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Lower Eocene carbonate cemented chimneys (Varna, NE Bulgaria): Formation mechanisms and the (a)biological mediation of chimney growth?

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Abstract

In the area of Pobiti Kamani (Varna, northeast Bulgaria), massive carbonate cemented columns ("chimneys", up to 1.5 m diameter and 8 m high) and horizontal interbeds (≤1.5 m thickness) occur in dispersed outcrops over an area of 70 km^2 within loose Lower Eocene sands. Field observations and petrographical and stable isotope geochemical characterisation of four studied locations reveal a relationship between these structures and processes of ancient hydrocarbon seepage. Column and interbed structures both consist of similar well-sorted silt- to sand-sized nummulitic host sediments, predominantly cemented by early diagenetic, low-magnesium calcite. Filamentous textures, about 10 μm in diameter and 80–650 μm long, are only locally detected within interparticle calcite cement of columns. Column samples from two sites reveal a similar, linear and inverse covariant trend of $\delta^{13}C$–$\delta^{18}O$ values, which was interpreted as a mixing trend between two end member fluid/precipitation conditions, i.e. (1) a methane- and/or higher hydrocarbon-derived carbon member characterised by $\delta^{13}C$ values as low as −43‰ and marine controlled precipitation conditions with $\delta^{18}O$ of -1 ± 0.5‰ V-PDB and (2) a member with less contribution of methane which was mixed most likely with less depleted carbon sources explaining $\delta^{13}C$ values ranging up to −8‰ V-PDB. The corresponding, depleted $\delta^{18}O$ values, with many samples clustering around −8‰ V-PDB, are interpreted in terms of precipitation at elevated temperatures. This suggests the venting system was not a true "cold" seep, sensu stricto. Furthermore, column cross-transects often document an internal pattern consisting of (concentric) zones with distinct isotopic signatures, which vary between the two end members. The mixing and internal pattern of column isotopic data, together with petrographical observations, are qualitatively interpreted as evidence of alternating precipitation conditions, controlled by varying seepage rates of a single fluid source at depth, during build-up of individual chimney pipes near the sediment surface. Based on several field observations, migration of the hydrocarbon-charged fluids in Lower Eocene times was possibly channelled along NE oriented faults. Isotopic signatures of calcite cemented horizontal interbeds, with depleted $\delta^{18}O$ ratios as low as −8.88‰ V-PDB and variable $\delta^{13}C$ (−1‰ to −16‰, mainly around −5‰ to −7‰) suggest that ascending fluids contributed to their cementation or resetted the calcite cement isotopic signature, predominantly during periods of active seepage of warmer fluids. Only few petrographical (and preliminary lipid-biomarker) evidence has been found, pointing to the presence or possibly former activity of microbiota, involved in carbon cycling and calcite precipitation, typical of cold seep settings. This may result from diagenetic alteration of organic components. However, considering

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the processes of chimney formation, a cementation process, governed by the inorganic oxidation of hydrocarbons in which interstitial oxygen is rapidly consumed without bacterial mediation, is considered.

Keywords: Authigenic carbonates; Cold seep; Methane oxidation; Eocene; Varna; Bulgaria

1. Introduction

Within the past decade, an increasing number of submarine locations of hydrocarbon seepage, often associated with characteristic chemosymbiotic invertebrates and carbonate deposits has been identified. Many of them have been intensively studied in order to understand the mechanisms of fluid venting and carbonate cementation. Furthermore, based on typical features defined in modern settings, fossil seep carbonates have been discovered in the geological record (Peckmann et al., 1999, 2002; Clari and Martire, 2000; Campbell et al., 2002; Clari et al., 2004). Studying these fossil records of hydrocarbon seepage can further contribute to our knowledge and understanding of venting processes and carbonate diagenesis at modern and fossil equivalents.

Seep carbonates are a well-known product of cold seeps. It is assumed that upward migrating methane and other gases, often channelled along permeable horizons such as fault planes, are oxidized near the sea floor yielding patchily distributed outcrops of carbonate cemented structures, ranging from small slabs, concretions, doughnut-like structures to large chimneys (Hovland et al., 1987; Ritger et al., 1987; Jensen et al., 1992; Jorgensen, 1992; Sakai et al., 1992; Peckmann et al., 2001; Díaz-del-Río et al., 2003). They form a fossil record of hydrocarbon-rich fluid expulsion and especially the stable isotopic composition of early diagenetic carbonate cements has been intensively studied as a window to the identification of the hydrocarbon source and precipitation conditions (Greinert et al., 2001; Peckmann et al., 2001; Campbell et al., 2002).

The typical low $\delta^{13}C$ signature (down to −80‰ V-PDB) of these deposits is due to the incorporation of methane- and/or higher hydrocarbon-derived carbon. When seepage rates are high enough, fluids can reach the sea floor where they are oxidized in aerobic conditions and may be actively expelled into the water column (Hovland et al., 1987; Aloisi et al., 2000; Peckmann et al., 2001). In the presence of free oxygen, aerobic methanotrophs can thrive on methane and produce CO_2 (Cavagna et al., 1999). When fluid seepage is slower, hydrocarbons are assumed to be effectively oxidized anaerobically within the sediment column by a coupled process of bacterial mediated sulphate reduction and methane oxidation (Hoehler et al., 1994; Aloisi et al., 2000). This coupled process increases levels of alkalinity and dissolved inorganic carbon (DIC) in the pore fluids, in this way favouring carbonate precipitation (Ritger et al., 1987; Aharon, 2000).

Some peculiar petrographic fabrics, such as filamentous textures and micritic cloths, enveloped within the carbonate cements have been interpreted as evidence of such fossil microbial activity in possible relation to seepage of hydrocarbons and/or other gases (Cavagna et al., 1999; Peckmann et al., 2001, 2002). In addition to petrography, molecular and stable isotope analyses have been able to identify the chemolithotrophic bacteria mediating the process of carbonate precipitation at cold seep settings, although the exact biogeochemical pathways are still not fully understood (Hoehler et al., 1994; Thiel et al., 1999; Boetius et al., 2000; Peckmann and Thiel, 2004).

We report here on the carbonate cemented structures of the Pobiti Kamani area, located near Varna (northeast Bulgaria). The area envelops several dispersed outcrops of massive, carbonate cemented vertical columns and horizontal interbeds contrasting with the loose surrounding sandy sediments. Morphological similarities with present-day forming seep-deposits in the northwestern Black Sea (Thiel et al., 2001; Michaelis et al., 2002; Peckmann et al., 2002) and abundant hydrocarbon seepage along the nearby Bulgarian coast (Dimitrov and Dontcheva, 1994; Dimitrov, 2002) have led to the hypothesis of a cold seep-related origin. Only a single preceding study has prudently addressed this hypothesis, based on a limited set of stable isotope data (Botz et al., 1993). However, the structures of the Pobiti Kamani are unique both regarding their good preservation, abundance (locally over 100 columns in a single outcrop) and immense dimensions. We present here newly gathered petrographical and a large set of stable isotope data of column and horizontal interbed structures from four locations which were studied during a first reconnaissance field trip. This study focuses on the processes controlling the formation of these structures and the question on the (micro)biological mediation of carbonate precipitation.