounding facies has been affected by hydrocarbon venting, which is evident from $\delta^{13}C$ values intermediate between the vent carbonates and the marine signatures of background carbonates. This is valid for both fossiliferous micrites directly adjacent to the vent deposits and for pieces of fossiliferous micrite that are embedded within hydrocarbon derived carbonate phases.
3. Typical features of the vent deposits are carbonate corrosion and stromatactoid pores. The enrichment of framboidal pyrite on the surfaces truncating the fossiliferous micrite indicates that H_2S-rich fluids might have been responsible for carbonate corrosion.

Lithification is an early event, which is evident from stromatactoid pores and the three-dimensional preservation of phytoplankton.

4. One factor that possibly influenced mound growth is the fluid transport through the stromatactis pore systems. In the mature mound the hydrocarbon-dominated fluids were diluted with increasing distance from the localized vent and lost their characteristic isotopic signatures. This explains the facies gradient from a hydrocarbon influenced mound core to the marine dominated periphery of the mud mound.
5. The core facies is a complex system of various neptunian dikes crosscutting the central portion of the mud mound. With increasing distance from the vent a hydrocarbon-dominated environment graded into a normal marine one. The seep-related nutrient flux and hardgrounds attracted sessile biota like filter feeding organisms (auloporid cnidarians) on the periphery of the core facies forming the outer ecological belt of the mud mound.
6. The bivalves of the core facies are arranged in clusters similar to the high abundance faunas of modern hydrocarbon-vents. Their abundance in the otherwise fossil-poor vent deposits accounts for a close relation to the ancient venting. It is likely that the Devonian bivalves were dependent on chemosynthetic pathways for their nourishment similar to the bivalves of modern vents and seeps. A similar preference for vent environments may be suggested for specific prasinophyte assemblages such as recorded here.
7. The onset and the end of the formation of the mud mound and its core facies coincides with major facies changes which are recognized as global events triggered by sea-level changes. This demonstrates the strong interdependence between general environmental conditions and local peculiarities, such as hydrocarbon venting.

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