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Palaeogeography, Palaeoclimatology, Palaeoecology 227 (2005) 48–66

PALAEO

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Lipid biomarkers preserved in hydrate-associated authigenic carbonate rocks of the Gulf of Mexico

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Received 10 March 2004; received in revised form 28 July 2004; accepted 11 April 2005

Abstract

Anaerobic oxidation of methane (AOM) is common in ocean-margin sediments, where it is mediated by consortia of Archaea and Bacteria and can result in the formation of authigenic carbonate, including extensive carbonate crusts. Previous work indicates that AOM is associated with Gulf of Mexico hydrocarbon seeps and is mediated by similar organisms as identified in other settings; however, biological investigations have not been done on the associated ^{13}C-depleted carbonates. Here, we show that ^{13}C-depleted archaeal and bacterial biomarkers are abundant in Gulf of Mexico authigenic carbonate rocks, revealing that AOM-mediating organisms are closely associated with carbonate authigenesis. Moreover, the rocks share general characteristics of the background (soft) sedimentary archaeal and bacterial community inferred from biomarker analysis, suggesting that the organisms associated with carbonate authigenesis are the same as those that live elsewhere in the hydrocarbon seep environment. This provides further evidence that AOM by Archaea and sulfate-reducing bacteria can result in the sequestration of significant quantities of methane-derived carbon in carbonate rocks.

Keywords: Anaerobic oxidation of methane; Archaea; Bacteria; Gas hydrates; Diether lipids; Hopanoids; Irregular isoprenoids; Authigenic carbonates

1. Introduction

Gas hydrates are widespread along continental margins of the world's oceans (Henriet and Mienert,

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doi:10.1016/j.palaeo.2005.04.035

1998; Kastner, 2001; Kvenvolden and Lorenson, 2001), including the Gulf of Mexico (Brooks et al., 1986; Roberts and Carney, 1997; Sassen et al., 1998), and are thought to represent approximately 0.25 to 1×10^{19} g of sequestered, but potentially transient, carbon (Kvenvolden and Lorenson, 2001; Milkov et al., 2003). The role of gas hydrates in the global carbon reservoir is of particular importance because they could represent an untapped energy source but are also potential agents of rapid climate change (Dickens et al., 1995; Kennett et al., 2000; Dickens, 2001). Currently, anaerobic oxidation of methane (AOM) consumes about 90% of the methane produced in anoxic marine sediments and plays an important role in controlling methane release into the atmosphere (Reeburgh, 1996). Gas hydrates are abundant in the Gulf of Mexico, perhaps representing ~10–14 trillion cubic meters of mainly methane but also C_2–C_5 hydrocarbon gases (Sassen et al., 2001; Milkov and Sassen, 2001); as these hydrates degrade releasing methane, AOM occurs in Gulf of Mexico sediments (Zhang et al., 2002, 2003) and plays an important role in carbon cycling and the development of biological communities (Sassen et al., 1993; Aharon and Fu, 2000).

As a consequence of AOM, bicarbonate concentrations are very high in pore waters and bottom waters associated with methane seeps, leading to the extensive precipitation of authigenic carbonate in sediment pore spaces and on the seafloor (e.g., Peckmann et al., 1999; Thiel et al., 1999; Greinert et al., 2002; Aloisi et al., 2002). In the Gulf of Mexico, authigenic carbonate rock occurs as extensive pavements, crusts, nodules, and cements. These carbonates increase the seafloor stability (Roberts and Aharon, 1994) and provide favorable surfaces for the development of invertebrate communities in the deep ocean (MacDonald et al., 1989; Nelson and Fisher, 1995; Sassen et al., 1998). Moreover, they are a critical component of carbon cycling at cold seeps as they represent the long-term sequestration of methane-derived carbon.

Until recently, the role of microorganisms in AOM was unclear. However, recent work, combining phylogenetic analyses, lipid biomarker quantification and stable isotopic analysis, indicates that consortia of sulfate-reducing bacteria and Archaea work in syntrophy to mediate the anaerobic oxidation of methane in methane-rich sediments (Boetius et al., 2000; Pancost et al., 2000; Orphan et al., 2001a). We have extended these analyses to Gulf of Mexico sediments; there, lipid biomarker abundances and carbon isotopic compositions (Zhang et al., 2002, 2003), as well as phylogenetic analyses (Lanoi1 et al., 2001; Mills et al., 2003), indicate that AOM is mediated by similar archaeal-bacterial consortia as has been reported elsewhere. However, there has been no comparable work on the authigenic carbonate rocks in the Gulf of Mexico; in fact, there have been relatively few biomarker-based investigations of modern cold seep carbonate crusts and other authigenic carbonates (Elvert et al., 2000, 2001; Thiel et al., 2001; Aloisi et al., 2002; Michaelis et al., 2002; Stadnitskaia et al., 2003). Here, we have determined biomarker distributions and carbon isotopic compositions in five authigenic carbonate rocks associated with Green Canyon, Gulf of Mexico, hydrocarbon seeps. These distributions are compared to nearby sediments and biomarker distributions in Black Sea (Thiel et al., 2001) and Mediterranean mud volcano (Aloisi et al., 2002) carbonates.

2. Material and methods

Samples were collected from the Green Canyon (GC) region of the Gulf of Mexico (Fig. 1) using the Johnson Sea-Link research submersible. The mechanical arm of the submersible was used to sample a slab of authigenic carbonate rock outcropping on the sea floor (at site GC185) and to excavate small carbonate nodules from <0.25 m depth in sediment (all other sites; Fig. 1). Details of sites are provided in Table 1. Gas hydrate occurs at sites GC185, 232, and 234, but is absent near the GC233 brine pool site because dense brines retard gas hydrate crystallization. All sites are associated with hydrocarbon-driven chemosynthetic communities characterized by tube worms that utilize H_2S and mussels with bacterial symbionts within their gill tissues that utilize methane.

2.1. Extraction and fractionation

Carbonate rocks were frozen at −20 °C immediately upon recovery at the sea surface and kept frozen until