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Methane Index: A tetraether archaeal lipid biomarker indicator for detecting the instability of marine gas hydrates

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ABSTRACT

Gas hydrates represent one of the largest pools of readily exchangeable carbon on Earth's surface. Releases of the greenhouse gas methane from hydrates are proposed to be responsible for climate change at numerous events in geological history. Many of these inferred events, however, were based on carbonate carbon isotopes which are susceptible to diagenetic alterations. Here we propose a molecular fossil proxy, i.e., the “Methane Index (MI)”, to detect and document the destabilization and dissociation of marine gas hydrates. MI consists of the relative distribution of glycerol dibiphytanyl glycerol tetraethers (GDGTs), the core membrane lipids of archaea. The rational behind MI is that in hydrate-impacted environments, the pool of archaeal tetraether lipids is dominated by GDGT-1, -2 and -3 due to the large contribution of signals from the methanotrophic archaeal community. Our study in the Gulf of Mexico cold-seep sediments demonstrates a correlation between MI and the compound-specific carbon isotope of GDGTs, which is strong evidence supporting the MI-methane consumption relationship. Preliminary applications of MI in a number of hydrate-impacted and/or methane-rich environments show diagnostic MI values, corroborating the idea that MI may serve as a robust indicator for hydrate dissociation that is useful for studies of global carbon cycling and paleoclimate change.

1. Introduction

In marine sediments, under a delicate balance of temperature and hydrostatic pressure, methane can be stored within rigid cages of water molecules, forming the ice-like crystalline deposits called gas hydrates (Hester and Brewer, 2009; Kvenvolden, 1993). The estimated carbon stored in marine gas hydrate reservoirs is 5000 to 10,000 Gt ($1\ \mathrm{Gt} = 10^{15}$ g) as CH_4, which constitutes the largest pool of readily exchangeable carbon on Earth's surface (Archer, 2007; Hester and Brewer, 2009; Kvenvolden, 1999). Even a small instability in the boundary conditions affecting this reservoir could potentially add a significant amount of methane into the oceans and atmosphere, resulting in profound global carbon cycle perturbations and climate change (Dickens, 2003). For instance, Dickens et al. (1995) suggested the Paleocene–Eocene thermal maximum event might have been a consequence of more than two thousand Gt methane catastrophically released from marine gas hydrates. After this pioneering work, the importance of gas hydrates has been increasingly recognized. For example, the “Clathrate Gun Hypothesis” has been proposed for the millennial-scale climate changes of the late Quaternary, based on the δ^{13}C of foraminiferal shell carbonates (Kennett et al., 2000). However, this study was met with criticism primarily concentrated on the usage of carbonate carbon isotope as an indicator of methane release: vital effects and diagenesis may distort the isotopic signals preserved in marine carbonates (Cannariato and Stott, 2004; Stott et al., 2002). The majority of currently inferred hydrate-dissociation events are either based on carbonate carbon isotopes (e.g. Jiang et al., 2003; Kennett et al., 2000) or conceptual models (e.g. Dickens et al., 1995). More direct evidence for methane-hydrate dissociation events was provided by a few biomarker-based studies that largely focused on aerobic methanotrophs (Hinrichs, 2001; Hinrichs et al., 2003; Ménot and Bard, 2010; Uchida et al., 2004). Since the respective aerobic methanotrophy presumably took place in an oxygenated, methane-laden water column, the respective signals are only preserved in the sedimentary record under exceptional conditions (e.g. those involving rapid sedimentation and/or low oxygen concentrations). Therefore, a more widely applicable, complementary proxy is needed to unambiguously evaluate the stability of gas hydrate reservoirs and to test the relationships between “hydrate-forcing” and climate change in the geological past.

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Up to 90% of the methane produced in marine sediments and waters is being oxidized anaerobically (Barnes and Goldberg, 1976; Reeburgh, 1976; Valentine and Reeburgh, 2000). The anaerobic oxidation of methane (AOM) is mediated by a consortia of methanotrophic archaea (ANME groups) and sulfate-reducing bacteria (Boetius et al., 2000; Hinrichs et al., 1999) through the reaction first proposed by Reeburgh in 1976 (Reeburgh, 1976):

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \quad (1)$$

This implies a close linkage between methane release from gas hydrates and the microorganisms (e.g. archaea) that are directly involved in the consumption of methane.

A large number of methane-metabolizing archaea synthesize glycerol dibiphytanyl glycerol tetraethers (GDGTs) as their core membrane lipids (Gambacorta et al., 1995; Koga et al., 1993; Koga and Nakano, 2008; Rossel et al., 2008). The GDGTs are quite stable and resistant to oxidation or degradation in geological formations (c.f. Kuypers et al., 2001). Therefore, GDGTs preserved in sediments could serve as biomarkers archiving abundant paleo-biology, ecology and environmental information (Brocks and Pearson, 2005; Eglinton and Eglinton, 2008). Gas hydrate and/or methane-rich deep sea environments exhibit distinct GDGT distribution profiles, namely by the predominance of GDGT-1, -2 and -3 (GDGTs with 1–3 cyclopentane rings, respectively), which are contributed by methane-oxidizing archaea associated with the methane hydrates (Blumenberg et al., 2004; Pancost et al., 2001). Analyses of polar lipid distributions in taxonomically-characterized natural archaeal methanotrophic communities suggest that the ubiquitous GDGT-producing ANME-1 clade is a primary player in AOM systems (Rossel et al., 2008). This implies that these compounds could potentially be used as biomarkers for detecting periods of instability of marine gas hydrates.

The Gulf of Mexico (GOM, Fig. 1) represents a unique system for biogeochemical and geomicrobiological studies of gas hydrates because of the wide occurrence of subsurface- and seafloor-breaching gas hydrates and cold seeps, as well as the presence of free gas venting, diverse microbial communities and authigenic carbonate platforms within the ~1.6 million km^2 gulf basin (Sassen et al., 2004; Zhang and Lanoil, 2004). Previous studies of lipids, stable isotopes and molecular biology have shown that the consortia of methanotrophic archaea and sulfate-reducing bacteria mediated-AOM in the GOM (Zhang and Lanoil, 2004). Because of the difficulties in locating and monitoring present-day gas hydrate destabilization and catastrophic release of methane events, we believe that cold-seep environments like the GOM where CH_4 is actively degassing from hydrate dissociation might be the best analogs for ancient hydrate instability, particularly in terms of the microbial community and their lipid profiles.

Here we report new geochemical and lipid biomarker studies in the sediment cores from the Gulf of Mexico and discuss them in the context of previously published results to explore the feasibility of using archaeal lipids as an indicator for the instability of marine gas hydrates in the geological past.

2. Materials and methods

2.1. Site description and sample collection

Sediment core samples were recovered from Mississippi Canyon Block 118 (MC 118), located on the northeastern gulf slope (Fig. 1).

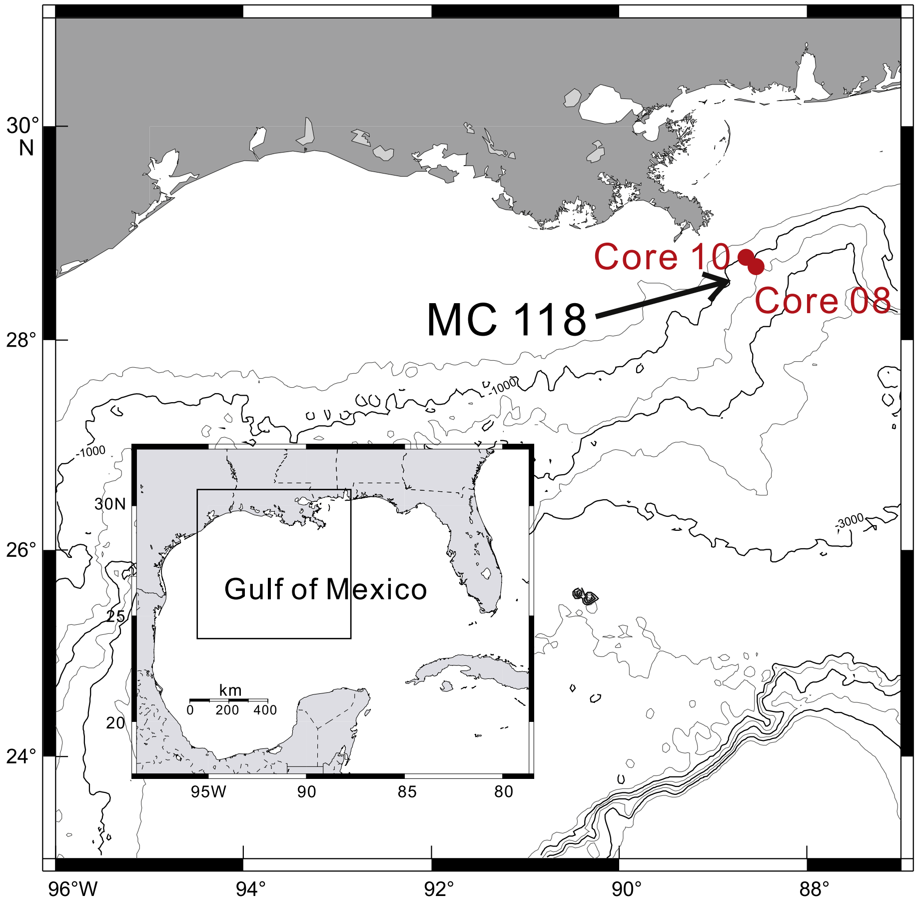

Fig. 1. Map shows the locations of Core 08 and Core 10, as collected from hydrate site MC 118, NE Gulf of Mexico.