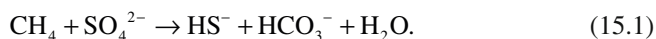


Chapter 15

Synergistic Roles of Microorganisms in Mineral Precipitates Associated with Deep Sea Methane Seeps

Huifang Xu

The discovery of huge deep sea methane reservoirs in the form of ice-like solid crystals of methane clathrate hydrates (methane hydrates or gas hydrate for short) and carbonate deposits at the Hydrate Ridge in the Cascadia subduction zone (Suess et al. 1985) has stimulated global exploration and extensive studies of cold methane seeps and vents associated with the hydrate deposits (Paull and Dillon 2001; Trehu et al. 2004). Many deep sea methane hydrate deposits have been discovered around the world, for instance, in the Gulf of Mexico (Pohlman et al. 2008; Sassen et al. 1998, 2004), Monterey Bay of California (Gieskes et al. 2005; Lorenson et al. 2002; Stakes et al. 1999), Black Sea (Peckmann et al. 2001), Sea of Okhotsk, Eastern Siberia (Greinert and Derkachev 2004), the Gulf of Cadiz (Stadnitskaia et al. 2008), the Kuroshima Knoll of southern part of the Ryukyu Arc (Takeuchi et al. 2007), and South China Sea (Han et al. 2008; Lu 2007). It has been estimated that there are about 1,000 ~24,000 Gt of carbon in global methane hydrate zones (Dickens et al. 1997; Harvey and Huang 1995; Kvenvolden 1988; MacDonald 1990; Makogon and Makogon 1997). Methane hydrates have the potential to be a future energy source however methane is also a greenhouse gas. The release of methane from the methane hydrate can have a profound effect on the global climate (Kvenvolden 1998). In geological record, the rapid global temperature change at the Paleocene-Eocene boundary at ~55 millions of years ago, the Paleocene-Eocene Thermal Maximum (PETM), may be related to catastrophic methane release from sea sediments (Dickens et al. 1995; Katz et al. 2001; Zachos et al. 2005). At the interface between uprising methane from dissociation of methane hydrate and sulfate from sea water, a distinct microbial consortium mediates anaerobic oxidation of methane (AOM) through a net reaction of



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The interaction results in a unique microbial ecosystem associated with AOM in deep sea environments (Jørgensen and Boetius 2007). The methane-fueled microbial communities in anoxic sediments above methane hydrates have the highest biomass in known marine ecosystems (Boetius et al. 2000; Michaelis et al. 2002). The interactions among pore fluids, ambient sediments and the metabolic products from coexisting syntrophic microorganisms result in distinctive mineral precipitations and mineral assemblages with Fe-sulfides, graphitic carbon, and variety of carbonate minerals.

In many cold methane seep and vent sites, chemosynthetic communities that derive energy from H_2S and methane oxidation have developed at the sea floor (Fig. 15.1) (Levin et al. 2000; Sassen et al. 1998; Treude et al. 2003). *Beggiatoa* spp, hydrogen sulfide-oxidizing organisms of tube worms, methane-utilizing clams (*Calyptogena*) and bivalves (*Acharax*) are distributed in the seep and vent sites according to the fluxes of up-rising hydrogen sulfide and methane (Bohrmann et al. 2002; Treude et al. 2003). The bacteria mats of *Beggiatoa* are associated with high uprising hydrogen sulfide and methane areas at the sea floor.

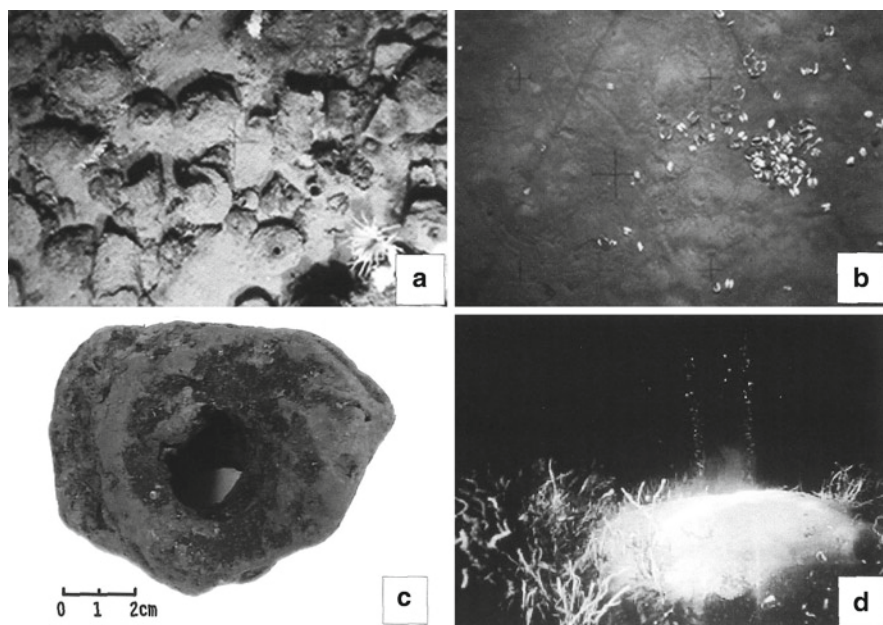


Fig. 15.1 (a) A photo showing carbonate deposit and carbonate chimneys at a seep site in the South China Sea. (b) A photo showing bio-mats of *Beggiatoa* (slightly yellowish) and bivalves on a carbonate deposit at a seep site in the South China Sea. (c) Hand specimen of a carbonate chimney (Lu 2007, used by permission). (d) A photo showing a typical methane hydrate mound (~2 m across) at the Bush Hill site with vents and a nearby chemosynthetic community of tube worms and *Beggiatoa* covering the mound (Sassen et al. 1998, used by permission)

Methane Production and Methane Hydrate Formation

There are three distinct processes that produce methane: biogenic through methanogenesis, thermogenic (thermal cracking at high temperature), and geothermal (or, abiotic) through serpentinization of Fe-bearing olivine. The methane-dominated gases produced through these three methane production processes have different isotopic signatures and chemical compositions. The source of the methane or methane production process can be determined using the ratio of methane to the sum of ethane and propane [$C_1/(C_2 + C_3)$] and carbon isotopic fractionation. The carbon fractionation is measured with respect to the standard Pee Dee Belemnite (PDB). The ratio difference ($\delta^{13}C$) of ^{13}C and ^{12}C is defined by:

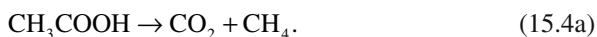
$$\delta^{13}C = [(^{13}C / ^{12}C)_{\text{Sample}} / (^{13}C / ^{12}C)_{\text{PDB}} - 1] \times 1000. \quad (15.2)$$

The factor 1,000 yields results expressed in thousandths, or *per mil* (‰), not %.

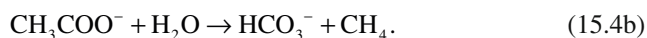
In similar way, the ratio (δD) of D (deuterium, 2H) and 1H in methane, and the ratio ($\delta^{18}O$) of ^{18}O and ^{16}O in carbonate can be obtained relative to their standards of standard mean ocean water (SMOW), or Vienna standard mean ocean water (VSMOW). Two diagrams in Fig. 15.2 illustrate the regions for different methane sources.

Biogenic Methane Production through Methanogenesis

Methanogenesis is the final step in the anaerobic degradation of organic carbon (Megonigal et al. 2003). Methanogens use H_2 and acetate generated by fermenting bacteria to produce methane through the following reactions:



or,



It is reported that 45% of all H_2 -consuming (hydrogenotrophic) methanogens can substitute formate for H_2 in the reaction (15.3) (Garcia et al. 2000). The reaction (15.4) is known as acetate fermentation or acetoclastic methanogenesis and is restricted to two genera of *Methanosarcina* and *Methanosaeta* (formally *Methanotherix*) (Megonigal et al. 2003).

The reaction (15.3) is for H_2 -consuming (or H_2 -scavenging) methanogens, and the reaction (15.4) is for acetate-utilizing methanogens. The reaction (15.4) will result in carbon isotope fractionation between CO_2 and CH_4 . The CO_2 generated in

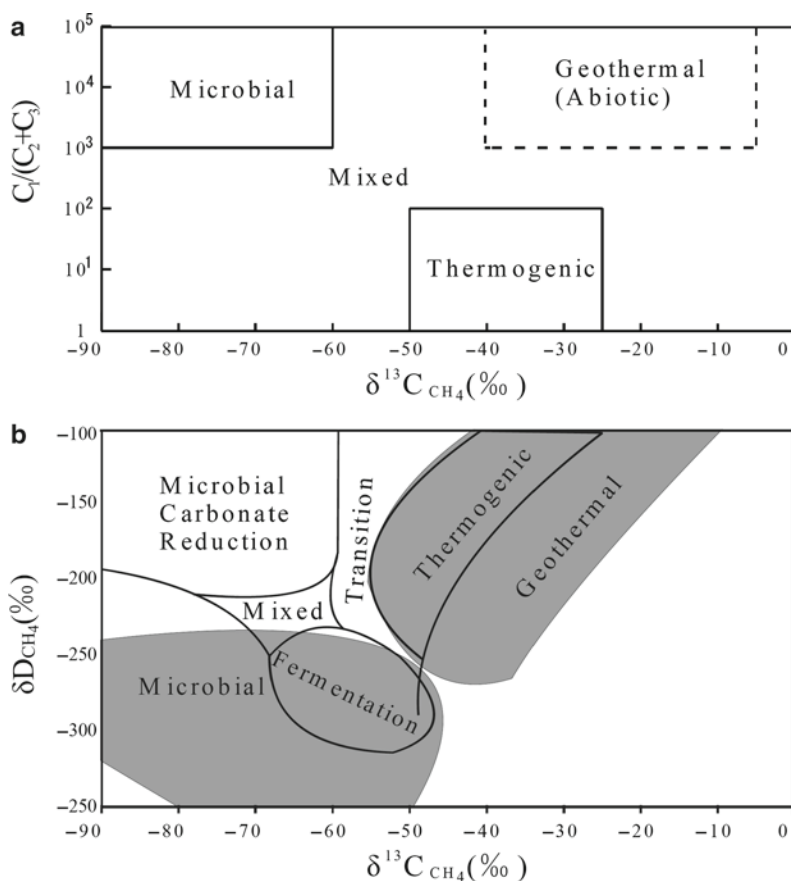
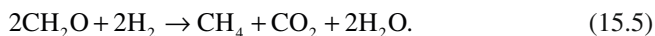


Fig. 15.2 (a) A plot of composition of C_1 (methane) and $C_1/(C_2 + C_3)$ ratio to distinguish biogenic, thermogenic, and geothermal (abiotic) methane. Modified from Claypool and Kvenvolden (Claypool and Kvenvolden 1983). (b): A plot of hydrogen and carbon isotopes to distinguish biogenic, thermogenic, and geothermal (abiotic) methane (Modified from Whitaker 1994; Lorenson et al. 2002)

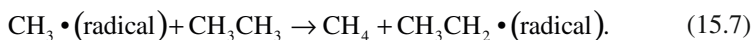
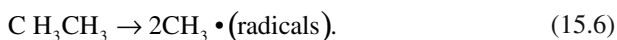
pore fluids will be enriched in ^{13}C , whereas the methane will be depleted in ^{13}C . Thus carbonate minerals formed in such kinds of environments will have high $\delta^{13}C$ values (Greinert et al. 2001; Mazzullo 2000). Consumption of H_2 by H_2 -scavenging methanogens promotes fermentation reactions with H_2 as part of the reaction products (Bryant et al. 1967). The two metabolically different types of micro-organisms (syntrophs) cooperate together and form a mutually dependent consortium and unique ecosystem. Because the fermenting bacteria and methanogens are in a symbiotic relationship, a general net reaction for decomposing bio-organics into methane may be written as:



Thermogenic Methane Production

Thermogenic degradation of pre-existing or buried organics releases CH₄ and other hydrocarbons when microbes are no longer active at high temperatures (T > 80°C). For instance, significant thermogenic gas vents and seeps into the water column occur at the Bush Hill site in the Gulf of Mexico (Sassen et al. 1998). This site is characterized by gas hydrate mounds that outcrop on the seafloor.

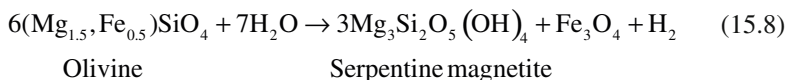
The thermogenic process is basically a thermal cracking of organics and oils breaking larger molecules into smaller ones. For instance, methane can be generated by breaking of C–C bond in ethane and through reactions of:



Thermogenic methane forms at a deeper depth relative to the biogenic methane produced through methanogenesis. Thermogenic methane-dominated gas generally contains a small amount of wet gas components ethane, propane and C₄₊-hydrocarbons, whereas the biogenic methane gas is very dry and pure and is dominated by methane. Both chemical and isotopic compositions can be used to differentiate between these processes (Fig. 15.2). The uprising thermogenic methane through faults can directly contribute to deep sea methane seeps and vents (Greiner et al. 2001; Sassen et al. 2004).

Geothermal Methane Production Through Serpentinization of Ultramafic Rocks

Both hydrogen and methane enriched fluids were observed in mid-ocean ridge hydrothermal systems and nearby the ridge systems (e.g., the recently discovered Lost City hydrothermal vent system) (Kelley et al. 2001, 2005). Circulation of ocean waters through the hydrothermal system results in a redox reaction between water and Fe (II) in olivine in an oxygen free environment which produces magnetite and hydrogen (Charlou et al. 1998). Although real olivine contains about 20 mole% of the fayalite component, and serpentine may contain small amount of Fe (II), the redox reaction at high temperatures can be simplified as (Reeburgh 2007):



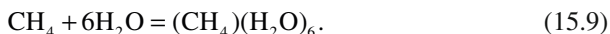
The hydrogen gas produced will react with dissolved carbon dioxide to form methane through the Fischer – Tropsch reaction in the presence of metal oxides and metal as catalysts through reaction (15.3).

This type of methane will have higher $\delta^{13}\text{C}$ values due to its carbon source from dissolved inorganic carbon in ocean water. The $\delta^{13}\text{C}$ values range from -8.8 to -13.6 in the Lost City fluids (Keir et al. 2005).

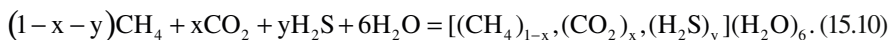
In low temperature hydrothermal systems like diffuse seeps away from mid-ocean ridges (German and Von Damm 2004), the dissolved hydrogen may also be used by methanogens to produce methane through the reaction (15.3). In the Lost City hydrothermal filed ecosystem, 16S rRNA gene sequence corresponding to the *Methanosarcinales* phylotype were found in high temperature chimneys, while a phylotype of anaerobic methanotrophic Archaea (ANME-1) was restricted to low-temperature, less vigorously venting sites (Brazelton et al. 2006). This type of methane is not important in the methane seeps, but it could be very important in the early anoxic Earth ~2 billion years ago.

Methane Hydrate Formation and Dissociation

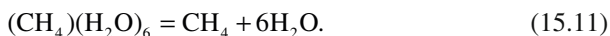
Both thermogenic and methanogenic methane gas are the main sources of the deep sea methane hydrate. Based on the methane hydrate phase diagram, at low temperature ($<4^\circ\text{C}$) and elevated pressure (>60 bar, or more than 600 m below sea level), methane and water or pore fluids form ice-like solid phases of methane clathrate hydrate, or methane hydrate $(\text{CH}_4)(\text{H}_2\text{O})_6$ in sediments (Kvenvolden 1988; Sloan 1998).



The oxygen isotope fractionation of reaction (15.9) will result in heavy oxygen in the solid methane hydrate with respect to sea-water and pore fluid. There are two major types of gas hydrate phases (structure I and structure II) with methane in large cage sites (Jeffrey and McMullan 1967). Neutral molecules of CO_2 , H_2S and ethane may also occupy the methane site in the structure of the methane hydrate crystals. The solid methane hydrate crystals in sea sediments can also serve a stable source for methane and carbon dioxide.



When temperature increases and/or overlying pressure decreases due to local structure change (faults, slide, and turbidite cuts), or large scale tectonic, climate changes, the solid methane hydrate becomes thermodynamically unstable and dissociates into water and methane. The process could be slow and gentle, or rapid and even catastrophic.



The methane generated through the slow dissociation process results in methane seeps and vents. In an ambient air environment, dissociation of 1 m^3 of methane

hydrate will produce 164 m^3 of methane gas and 0.8 m^3 of liquid water. Water from the dissociation of methane hydrate may also contribute to cold methane seeps.

Anaerobic Oxidation of Methane (AOM) at the Sulfate-Methane Transition (SMT) Zone

Anaerobic oxidation of methane (AOM) occurs in the marine environment is one of the global major methane sinkers (Reeburgh 2007). A net reaction for the anaerobic oxidation of methane at SMT zone can be written as reaction (15.1).

The reaction will increase the alkalinity, but also slightly lowers the pH of sea water-dominated pore fluids (Mazzullo 2000; Pohlman et al. 2008). A linear relationship between alkalinity and HS^- concentration was observed in fluids from methane hydrate seep sites (Gieskes et al. 2005). The reactions result in carbonate precipitation and pyrite formation, if there is Fe(II) from surrounding and ambient sediments and solutions. The coupled methane oxidation and sulfate reduction at the sulfate-methane transition (SMT) zone results in sharp decreases in sulfate and methane concentrations in sediment depth profiles (Fig. 15.3). The reaction rate at the SMT zone is very high and the reaction rate drops dramatically away from the SMT zone (Dale et al. 2008; Knab et al. 2008). AOM for general marine environments has been reviewed recently by several authors (Kasten and Jørgensen 2000; Megonigal et al. 2003; Reeburgh 2007). In most marine AOM, methane in the pore fluid above SMT zone is nearly depleted, and concentration of dissolved sulfides drops to zero very fast (Kasten et al. 1998; Niewöhner et al. 1998). In the AOM in methane seep and vent sites, a high biomass above the methane hydrate (may reach $\sim 10^{12}$ cells per cm^3) (Boetius et al. 2000; Treude et al. 2007) results in surplus hydrogen sulfide and bisulfide in pore fluids and seep and vent fluids

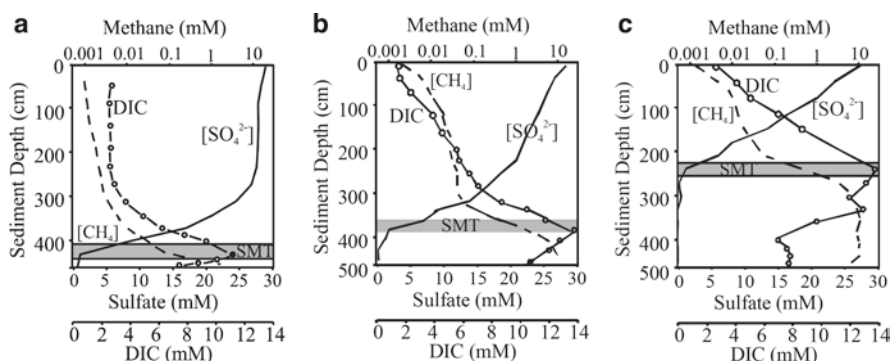
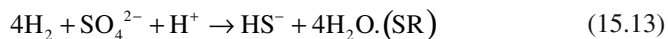
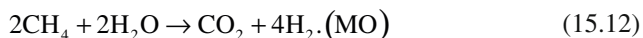


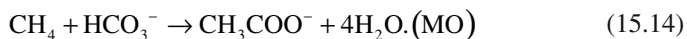
Fig. 15.3 Pore fluid chemistry profiles of the biogeochemically active pore fluids from seep sites in Keathley Canyon in the northern Gulf of Mexico. (a) An extreme concavity site (KC03-05), (b) an intermediate concavity site (KC03-07), (c) a slight concavity site (KC03-19). All figures are modified from Pohlman et al. (2008). DIC = dissolved inorganic carbon

(Pohlman et al. 2008). Both dissolved sulfides and methane in seep and vent fluids provide nutrients for the chemosynthetic communities (like sulfide-oxidizing bacteria, tube worms and methane-consuming mussels and clams) at seep and vent sites (Figs. 15.1 and 15.3).

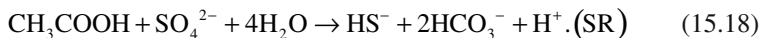
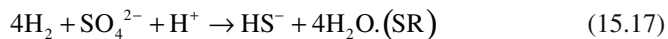
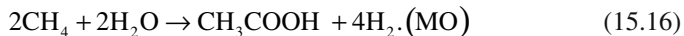
Recent studies indicate that there are two types of microorganisms (anaerobic methane oxidizers and sulfate-reducing bacteria (SRB) partnering together in an obligate syntrophic relationship to carry out reaction (15.1). Results from 16S rRNA gene sequence and carbon isotope signatures from the microorganisms collected from methane seep sites indicate that *Archaea* related to *Methanosarcinales* are the dominant anaerobic methanotrophs that produce acetate and hydrogen for the associated SRB (Boetius et al. 2000; Hinrichs et al. 1999; Orphan et al. 2001a). Two groups of methanogens, specifically archaeal genes, ANME-1 and ANME-2 were identified in the anaerobic methane oxidation Archean- SRB consortium in seep site SMT zones (Boetius et al. 2000; Hinrichs et al. 1999; Orphan et al. 2001a, b). Three possible reverse methanogenesis processes were proposed for AOM at the SMT zone for methane oxidation (MO) and sulfate reduction (SR) (Hoehler et al. 1994; Megonigal et al. 2003; Reeburgh 2007). The first hypothesis is an analog to reverse hydrogenotrophic methanogenesis:



The second hypothesis includes reactions of:



The third hypothesis includes reactions of:



The third mechanism may be more realistic because it is more thermodynamically favorable (Valentine and Reeburgh 2000). It was reported that *Archaea* of the ANME-2 group are associated with high methane flux seeps and vents, whereas, ANME-1 group are associated with low flux methane seeps (Stadnitskaia et al. 2008). The overall redox reactions involved in AOM can be expressed in Fig. 15.4.

The interaction between uprising methane and dissolved sulfate in pore fluids and sea water produces unique ecosystems. Amount of dissolved methane and sulfide varies at different sites and different levels. The interactions among pore

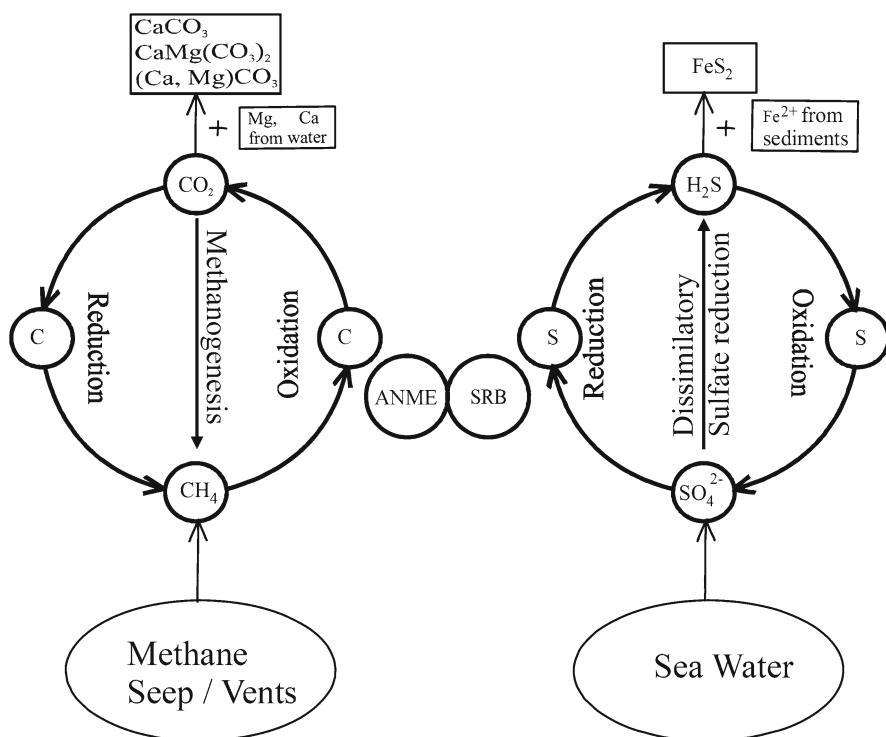


Fig. 15.4 Simplified cycles for carbon and sulfur performed by an ANME-SRB consortium in seep and vent sites. C and S mean elemental C and S or organic C and S, respectively

fluid and sea water, products from microbial metabolisms and ambient sediments result in distinctive mineral precipitates of carbonates and sulfides associated with methane hydrates and seeps vents.

Mineral Precipitates

Precipitation of Pyrite and Graphitic Carbon

Framboidal pyrite is very common in the sediments associated with methane hydrates through AOM. Precipitation of pyrite and other sulfide minerals is controlled by HS⁻ from the dissimilatory sulfate reduction of reaction (15.1) and Fe in the sediments. The dissimilatory sulfate reduction in marine environments is a very important process in controlling sulfur and carbon cycling (Jørgensen 2000). The process accounts more than half of total organic carbon oxidation (Canfield et al. 1993; Jørgensen 1982). At SMT zone, the SRB-generated H₂S (dominated by HS⁻ in circumneutral pH condition) (Stumm and Morgan 1996) will react with Fe(II)

and Fe(III) from the sediments and precipitates Fe-sulfides. The metastable Fe-monosulfide, FeS, will react with intermediate sulfur species (elemental S⁰ and poly-sulfides) and transforms into pyrite as a final product (Berner 1984). Intermediate sulfur species could form by HS⁻ oxidation (Jørgensen 2000). The reaction may be simplified as:

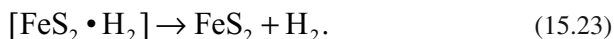
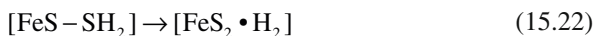
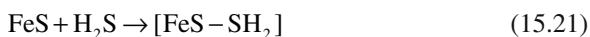


and



Intermediate sulfide structures like greigite (Fe₃S₄) and pyrrhotite (Fe_{1-x}S) may also occur in low concentration gradients of methane near disseminated methane hydrate (Larrasoana et al. 2007). The filamentous structure of pyrite framboid pseudomorphs after *Beggiatoa* was reported in a gas hydrate mound at Bush Hill, Gulf of Mexico (Sassen et al. 2004). This type of pyrite may be formed through this process at the sea floor because the presence of internal sulfur granules in *Beggiatoa* is commonly seen.

Another proposed mechanism for pyrite formation is the reaction between FeS and H₂S with hydrogen as a by product (Rickard 1997; Rickard and Luther 1997; Theberge and Luther 1997), although it is very difficult to simulate the process in the laboratory due to the very low hydrogen concentration. The reactions may be written as:



A net reaction is:



A third mechanism for the formation of pyrite is by direct precipitation through reactions of Fe(II), sulfur and polysulfide when the solution is undersaturated with respect to amorphous FeS (Giblin and Howarth 1984; Howarth 1979; Luther 1991).

SEM images show framboidal pyrite clusters associated with carbonate (protodolomite) (Fig. 15.5a) from site 1 of South China Sea, and a pyrite micro-chimney, or micro-chimney-like pyrite from site 2 of South China Sea (Fig. 15.5b–e). SEM images shows framboidal pyrite core surrounded by elongated pyrite crystals that form pyrite spherules (Fig. 15.5d). High-resolution TEM image shows planar defects in the pyrite spherules (Fig. 15.5e). The pyrite (P) spherules contain marcasite (M)

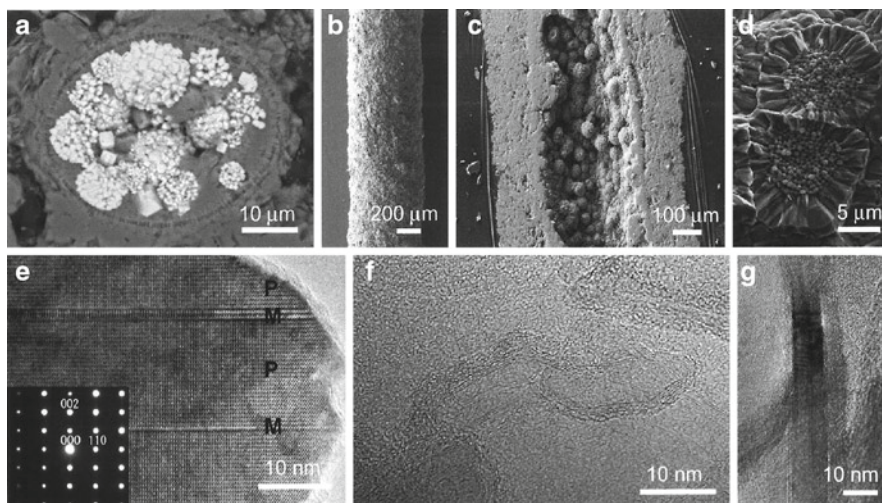


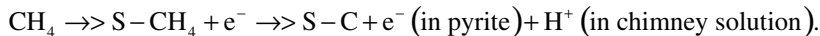
Fig. 15.5 SEM image showing pyrite framboids and protodolomite filling chamber of a foraminifer from site 1 of the South China Sea (a). (b) A pyrite micro-chimney composed of many spherical aggregates. (c) SEM image showing the inner wall of the chimney pyrite. (d) High-magnification SEM image showing spherical pyrite aggregates consist of a framboidal core with pyrite spherules. (e) High-resolution TEM image showing a pyrite spherule contains marcasite lamellar domains. (f) High-resolution TEM images showing a nanotube-like carbon, and (g) a graphitic nano-plate

domains along (001) of pyrite. The marcasite and pyrite host keep a strict orientation relationship: marcasite (101)//(001) of pyrite, and [010] direction of marcasite//[100] of pyrite. This is the least misfit plane between pyrite and marcasite. A similar micro-structure was observed in a hydrothermal pyrite spherule (Dodony et al. 1996).

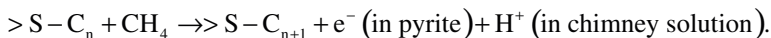
Both pyrite and marcasite have the same composition but different crystal structures. Pyrite is the stable polymorph of FeS_2 . In general, the presence of neutral H_2S species (i.e., relatively lower pH) is required in order to precipitate marcasite (Murowchick et al. 1986; Schoonen and Barnes 1991a, b). The observed texture of a spherule pyrite rim with marcasite domains surrounding a framboidal pyrite core (Fig. 15.5d) indicates different solution conditions during the pyrite precipitation. The chimney-like pyrite precipitates in worm tubes serve as channels for methane and HS^- -bearing seep fluids. The reaction (15.1) results in an increase in alkalinity and slightly lowers the pH if there is no pyrite precipitation. In circumneutral (lightly basic) solutions, pyrite precipitates and forms pyrite framboids.

Graphitic nano-crystals and nano-tube-like carbon are closely associated with the pyrite spherules (Fig. 15.5f and g). This type of elemental carbon (instead of by the complete oxidation of methane) may indicate gas-phase methane in the fluid besides dissolved methane. Carbon nanotubes can also be synthesized in aqueous solutions with solid catalysts (Gogotsi et al. 2001; Hata et al. 2004). In the methane seeps areas, there is methane in dissolved and gas phase states even at the SMT zone. The uprising methane and dissolved sulfides will interact with the pyrite surface. The close relationship between nano-tube-like carbon and pyrite spherules indicate

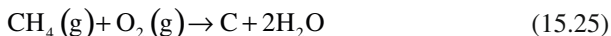
that pyrite, a semiconductor, serves as a catalyst during the reaction from methane to elemental carbon. Partial oxidation of methane occurs through sorption of methane molecules on pyrite surface (notation: >S) and pre-formed C on pyrite surface (notation: >S-C_n) followed by electron donation to pyrite crystals:



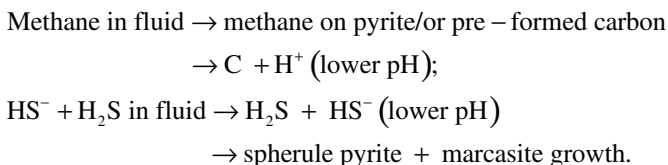
and,



Whereas, ambient electron acceptors like Fe(III), Mn(IV) and oxygen gain electrons from the neighboring pyrite. The pyrite-catalyzed net reaction may be expressed as:



The above pyrite-catalyzed reaction process results in acidification of the solution in the pyrite-chimney chamber which will increase the ratio between neutral [H₂S] species and bisulfide [HS⁻]. Lower pH and increasing [H₂S] will result in marcasite growth on pyrite substrate (Murowchick et al. 1986; Schoonen and Barnes 1991a, b) and formation of pyrite spherules as showed in Fig. 15.5d and e. The coupled methane oxidation on pyrite surface, pH change in the chimney solution, and the growth of marcasite and pyrite spherules can be expressed as:



There is no carbonate in all the observed pyrite chimneys that also indicates a low pH condition during the spherule pyrite and nanotube-like carbon formation.

Precipitations of Carbonate Minerals

AOM will result in alkalinity increase of pore fluids and carbonate precipitation (Gieskes et al. 2005). Stoichiometric dolomite CaMg(CO₃)₂ should precipitate from sea-water and sea-water-derived pore fluids according to thermodynamic equilibria (Hardie 1987). However, aragonite precipitates from modern sea water because solvent water that has large dipole moment forms a strongly hydrated Mg²⁺ surface complex and inhibits dolomite and calcite nucleation and growth (Lippmann 1973). Minerals of aragonite, calcite, low-magnesian calcite (LMC), high-magnesian calcite

(HMC), protodolomite (proto), disordered dolomite, and dolomite (actually Ca-rich dolomite, not stoichiometric dolomite) occur in the carbonate precipitates associated with methane seeps and vents (Greiner et al. 2001; Naehr et al. 2007; Takeuchi et al. 2007). The carbonate minerals may form tube-like chimneys that are channels for seeping and venting fluids (Fig. 15.1c). Framboidal pyrite may coexist with HMC, dolomite, or protodolomite (Fig. 15.5a). Calcite and LMC can be biogenic or bioclasts of coccoliths and foraminifera fragments. The boundary between LMC and HMC ranges from 8 mole % of MgCO_3 to 11 mole % of MgCO_3 . In sea-water, most biogenic magnesian calcite contains ~11 mole % of MgCO_3 that may have same solubility of aragonite. Figure 15.6a shows X-ray diffraction patterns of carbonate deposits from three different methane seep sites in South China Sea. The carbonate could be dominated by dolomite, mixture of HMC and protodolomite, and mixture of aragonite and HMC. Protodolomite with a very broad (104) diffraction peak indicates both structural (Mg–Ca disordering) and compositional heterogeneity. High-resolution TEM image and Fourier transform patterns from different areas show disordered dolomite (without super lattice reflections) and weakly ordered dolomite (protodolomite) (Fig. 15.7).

Recent studies in some marine AOM areas without obvious methane seeps and vents indicate dolomite and protodolomite are closely related to the methanogenesis zone and lower part of the SMT zone (Mazzullo 2000). The concentration of methane in pore fluids above SMT zone is about zero. However, protodolomite (~40–44 mole % of MgCO_3) and HMC can precipitate above SMT zones in methane

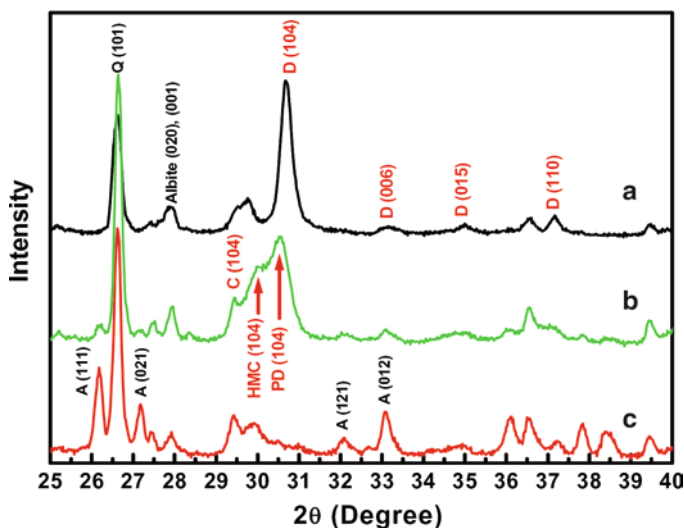


Fig. 15.6 XRD patterns (using Cu K α radiation) from three methane seep sites in South China Sea. *Top pattern*: dolomite is the major minerals (~45 mole % of MgCO_3); *Middle pattern*: protodolomite (~40–44 mole % of MgCO_3) and HMC are the major minerals; *Bottom pattern*: aragonite and HMC are the major minerals. Very broad (104) diffraction peak characterizes disordered dolomite and protodolomite (PD) with composition range of ~40 to 44 mole% of MgCO_3 . C = calcite, Qtz = quartz, Ab = albite

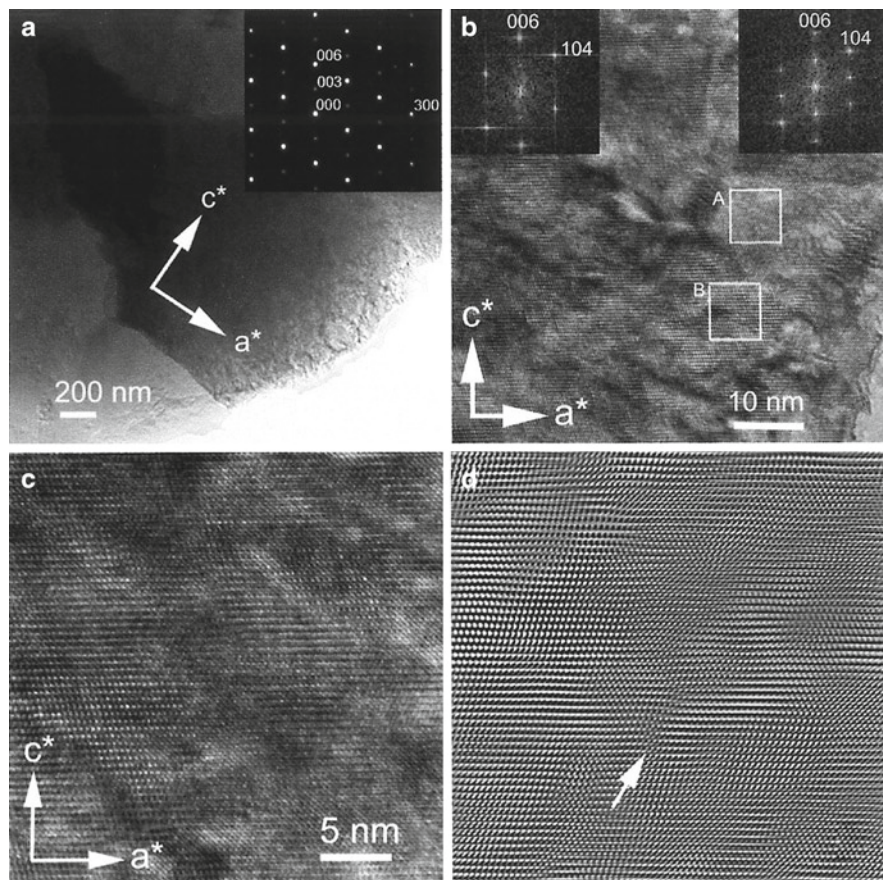


Fig. 15.7 Bright-field (a) and high-resolution TEM images (b) of the protodolomite with nano-domains and low-angle boundaries among the neighboring crystals. An inserted electron diffraction pattern shows weak supper lattice reflections characterizing poorly ordered dolomite structure. There are domains with dolomite and calcite structures (see inserted Fourier transform patterns from two selected areas). Some areas show anti-phase-domain-like boundaries (c, d) that result from Mg–Ca ordering-induced phase transition. Image D is a filtered inverse Fourier transform of image C, and clearly shows the domain boundary, i.e., off-set of (001) dolomite lattice fringes (indicated by arrow) between neighboring domains

seep and vent areas (Takeuchi et al. 2007). The dehydration and desolvation of the hydrated Mg^{2+} ion and dolomite surface Mg^{2+} –water complex is the key to the dolomite formation. Both dissolved methane and hydrogen sulfide have low molecular dipole moments and serve as catalysts for lowering dehydration energy of Mg^{2+} –water surface complex. Our synthesis experiments indicate that concentration of MgCO_3 in HMC and dolomite is related to molecular dipole moments (μ) of dissolved molecules that serve as catalysts at a given temperature (Fig. 15.8). Increasing temperature will enhance Mg incorporation into HMC and dolomite

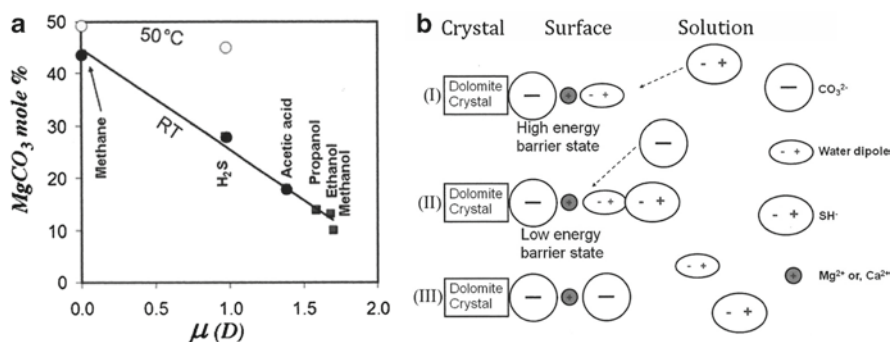


Fig. 15.8 (a) Diagram showing relationship between molecular dipole moment (μ) of added catalysts and mole % of MgCO_3 in the crystallized calcite or disordered dolomite at about room temperature (RT). All the solutions are with 5:1 Mg/Ca ratio. Data for methanol, ethanol, and propanol are from published data (Falini et al. 1996). Molecular dipole moments are from Lide (2004). The unit for dipole moment is debye (D). Two 50°C data of disordered dolomite are plotted in circles. (b) Diagram showing 1-dimensional crystals diagrams showing catalytic role of dissolved bisulfide on lowering dehydration energy of Mg^{2+} on calcite or dolomite surface. (I) Water dipole bonding with the surface Mg^{2+} due to strong hydration of Mg^{2+} ; (II) Interaction between dissolved bisulfide with the surface water results in orientation/distance change of the water dipole, and weakening bonding between the Mg^{2+} and surface water; (III) Aqueous carbonate can repel the water dipole and form bonds with the surface Mg^{2+} . The calcite crystal grows through this process

dramatically in the presence of the catalysts. The presence of dissolved sulfides result in precipitation of HMC at low temperatures and disordered dolomite at temperatures of 40°C or higher. Presence of dissolved methane results in the formation of protodolomite or disordered dolomite (due to fast precipitation and growth). In solutions without methane and dissolved sulfides, no dolomite precipitates. Laboratory synthesis experiments also show that aragonite precipitates if elemental sulfur also exists with the catalysts in forms of colloids. The mechanism by which elemental sulfur inhibits HMC and dolomite precipitation is still not clear. Observed carbonate deposits with HMC and dolomite chimneys above SMT zone, and aragonite at sea floor level in the Kuroshima Knoll of southern part of the Ryukyu Arc can be explained based on newly obtained experimental results (Fig. 15.8). HMC and dolomite chimneys can precipitate in sediments above the SMT zone due to the presence of both methane and sulfide in pore fluids. Only aragonite precipitates at the sea floor (above the carbonate chimney layer) because of oxidation of sulfide and/or formation of elemental sulfur.

The dolomite or protodolomite formed in the methanogenesis zone will have high $\delta^{13}\text{C}$ values (Greinert et al. 2001; Mazzullo 2000). The carbon isotope fractionation will enrich ^{13}C in bicarbonate and deplete ^{13}C in methane. The dolomite formed in this environment will have high $\delta^{13}\text{C}$ values, i.e., group A carbonate (Figs. 15.9 and 15.10). The dolomite or calcian dolomite formed in these areas generally contains small amounts of Fe(II) or FeCO_3 . In extreme cases, even

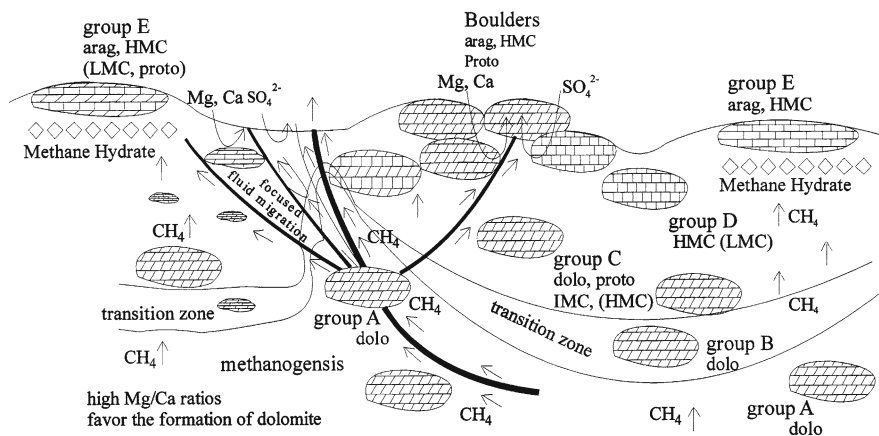


Fig. 15.9 Schematic diagram showing the origin of petrographically and isotopically different carbonate rocks relative to the controlling diagenetic environments. Group A carbonates are restricted to the deep methanogenic zone resulting in the formation of dolomite. Group B carbonates, also dolomite dominated, are representative of the transition between sulfate-reduction and methanogenesis. Group C carbonate, with typical methane-derived values but protodolomite and dolomite as major carbonate phases have formed in the sulfate-reduction zone. Group D carbonates without obvious dolomite contain carbon from mixture of degraded organic matter and methane oxidation and are generated close to surface. Group E are aragonite-rich carbonates formed at the surface or near surface environments, with carbon from methane oxidation (Modified from Greinert et al. 2001)

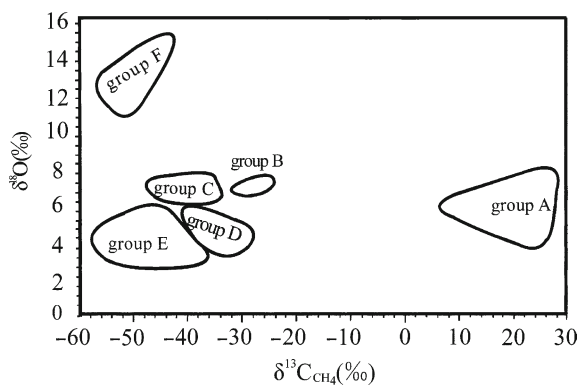
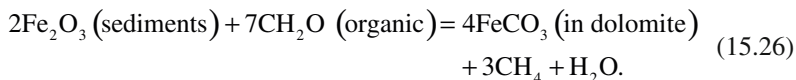


Fig. 15.10 Carbon and oxygen isotope values of carbonate from the northern summit of the Hydrate Ridge. Five distinctive six groups (group A to F) can be distinguished in their dominate carbonate cement phases as well as their carbon source sources and formation conditions illustrated in Fig. 16.9. The carbonate directly associated with methane hydrate falls in group F. Its carbon isotopes are typical methane-generated carbon source, whereas their extremely high $\delta^{13}\text{C}$ value is still unsolved (Greinert et al. 2001)

siderite can precipitate. The existence of Fe^{2+} in dolomite also indicates a reducing dolomitizing fluid that contains dissolved methane and other organics that are responsible for the dolomite precipitation. It has been shown that fermenting bacteria can transfer electrons to Fe(III) in sediments (Lovley 2000). The cooperative metabolism between methanogens and fermenting bacteria results in CO_2 or dissolved HCO_3^- as the common product of all these reactions which can result in Fe^{2+} -bearing carbonate (Coleman and Raiswell 1993) through a general net reaction of,



The produced methane in the above reaction serves as a catalyst for dolomite formation.

If the methane is produced mainly through the reaction (15.26), the dolomite precipitated in this zone will have high $\delta^{13}\text{C}$ values (Fig. 15.10) (Greinert et al. 2001; Mazzullo 2000). However, the dolomite formed in SMT zone will be depleted in ^{13}C and Fe due to AOM (Mazzullo 2000). HMC and dolomite associated with methane seeps/vents in and above SMT zone are also depleted in ^{13}C and Fe (Greinert et al. 2001; Takeuchi et al. 2007). The AOM of reaction (15.1) will result in ^{13}C -depleted dissolved inorganic carbon. Precipitation of pyrite results in Fe-depleted HMC and dolomite.

Geological Records and Biosignatures

Reported methane seeps and vents in the rock record are based on large carbon isotope excursions, tepee like structures in rocks, ^{13}C -depleted carbonate, associated pyrite framboids, and lipids of microorganisms preserved in carbonate rocks. One well studied site is a Neoproterozoic postglacial cap carbonate (Doushantuo cap carbonate) in Yangtze platform of south China (Jiang et al. 2003, 2006). The cap carbonate formed during destabilization of methane hydrate during the deglaciation at ~635 Ma (millions of years ago). The cap carbonate consisting of disrupted limestone and/or dolomite (with micrite, dolomicrite, pyrite framboids, and barite) (layer 1), and laminated limestone and/or dolomite with tepee-like structures (layer 2). The mineral assemblage and texture is similar to some modern methane seep and vent-induced carbonate deposits. The cap carbonate overlies the glacio-genic diamictite (poorly or non-sorted conglomerate with a wide range of clasts and clay minerals) (Jiang et al. 2003). The tepee-like structures indicate paleo-methane vents. A huge carbon isotope excursion ($\delta^{13}\text{C}$ ranges from +5‰ to -40‰) was observed in a thin layer right above the tepee-like layer. This ^{13}C -depleted layer was formed during AOM of uprising methane from dissociation of methane hydrate. Global deglaciation (or the end of Snowball Earth) resulted in a massive dissociation of methane hydrate (Jiang et al. 2003, 2006).

Another case is the Late Cretaceous (Campanian) Tepee Buttes (limestone) in the Western Interior Seaway, USA (Birgel et al. 2006, 2008; Birgel and Peckmann 2008). Highly ^{13}C -depleted archaeal lipids ($\delta^{13}\text{C}$ ranges from -102‰ to -118‰) and bacterial biomarkers ($\delta^{13}\text{C}$ ranges from -51‰ to -73‰), corroborating a syntrophic consortium of *archaea* and bacteria mediating AOM were reported in the limestone Tepee Buttes (Birgel et al. 2006). In the relatively recent geologic past, it is proposed that the sudden release and oxidation of methane hydrate at the Paleocene-Eocene boundary contributed to a rapid global temperature change at the Paleocene-Eocene Thermal Maximum (PETM) (Dickens et al. 1995; Katz et al. 2001).

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