



Time integrated variation of sources of fluids and seepage dynamics archived in authigenic carbonates from Gulf of Mexico Gas Hydrate Seafloor Observatory



Dong Feng ^{a,*}, Daniel Birgel ^{b,*}, Jörn Peckmann ^b, Harry H. Roberts ^c, Samantha B. Joye ^d, Roger Sassen ^e, Xiao-Lei Liu ^f, Kai-Uwe Hinrichs ^f, Duofu Chen ^a

^a Key Laboratory of Marginal Sea Geology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China

^b Department of Geodynamics and Sedimentology, Center for Earth Sciences, University of Vienna, 1090 Vienna, Austria

^c Coastal Studies Institute, Department of Oceanography and Coastal Sciences, School of the Coast and Environment, Louisiana State University, Baton Rouge, LA 70803, USA

^d Department of Marine Sciences, University of Georgia, Athens, GA 30602, USA

^e Environmental Research Group, Texas A&M University, College Station, TX 77845, USA

^f Organic Geochemistry Group, MARUM Center for Marine Environmental Sciences & Department of Geosciences, University of Bremen, 28359 Bremen, Germany

ARTICLE INFO

Article history:

Received 28 December 2013

Received in revised form 4 July 2014

Accepted 21 July 2014

Available online 30 July 2014

Editor: Michael E. Böttcher

Keywords:

Authigenic carbonate

Hydrocarbon seep

Gas hydrate

Gulf of Mexico

ABSTRACT

Authigenic carbonate rocks recovered from the Gulf of Mexico Gas Hydrate Seafloor Observatory in Mississippi Canyon block 118 (MC118) at approximately 900 m water depth were studied using mineralogical, bulk geochemical, and lipid biomarker analyses. Carbonate rocks occurred as fractured blocks and nodular masses incorporated in carbonate breccias. The carbonates were comprised mainly of high-Mg-calcite and aragonite. The stable carbon isotope composition ($\delta^{13}\text{C}$) of authigenic carbonate varied from -29.8% to -18.1% vs. V-PDB, suggesting a complex mixture of various carbon sources, including dissolved marine inorganic carbon (DIC), oil, as well as methane. Oxygen isotopes ($\delta^{18}\text{O}$) varied from $+3.4\%$ to $+5.8\%$. The observed ^{18}O -enrichment in relation to calculated equilibrium values in the carbonates probably reflects decomposition of gas hydrates. The most abundant lipid biomarkers in the carbonates were isoprenoidal glycerol dibiphytanyl glycerol tetraethers (GDGTs), predominated by GDGT-2 and GDGT-3, which are typically indicators of anaerobic methane oxidizing archaea (ANMEs). Mono- and bicyclic biphytanes (derived after ether cleavage of GDGT-2 and GDGT-3) showed strong ^{13}C -depletion, which is characteristic for ANMEs. Interestingly, large differences between the $\delta^{13}\text{C}$ values of the archaeal diether archaeol and acyclic biphytane on the one hand and monocyclic biphytane on the other hand suggest the presence of archaea other than ANMEs. Archaeol and GDGT-0 (containing two acyclic biphytane moieties) are commonly assigned to various methanogenic archaea. Where methane seepage activity is intermediate or low within acoustic wipeout zones at the MC118 gas hydrate site nowadays, microbial communities must have coped with changing conditions as well as longer-term fluctuations in oil and gas seepage or the temporary cessation of hydrocarbon flux in the past. The change from methane seepage to oil seepage or vice versa in addition to flux variability apparently favors the establishment of complex prokaryotic communities dominated by archaea. In addition to anaerobic oxidation of methane, local production of methane is apparently prominent at the study site based on the occurrence of biomarkers of methanogens in the authigenic carbonate. This finding adds to the ongoing multidisciplinary effort to better constrain the environment at the MC118 observatory site and to determine the locally dominant biogeochemical processes.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Authigenic carbonate rocks are common at cold hydrocarbon seeps in marine settings worldwide (e.g. Campbell, 2006; Judd and Hovland, 2007). Carbonates in such settings are a product of hydrocarbon oxidation (chiefly methane), which is mediated by consortia of methane-oxidizing archaea and sulfate-reducing bacteria (e.g. Ritger et al.,

1987; Boetius et al., 2000; Joye et al., 2004; Naehr et al., 2009). Such carbonates provide insight into past seepage and associated environmental parameters (Bohrmann et al., 1998; Aloisi et al., 2000; Peckmann et al., 2001; Peckmann and Thiel, 2004; Bayon et al., 2007; Naehr et al., 2007; Bayon et al., 2009; Feng et al., 2009; Campbell et al., 2010; Feng et al., 2010a,b; Haas et al., 2010; Luzinova et al., 2011; Bayon et al., 2013; Crémière et al., 2013).

Numerous recent studies indicated that physical, chemical, and biological characteristics of cold seeps are highly variable in space and time (see Boetius and Wenzhöfer, 2013 and references therein).

* Corresponding authors. Tel.: +86 20 89022336; fax: +86 20 84451672.

E-mail addresses: feng@scsio.ac.cn (D. Feng), daniel.birgel@univie.ac.at (D. Birgel).

Furthermore, environmental change is commonly archived by different mineralogical and geochemical features in authigenic carbonates (e.g. Peckmann and Thiel, 2004; Campbell, 2006; Naehr et al., 2007; Bayon et al., 2009; Feng et al., 2009; Peckmann et al., 2009; Feng et al., 2010a,b; Haas et al., 2010; Birgel et al., 2011; Bayon et al., 2013; Hagemann et al., 2013).

Seep carbonates usually display considerable mineralogical complexity, represented by aragonite, high-Mg-calcite (HMC), low-Mg-calcite (LMC), and dolomite phases (e.g. Naehr et al., 2000; Greinert et al., 2001; Peckmann and Thiel, 2004; Naehr et al., 2007, 2009; Roberts et al., 2010; Feng et al., 2014). Aragonite seems to be favored in high sulfate environments, whereas the formation of HMC – mostly in the form of micrite (i.e. microcrystalline calcite) – preferentially occurs at low sulfate concentrations (Burton, 1993; Savard et al., 1996; Peckmann et al., 2009; Haas et al., 2010).

The $\delta^{13}\text{C}$ values of seep carbonate indicate the sources of carbonate ions that are incorporated in the carbonate mineral lattice (e.g. Roberts and Aharon, 1994; Peckmann and Thiel, 2004). The large variability in $\delta^{13}\text{C}$ values of seep carbonates (from as low as -76% to up to $+26\%$ V-PDB; Campbell, 2006; Naehr et al., 2007), indicates complex carbon sources that include ^{13}C -depleted biogenic and thermogenic methane, crude oil, seawater carbonate, and ^{13}C -enriched residual carbon dioxide from methanogenesis. Anomalously positive $\delta^{18}\text{O}$ values of carbonates from gas hydrate environments are usually interpreted to reflect formation in an environment affected by gas hydrate dissociation (e.g. Böhrmann et al., 1998; Aloisi et al., 2000; Greinert et al., 2001), because ^{18}O is enriched in gas hydrate (Davidson et al., 1983).

The anaerobic oxidation of methane (AOM) at cold seeps is driven by the AOM consortium (e.g. Boetius et al., 2000). In young, immature sediments, the preservation of archaeal membrane lipids, including diether (e.g. archaeol) and tetraether (glycerol dibiphytanyl glycerol tetraethers; GDGTs) lipids, is excellent and their source organisms can be elucidated by comparing lipid profiles with 16S rRNA data (e.g. Hinrichs et al., 1999; Niemann et al., 2006). Some of the molecular fossils (i.e. lipid biomarkers) of AOM-performing prokaryotes have a high preservation potential in seep carbonates, such as biphytanes and other isoprenoid hydrocarbons (Birgel et al., 2008b). The activity and abundance of methane-oxidizing archaea in seep environments are mirrored by their biomarker distributions and compound-specific carbon isotope signatures (e.g. Niemann and Elvert, 2008). Whether seep environments are dominated by ANME-1 or ANME-2 – two groups of ANME adapted to different conditions – can commonly be assigned by the biomarker inventory even when no other information is available (Niemann and Elvert, 2008). Rather than preserving microbial biosignatures at one spot at a single point in time, biomarker patterns preserved in seep carbonates integrate over longer time periods, but are excellent tools to record the key players involved in biogeochemical processes that imprinted seep sites (Peckmann and Thiel, 2004; Gontharet et al., 2009; Birgel et al., 2011).

The Gulf of Mexico (GOM) Mississippi Canyon block 118 (MC118) gas hydrate and cold seep site has been designated as the first National Gas Hydrate Seafloor Observatory, where gas hydrate dynamics are monitored (e.g. McGee, 2006; Lapham et al., 2008; Ingram et al., 2010). The physical and biogeochemical processes associated with gas hydrates and cold seep systems are increasingly understood (e.g. Macelloni et al., 2013; Simonetti et al., 2013; Wilson et al., 2014), but little is known about how biogeochemical processes other than AOM impact carbonate formation. Seep carbonates represent an archive that can provide insight into the long-term dynamics of these processes, integrating the key biogeochemical processes over time. Here, we investigate authigenic carbonate rocks retrieved from the seafloor and the shallow subsurface at hydrocarbon seeps of the MC118 gas hydrate site, GOM. Petrography, mineralogy, stable isotope, and biomarker analyses of authigenic carbonates were applied to constrain the long-term environmental conditions under which carbonate formation occurred. The resulting data are used to constrain environmental conditions and

to identify the dominant biogeochemical processes at the time of carbonate formation.

2. Site characteristics

The MC118 (Fig. 1) gas hydrate site is located on the eastern side of Mississippi Canyon along the continental slope of the northern GOM. It is home to a seafloor observatory where gas hydrate dynamics are monitored (McGee, 2006; Lapham et al., 2008; Macelloni et al., 2013). The site was discovered during dives of the Johnson Sea Link (JSL) research submersible in 2002 (dives 4414 and 4415). Water depth at the site is approximately 900 m and the bottom water temperature is typically around $6\text{ }^{\circ}\text{C}$. The geologic setting of this site has been described in detail by Sassen et al. (2006) and McGee et al. (2008, 2009a,b). Briefly, hydrocarbon gases and oil seep to the seafloor via fault migration-conduits derived from an isolated salt body some hundreds of meters beneath the seafloor. Seep gas rapidly crystallizes as massive fracture-fillings of gas hydrate at the seafloor. Living and dead clams are common around the hydrate mounds but tubeworms are rare. Mussels are abundant especially in areas associated with active gas seepage.

3. Materials and methods

The carbonate samples analyzed in this study were collected during dives with the deep submergence vessel (DSV) JSL (in 2002) and with the DSV Alvin and remotely operating vehicle (ROV) Jason (in 2010; Fig. 1 and Table 1). Samples were obtained from the seafloor and the shallow subsurface, and some of the samples were closely associated with outcropping gas hydrates (Fig. 2). Seafloor observations indicate various seafloor morphologies of seep carbonates at MC118 (Fig. 2), including carbonate crusts, pavements, mound-like buildups, large carbonate slabs associated with chemosynthesis-based communities and outcropping gas hydrate (cf. Macelloni et al., 2013). Carbonate crusts are generally less than 20 cm in diameter and were scattered on the seafloor (Fig. 2A). Carbonate pavements as large as half a meter in diameter were commonly colonized by corals and crabs (Fig. 2B). Large carbonate slabs more than 1 m in diameter were found to be settled by chemosynthesis-based communities and associated with outcropping gas hydrates (Fig. 2C). Carbonate samples were obtained from isolated blocks, mound-like buildups, pavements on the seafloor and nodules in the subsurface sediment ($<50\text{ cm}$). Samples JSL-4414-3 and JSL-4415-1 were in contact with gas hydrates at the time of sampling while the other nine samples were not (Table 1). Macroscopic textures of the block and outcrop samples were characterized by large irregular intraclasts, representing composite aggregates cemented by micrite, and bioclasts (Fig. 3). Bioclasts consisted predominantly of broken bivalve shells up to several cm in length. Much of the carbonate rock is intensively brecciated. Nodules retrieved from subsurface sediments are homogenous, characterized by smooth surfaces, and up to approximately 2 cm in diameter (Fig. 3B).

Semiquantitative mineralogy of the bulk samples was determined by X-ray diffraction (XRD; Rigaku DXR 3000) at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG, CAS). Sample preparation and measurements were described by Roberts et al. (2010). Calcite with less than 5 mol% MgCO_3 is considered as low-Mg-calcite (LMC), whereas calcite with 5–20 mol% MgCO_3 is referred to as high-Mg-calcite (HMC) after Burton and Walter (1991). Carbonate phases with 30–40 mol% MgCO_3 are classified as protodolomite, and carbonates containing 40–55 mol% MgCO_3 are referred to as dolomite (Naehr et al., 2007). Carbonate contents [expressed as weight percent (wt.%) CaCO_3] of the samples were determined by comparing sample weight before and after removing the volatile CaCO_3 fraction using 5% HNO_3 . Petrographic observations of thin sections were made with an optical microscope.

Samples for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ analyses were taken from the surfaces of polished slabs using a microdrill. The CO_2 was analyzed by reacting

Download English Version:

<https://daneshyari.com/en/article/4698718>

Download Persian Version:

<https://daneshyari.com/article/4698718>

[Daneshyari.com](https://daneshyari.com)