

Magnitude of dissociation of methane hydrate reservoir associate with climate change

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Abstract—Methane hydrates are found in enormous quantities along all the continental margins. The magnitude of the carbon pool locked in the methane hydrate reservoir is not known precisely, but estimates range from 10^3 to 10^6 Gt C. Methane hydrates are also of interest because of their potential role in climate change. When these marine methane hydrates begin to dissociate, the methane trapped in the methane hydrates is released into the ocean and the atmosphere. This review focuses on the dissociation mechanism of methane hydrates that are rather unique and involve a number of conditions, and presents current understanding of the effects of methane hydrate on the chemical and physical properties of seawater. We discuss past events about the dissociation of methane hydrate in the various geological periods. It will be shown how the previously mentioned sufficient flux of methane from hydrate dissociation can cause an oceanic anoxic event and a major global warming. These events maybe are occurring and will be believed to influence the climate change in the future.

Keywords—methane hydrate; dissociation; greenhouse gas; climate change

I. INTRODUCTION

Gas hydrates are ice-like structures where cages of water molecules are stabilized by gas molecules [1] and are principally composed of methane and water that occur naturally in the pore space of marine sediments where appropriate high pressure and low temperature conditions and an adequate supply of methane exist [2]. Methane hydrates have been discovered in the subsurface in permafrost regions, but most occur in oceanic sediments hundreds of meters below the sea floor where water depths are greater than about 500 m. As it is shown in Fig.1 natural methane hydrates have been discovered at numerous locations along continental margins as well as in the Arctic.

Huge deposits of oceanic methane hydrate exist on the seafloor on continental margins. An extensive hydrate prone layer, extending to as deep as 1400 ± 200 m over an area of $50,000$ km², is predicted by the thermal data and hydrate

stability field. Comparison of the predicted maximum depths of methane hydrate stability with the maximum depths of hydrate occurrences in 52 wells shows general agreement in the areas of thick offshore and onshore permafrost. Differences in several areas of up to 400 m between the thermally predicted hydrate base and the deepest detected hydrates can be explained by changes in gas composition. Otherwise low near-surface thermal gradients of approximately 15 mK/m to 20 mK/m would be needed to explain the existence of deep hydrates in the area of the southern Mackenzie Delta trough and offshore north of 71° N latitude [3]. Unfortunately there is no reliable industrial temperature observation from wells to support the latter. Such regional studies of the distribution of methane hydrates, including the stability of those deposits, form a crucial component of an assessment of the influence of methane hydrate formation and decomposition on the proportion of methane present in the earth's atmosphere. Current estimates suggest that between 10^3 to 10^6 Gt of methane may be presently locked in methane hydrate deposits [4]. To fully assess the total amount and the potential contribution to global warming, similar regional assessments are needed for each of the major areas of occurrence, especially in the circumpolar regions which are subject to the greatest increase in temperature conditions.

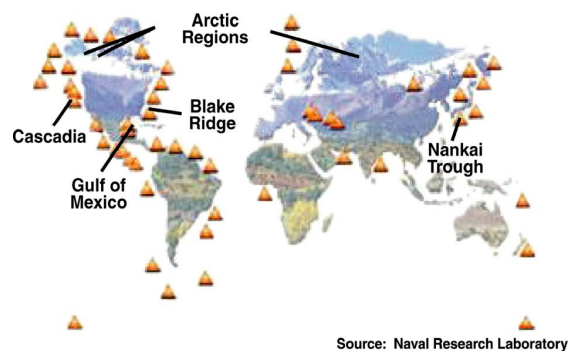


Fig.1. Distribution of natural methane hydrates around the globe

The purpose of this paper is to review the past events in

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the geological periods due to the dissociation of methane hydrate reservoir. Dissociation mechanism of methane hydrates are discussed briefly in this paper and related research opportunities are identified. This study also indicates the current understanding of the effects of methane from methane hydrate reservoir on climate. For these reasons, the study of possible countermeasures should be actively considered.

II. DISSOCIATION MECHANISM OF METHANE HYDRATE RESERVOIR

Methane hydrate can stably exist under the appropriate conditions of temperature and pressure, and the change of these conditions may induce its decomposition and release methane [5]. The decomposition of methane hydrates triggered by an increase in near surface temperatures and the subsequent upward migration of released gases is occurring, either as a result of warming bottom water, or as a result of a pressure drop due to a reduction in sea level (such as during the ice age). The change of temperature and pressure will induce conversion between methane hydrate and gas. This is a dynamic process [6], which affects the balance between methane and carbon in the lithosphere-hydrosphere-atmosphere. This process has occurred several times during the geological period and has affected the changes in the global climate [7-12] and carbon cycle [13-14].

Methane hydrate transforms into water and methane gas in bubbles when it dissociates in seawater. That CH_4 may be oxidized (via bacteria) into CO_2 before the bubbles rise to the sea surface or dissolve into seawater again. Chung-Chieng found a good agreement between “apparent oxygen utilization” (AOU) and “virtual oxygen utilization” (VOU) at depth greater than the level where hydrates dissociate [15]. The VOU is less than AOU in the layer of seawater beneath the euphotic zone. That is attributed to the escape of CO_2 into the atmosphere. However, the stability of methane hydrates is affected by the conditions of temperature and pressure. Any assessment of the total methane contribution to the atmosphere and the rate of the release require knowledge of the distribution, spatially and with depth, the temperature and composition of the methane hydrate reservoir.

III. EFFECTS OF DISSOCIATION OF METHANE HYDRATE ON CLIMATE CHANGE

Methane is an important greenhouse gas. It is released into the atmosphere by a wide variety of sources, both natural and anthropogenic. Natural methane emissions arise from wetlands, termites, other wild ruminants, oceans, and methane hydrates [16]. Donner and Ramanathan [17] calculated that the presence of methane at current levels causes the globally-averaged surface temperature to be about 1.3 K higher than it would be without methane [18]. However, it should also be recognized that the dissociation of methane eventually produces carbon dioxide, leading to additional

climatic forcing from methane emissions from fossil sources. Permafrost has been suggested as a high-latitude source of methane during global warming [19]. Moreover, the oceanic methane hydrate provides a huge biochemical fuel source to generate heat internal to world oceans. This may explain the observed ocean warming at the intermediate depth during last several decades. Release of methane from large marine reservoirs has been linked to climate change, as a causal mechanism and a consequence of temperature changes, during the Quaternary and the Paleocene. The role of microbes in altering the chemical and physical properties of seawater and the course of climate change can not be ignored.

A. *The Paleocene–Eocene Thermal Maximum (PETM)*

At the PETM, foraminiferal magnesium/calcium ratios indicate that ocean bottom waters warmed by 4 to 5°C, similarly to the sea-surface temperatures in the subtropical and tropical ocean, implying that similar magnitudes of warming occurred in regions of deepwater formation under ice-free conditions [20]. These authors suggest intermediate waters warmed, in association with downwelling in the North Pacific and reduced Southern Ocean convection, before the PETM and suggest methane hydrate release as the trigger mechanism. A switch to deep convection in the North Pacific at the PETM onset could have amplified and sustained warming. Zachos et al. provide evidence that a large mass of carbon dissolved in the ocean at the Paleocene–Eocene boundary caused the CCD to shoal rapidly (<10,000 years) by more than 2 km, and that it gradually recovered (>100,000 years) by carbon sequestration through silicate weathering feedback [21].

A primary concern with regard to the pattern of changes in climate is the apparent modulation of natural climatic trends with atmospheric concentrations of greenhouse gases. The rapid increase in atmospheric CH_4 during the Late Quaternary is closely associated with intervals of rapid warming. Especially, large, rapid increase in CH_4 occurred at glacial terminations. CH_4 concentrations essentially doubled from LGM values (350 ppbv) approaching concentrations typical of the Late Holocene (~700 ppbv). This large increase in CH_4 occurred in less than a few decades [22,23]. Recently, several studies have investigated the geochemistry of deep-sea sediments, ice cores, and other geological indicators to document past episodes of rapid changes in climate and to assess possible linkages to variations in atmospheric concentrations of greenhouse gases [24]. There seems to be widespread acceptance that changes in the methane hydrate reservoir played a role in the climate history before the Quaternary. The origin of several brief episodes of global warming has been linked with massive dissociation of hydrates and CH_4 transfer into the atmosphere [25]. These along with the hypothesis proposed by several earlier researchers that the formation and dissociation of methane hydrate within terrestrial and marine sediments may have been key factors. Dickens argued that released methane from

methane hydrate played a very important role in the Late Paleocene thermal maximum (LPTM) [26], and indirect evidence of the rapid release of methane by methane hydrate decomposition has been invoked to explain negative $\delta^{13}\text{C}$ excursions in Early Jurassic sediments [12], Late Jurassic deposits [27], and Paleocene marine and terrestrial carbonate components [28]. Nisbet related the present global warming to methane release from methane hydrate in the last glacial termination about 13 500 and argued that in global warm period [29], the released methane from methane hydrate of polar region had entered atmosphere and induced global climate warming.

B. Oceanic anoxic events

1) The Permian–Triassic boundary (PTB) anoxic events

The end-Permian mass mortality is a unique 1-2-m-thick layer consisting of 5-20-cm-long crystals of calcite that occurs precisely at the PTB in Iran, Armenia, Turkey, and China. This layer is interpreted as syndepositional, abiotic, seafloor cement indicative of precipitation from a highly carbonate supersaturated seawater.

The Upper Permian accumulation period of methane hydrates ended abruptly adjacent to the PTB and the dissociation event began releasing 3.2 to 4.7×10^{18} g CH_4 into the ocean. Oxidation of CH_4 in the water column created a seawater that was charged with CO_2 and had lower than normal O_2 content. This oceanic acid bath first dissolved suspended fine-grained carbonate particles and small calcareous organisms, followed by extensive dissolution of platform carbonates raising Ca^{2+} and HCO_3^- concentrations of seawater. When the release of CH_4 declined, the acid-bath ocean became a soda ocean precipitating massive amount of seafloor cements observed globally at the PTB.

Heydari and Hassanzadeh suggests that prior to cement precipitation, the PTB ocean was charged with CO_2 , warm, had low oxygen, high Ca^{2+} , and high HCO_3^- concentrations. These conditions collectively created stressful conditions causing the marine mass mortality [30]. The leakage of CH_4 to the atmosphere produced a super-hot climate resulting in the biological devastation on land. The proposed kill mechanism is developed on the basis of the physical clue-the cement layer-left behind by the killing process-the change in ocean chemistry.

The accumulation-dissociation cycles of methane hydrates also explain the periodicity of mass extinction events during the Phanerozoic (Fig. 2). Accumulation periods were long (5 to 20 My) providing favorable conditions for ecosystem development (Pardeess phase). The dissociation events were short and catastrophic (10 to 500 Ky) causing low oxygenation, super-hot climate, and biological devastation (Doozakh phase). It appears that most mass extinctions of the Phanerozoic have been related to the internal working of the Earth system.

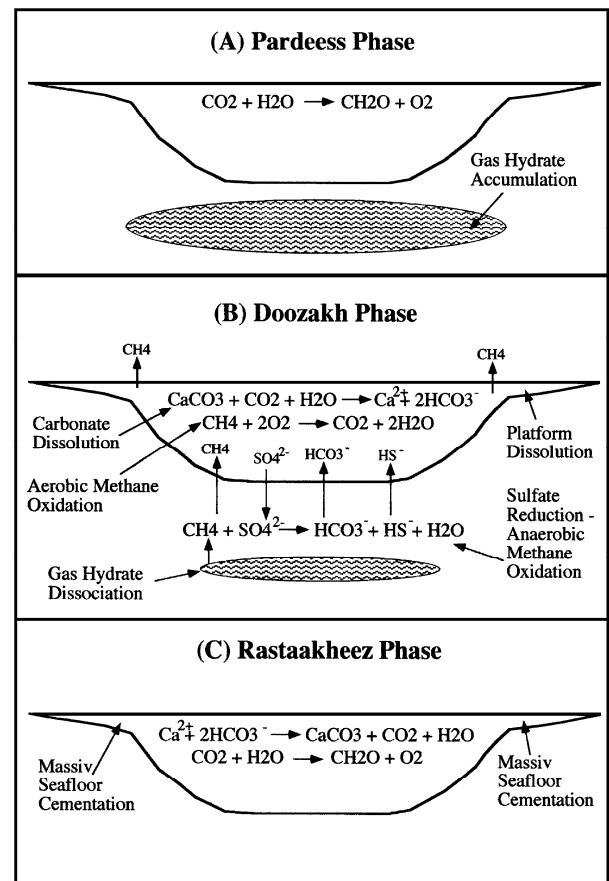


Fig.2. Accumulation–dissociation cycle(Heaven-Hell cycle)of methane hydrates adjacent to the PTB interval [30].

(A)The accumulation period-Pardeess (paradise, heaven) phase-resulted in production of organic matter and accumulation of a large amount of methane hydrates in continental margins.

(B)Dissociation interval-Doozakh (inferno, hell) phase- promoted catastrophic release of methane hydrate CH_4 .Aerobic CH_4 oxidation in the water column and anaerobic oxidation by sulfate reduction in sediments generated a seawater that was CO_2 -charged, had lower than normal dissolved O_2 and high concentrations of Ca^{2+} and HCO_3^- .This change in seawater composition combined with warm shallow water caused the marine mass mortality. The leakage of CH_4 into the atmosphere created a super-hot climate resulting in death on land.

(C)The Rastaakheez (resurrection) phase encompasses the cessation of CH_4 injection to the ocean, leading to abrupt end to generation of CO_2 resulting in the development of a soda ocean, highly supersaturated with respect to calcium carbonate. Massive precipitation of seafloor marine cement occurred. The organisms that survived the mass extinction struggle for a new beginning for the continuation of life on Earth.

2) The Early Toarcian oceanic anoxic event

The marked 3-8‰ negative carbon isotope excursion associated with the Early Toarcian oceanic anoxic event (OAE; ~183 myr ago) in the Early Jurassic period is thought to represent one of the most important perturbations of the C-cycle in the last 200 myr. However, the origin of this excursion remains strongly debated, primarily due to

uncertainties in the estimation of its duration, which ranges from ~200 kyr to 1 myr. Guillaume et al. found a new orbital calibration of the Early Toarcian carbon isotope excursion, based on spectral analyses of two independent datasets generated from the sedimentary record of two hemipelagic sections from Portugal (Peniche) and SW Germany (Dotternhausen), in order to better constrain the timescale and hence the origin of this excursion [31]. These analyses reveal that orbital cycles exert a strong influence on both the calcium carbonate content in Portugal and on the greyscale of black shales in Germany, which allow us to propose a duration of ≥ 1.9 myr for the Early Toarcian and of ~900 kyr for the entire carbon isotope excursion. The shift towards lower carbon isotope values lasted ~150 kyr, and carbon isotope values remained low for ~450 kyr; the subsequent increase of carbon isotope values lasted ~300 kyr. This calibration suggests that the sustained input of isotopically light carbon at the origin of the excursion occurred over ~600 kyr and thus dismisses causal mechanisms implying relatively small source reservoirs such as the massive dissociation of methane hydrates. And the results show that the C-isotope perturbation coincided with a transition from precession-eccentricity-dominated cycles to obliquity-eccentricity-dominated cycles, suggesting that the OAE was marked by a fundamental change in the response of the climate system, which allowed the obliquity signal, normally better recorded at high latitudes, to be a dominant forcing factor of short-term sedimentary cycles at tropical latitudes.

C. *Deglacial methane emission signals of Lake Baikal*

The carbon isotopic record of Lake Baikal is the first continental evidence for climatically caused changes in a methane gas hydrate reservoir. The organic carbon stable isotope record from Lake Baikal during the past 130,000 years registers regular emissions of isotopically light carbon by the occurrence of distinct negative shifts of 3-5% at every major orbitally forced cold-to-warm climatic transition during the past 130,000 years. Alexander et al. concluded that these emissions were associated with decomposition of sedimentary clathrates, widespread in the Baikal basin [32]. Among potential hypotheses to account for these methane episodes, the most probable appears to be hydrate dissociation due to deglacial warming of lake water. We estimate that as much as 12-33 Tg of methane could have been released with each episode. By recording the systematically recurring episodes of massive methane clathrate decomposition closely linked with the northern hemisphere temperatures during major orbital warmings, the new Baikal $\delta^{13}\text{C}$ record provides further evidence for the potential involvement of clathrate reservoir in rapid deglacial rises of atmospheric methane levels.

D. *Anaerobic oxidation of methane in the Gulf of Mexico*

Anaerobic oxidation of methane (AOM) occurs in the Gulf of Mexico methane hydrate systems. Here lipid biomarker and isotopic evidence that archaea are involved in

AOM. Chuanlun et al. found archaeal lipid biomarkers in the Gulf of Mexico hydrate samples are dominated by archaeal and sn-2 hydroxyarchaeol and have extremely low ^{13}C values (69 to 99%) [33]. These results are consistent with ^{13}C -depleted lipid biomarkers of sulfate-reducing bacteria and suggest that AOM is mediated by consortia of archaea and sulfate-reducing bacteria. The distribution of archaeal lipids in the Gulf of Mexico is similar to that observed in California Margin and Hydrate Ridge [34]; however, different isotopic fractionations between substrate methane and archaeal and bacterial lipids suggest a diversity of microorganisms, reaction kinetics and pathways. Extensive oxidation of oil hydrocarbons also occurs in the Gulf of Mexico [35,36], which not only adds to the accumulation of enormous volumes of carbonate from AOM but also contributes to the complexity of carbon cycling mediated by different microbial processes.

The estimated abundance of total archaeal lipids ranges from 44.8 to 60.4 mg/g (dry sediment) in hydrate-bearing samples but is below detection limit in the hydrate-free sample. The ^{13}C values of archaeal lipids range from 69 to 99% in hydrate-bearing samples. These results suggest that biomass of archaea is significantly enhanced through AOM at the methane hydrate deposits. These data also support a currently acknowledged mechanism of AOM mediated by a consortium of sulfate-reducing bacteria and archaea observed in a variety of methane-rich marine settings. Anaerobic oxidation of oil hydrocarbons also occurs in the Gulf of Mexico methane hydrate systems as shown by degradation of n-alkanes ($>\text{C}_{15}$) in the anoxic sediments. These processes convert hydrocarbons to carbon dioxide and increase pore water alkalinity, which promotes the precipitation of enormous volumes of authigenic carbonate rock depleted in ^{13}C . This long-term geologic sequestration of carbon, may affect models of global climate change.

IV. CONCLUSIONS

The possible destabilization of methane hydrates due to anthropogenic climate warming, and the resulting outgassing of methane, could lead to a major increase of the global Greenhouse effect, with dramatic consequences for Humanity [37]. At present, support for the idea that methane hydrate is an important factor with respect to global change comes from both marine and terrestrial carbon isotopic records. The dissociation of hydrate alters the heat content of seawater at various depths. The oxidation of CH_4 into CO_2 within seawater might be the cause of the relatively smaller atmospheric concentration of CH_4 compared to that of CO_2 . Because CO_2 is less powerful as a greenhouse gas than CH_4 is, this sets a brake on the atmospheric greenhouse effect. Recent increase of atmospheric CH_4 concentration may imply a change of ocean dynamics, chemistry and biology.

Opening of this reservoir, either purposefully to extract the energy or inadvertently, will release the sequestered carbon into the environment, increasing radiative forcing and

exacerbating the ongoing global warming trend. Data from the historical record and recent modeling results suggest that hydrate destabilization and methane outgassing may have catalyzed a number of runaway global warming episodes in the past. A careful reassessment of the role of methane in various climate change scenarios therefore appears warranted as well as an evaluation the vulnerability of the hydrate reservoir to unintentional destabilization.

More research is needed to fully understand the role of methane hydrates dissociation has played in the various geological periods and its future projection. More complete analyses will require increased coordination between programs measuring methane dissolution abundances and exchange fluxes, and modeling efforts that oceanic ecosystem with methane hydrate decomposition processes.

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