



The Pobiti Kamani area (Varna, NE Bulgaria) – study of a well-preserved paleo-seep system

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„Побити камъни“ (Варна, СИ България) – изследване на една добре запазена палеометанова изворна система

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Резюме. Атрактивните цилиндрични колони (с височина до 10 m и около метър в диаметър) в природен парк „Побити камъни“ се разкриват сред долноеоценски пясъци и пясъчници (Дикилиташка свита), на около 20 km западно от гр. Варна, Североизточна България. Те са били обект на много геоложки изследвания като основният въпрос е бил начина, по който са формирани. В настоящата статия се дискутират резултатите от няколкогодишно (и все още продължаващо), целенасочено изследване на генезиса на тези калцит-цементирани образувания (конкреции) от гледна точка на връзката им с палеометанови извори. Систематичното картиране на морфологията и 2D-пространственото разпределение на колоните показва, че: а) палеогенският структурен план е играл важна роля, направлявайки миграцията на флуиди към дъното на съществуващия тогава палеобасейн и б) морфологията на различните типове колони се е контролирала от субвертикални миграционни пътища на обогатени с газ флуиди през неконсолидираните седименти, както и от литоложките особености на вместващите скали и латералните разлики на самите извори. Базирайки се на резултатите от детайлни петроложки, геохимични и липид-биомаркерни изследвания на колоните е доказано, че нискомагнезиалната калцитна циментация на пясъците около изходната на издигащите се обогатени с метан флуиди се е осъществила на относително малка дълбочина под морското дъно и е била провокирана от микробиално, анаеробно окисляване на метана.

Ключови думи: метанови извори, автогенни карбонати, геохимия, миграция на флуиди, Еоцен, Варна, СИ България.

Abstract. In the Pobiti Kamani area, up to 10 m high and meter-diameter tubular concretions (so-called columns) are exposed within Lower Eocene sands and sandstones (Dikili Tash Formation) about 20 km west of Varna (NE Bulgaria). These calcite-cemented sandstone concretions have been a subject of many geological studies addressing their formation. In the present contribution a short review is presented as result of a recent (and still ongoing) study about the origin of these structures in relation to past methane seepage. The systematic mapping of the morphology and 2D-spatial distribution of the tubular concretions indicated that: a) the Paleogene structural framework likely played an important role in directing fluid movement to the paleo-seafloor and b) the morphology of different types of tubular concretions was controlled by the subvertical path of ascending gas-bearing fluids through the unconsolidated host sediments as well as by the characteristics of the host lithology and lateral differences in seepage conditions. Based on a detailed petrographical, geochemical and lipid biomarker study, it was furthermore shown that interparticular low-magnesian calcite cementation of the unconsolidated host sediments around the rising methane-bearing fluid plume, occurred at shallow depth below the seafloor and was triggered by the microbial mediated anaerobic oxidation of methane.

Key words: methane seepage, authogenic carbonate, geochemistry, fluid flow, Eocene, Varna, NE Bulgaria.

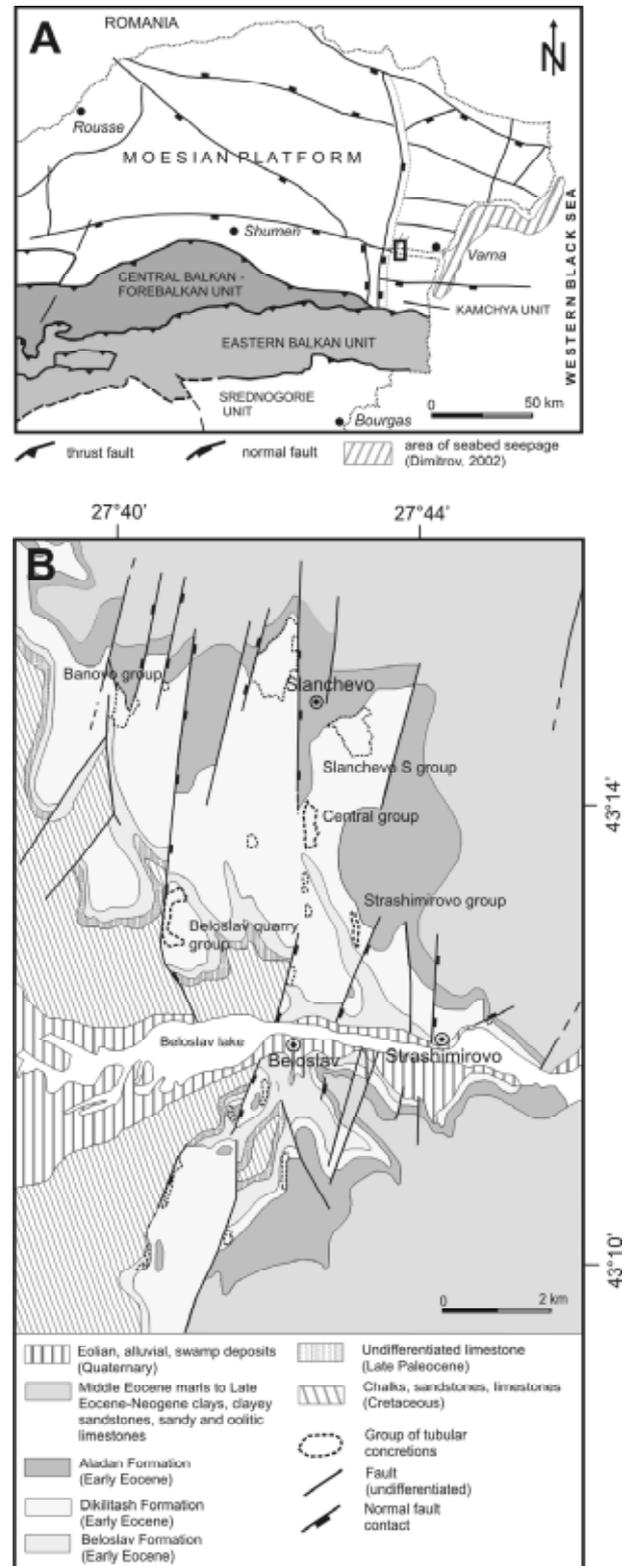
Introduction

The columnar structures of the Pobiti Kamani area, located about 20 km west of Varna (Fig. 1A), have attracted the attention of many scientists since the early 1800's, sparking off various theories for their origin (e.g. Nachev et al., 1986; Iliev et al., 1998; Nachev, Nachev, 2001, and references therein). The mostly cylindrical sandstone "columns", enveloped within the Lower Eocene Dikili Tash Formation (Fig. 2) are often upright standing and can reach heights in outcrop of up to 10 m. They are entirely composed of carbonate-cemented host sands and occur within a 70 km² area around the village of Beloslav (Fig. 1B), often with over 100 individual columnar structures together in different "clusters", jointed into so-called "groups". Theories addressing their origin can be roughly subdivided in non-biogenic models (e.g. "Infiltration theory") and more favored biogenic hypotheses invoking the role of algae (and microbiota) in the column build-up (e.g. the "Algal bioherm model") (Nachev et al., 1986; Nachev, Nachev, 2001).

One of the later models (Botz et al., 1993; Walther, 1994) suggested the key-role of oxidation of hydrocarbon-bearing fluids in carbonate precipitation. This link between methane seepage, and the formation of the carbonate-cemented sandstone columns was recently confirmed by the strongly depleted $\delta^{13}\text{C}$ signatures (as low as -44.5‰ VPDB) of the columnar carbonate cements (De Boever et al., 2006, De Boever et al., in revision). Noteworthy is that similar active methane seepage occurs at present along e.g. the Bulgarian Black Sea shelf (Dimitrov, 2002).

Hydrocarbon seep systems are locations where reducing hydrocarbon-bearing fluids migrate upwards to the seafloor and affect geological, hydrological and (micro)biological processes (Suess et al., 1999; Campbell et al., 2002; Birgel et al., 2006; Bojanowski, 2007). Authigenic carbonate precipitation (calcite, aragonite, dolomite) and the formation of diverse carbonate-cemented structures are well-known phenomena at the seafloor and/or shallow subsurface at these sites. They allow tracing of the fluids involved, as well as the reconstruction of the fluid migration patterns and unraveling the unique geobiological interactions (Ritger et al., 1987; Peckmann et al., 2001; Peckmann, Thiel, 2004).

The aim of this contribution is to present a short review of an ongoing study of the Pobiti Kamani methane seepage-related tubular concretions. At first, controlling factors on the morphology and 2D-spatial distribution of the tubes were investigated (De



Boever et al., in press). Secondly, a detailed study of individual tubes aimed at revealing the process of carbonate cementation based on an integrated petrographical, geochemical and lipid biomarker study (De Boever et al., in revision). This research frames within an overall study that aims at a better understanding of processes and controlling factors on methane-bearing fluid migration and related carbonate diagenesis at different evolution stages of a methane seep system, based on the study of the ancient Pobiti Kamani seep system.

Geological setting

The Pobiti Kamani area is located within the north-eastern Bulgarian part of the Moesian Platform, forming the relatively stable foreland of the Cretaceous-Paleogene Carpatho-Balkan chain (Bokov et al., 1993) (Fig. 1A). The Cretaceous to Neogene sediments in outcrop are subhorizontally bedded. The tubular sandstone concretions are confined to the Lower Eocene (Upper Ypresian) unconsolidated silt- to sand-sized sediments of the Dikili Tash Formation (Aladjova-Khrischeva, 1984) (Fig. 2) and occur over its entire stratigraphic thickness. The poorly to well sorted, rather homogeneous to parallel-bedded sands reflect deposition in the shallow mid to outer ramp zone of an open epicontinental sea along the northern Tethys border. Often poor stratification relates to intense bioturbation. Foraminifera (e.g. nummulites) dominate the bioclast content. The unconsolidated sediments are interbedded with cemented, decimetre to meter-thick subhorizontally elongated sandstone concretions and continuous cemented beds, corresponding to e.g. marine hardgrounds and cemented lag deposits. More distal facies can be found to the south where the ramp rapidly deepened to the Balkan foredeep basin (Aladjova-Hrisceva, 1991; Sinclair et al., 1997). The overlying Aladan limestones prograded southwards over the Dikili Tash sediments marking a distinct and traceable relative sea level lowering (Aladjova-Hrisceva, 1991; Sinclair et al., 1997).

Superimposed Mesozoic-Cenozoic extensional, compressive, transpressive and transtensional tectonic events created and reactivated the deeper block-faulted structure of the Moesian Platform unit. N-S oriented normal faults (with deviation from NNE to NNW) actually predominate the structural pattern of the study area (Fig. 1B), whereas at depth major N-S and E-W-running faults cross-sect each other (Bokov et al., 1978). Tube clusters can both be positioned in the hanging and footwall of the present-day outcropping faults in the study area. The major Alpine tectonic events, culminating in large-scale sinistral transpression during the Middle Eocene (Doglioni et al., 1996; Sinclair et al., 1997; Georgiev et al., 2001) resulted in a N50E to EW left lateral and a N20E to N20W right lateral conjugate strike slip faults and a system of conjugate N10W to N20E trending normal faults in the central-eastern Moe-

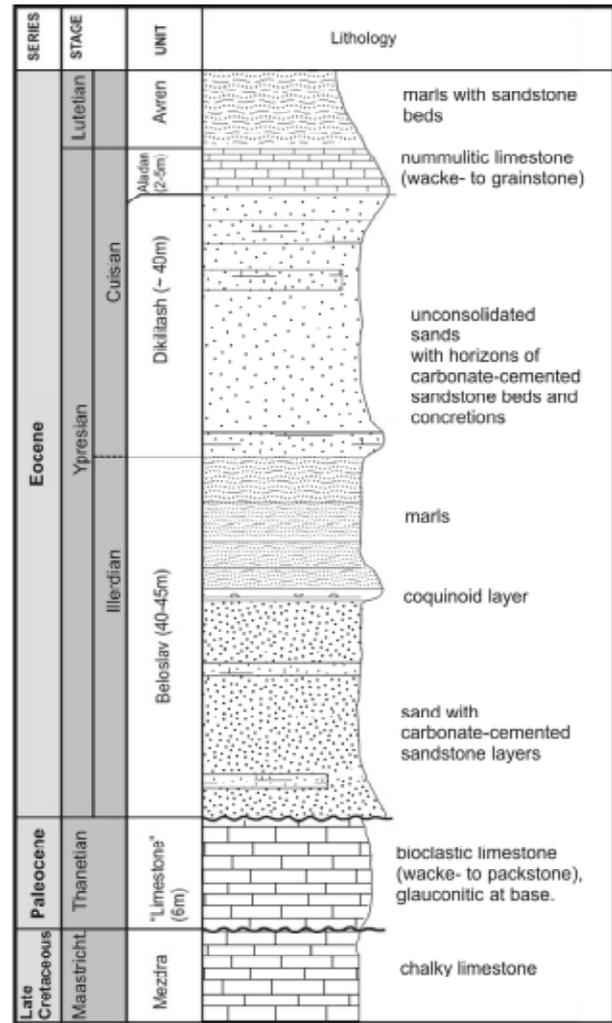


Fig. 2. Stratigraphic column of the study area (modified after Aladjova-Khrischeva, 1984; Sinclair et al., 1997)

Фиг. 2. Обобщена литостратиграфска колонка на изследвания район (модифицирана по Aladjova-Khrischeva, 1984; Sinclair et al., 1997)

sian Platform (Bergerat et al., 1998). The present structural pattern of the study area also reflects at least the latter fault system.

Methodology

Morphology of tubular concretions

A morphological study of the tubular concretions allowed defining four main field-based types (Fig. 3). Two locations, i.e. the Strashimirovo group and Central group (Fig. 1B), were selected for a more detailed and systematic study of the spatial variations in morphology and the 2D-spatial distribution of the tubes. The former Beloslav sand extraction quarry (Fig. 1B) was included

for descriptive purposes because of the exceptional lateral and vertical exposure of tubular concretions within the hanging wall block of a major N–S oriented fault contact.

2D-field mapping and geostatistics

For each individual tube, the longitude-latitude position (N43° – E27°) was documented during a systematic survey by means of a portable GPS (1 ± 0.2 m

precision). Data handling within a Geographical Information System (GIS) allowed investigating whether the distribution of tubular concretions is random or shows a spatial pattern. Details on the analysis procedure are given by De Boever et al. (in press).

Systematic measurements of tube circumferences (m, $\pm 3\%$) (Fig. 3A) in the Strashimirovo and Central group were furthermore used in a geostatistical analysis (see Isaaks, Srivastava, 1989) to investigate the 2D-spatial structure of tube circumferences, based

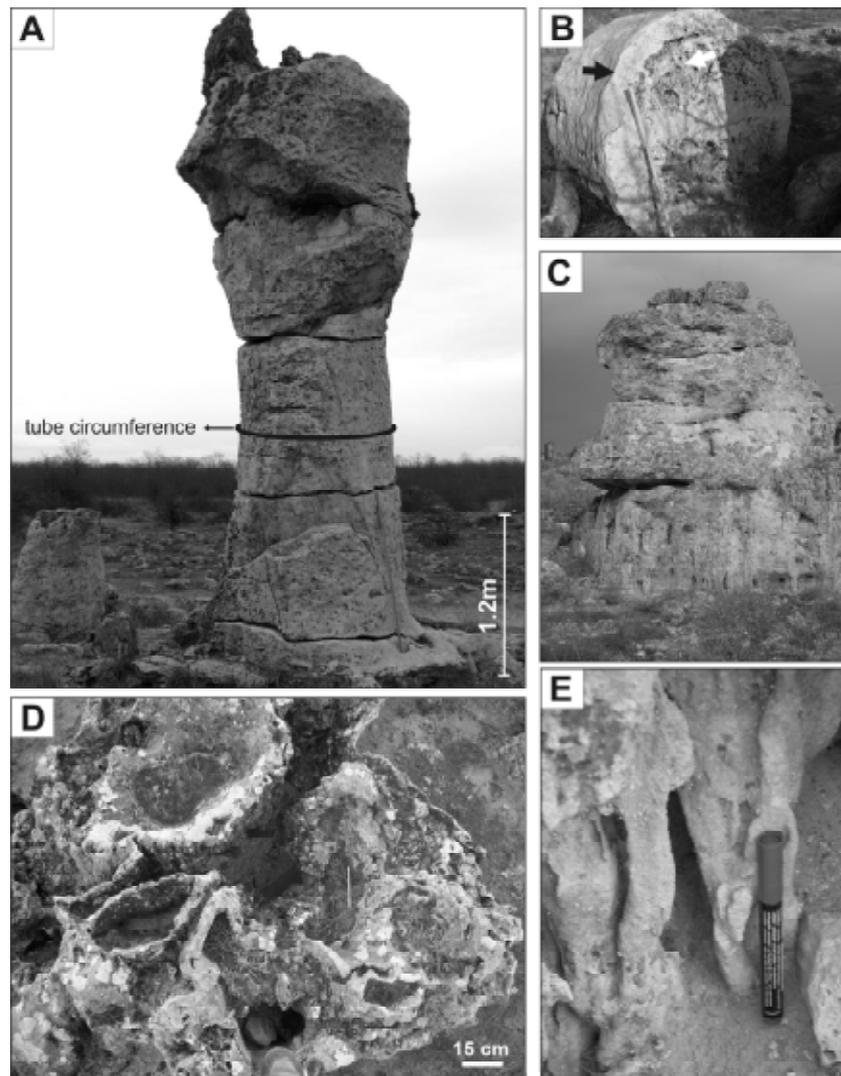


Fig. 3. Four morphological types of tubular concretions

A, cylindrical type 1 tube (Central group); *B*, cross-section of type 1 tubular concretion, black arrow – well-cemented peripheral tube wall, white arrow – partly cemented axial tube conduit (Central group); *C*, bulbous type 2 tube. A central conduit is less clear compared to type 1 tubes. Hammer for scale (Banovo group); *D*, strongly clustered, more irregular shaped type 3 concretions (Slanchevo S group); *E*, strongly clustered, entirely cemented type 4 tubes (Banovo group)

Фиг. 3. Четири основни морфоложки типа на калцит-цементираните образувания

A – цилиндрични колони от тип 1 (Централна група); *B* – разрез на цилиндрична колона от тип 1, с черна стрелка е показана силно цементираната външна стена, с бяла стрелка – частично цементираната стена около вътрешната кухина (Централна група); *C* – гъбообразни ниски колони от тип 2. Централната вътрешна кухина е по-слабо развита отколкото тази при тип 1. Геоложки чук за мащаб (група Баново); *D* – строго групирани ниски колони с неправилни форми – тип 3 (група Слънчево Юг); *E* – строго групирани, изцяло цементиран ниски колони – тип 4 (група Баново)

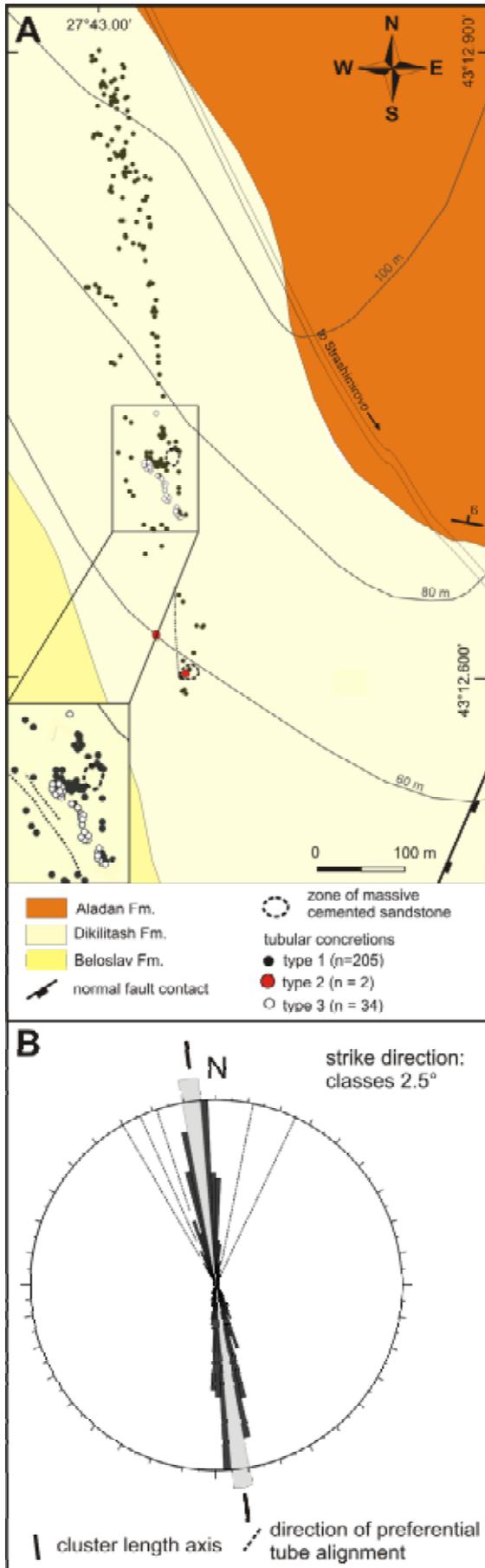


Fig. 4. Strashimirovo group

A, geological map with tube cluster geometry and mapped individual tubular concretions; *B*, rose diagram with the orientations of connection lines between all possible tube pairs ($n = 11460$; tube spacing >24 m; strike accuracy: $\pm 1.6^\circ$). The grey shaded area marks the most prominent directions of tube alignment, which coincide with the tube cluster length axis (modified after De Boever et al., in press).

Фиг. 4. Страшимировска група

A – карта на местоположението на 98% от колоните върху геоложка основа; *B* – роза диаграма на ориентацията на колоните по всички възможни двойки ($n = 11460$; разстояние между двойките >24 m; точност на направленията: $\pm 1,6^\circ$). Зоната в сиво маркира най-значимото направление на ориентация, което напълно съвпада с ориентацията на разкритията (видоизменено по De Boever et al., in press).

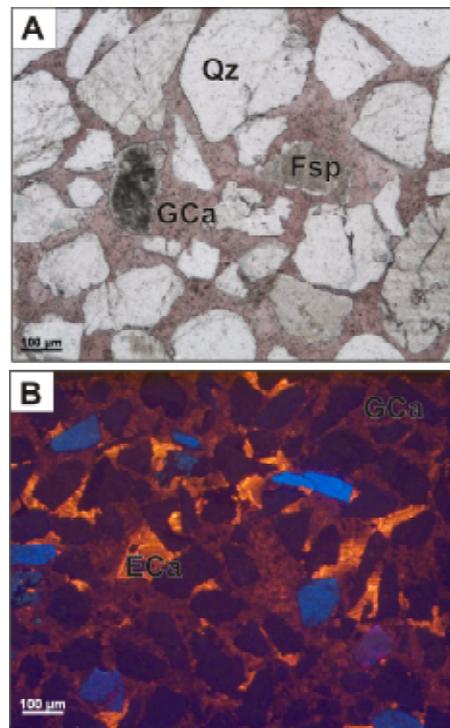


Fig. 5. Microscopic characteristics of the investigated tubular concretions. Qz = quartz grain; Fsp = feldspar grain. *A*, the reddish-stained, interparticular granular calcite (GCa) cement is cloudy. GCa crystals are replacive with respect to the altered feldspar grain and its overgrowth. Plane polarized light, Central group. *B*, cathodoluminescence image of interparticle porosity, cemented by dark brown dull luminescent GCa cement, sometimes with a non luminescent crystal core. Interparticle, euhedral ECa crystals are characterized by alternating dull brown luminescent and brighter orange-yellow zones (Beloslav quarry group).

Фиг. 5. Микроскопска характеристика на калцит-циментираните образувания

Qz – кварц, Fsp – фелдшпат

A – аморфните GCa кристали са оцветени в червено и са репликирани с фелдшпат; *B* – катодолуминисцентен образ на поровото пространство, запълнено от GCa цимент. Евхедралните ECa кристали се характеризират с редуване на матово-кафяви и по-ярки, оранжево-жълти зони (кариера Белослав).

on a three-stage exploratory variogram analysis (De Boever et al., in press). Variogram values are calculated as half of the average squared difference between variable values (circumferences) over the entire studied area, separated by a distance h (m) (lag spacing) (Isaaks, Srivastava, 1989). The presence of a spatial pattern in the distribution of tube circumferences is shown by increasing variogram values with increasing distance between two tubes. This demonstrates that the similarity between the tube circumferences decreases with distance and that closer-spaced tubes tend to have more similar dimensions.

Petrographical and geochemical techniques

Half-stained, epoxy-impregnated thin sections are studied by conventional microscopy, UV fluorescence and cold cathodoluminescence microscopy. Point counting was carried out to quantify the volume percentage of different authigenic and detrital components. A scanning electron microscope (SEM) equipped with an energy dispersive detector (EDX) was used for detailed observations and qualitative chemical analyses. Individual carbonate cement phases were analyzed for their Ca, Mg, Sr, Fe and Mn content by electron probe microanalysis (EPMA). The relative standard deviation is generally <20%. The detection limits (3σ) are 0.05 wt.% for MgO and SrO and 0.10 wt.% for MnO and FeO. Drilled carbonate samples were analyzed for their stable carbon and oxygen isotopic signature at the University of Erlangen (Germany). All values are reported relative to VPDB. Reproducibility is better $\pm 0.06\text{‰}$ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (1σ). For details on the procedures of the different techniques, the reader is referred to De Boever et al. (in revision).

Lipid extraction and analysis

Analysis of lipid biomarkers was done on pooled samples from the Beloslav quarry and Central group (Fig. 1B), containing several hand-drilled plugs. Following sample crushing, a cleaning procedure and subsequent dissolution was applied to extract pristine signatures. An extended description of the methodology can be found in Birgel et al. (2006) and De Boever et al. (in revision). The four separated fractions, i.e. 1) hydrocarbons; 2) ketones/esters; 3) alcohols and 4) carboxylic acids were examined using gas chromatography-mass spectrometry (GC-MS) with a Thermo Electron Trace MS equipped with a 30m RTX-5MS fused silica column. Identification of compounds was based on GC retention times and published mass spectral data. Compound specific carbon isotope analysis (standard deviation <0.4‰ VPDB) was performed with a Hewlett Packard 5890 series II gas chromatograph connected via a Finnigan combustion interface-II to a Finnigan MAT 252 mass spectrometer.

Results and interpretation

Morphology and spatial distribution of tubular concretions

Tubular concretions are well-known products described from different ancient seep systems where they are interpreted as part of the focussed, shallow subsurface plumbing system of past methane seepage (Clari et al., 2004). For this study, the tubular concretions were classified in four main field-based types of which the regular cylindrical type 1 tubes (the so-called “columns”) are the most common (Fig. 3A). They are often characterized by a central uncemented or only partly cemented “conduit” zone, which contrasts with an outer, decimetre-thick, well-cemented peripheral wall (Fig. 3B). Tube circumferences are rather constant along the tube length axes, varying between 0.5 m and 12 m, with the majority being between 2 and 4 m. The tubes are mostly in upright position with their length axes at high angles to the subhorizontal bedding plane (Fig. 3A), indicating their preservation in original position. When visible, the bedding can be traced with minor modifications through the tube-sediment contact. Large and rather bulbous type 2 (Fig. 3C) and densely grouped type 3 (Fig. 3D) tubular concretions are less common, but may occur within the same stratigraphical level as type 1 structures, in contrast to the small, entirely cemented type 4 tubes (Fig. 3E). The latter can often be found below type 1 or type 2 structures.

The orientation of the length axis of seepage-related tubular concretions documents the direction of the focussed, advective fluid flow that passed through it. Carbonate will precipitate around the methane-bearing fluid plume where it meets the marine porewater, becomes oxidized anaerobically, inducing carbonate supersaturation (Kulm, Suess, 1990). It is therefore suggested that the regular, cylindrical morphology of most tubular concretions is primarily the consequence of cementation around the buoyancy-driven, vertically upward directed fluid path of a gas-bearing fluid through the Dikili Tash host sands, which lack significant hydraulic conductivity contrasts over several meters vertical distance. The large, meter-scale dimensions of the tubular concretions, especially of the type 1 tubes likely relates also, at least partly, to the large hydraulic conductivity of the host sediments (Peckmann et al., 2001; Clari et al., 2004). In addition to the characteristics of the host lithology, differences in seepage conditions (e.g. fluid volume, flux) might explain the co-occurrence of different tube types within the same stratigraphic horizon.

Mapping of each individual tubular concretion in the Strashimirovo and Central group shows that clusters of tubular concretions are systematically aligned and elongated along N–S to NNW–SSE directions (Fig. 4A). These directions fall within the range of orientations of post-Paleocene normal and strike-slip faults in the central-eastern Moesian Platform area (Bergerat et al., 1998), strongly suggesting

that the locations of Early Eocene focused fluid migration were controlled by the structural framework. Furthermore, when looking at the scale of a single cluster, tubes occur at distances up to 80 m away from the assumed master fault contact. In addition, tubes are aligned over distances of up to 50 meters along certain directions, which deviate $\leq 36^\circ$ from the assumed fault-parallel cluster length axis (Fig. 4B). Also the geostatistical analysis of the tube circumferences (m) from the most common type 1 tubes underlines this spatial structure. The computed directions of maximal spatial correlation of tube circumferences over distances > 100 m fall within the range of directions of preferential tube alignment. The tube circumference can be considered as a measure of the general dimension of the past fluid plume, suggesting that along these directions, consistent fluid flow could be maintained over a certain distance and time. A model is proposed whereby the spatial distribution of the tubular concretions within a single tube cluster might relate to the complex geometry of deformation structures such as subsidiary faults and fracture sets in the fault damage zones surrounding the master fault. Especially where fault segments interact and link, subsidiary deformation structures can have orientations oblique or at a high angle to the master fault (e.g. Davatzes, Aydin, 2003; Balsamo et al., 2008). These locations have indeed been previously described as sites of preferential hydrocarbon escape to the surface (Peacock, Sanderson, 1994).

Methane-related calcite cementation in tubular concretions

Microscopic observations reveal a subarkosic sandstone, cemented by non-ferrous calcite cements (Fig. 5A). The fabric and sequence of diagenetic phases are similar throughout a single tube and between various tubes from different locations. Altered feldspar grains are locally surrounded by an authigenic K-feldspar overgrowth, which precedes the predominant interparticular dull luminescent granular calcite cement (GCa) (Fig. 5). Bulk stable isotope values of predominantly GCa-cemented tube samples indicate calcite cementation in equilibrium with Lower Eocene seawater at ambient seafloor temperatures ($\delta^{18}\text{O} = -0.5$ to $+0.5\%$ VPDB).

$\delta^{13}\text{C}$ values as low as -44.5% VPDB reveal that the carbon is predominantly methane-derived. Based on studies of modern methane seeps, the $\delta^{13}\text{C}_{\text{methane}}$ value can be up to 40% lower compared to the lowest $\delta^{13}\text{C}_{\text{calcite}}$ value (Peckmann, Thiel, 2004). This would suggest a $\delta^{13}\text{C}_{\text{methane}}$ signature down to -84% , indicating a significant contribution of microbial methane-derived carbon. A linkage of the methane-related tubular concretions to a known hydrocarbon source in the Eastern Bulgarian – Black Sea region based on this information is speculative, but some suggestions can be put forward. In Eastern Bulgaria known source rocks are the more 2.5 km thick the Triassic marine clastics and Lower-Mid-

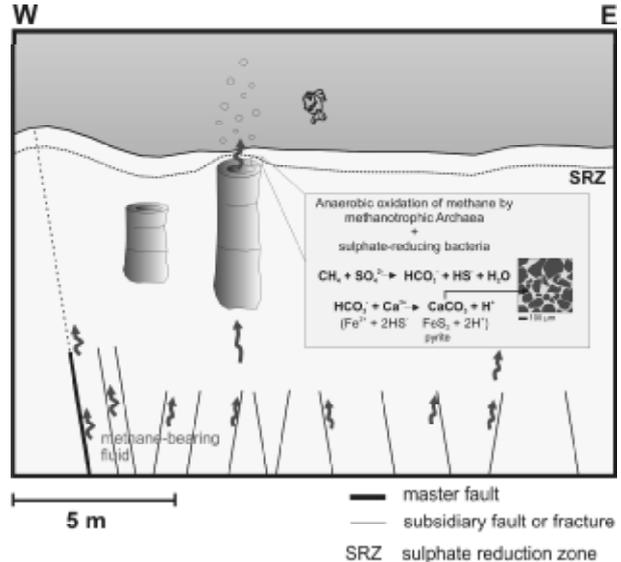


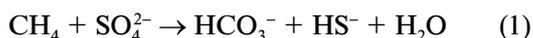
Fig. 6. Conceptual model for the formation of the “Pobiti Kamani” tubular sandstone concretions

Фиг. 6. Концептуален модел на формиране на циментираниите с калцит образувания от Природен парк „Побити камъни“

dle Jurassic turbiditic and black shale lithologies along the southern Moesian Platform margin and buried below the thrust sheets in the Eastern Balkan region, up to 50 km south of the study area (Georgiev, 1996; Tari et al., 1997; Georgiev et al., 2001). Time-equivalent lithologies in the region of Varna have reduced thicknesses (generally < 1 km), consisting of shallower clastic and carbonate lithologies. However, both the Triassic-Upper Jurassic deposits have source rock potential and thermogenic and biogenic gas occurrences along the northern margin of the Kamchia Depression are believed to be sourced by these lithologies.

Strong variations in $\delta^{13}\text{C}$ values (-44.5% up to -8% VPDB) and $\delta^{18}\text{O}$ values (as low as -9% VPDB) for different samples from a single tubular concretion are presumably partly related to recrystallization and cementation by brighter luminescent to cyclic zoned equant cements (ECa) (Fig. 5B) due to the infiltration of meteoric waters through the permeable host sediments and the central tube conduit.

The presence of ^{13}C -depleted archaeal biomarkers, such as arachaeol and hydroxyarchaeol ($\delta^{13}\text{C}$ values down to -111% VPDB), enclosed within the GCa-cemented tubes, indicates the importance of the microbially mediated anaerobic oxidation of methane (AOM) (Hinrichs et al., 1999; Stادنitskaia et al., 2005) (net reaction 1). These archaeal methanotrophs possibly operated in consortium with sulphate reducing bacteria (SRB) but only faint ^{13}C -depleted SRB biomarker signals such as terminally-branched alcohols and dialkylglyceroldiethers ($\delta^{13}\text{C}$ values = -103 to -67% VPDB) (Elvert et al., 2003) could be detected.



The pore fluid alkalinity and dissolved inorganic carbon (DIC) concentration increase, resulting from AOM (net reaction 1), is considered the prime factor driving early diagenetic ^{13}C -depleted calcite precipitation (Ritger et al., 1987) (reaction scheme 2).

Conclusions

A review of the results of an ongoing study on the origin of the “Pobiti Kamani” tubular sandstone concretions near Varna (NE Bulgaria) in relation to processes of methane seepage during the Early Eocene is presented (Fig. 6).

The tubular sandstone concretions document part of the shallow subsurface pathways of past methane seepage. The large dimensions and subvertical, cylindrical shape of the most common tube type primarily reflects the buoyancy-driven, vertical path of an ascending gas-bearing fluid through permeable, mainly unconsolidated sandy host sediments. The tube morphology might also document differences in former seepage conditions. Mapping of > 800 tubular concretions showed the NNW–SSE and NNE–SSW alignment of tubes. This suggests that Paleogene fault and fracture systems played a major role in channelling the fluids. In addition, within a single tube cluster, tubes are preferentially aligned over distances up to 50 m along directions at an angle $\leq 36^\circ$ with respect to the inferred, cluster-parallel fault orientation. Similar directions of alignment are also documented for cylindrical tubes with analogue dimensions. It is hypothesized that this spatial distribution of tubular concretions within tube clusters

reflects the complex geometry of deformation structures in fault damage zones along which the methane fluids were preferentially focussed.

Stable isotope geochemical data show that during the Early Eocene predominantly microbial methane-bearing fluids escaped to the seafloor and provided a ^{13}C -depleted carbon source for pervasive interparticle low-Mg-calcite cementation ($\delta^{13}\text{C}$ as low as -44.5% VPDB) within the Dikilitash sediments, surrounding the ascending fluid plume. The lipid biomarker study demonstrates that methane-related calcite cementation was primarily related to a pore water alkalinity and DIC concentration increase, resulting from the sulphate-dependant anaerobic oxidation of methane. Thus, the results presented here, unequivocally indicate a microbial-mediated process driving calcite precipitation in the sandstone ‘columns’, which is related to the upward migration of deeper-sourced methane-bearing fluids.

Acknowledgements: This research is financed by the Institute for the Promotion of Innovation through Science and Technology in Flanders (IWT). J. Wautier is thanked for his assistance with the EPMA analyses (UCL), Dr. M. Joachimsky (University of Erlangen) for the stable isotope analyses and H. Nijs for preparing the thin sections. Dr. M. Huysmans (K.U.Leuven) is acknowledged for the geostatistical data analyses. We are grateful to Prof. J. Peckmann and Dr. D. Birgel (University of Bremen) and Prof. V. Thiel (University of Göttingen) for the lipid biomarker analyses. Thanks also go to Prof. D. Vangelov and Prof. S. Juranov (“St. Kliment Ohridski” University) for providing background information on the stratigraphic and sedimentological framework. We furthermore wish to thank Mrs. Tumbarkova and Mr. Stilian Markov for their support of this research.

References

- Aladjova-Khrischeva, K. 1984. Stratigraphie des dépôts éocènes aux environs du village Beloslav, département de Varna. – *Rev. Bulg. Geol. Soc.*, 45, 1, 33–44 (in Bulgarian, with French abstract).
- Aladjova-Hrisceva, K. 1991. Stratigraphic subdivision and correlation of Paleogenic deposits in Northeast Bulgaria. – *Geologica Balc.*, 21, 2, 12–38 (in Russian, with English abstract).
- Balsamo, F., F. Storti, B. Piovano, F. Salvini, F. Cifelli, C. Lima. 2008. Time dependent structural architecture of subsidiary fracturing and stress pattern in the tip region of an extensional growth fault system, Tarquinia basin, Italy. – *Tectonophysics*, 454, 54–69.
- Bergerat, F., P. Martin, D. Dimov. 1998. The Moesian Platform as a key for understanding the geodynamical evolution of the Carpatho-Balkan alpine system. – In: Crasquin-Soleau, S., E. Barrier (Eds.). *Peri-Tethys Memoir 3: Stratigraphy and Evolution of Peri-Tethyan platforms*, 29–150.
- Birgel, D., V. Thiel, K. U. Hinrichs, M. Elvert, K. A. Campbell, J. Reitner, J. D. Farmer, J. Peckmann. 2006. Lipid biomarker patterns of methane-seep microbialites from the Mesozoic convergent margin of California. – *Organic Geochem.*, 37, 10, 1289–1302.
- Bojanowski, M. J. 2007. Oligocene cold-seep carbonates from the Carpathians and their inferred relation to gas hydrates. – *Facies*, 53, 3, 347–360.
- Bokov, P., P. Gocev, R. Ognyanov. 1993. Tectonic position, hydrocarbon exploration and future potential of Bulgaria. – *Geologica Balc.*, 23, 3, 3–24.
- Botz, R. W., V. Georgiev, P. Stoffers, K. Khrishev, V. Kostadinov. 1993. Stable isotope study of carbonate-cemented rocks from the Pobitite Kamanie area, north-eastern Bulgaria. – *Geol. Rundschau*, 82, 663–666.
- Campbell, K. A., J. D. Farmer, D. Des Marais. 2002. Ancient hydrocarbon seeps from the Mesozoic convergent margin of California: carbonate geochemistry, fluids and palaeoenvironments. – *Geofluids*, 2, 2, 63–94.
- Cheshitev, G., V. Milanova, N. Popov, E. Kojumdgieva. 1992. *Geological map of Bulgaria. Sheet Varna and Resort Zlatni Pjasaci*. Sofia, Committee mineral and energy resources, Department of geological prospecting and geological mapping.
- Clari, P., S. Cavagna, L. Martire, J. Hunziker. 2004. A Miocene mud volcano and its plumbing system: A chaotic complex revisited (Monferrato, NW Italy). – *J. Sed. Research*, 74, 5, 662–676.

- Davatzes, N. C., A. Aydin. 2003. Overprinting faulting mechanisms in high porosity sandstones of SE Utah. – *J. Structur. Geology*, 25, 1795–1813.
- De Boever, E., R. Swennen, L. Dimitrov. 2006. Lower Eocene carbonate cemented chimneys (Varna, NE Bulgaria): Formation mechanisms and the (a) biological mediation of chimney growth? – *Sed. Geology*, 185, 3–4, 159–173.
- De Boever, E., M. Huysmans, R. Swennen, P. Muchez, L. Dimitrov. Controlling factors on the morphology and spatial distribution of hydrocarbon-related tubular concretions – study of a Lower Eocene seep system. – *Marine and Petroleum Geology*, doi:10.1016/j.marpetgeo.2008.11.004.
- De Boever, E., D. Birgel, V. Thiel, P. Muchez, J. Peckmann, L. Dimitrov, R. Swennen. The formation of giant tubular concretions triggered by anaerobic oxidation of methane as revealed by archaeal molecular fossils (Lower Eocene, Varna, Bulgaria). – *Palaeogeography*, doi:10.1016/j.palaeo.2009.05.010.
- Dimitrov, L. 2002. Contribution to atmospheric methane by natural seepages on the Bulgarian continental shelf. – *Continental Shelf Research*, 22, 2429–2442.
- Dogliani, C., C. Busatta, G. Bolis, L. Marianini, M. Zanella. 1996. Structural evolution of the eastern Balkans (Bulgaria). – *Marine and Petroleum Geology*, 13, 2, 225–251.
- Elvert, M., A. Boetius, K. Knittel, B. B. Jorgensen. 2003. Characterization of specific membrane fatty acids as chemotaxonomic markers for sulfate-reducing bacteria involved in anaerobic oxidation of methane. – *Geomicrobiology J.*, 20, 4, 403–419.
- Georgiev, G. 1996. Overview of the oil and gas exploration and production of Bulgaria. – In: Wessely, G., W. Lieble (Eds.). *Oil and gas in Alpidic thrustbelts and basins of Central and Eastern Europe*. European Association of Petroleum Geologists, 29–33.
- Georgiev, G., Ch. Dabovski, G. Stanisheva-Vassileva. 2001. East Srednogorie-Balkan Rift Zone. – In: Ziegler, P. A., W. Cavazza, A. H. F. Robertson, S. Crasquin-Soleau (Eds.). *Peri-Tethys Memoir 6: Peri-Tethyan Rift/Wrench Basins and Passive Margins*. Mém. Mus. Natn. Hist. Nat., 259–293.
- Hinrichs, K. U., J. M. Hayes, S. P. Sylva, P. G. Brewer, E. F. DeLong. 1999. Methane-consuming archaeobacteria in marine sediments. – *Nature*, 398, 6730, 802–805.
- Iliev, Z., G. Nikolov, K. Kourtev. 1998. “Pobitite kamani” (“Dikili tash”, the upright stone columns), a unique natural and geological phenomenon. – *Geologica Balc.*, 28, 3–4, 87–90.
- Isaaks, E. H., R. M. Srivastava. 1989. *An introduction to applied geostatistics*. New York, Oxford University Press, 561 p.
- Kulm, L. V. D., E. Suess. 1990. Relationship Between Carbonate Deposits and Fluid Venting: Oregon Accretionary Prism. – *J. Geoph. Research*, 95, B6, 8899–8915.
- Nachev, I. K., P. D. Mandev, S. K. Zhelev. 1986. “Pobitite kamani” – algal bioherms. – *Rev. Bulg. Geol. Soc.*, 47, 3, 1–12 (in Bulgarian with English abstract).
- Nachev, I. K., Ch. Nachev. 2001. “Pobitite kamani” – bakteriyalno-vodoraslovi koloni (“Pobitite kamani” – bacterial-algal columns). Sofia, Artik, 110 p. (in Bulgarian, with English summary).
- Peacock, D. C. P., D. J. Sanderson. 1994. Geometry and Development of Relay Ramps in Normal Fault Systems. – *AAPG Bulletin*, 78, 2, 147–165.
- Peckmann, J., A. Reimer, U. Luth, B. T. Hansen, C. Heinicke, J. Hoefs, J. Reitner. 2001. Methane-derived carbonates and authigenic pyrite from the northwestern Black Sea. – *Marine Geology*, 177, 129–150.
- Peckmann, J., V. Thiel. 2004. Carbon cycling at ancient methane-seeps. – *Chem. Geology*, 205, 3–4, 443–467.
- Ritger, S., R. Carson, E. Suess. 1987. Methane-derived authigenic carbonates formed by subduction-induced pore-water expulsion along the Oregon/Washington margin. – *Geol. Soc. Am. Bull.*, 98, 147–156.
- Sinclair, H. D., S. G. Juranov, G. Georgiev, P. Byrne, N. P. Mountney. 1997. The Balkan Thrust Wedge and Foreland Basin of Eastern Bulgaria: Structural and stratigraphic development. – In: Robinson, A. G. (Ed.). *Regional and petroleum geology of the Black Sea and surrounding region*, 91–114.
- Stadnitskaia, A., G. Muyzer, B. Abbas, M. J. L. Coolen, E. C. Hopmans, M. Baas, T. C. E. van Weering, M. K. Ivanov, E. Poludetkina, J. S. Sinninghe Damsté. 2005. Biomarker and 16S rDNA evidence for anaerobic oxidation of methane and related carbonate precipitation in deep-sea mud volcanoes of the Sorokin Trough, Black Sea. – *Marine Geology*, 217, 1–2, 67–96.
- Suess, E., M. E. Torres, G. Bohrmann, R. W. Collier, J. Greinert, P. Linke, G. Rehder, A. Trehu, K. Wallmann, G. Winckler, E. Zuleger. 1999. Gas hydrate destabilization: enhanced dewatering, benthic material turnover and large methane plumes at the Cascadia convergent margin. – *Earth Planet. Sci. Lett.*, 170, 1–15.
- Tari, G., O. Dicea, J. Faulkerson, G. Georgiev, S. Popov, M. Stefanescu, G. Weir. 1997. Cimmerian and Alpine stratigraphy and structural evolution of the Moesian Platform (Romania/Bulgaria). – In: Robinson, A. G. (Ed.). *Regional and petroleum geology of the Black Sea and surrounding region*, 63–90.
- Walther, H. 1994. The Stone Forest near Varna, Bulgaria – Tertiary Rock Pillars of Unknown Origin. – *Z. Angew. Geol.*, 40, 1, 50–55.

(Постъпила на 12.12.2008 г., приета за печат на 24.02.2009 г.)
Отговорен редактор Елена Колева-Рекалова