Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Palaeogeography, Palaeoclimatology, Palaeoecology 227 (2005) 31–47
PALAEO
www.elsevier.com/locate/palaeo

Lipid geochemistry of methane-seep-related Black Sea carbonates

Thomas Pape [a], Martin Blumenberg [a], Richard Seifert [a], Victor N. Egorov [b], Sergei B. Gulin [b], Walter Michaelis [a,*]

[a] Institute of Biogeochemistry and Marine Chemistry, University of Hamburg, Bundesstr. 55, 20146 Hamburg, Germany
[b] Institute of Biology of the Southern Seas (IBSS), 2 Nakhimov Av., Ukrainian Academy of Sciences, Sevastopol, UA-99011, Ukraine

Received 14 May 2004; received in revised form 30 November 2004; accepted 11 April 2005

Abstract

Carbonates recovered from anoxic waters between 235 and 1555 m depth in the northwestern Black Sea were analyzed for lipid biomarkers and stable carbon isotopic compositions. In addition, a methane-seep-related microbial mat and a sample of surface sediment recovered from a non-seep site were studied for comparison. High concentrations of strongly ^{13}C-depleted lipids attributed to bacteria and archaea mediating the anaerobic oxidation of methane (AOM) were found in all samples except for the sediment. Differences of the dominant AOM-performing communities between the carbonates indicated by specific lipid patterns appear to be caused by the respective biogeochemical settings. High proportions of ANME-2 consortia are found at sites of assumingly high partial pressures of methane while ANME-1 associations dominate at locations of moderate methane supply. In the sedimentary concretion, a complex mixture of biomarkers for terrestrial and planktonic organisms was found. Different molecular structures along with strong variations in the stable carbon isotopic compositions ($\delta^{13}C = -20.2‰$ to $-94.3‰$) allow for an estimation of the proportions of tetraether-bound biphytanes derived from planktonic *Crenarchaeota* and methanotrophic *Euryarchaeota*. Our data imply that the shape of AOM-derived carbonate precipitates in Black Sea environments is crucially influenced by the respective methane supply. Active AOM-driven chimney-like bioherms, similar to those previously observed on the Ukrainian shelf, might also develop in the deep euxinic zone at 1555 m water depths.

Keywords: Authigenic carbonate; Anaerobic oxidation of methane; Stable carbon isotopes; Black Sea; Methanotrophy

1. Introduction

The anaerobic oxidation of methane (AOM) has been recognized as a key process within anoxic, methane-rich and sulfate-bearing settings (Reeburgh, 1976; Reeburgh et al., 1991; Hoehler et al., 1994; Valentine, 2002). This process is of major relevance

* Corresponding author. Fax: +49 40 42838 6347.
E-mail address: michaelis@geowiss.uni-hamburg.de (W. Michaelis).

0031-0182/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.palaeo.2005.04.030

not only for the contemporary carbon cycle but also within studies concerning the deep biosphere and life on early Earth, for which conditions of low oxygen and high methane concentrations are supposed to be common. With a suggested chemical net reaction of

$$CH_4 + SO_4^{2-} \rightarrow H_2O + HS^- + HCO_3^-$$

AOM results in an increase of alkalinity favoring carbonate precipitation (Reeburgh, 1980; Ritger et al., 1987, see Valentine, 2002 for a review). Carbonates might persist through geological times and organic matter entrapped is protected against diagenetic transformation to a large extent (Peckmann and Thiel, 2004). Hence, carbonates are an excellent archive of information on (sub)recent and especially fossil AOM settings. So far, a considerable number of authigenic carbonates relating to methane seepages covering a time span from Recent to Paleozoic has been reported (Peckmann and Thiel, 2004 and refs. cited therein). To decipher the information offered by the fossil deposits, thorough studies of recent structures built within active AOM environments are needed. Recent AOM-derived authigenic carbonates have been observed e.g., at pelagic hydrocarbon seeps even at water depths of about 2000 m both in the Mediterranean (Aloisi et al., 2000) and in the Black Sea (Stadnitskaia et al., 2002), and at about 4800 m on the Aleutian accretionary margin (Elvert et al., 2000).

Several recent advances indicate that the AOM is driven by at least two phylogenetically distinct archaeal lineages (namely ANME-1 and ANME-2) frequently observed in physical and physiological coupling to sulfate-reducing (proteo)bacteria (SRB) of the *Desulfosarcina*/*Desulfococcus* group (Hinrichs et al., 1999, 2000; Boetius et al., 2000; Orphan et al., 2001, 2002; Hinrichs and Boetius, 2002; Blumenberg et al., 2004). Even though the co-occurrence of both phylotypes is known from several methane-rich habitats, distinct population structures, including a preferred occurrence of a specific ANME group, were found at certain AOM-sites (Hinrichs et al., 1999; Boetius et al., 2000; Orphan et al., 2001, 2002; Michaelis et al., 2002; Teske et al., 2002; Blumenberg et al., 2004; Knittel et al., 2005). Strong depletions in ^{13}C of the bulk biomass and specific archaeal and bacterial lipids (e.g. isoprenoid hydrocarbons, archaeol, *sn*-2-hydroxyarchaeol, glycerol dialkyl glycerol tetraethers, carboxylic acids), due to the incorporation of methane-derived carbon, are commonly observed for AOM-performing consortia (Thiel et al., 1999, 2001; Michaelis et al., 2002).

The Black Sea provides a unique opportunity to study methane-consuming processes in the marine environment and especially AOM. It represents the world's largest anoxic water mass and numerous methane gas seepages distributed over the total water depth range from surface down to below 2000 m were detected by conducting hydroacoustic surveys (Polikarpov et al., 1992; Shnukov et al., 2004). Concentrations of dissolved methane of up to 18 μM are reported (Seifert et al., 2003). Generation and consumption of methane are two of the main microbial processes within the anoxic water column and sediments. Large bioherms (carbonate towers) built by AOM-performing microbial associations have been found to prosper in the anoxic waters, where gas leaks from the sediments (Michaelis et al., 2002); no similar modern structures have been discovered so far anywhere else. With the situation given today, the Black Sea might be the best analogue on-hand to an early oxygen-poor and methane-rich ocean.

Lipid distribution patterns in combination with stable carbon isotopic compositions determined for carbonate precipitates have provided important information on the microbial community structures and on ecological functions of certain microbial groups at contemporary and ancient methane-seeps (Peckmann et al., 1999, 2004; Thiel et al., 1999, 2001, 2003; Pancost et al., 2001b; Aloisi et al., 2002; Michaelis et al., 2002; Blumenberg et al., 2004; Peckmann and Thiel, 2004). We here report on lipid characteristics of a sediment sample, a sedimentary concretion, and carbonate structures, as well as a carbonate appended microbial mat, recovered from seep- and non-seep-related areas west of the Crimean Peninsula. Multiple lipid biomarkers attributed to higher plants, pelagic prokaryotes and eukaryotes, and in particular AOM-performing prokaryotes were recovered in our sample set. The results are discussed, with respect to local depositional settings and the presence of gaseous methane, which apparently influence the morphological development of such carbonate crusts. Thus, variations in lipid inventories preserved in authigenic carbonates allow for a characterization of the methane-