



GAS HYDRATES OCCURRENCE, DESTABILIZATION AND POTENTIAL ENERGY RESOURCES: A REVIEW BASED ON FAUNAL, GEOCHEMICAL AND GEOPHYSICAL INVESTIGATIONS WITH SPECIAL REFERENCE TO THE BLAKE RIDGE, NW ATLANTIC

AJOYK. BHAUMIK^{*}, AKANKSHA GUPTA, ANIL K. GUPTA^{2,3}, SHIV KUMAR¹, SHILPI RAY¹ and SANJIB BISWAS¹

¹DEPARTMENT OF APPLIED GEOLOGY, INDIAN SCHOOL OF MINES, DHANBAD – 826 004, JHARKHAND, INDIA

²DEPARTMENT OF GEOLOGY AND GEOPHYSICS, INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR – 721 302, WEST BENGAL, INDIA

³PRESENT ADDRESS: WADIA INSTITUTE OF HIMALAYAN GEOLOGY, DEHRA DUN, UTTARAKHAND – 248 001, INDIA

*Corresponding author: E-mail: ajoyism@gmail.com

ABSTRACT

Gas hydrate, a naturally occurring frozen methane, has been identified as a promising future energy resource. Gas hydrate deposits are found in both continental and marine realms as cage of water and methane molecule under suitable pressure and temperature conditions. Numerous geophysical, geochemical and palaeontological proxies have been used to identify gas hydrate horizons in the marine environments. These include bottom simulating reflectors or BSRs, depleted chlorine anomaly, stable carbon isotope values of foraminiferal calcitic tests and certain species of benthic foraminifera. Study of cores from the Ocean Drilling Program Leg 164, Hole 994C from the Blake Ridge in the northwest Atlantic suggests a close association between certain species of benthic foraminifera and methane emissions. Such species will prove to be good proxy in any future exploration of gas hydrate. Low stable carbon isotope values have also been observed during intervals of methane releases, whereas enriched values suggest *in situ* formation of gas hydrates. Changes in foraminiferal distribution at around 3 Ma suggest destabilization of gas hydrates by the reduction of hydrostatic pressure during intense Northern Hemisphere Glaciation. Bottom water warming also can be another vital factor for submarine gas hydrate destabilization. Highly metastable properties of gas hydrates allow its dissociation into gaseous methane by shifting of the position of gas hydrate stability zone owing to little changes in temperature and pressure which ultimately lead to increase in atmospheric methane. The continental or permafrost gas hydrate deposits are being exploited because of recently developed technologies; the marine gas hydrate deposits have just begun to be exploited and require more developed technology for commercial production. Besides economic importance, gas hydrates are also driver of climate change owing to its high green house potentiality and geohazards along the continental margins. Thus, there is a need to understand different aspects of gas hydrate through the Neogene. India is depleted in conventional natural resources and rich in submarine gas hydrate. Commercial production of gas hydrate can fulfil the energy crisis of the country. Also, controlled production of gas hydrate will be helpful to restrict excess methane input to the atmosphere and lowering global warming.

Keywords: Gas hydrate, methane, geophysical and geochemical proxies, benthic foraminifera, global warming

INTRODUCTION

Increasing energy demand for economic development is compelling the emerging as well as the developed economies to search for alternative energy resources. Most of our energy requirements are met by conventional energy resources whereas unconventional energy resources contribute little. Till date, we have been able to generate energy from a few unconventional resources such as solar, wind and wave-energy resources. Yet, the discovery and exploitation of unconventional energy resources bears immense importance to the human society. Coal bed methane, shale gas, etc. are some of the potential natural resources which have successfully been explored and are being commercially exploited from different part of the globe. However, gas hydrate, another unconventional natural energy resource, is yet to be exploited for commercial production for the use of society.

Gas hydrate is a naturally occurring solid, ice-like highly metastable crystal consisting mainly of methane and water molecule that has enormous potentiality as a future energy resource (Fig. 1). It has been established that 1 cubic meter of solid structure-I gas hydrate can yield up to 164 cubic meter of methane in standard temperature and pressure conditions (Hunt, 1979). The global distribution of permafrost and submarine gas hydrate show its potentiality to produce methane at about 1 to 5×10^{15} cubic meters (Milkov, 2004). The numbers of observed and inferred gas hydrate reserves are around 220 as shown in Fig. 2 (Ginsburg and Soloviev, 1998;



Fig. 1. Photograph of recovered gas hydrate chunk from well no. 10D, Krishna-Godavari Basin during the drilling of NGHP-01 expedition (Courtesy: Dr. Pushpendra Kumar, ONGC).

Maslin *et al.*, 2010). Most of these gas hydrate reserves are mainly identified by the presence of Bottom Simulating Reflectors (BSR, e.g., Peru Trench, Blake Outer Ridge, Krishna-Godavari Basin, etc.) and a few are identified by direct collection of hydrated cores (e.g., Okhotsk Sea, Cascadian Basin, etc.), freshening of pore water (e.g., Alcutian Trench, Japan Trench etc.), well logs (e.g., Sverdrup Basin) and Acoustic Velocity-

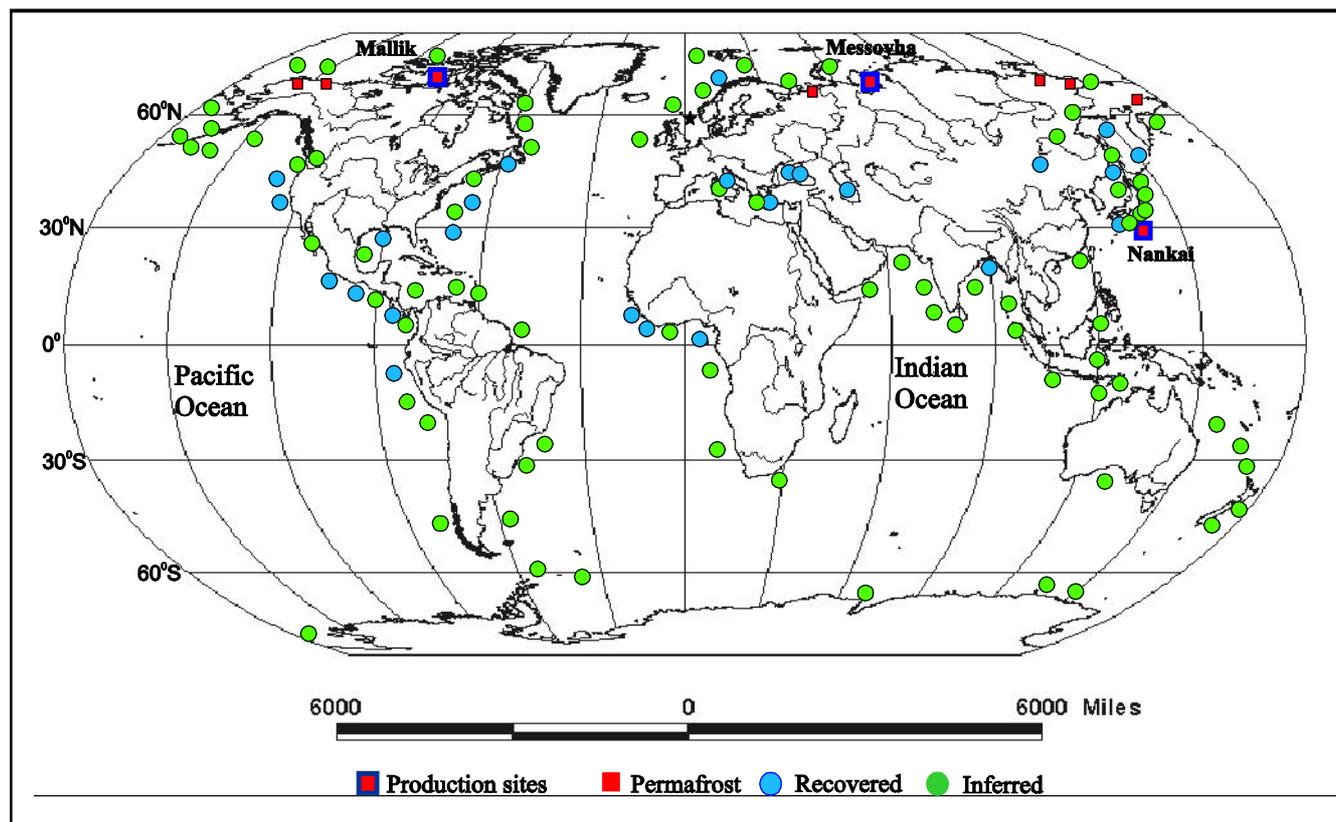


Fig. 2. Global distribution of gas hydrates deposits. Filled squares and circles indicate status of gas hydrate sites.

AMPLITUDE (VAMP, e. g., Bering Sea). In the permafrost region, gas hydrate is present within the permanent ice cap on the surface (e.g. Mallik hydrate field in Mackenzie Delta).

COMPOSITION AND STRUCTURE OF GAS HYDRATE

Gas hydrate is mainly composed of gaseous hydrocarbons (mainly methane/ C_1) and water molecule in the form of ice. Analysis of global gas hydrate deposition reveals that among the gaseous components the most dominant one is C_1 (99.99 to 29.7%) along with C_2 (15.3 to 0.02%), C_3 (36.6 to 0.1%), $i-C_4$ (9.7 to 0.09%), $n-C_4$ (4 to 0.1%), C_5 (4.8 to 0.0%), CO_2 (0.63 to 0.1%) and N_2 (1.4 to 0.77%) (Makogon *et al.*, 2007). Sometimes, H_2S may be present in the hydrate. Biogenic gas hydrate mostly contains more than 98% methane whereas thermogenetic gas hydrate contains more amounts of long chain gaseous hydrocarbons.

In gas hydrate lattice structure, water molecules act as the host by forming cage-like structure within which the methane molecules (as guest molecules) are enclosed. In addition to methane, CO_2 and H_2S may form hydrates which are less frequent in nature. Gas hydrates are mainly crystallized in isometric systems (Structure I and II) and occasionally in Hexagonal system like ice (Structure H). Among them, structure I is the most frequent one. The unit cell of Structure I contains eight cages of two different types. These cages may entrap gas molecules like CH_4 , CO_2 or H_2S which having smaller diameter than propane molecule and indicates biogenic hydrates. Unit cell of structure II gas hydrate consists of 24 cages (16 small cages and 8 large cages). Structure II gas hydrate contains mixture of long chain hydrocarbons (larger

than ethane and smaller than pentane) and generally formed thermogenic hydrates. Structure H is a more complicated and form smaller cages; it contains a cage in which 12-sided shapes consisting of squares, hexagon and pentagon cages are present. This structure can fit much larger molecules of hydrocarbons than methane such as methyl cyclohexane (Maslin *et al.*, 2010).

ENVIRONMENT OF GASHYDRATE ACCUMULATION

Gas hydrate deposits show wide geographical distribution. Most of the deposits are found in the equatorial zone and Northern Hemisphere, whereas a few deposits are reported from the Southern Hemisphere. They are mainly concentrated in the continental margin where ocean water depth is greater than 500m with low temperature, high pressure and adequate amount (2.0–3.5%) of sedimentary organic carbon (SOM) (Ginsburg and Soloviev, 1998; Fehn *et al.*, 2000). The other influencing factors include salinity, composition of gas, geological structure, fluid migration and pore space of sediments (Ginsburg and Soloviev, 1998; Dickens, 2001). In Polar Regions (permafrost regions), gas hydrate may exist at subsurface depth ranging from about 130m to 2000m (Kvenvolden, 1998).

Temperature and Pressure

Temperature and pressure play a major role in gas hydrate formation. Hydrate forms at pressure 2.6 MPa and above, for the system 'liquid fresh water – pure gas' at 0° C temperature. Hydrate formation curve for methane, for the temperature range -10° C to 0° C, can be represented by the following formula (Istomin and Yakushev, 1992):

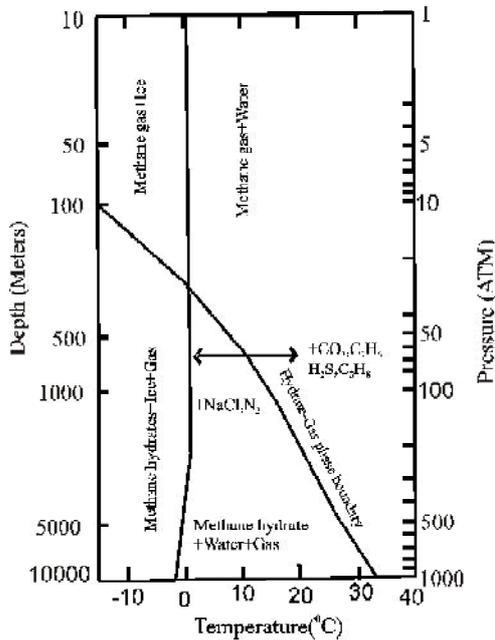


Fig. 3. Phase diagram showing the boundary between free methane gas and methane hydrate for a ‘pure water and pure methane’ system. Addition of NaCl to water shifts the curve to the left. Addition of CO₂, H₂S, C₂H₆, C₃H₈ to methane shifts the boundary to the right and thus increase the area of the hydrate stability field (Kvenvolden, 1998).

$$nP = 8.968 - 2196.62 \dots\dots\dots(i)$$

where P = Pressure in MPa ; T = Temperature in Kelvin scale

For the temperature range 0° C to 12° C the formula is:

$$nP = 29.112 - 7694.3/T \dots\dots\dots(ii)$$

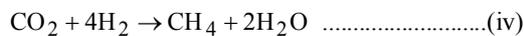
Fig. 3 gives an outline of the effect of pressure and temperature for the formation of gas hydrate. These are ‘temperature – pressure’ phase diagram for the ‘pure methane – pure water’, ‘pure methane – sea water (Sw)’ system at high methane concentration. Fig. 3 is the redrawn phase diagram showing boundary between free methane gas and methane hydrates for a ‘pure water - pure methane’ system along with depth (Kvenvolden, 1998).

Total Organic Carbon

Adequate SOM (generally represents as CH₂O) is necessary for the formation of significant amount of methane, which is the main component of methane hydrate. Gas hydrate forming methane may be of biogenic or thermogenic origin. Biogenic methane is formed by the bacterial decomposition of SOM (methanogenesis) in low temperature and anaerobic conditions at shallow depths. SOM is degraded by the following reaction:



Carbon dioxide produced may convert into methane, theoretically, if adequate amount of hydrogen is present according to the reaction:



Cracking of SOM in deep-seated conditions at high temperature (80°C to 150° C) produce hydrocarbon liquid and gas. The co-genic gas with liquid is called primary thermogenic gas and thermal cracking of liquid at high temperature into gas is called secondary thermogenic gas.

Gas hydrate formed from biogenic hydrocarbon is composed mainly of 99% pure methane, whereas thermogenic gas hydrate contains less amount of methane along with other short chain hydrocarbons such as ethane, propane, butane, etc. Organic carbon studies from various Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) sites show that 1% to 3.5% of Total Organic Carbon (TOC) is present in case of *in situ* gas hydrate deposits. Observations on the present-day organic matter content of *in situ* gas hydrate containing sediments offshore Guatemala show value in between 2% and 3.5%, whereas in Blake Outer Ridge it is 0.5% to 1.6% (Bhaumik and Gupta, 2007; Bhaumik *et al.*, 2011). But for the formation of gas hydrate the organic carbon content in the sediment was undoubtedly higher, perhaps double the present amount.

Porosity

Porosity plays an important role in the genesis and distribution of gas hydrates. Capillary force between the sediment grains is inversely proportional to the radius of the menisci of the interstitial water (Pierre *et al.*, 2000), which acts as a factor for the nucleation of gas hydrate. Large and round pore spaces between the grains decreases the capillary force and act as an ideal nucleation site for the formation of gas hydrate. Marine hydrates are found within unconsolidated sediment containing silt or clay (sometimes sand) with high porosity, about 35% to 60% of the sediment volume. The porosity of the upper gas hydrate zone (180 m to 260m) in Blake Outer Ridge (Site 994, Hole C, Leg 164) shows high value in between 60% to 68% (Paull *et al.*, 2000). Generally, the hydrate content of these sediments does not exceed 15% of the pore spaces.

Salinity and Composition

Salinity of the seawater is mainly caused by the huge concentration of NaCl in it. The freezing point of brine water is much less than the freezing point of pure water. So, the phase boundary of ‘methane hydrate-water-gas and methane-gas-water’ in ‘pure water–pure methane’ system moves towards the left in the ‘saline water- pure methane’ system. Presence of salts in seawater shifts the base of hydrate stability zone (HSZ) to shallower depths and causes a small reduction in the solubility of methane (Kvenvolden, 1998). On the other hand, presence of other components like carbon dioxide, ethane, propane, hydrogen sulphide etc., shifts the phase boundary of ‘methane hydrate-water-gas and methane gas-water’ in ‘pure water–pure methane’ system towards right and thus increases the area of the hydrate stability field (Fig. 3).

Gas hydrates quickly transformed in gaseous methane and pure water owing to the depressurization during recovery of core. Thus, input of significant quantity of fresh water caused the dilution of salinity of the pore water which is used as marker for the identification of gas hydrate and commonly known as freshening of pore water. The Blake Ridge gas hydrate reserve shows minimization of pore water chlorine concentration up to a tune of 450 μm and is the classical example of freshening of pore water.

Mechanism for the formation of gas hydrates

Several mechanisms have been proposed to explain the formation of gas hydrate. The Cryogenetic model indicates external cooling of sediments which in-turn is responsible for the entrapment of molecular methane gas within the ice cage in

the permafrost region (Ginsburg and Soloviev, 1998), whereas transgression model states that in warm intervals, sea-level rise due to marine transgression is responsible for the increase in formation pressure. In addition, melting of ice in the permafrost region is also responsible for lowering temperature owing to the required latent heat for melting of ice. The buffering of latent heat lower down the temperature in such a way that the gas hydrate can be stable increasing of temperature 1 to 7°C (Ginsburg and Soloviev, 1998; Majorowicz *et al.*, 2011). The sedimentation model is a hypothetical model for the formation of gas hydrates. Mass sediment flow owing to avalanche, gravity etc. can entrap free gas or gas bubbles present within the flow and may form buried hydrate accumulation in favourable conditions (Ginsburg and Soloviev, 1998). The authigenic-diagenetic model expresses the *in situ* formation of biogenic gas hydrates. This is complex and combined process which includes formation of biogenic methane by the degradation of sedimentary organic matter during early diagenesis, removal of methane by diffusion, removal of salts by diffusion, osmotic transport of water and lithification of sediments. Solubility of methane in water at different depths is also an important factor in this model (Ginsburg and Soloviev, 1998). Filtration model states that hydrate forming fluid is supplied by fluid flow to the hydrate stability zone. The fluid can be emerged and supplied outward by the squeezing of sediments or hydrothermal system may produce hydrate forming fluid or can be of free gas flow. However, it is important to note here that the solubility of methane in pure water system varies directly with temperature and pressure (Ginsburg and Soloviev, 1998).

PROXIES FOR THE IDENTIFICATION OF GAS HYDRATE

Geophysical and Geochemical proxies

The gas hydrate deposits may be identified by using several proxies. Among them, the most important geophysical proxy is the presence of Bottom Simulating Reflector (BSR) in the subsurface condition. Geophysical investigation is an indirect procedure to obtain knowledge about the gas hydrate-bearing horizon. Most of the gas hydrate deposits in the marine environments were detected from the seismic reflection profile, where it produces remarkable BSR. This marks an interface between hydrate-cemented sediment having higher sonic velocity and uncemented sediments below with lower sonic velocity. Gas hydrate bearing sediments have higher compressional wave velocity than water saturated and free gas-bearing sediments (MacKay *et al.*, 1994). Seismic profile data not only provides us with the knowledge about the BSR, but is also helpful in giving us idea about the amount of gas hydrate, porosity of the sediment, lateral as well as vertical extension of gas hydrate zone, stability zone of gas hydrate, etc. The strong BSR in the eastern flank of the Blake Outer Ridge has enabled to locate the base of the gas hydrate stability zone (Fig. 4, Paull *et al.*, 1996). However, gas hydrate deposits were recovered by direct coring from different areas where BSR is absent, e.g. ODP Hole 994C at Blake Ridge, Southeast U. S. Cost, and Shenhu area in northern South China Sea (Paull *et al.*, 1996; Yang *et al.*, 2011).

Except this among the geochemical proxies most important are halide studies, pore water sulphate study, barium fronts and isotopic study of carbonates. Sodium chloride (NaCl) in

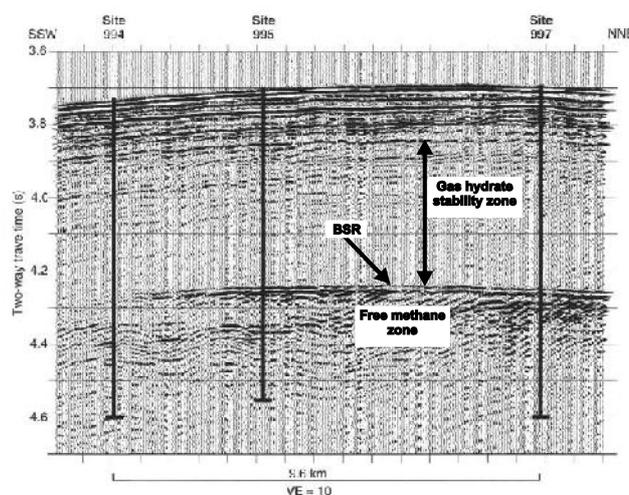
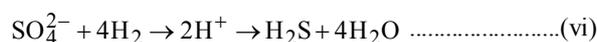
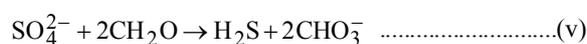


Fig. 4. Seismic profile (CH-06-92 Line 31) of Blake Outer Ridge showing BSR, free methane zone and gas hydrate stability zone. Solid gas hydrate is recovered from Site 994 though BSR is absent there (Modified from Paull *et al.*, 1996).

the seawater is the main source of Cl^- . Gas hydrate bearing zone always represents depleted Cl^- concentration than the surroundings. This happens due to the exclusion of dissolved Cl^- at the time of the formation of lattice of pure water and methane within the sea floor in an open system. For this reason, the salinity of the surrounding water increases due to percolation of the Cl^- . If water samples are recovered from gas hydrate zone after its dissociation at the time of core recovery, it shows less Cl^- concentration due to the dissociation of pure water from the lattice of hydrates which has no Cl^- in it. The classical example of chlorine depletion in recovered pore water samples from gas hydrate zone is observed in Blake Outer Ridge (Site 994, Leg 164) where gas hydrate layer lies in between 180m to 450m below sea floor (Paull *et al.*, 1996). Iodide (I^-) and Bromide (Br^-) are present in very little amounts in sea water in comparison to Cl^- whereas they may be present in higher amount in SOM. Water in the biogenic gas hydrate zone is always rich in I^- and Br^- concentration than the surrounding. I^- and Br^- present in the SOM come out in the free water by the bacterial decomposition of SOM, which is absolutely related to the genesis of the gas hydrate (Fehn *et al.*, 2000).

In general, pore water sulphate concentration decreases with increasing depth. The oxygen present in the sulphate is used for the oxidation of sedimentary organic matter present within the sediments and produces toxic H_2S . Thus the increased number of sulphate reducing bacterial population and decreased pore water sulphate indicate biogenic cracking of organic carbon. On the other hand, sulphate reducing bacteria also used pore water sulphate for the anaerobic oxidation of *in situ* generated or upward migrated methane from the deeper part. Thus the interface between pore water sulphate and methane may be important for determination of extent of methane within the sediments (Martens *et al.*, 1999). The chemical reactions for the degradation of sedimentary organic matter and anaerobic oxidation of methane are as follows:



Barium is present in the pelagic sediments either in aluminosilicate or microscopic barite crystal which is also used as an important indirect proxy to understand the occurrence and distribution of marine gas hydrate. Barium present in aluminosilicate is typically immobile where as present in barite is mobile in nature. Solubility of barite to produce Ba^{2+} greatly reduced with increasing depth and increased in depleted pore water SO_4^{2-} condition at shallower depth. During the sedimentation, dissolved Ba^{2+} moves downwards from high pore water SO_4^{2-} bearing zone to low pore water SO_4^{2-} bearing zone. Again the dissolve Ba^{2+} diffuses upward from depleted SO_4^{2-} to enriched SO_4^{2-} bearing zone and get participated there. Thus, upward diffusion of Ba^{2+} exceeds downward burial and barium front created. In this way, Ba^{2+} front marks the depth where paleo-pore water SO_4^{2-} concentrations were nearly zero in the past (Dickens, 2001).

The carbon isotopic ($\delta^{13}C$) composition of methane is directly related to its genesis. Methane formed by methanogenesis shows very high negative $\delta^{13}C$ values lighter than -60% relative to the Pee Dee Belemnite (PDB) standard (Kvenvolden, 1998; Paull *et al.*, 2000). Consistent trend of the carbon isotopic value in methane and CO_2 in a particular zone indicates formation of methane resulted from the microbial reduction of CO_2 derived from the organic matter (as per equation number iv). In case of thermogenic methane, the $\delta^{13}C$ values are relatively heavier ranging from -40% to -60% . The $\delta^{13}C$ values of methane and methane-ethane ratio in the graph (Fig. 5) can give an idea about the genetic history of methane formation (Paull *et al.*, 2000). In Blake Outer Ridge, for example, the carbon isotopic composition increases towards the depth from -94% to -66% , indicating microbial origin (Galimov and Kvenvolden, 1983). Other studies in Offshore Peru, Offshore northern California and Gulf of Mexico also show highly negative $\delta^{13}C$ values in the range of -79% to -44% relative to the PDB standard (Kvenvolden, 1998). On the other hand, gas hydrate associated with mud volcanoes in the Caspian Sea shows isotopic composition ranging from -57.3% to -44.8% indicating thermogenic origin of methane (Bernard *et al.*, 1976).

For the determination of formation age and genesis of methane, ^{129}I study is useful as iodine enrichment reflects the

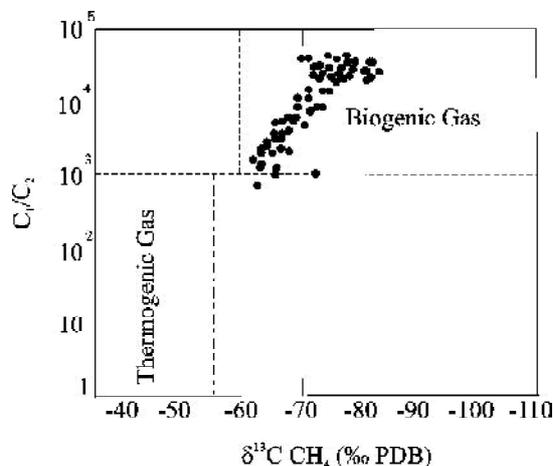


Fig. 5. Carbon isotopic plot of methane vs methane-ethane ratio plot from Blake Outer Ridge shows methanes are biogenic in origin (Paull *et al.*, 2000)

release of iodine from the decomposition of organic matter (biophilic character of iodine) in marine sediments (Fehn *et al.*, 2000).

The Calcium carbonate ($CaCO_3$) content of the sediments is also an important factor for gas hydrate formation. In Blake Ridge, $CaCO_3$ concentration within the hydrate bearing sediments is less. Owing to the lack of cementing agent $CaCO_3$ and abundance of siliceous microfossils which in turn is responsible for the formation of large well rounded pore, porosity within the sediments remains higher. Increasing siliceous microfossils also decreases the capillary force between the grains and increase inhabitation of hydrate or formation of large clathrate cage (Pierre *et al.*, 2000).

Foraminiferal proxy

Numerous studies have been carried out to understand the relation between foraminiferal distribution and seep/gas hydrate environment (e.g., Sen Gupta *et al.*, 1997; Rathburn *et al.*, 2000; Torres *et al.*, 2003; Hill *et al.*, 2003, 2004; Panieri, 2005; Bhaumik and Gupta, 2007). These studies showed that certain species of benthic foraminifera have higher tolerances to stressful environments associated with seeps (Rathburn *et al.*, 2000). Akimoto *et al.* (1994) suggested that the occurrence of *Rutherfordoides cornuta* and *Bolivina tumida* are related to high methane gas content in marine sediments. Benthic foraminifera from modern seep environments have been studied primarily in the Gulf of Mexico (Sen Gupta *et al.*, 1997), northern California Margin, USA (Rathburn *et al.*, 2000), Monterey, USA (Bernhard *et al.*, 2001), Santa Barbara Basin, California (Hill *et al.*, 2003) and offshore Japan (Akimoto *et al.*, 1994), Blake Outer Ridge (Bhaumik *et al.*, 2011). These studies showed that some particular taxa of benthic foraminifera, including the genera *Bolivina*, *Bulimina*, *Cassidulina*, *Fursenkoina*, *Epistominella*, *Melonis*, *Nonionella*, *Uvigerina*, etc. may be adapted to the high organic carbon, low oxygen reducing environment of methane seeps. The study by Hill *et al.* (2003) in methane seep rich Santa Barbara channel has shown that *Epistominella pacifica*, *Bolivina tumida*, *Oridorsalis umbonatus* and *Uvigerina peregrina* are common assemblage found near active methane seeps and may be an indication of high concentrations of methane as well as low oxygen and organic carbon rich environment. It has been found that *Bolivina seminuda* and *Nonionella auris* show their parallel excursions in methane rich environment and can be used as proxy for inferring high concentrations of biogenic methane in pore waters just below the sediment surface (Wefer *et al.*, 1994). However, few workers suggested that no foraminifera are endemic to seep environment.

It is evident that methane rich environment is always rich in bacteria (Wellesbury *et al.*, 2000) and there are some benthic foraminiferal species (e.g., *Chilostomenella oolina*, *Melonis barleeianum*, *Uvigerina peregrina* etc.) which prefer to feed on bacteria. Thus the population of bacteria as well as these benthic foraminifera may be an indicator of generation of biogenic methane by bacterial degradation of SOM (Bernhard *et al.*, 2001; Rathburn *et al.*, 2000; Panieri, 2005).

Depleted foraminiferal carbon isotopic values are also another proxy for identifying methane rich environments (Wefer *et al.*, 1994; Rathburn *et al.*, 2000). Highly depleted ^{13}C values of infaunal benthic foraminiferal shell may go up to -21% (Hill *et al.*, 2004) in methane rich settings. Bacterial degradation of organic carbon produces CH_4 and CO_2 (see

equation number iii). Anaerobic oxidation of methane in the presence of pore water SO_4^{2-} can also be responsible to produce O_3^- (see equation number vii). Thus, fractionation of ^{13}C and ^{12}C present with the organic matter took place during this time. Isotopically lighter carbon (^{12}C) preferentially enters the lattice of methane and isotopically heavier carbon (^{13}C) enters CO_2 . This isotopic fractionation may go upto 80% in between them (Rosenfeld and Silverman, 1959). Syndepositional formation of gas hydrate entrap methane quickly, leaving no time for its breakdown and thus the surrounding water becomes enriched in ^{13}C which in turn is responsible for enriched ^{13}C values in foraminiferal shell calcified during formation of gas hydrate. On the other hand, dissociation of gas hydrates or methane is responsible to contribute ^{12}C carbon to the ocean water and thus calcification of foraminiferal shell during this time bears highly depleted carbon isotopic signature.

DESTABILIZATION OF GAS HYDRATE

In recent years, numerous attempts have been made to determine paleo-methane fluxes from gas hydrate reservoirs using various proxy records (Wefer *et al.*, 1994; Rathburn *et al.*, 2000; Dillon *et al.*, 2001; Holbrook *et al.*, 2002; Ryskin, 2003; Cannariato and Stott, 2004). Dillon *et al.* (2001) and Holbrook *et al.* (2002) used geophysical proxies to estimate the release of methane from the Blake Ridge area. Highly depleted carbon isotope values of benthic and planktic foraminifera, organic carbon and different organic compounds (Diplopetrol, Archaeol) have also been used to detect methane fluxes in the Blake Nose area as well as Santa Barbara Basin (Kennett *et al.*, 2000; Cannariato and Stott, 2004).

It is well constrained that good amount of biogenic methane from the Blake Ridge was released at the time of Palaeocene-Eocene Thermal Maximum (PETM, Katz *et al.*, 1999) and in the Pliocene-Pleistocene intervals (mainly in the last 2.5 Ma, Dillon *et al.*, 2001; Dickens, 2001; Holbrook *et al.*, 2002; Bhaumik and Gupta, 2007). Methane emission across PETM was identified using benthic fauna and highly negative $\delta^{13}\text{C}$ isotope values (Katz *et al.*, 1999). During the Pliocene and Pleistocene, the methane release was identified mainly using the geophysical investigations. According to Holbrook *et al.* (2002), approximately 0.6 giga ton methane was released from this zone since the last 2.5 Ma. It has been argued that at any oceanic location where a methane-driven eruption occurs once, similar eruptions are likely to occur, roughly periodically (Ryskin, 2003). So from the previous work as discussed above, it may be said that a gas hydrate rich zone might have experienced several episodic methane flux events in the geologic past and can be identified by the selective benthic faunal presence or highly depleted carbon isotopic values.

Gas hydrates are highly metastable and easily converted into gaseous methane and fresh water owing to little bit changes in the temperature and pressure conditions. Two major models have been proposed by different workers to support the gas hydrate destabilization mechanism owing to the reduction of hydrostatic pressure as well as fluctuation in bottom water temperature. It has been argued that lowered sea level causes reduction of hydrostatic pressure that destabilizes solid gas hydrate into the gaseous phase (Kayen and Lee, 1991; Haq, 1998; Maslin *et al.*, 1998). On the other hand Kennett *et al.* (2000) and Hill *et al.* (2003) have linked dissociation of gas

hydrate in the Quaternary interstadials to increase in bottom water temperatures. Holbrook *et al.* (2002), on the other hand, related destabilization of gas hydrates to the creation of gas migration pathways by the formation of sediment waves and related erosion at Blake Outer Ridge after 2.5 Ma.

Case study from Blake Outer Ridge

The Blake Ridge is located ~200 Km off the east coast of the United States of America in the NW Atlantic Ocean. Presence of strong BSR and recovery of gas hydrate lumps during coring were the evidence of the presence of disseminated gas hydrate within 185 to 450 meter below sea floor (mbsf) in this zone. This case study is presented from the published data generated and obtained from Ocean Drilling Program (ODP) Hole 994C (31° 47.139' N; 75° 32.753' W; present day water depth 2799.1 m; core penetration 703.5 mbsf) (Paull *et al.*, 1996). Blake Ridge is an ideal site for the gas hydrate study and numerous studies have been carried out to understand different aspects of gas hydrate accumulation.

Presence of solid gas hydrate at Blake Ridge above the BSR with free gaseous methane below would suggest saturation of methane in the hydrate-bearing sediment (Paull *et al.*, 1996). The question is how gas hydrate was formed within the interval between 195 and 450 mbsf in this zone (5 to 2.95 Ma at ODP Hole 994C). High pressure, low temperature, high organic carbon, high porosity, adequate amount of methane and pore water, and rapid sedimentation rate are the primary requirements for the formation of gas hydrate (Kvenvolden, 1998). The gas hydrate zone of the Blake Ridge is typically characterized by the presence of high pressure (water depth ~3000 m and 195 m overlying sediment thickness), low temperature (~3°C), high sedimentation rate (12.75 cm/kyr), high porosity (50-65%), opal concentration (~8%), organic carbon (0.7-2.1 wt %) and low CaCO_3 concentration (~4 to ~15%, Paull *et al.*, 1996; Kraemer *et al.*, 2000; Fig. 6).

Presence of higher opal make the sediment highly porous which in turn acted as the nucleation site for generation of solid gas hydrates (Kraemer *et al.*, 2000). Abundance of diatoms within the sediments is responsible for the well rounded large pores and gas hydrate nucleates in these pores due to feeble capillary force (Kraemer *et al.*, 2000). Lower CaCO_3 concentration also decreases the cementing nature of the sediments and help in the formation of gas hydrate (Paull *et al.*, 1996; Balsam and Damuth, 2000). Increased abundances of well known organic carbon rich taxa (*Uvigerina hispida*, *U. hispidp-costata*, *U. peregrina*, *U. proboscidae* and *M. barleeianum*) and high TOC concentration in the gas hydrate and free methane intervals definitely indicate presence of high organic carbon in these zones (Fig. 7). High bacterial population (Wellesbury *et al.*, 2000) may indicate consumption of organic carbon in the formation of methane by methanogenesis. Absence of Miliolids (*Quinqueloculina weaveri*, *Q. seminulum*, *Q. pygmaea*, *Pyrgo depressa*, *P. lucernula*) in hydrate rich zone from this site indicates presence of methane which in turn was responsible for such highly redox environment.

Previous studies on benthic foraminifera from seeps and organic carbon rich environments enabled to classify benthic foraminifera at Hole 994C into two groups as seep-related (*Bolivina paula*, *Cassidulina carinata*, *Chilostomella oolina*, *Fursenkoina fusiformis*, *Globobulimina pacifica*, *Nonionella auris*, *Trifarina bradyi*) and organic carbon-related (*Uvigerina*

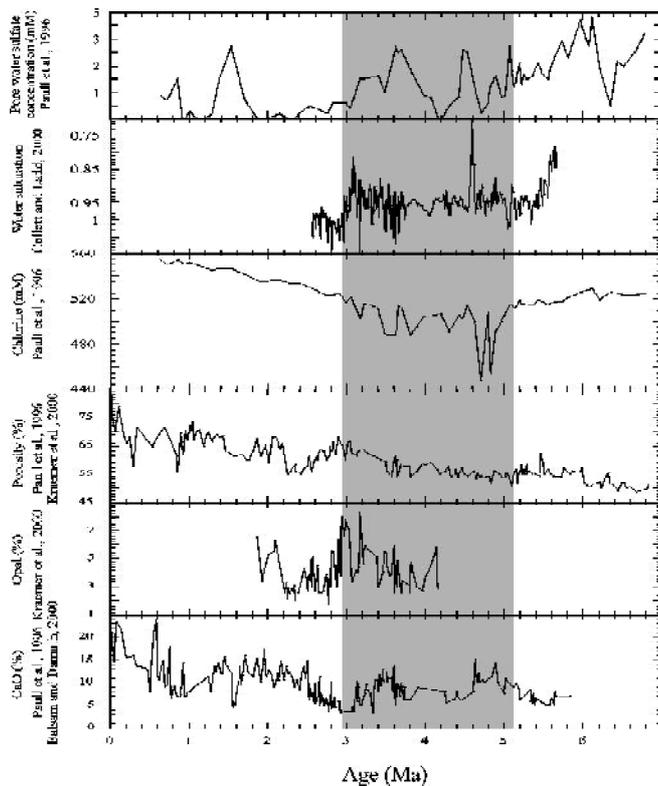


Fig. 6. Composite graphs showing variations of different geochemical, porosity and Opal data within the gas hydrate zone. Gas hydrate zone is shaded by grey colour.

peregrina, *U. hispida*, *U. hispidocostata*, *U. proboscidea* and *Melonis barleeanum*) taxa (Bhaumik and Gupta, 2007). The cumulative census data of these species are combined with total number of species and individuals data, oxygen and carbon isotope values and global sea-level fluctuation curve (Haq *et al.*, 1988) for better understanding of the generation and paleo-methane flux history at Blake Ridge (Fig. 7). At Hole 994C, seep-related and high-organic carbon taxa show opposite trends during the studied sequence. The interval late Miocene to mid Pliocene (~7 to 3.6 Ma) is dominated by higher abundances of high-organic carbon taxa, whereas mid-Pliocene (3.6 Ma) to the Holocene is dominated by an increased population of seep-related taxa, coinciding with the beginning of Northern Hemisphere Glaciation (Fig. 7). The major changes in seep-related taxa, high organic carbon taxa, total species and total individuals are observed at around 3 Ma which is coinciding with the boundary of hydrate rich and hydrate free zone and might be the indicator of a shift from a stressful environment (methane rich) to a favourable environment (methane free). Enriched population of high organic carbon taxa during 7 to 3.6 Ma indicates input of high organic carbon to the sea floor which in turn is responsible for generation of biogenic methane. Increased population of seep-related taxa coinciding with sea-level lowstands indicates dissociation and upward migration of gas hydrates in terms of methane owing to the lowering of hydrostatic pressure (Fig. 7).

Enriched $\delta^{13}\text{C}$ values in the interval 5 to 3.6 Ma may also be indicator of syndepositional formation of gas hydrate (Bhaumik and Gupta, 2005, 2007). The *in situ* generated biogenic $^{12}\text{CH}_4$ (having depleted $\delta^{13}\text{C}$) may quickly get entrapped within the sediments as solid gas hydrate owing to the presence of

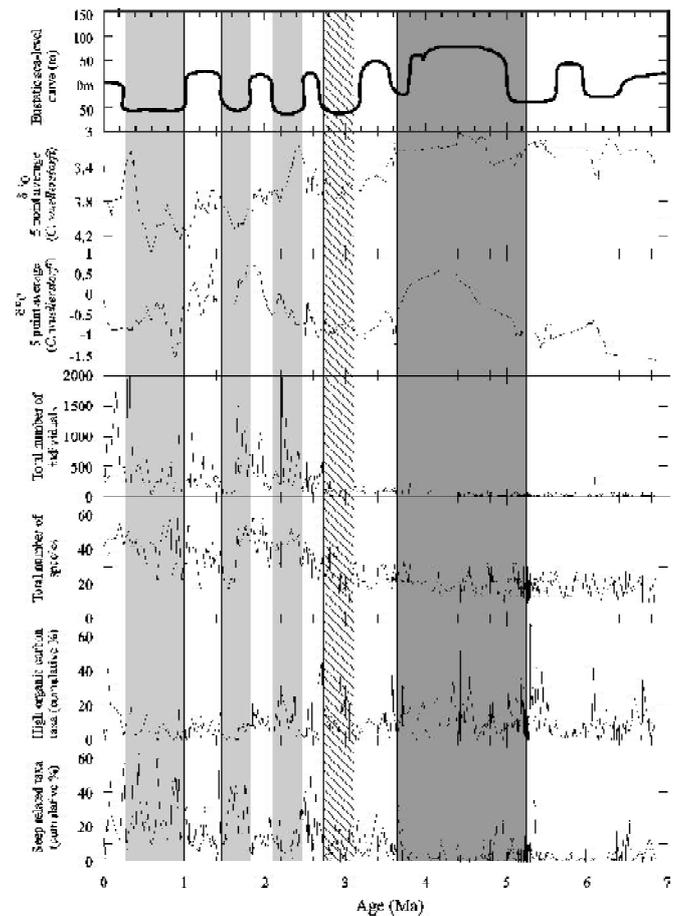


Fig. 7. Composite graph of faunal data, isotope data and sea level curve showing their variation within gas hydrate rich zone and probable paleo-seep intervals. Dark grey bar designates gas hydrate rich zone, hatched zone indicates transition zone coinciding with the boundary between hydrate rich and free zone where as light shaded bars indicate probable paleo-seep intervals.

suitable environment leaving behind $^{13}\text{CO}_2$ (as per equation no. iii). This $^{13}\text{CO}_2$ may take part in the formation of carbonate test of foraminifera which bears elevated carbon isotopic values. Also, the work carried out by Paull *et al.* (2000) on methane-ethane ratio also indicates that methane present at Hole 994C is biogenic in origin (Fig. 5) and corroborates our results. However, Bhaumik *et al.* (2011) relates the faunal carbon isotopic data with bottom water hydrography.

Presence of gas hydrate within the sediments makes it non-porous and non-permeable. Thus, the hydrate rich sediments resist upward flow of gaseous methane present below the BSR. Gas hydrate can only be formed and be stable within the gas hydrate stability zone (GHSZ). The GHSZ can move upward only if the pressure increases and/or temperature decreases and move downward if the reverse conditions are there. Changes in the position of GHSZ are responsible for the dissociation of gas hydrates into gaseous methane. The gaseous methane produced by the dissociation of gas hydrate can escape from the sediments and the methane present below the BSR again took part in the formation of solid gas hydrates. Free gaseous methane cannot directly go to the oceanic water owing to the presence of non-porous hydrated sediments in the GHSZ.

SIGNIFICANCE OF GAS HYDRATE STUDY

Though the beginning of gas hydrate research goes back to 1965, its study gained momentum over the last three decades when research workers found that it could be a potential energy resource, a submarine geohazard agent and a driving force for global climate change. Investigations by John *et al.* (1994) suggest that gas hydrate has some beneficial use in biotechnology, chemical processing and semiconductor industries or in emulsion manufacturing.

Potential energy resource

Gas hydrate is attractive potential energy resource owing to its enormous amount of methane within the clathrate structure. Theoretically it is established that one cubic meter (1m³) of fully saturated structure-I methane hydrate can yield up to one hundred sixty four cubic meter (164m³) of methane gas at standard PT conditions (Hunt, 1979). The energy density of gas hydrate is almost same as the energy density of Compressed Natural Gas (CNG) and less than the energy density of Liquefied Natural Gas (LNG). The amount of energy stored in the gas hydrate is twice of the sum of the energy stored in other fossil fuels (Sloan, 2003). Till date the estimated amount of carbon trapped within the ocean sediments in terms of gas hydrates ranges from 500 to 10,000 giga tonnes. Whereas, estimated trapped carbon in the Arctic permafrost region is about 400 giga tonnes (Maslin *et al.* 2010). Geological structures like seal or dome like reservoir with high porosity and permeability lying between impermeable strata are favourable to trap the dissociated methane from gas hydrates. Economic production of methane from gas hydrate is still a difficult task. The estimation of world energy balance during 1850 to 2050 is done by Makogon *et al.* (2007). He showed that the demand of wood, coal and oil is gradually decreasing and demand of natural gas and hydropower are gradually increasing along with nuclear power. The demand of gas hydrate increased with a high momentum since 2000 and probably it will be the main factor to meet our energy requirement in near future. The time of formation of gas hydrate is also not restricted globally like oil. About 90% of the total oil reserves are generated within the six major geologic intervals (Silurian – 9%, Upper Devonian – 8%, Pennsylvanian to lower Permian – 8%, upper Jurassic – 25%, middle Cretaceous – 29% and Oligocene-Miocene – 12.5%; Klemme and Ulmishek, 1991). On the other hand, world coal reserves are also generated mainly in two time slices, during Gondwana and Tertiary. In this respect, the generation of gas hydrate is not time restricted and is a continuous process. Formation of methane by the bacterial degradation of SOM within the sea floor is a continuous process. Trapping of the methane as gas hydrate in favourable condition can be a continuous source of future energy.

At present, production of gas hydrate is undergoing in three fields (Mallik field in Mackenzie Delta, Messoyha field in East Siberia and Nankai field in Japan; Makogon *et al.*, 2007). Gas hydrate production initially started in Messoyha permafrost deposit during the 1970s. Owing to the rapid production of gas hydrate the reservoir pressure dropped and the dissociation continued for long time (1979-1982) when the production was stopped. The production rate during the year 2007 from this site is about 400 million cubic meters per year (Makogon *et al.*, 2007). Methanol injection method is a mechanical way to recover methane from naturally occurring gas hydrate reservoir, although more expensive, but has been

successfully used to exploit methane from Messoyakha Gas Field. The resource potential of gas hydrate is yet unknown, but considering the possibility of enormous gas reservoirs, gas hydrate will continue to attract our attention until the wide scale recovery procedure is economically viable.

Submarine geohazards

Prior to gas hydrate formation in normal geological setting in an area, huge amount of methane and water are freed to migrate within the pore spaces of the sediment. After the formation of gas hydrate, water and methane become immobilized solid, restricting pore spaces and retarding the migration of fluids. Thus, solid water, not liquid water, occupies the pore spaces and the sedimentological process of consolidation and concentration of minerals are greatly inhibited, although gas hydrates themselves can act as metastable cementing agents. The permeability of the sediments decrease after the formation of solid gas hydrates. Eventually, the gas hydrates may occupy much of the sedimentary pore spaces within the zone of gas hydrate stability. Continuous sediment formation leads to deeper burial of the gas hydrate. Finally, the gas hydrate is buried so deeply that temperature at the base of the stability zone is reached, at which the gas hydrate is no longer stable and the solid gas hydrate transforms into “liquid gas–water” mixture. Thus, the basal zone of gas hydrate becomes weak possibly due to the pressure of the newly released gas, leading to a zone of weakness where failure could be triggered by the gravitational loading or seismic disturbance, and submarine landslides result (Kvenvolden, 1998). The same conditions that cause the gas hydrate dissociation during continuous sedimentation can also be brought by the lowering of sea level or by increasing bottom water temperatures (Katz *et al.*, 1999; Kennett *et al.*, 2000; Maslin *et al.*, 1998; Bhaumik and Gupta, 2007). These processes change the *in situ* pressure and temperature regime; thus gas hydrate stability zone also varies. While adjusting the new pressure–temperature conditions, the gas hydrate dissociates producing an enhanced fluidized layer at the base of gas hydrate zone. Submarine slope failure can also destabilize the solid gas hydrate in the deepest sediments. Similarly, gas hydrate may play an important role in sediment tectonics, strengthening the sediment above and weakening the sediment at the base of the gas hydrate stability zone. Besides these large scale geohazards created by destabilized gas hydrate, small scale (local) hazards also result in uncontrolled release of methane gas by dissociation of solid gas hydrate which can cause failure and subsidence of the gas releasing site (Yakushev and Collett, 1992).

Possible connection between gas hydrate boundaries and submarine slides and slump surfaces was first recognized by McIver (1977) and several possible examples have been described later. Some of them are surficial slides and slumps on the continental slope and rise of SW Africa (Summerhayes *et al.*, 1979), slumps on the U.S. Atlantic continental slope (Carpenter, 1981), large submarine slides on the Norwegian continental margin (Bugge *et al.*, 1987), sediment blocks on the sea floor in British Columbia fjords (Bornhold and Prior, 1989) and massive bedding plane slides and rotational slumps on the Alaskan Beaufort Sea continental margin (Kayen and Lee, 1991). Submarine mud volcanoes, another kind of geohazards, have also been attributed to the release of gas from gas hydrates in the Caspian Sea (Ginsburg *et al.*, 1992) and offshore North Panama (Reed *et al.*, 1990).

Global climate change

Methane is an important component of the atmosphere having a present-day concentration of about 4.9×10^{15} g (3.7×10^{15} g methane carbon). It is the most abundant greenhouse gas in the troposphere, after water and carbon dioxide. Both on the molecule and mass basis, additional methane is actually much more effective as a greenhouse gas than additional carbon dioxide. Methane is also the most abundant reactive trace gas in the troposphere and its reactivity is important to both tropospheric and stratospheric chemistry. The oxidation of methane by hydroxyl (OH[•]) ions in the troposphere leads to the formation of formaldehyde (CH₂O), carbon monoxide (CO) and ozone (O₃), in the presence of sufficiently high levels of nitrogen oxides (NO_x). Along with carbon monoxide, methane helps to control the amount of hydroxyl ion in the troposphere. Methane also affects the concentration of water vapour and ozone in the stratosphere and plays a key role in the conversion of reactive chlorine to less reactive HCl in the stratosphere (Wuebbles and Hayhoe, 2002).

In the total atmospheric methane, the contribution of oceanic methane is about 6%, whereas the share of other contributors is as follows: termites (13%), wet lands (72%) and other sources (9%) (Khalil, 2000). The outgassing of methane from gas hydrates due to pressure and temperature change may affect the Earth's climate since methane is a greenhouse gas. It is assumed that the release of methane from marine hydrates during PETM (Katz *et al.*, 1999) and during the Quaternary climatic maxima and minima has played a significant role in the climate change (Kennett *et al.*, 2000). Earth has witnessed several intervals of climate oscillations typified by rapid drops and rise in the sea level due to rapid cooling and warming. It is believed that the release of methane from marine hydrates has played a significant role to warm the Earth's climate. Several of these time intervals of climate change are characterized by major inputs of carbon to ocean and atmosphere, and the change in pressure-temperature conditions during these time slices may have reduced the stability of the gas hydrate reservoirs. During glaciations, when sea level drops, large volumes of methane may be released. Conversely, when sea level rises, the lower limit of gas hydrate stability moves downward releasing methane from the upper zone and may trap more methane gas, as gas hydrate move downward. The concentration of atmospheric methane is increasing at a rate of almost 1% per year (Watson *et al.*, 1990). Methane's contribution is important because its global warming potential can reach 72 times more in 20 years span than carbon dioxide (CO₂) (IPCC, 2007). Methane is also a strong green house gas and having global warming potentiality 21 times than CO₂ (Heimann, 2010). Continuous increase in the concentration of greenhouse gases may intensify global warming in near future, thus disturbing the world climate regimes including the Indian monsoon. As per the report of IPCC (2007), the global temperature may increase during 2100 is about 1.1 to 6.4° C (best estimation is about 4°C) which may accelerate global warming and increase in polar ice melting as well as sea level. This global warming and sea-level high may be responsible for more input of methane to the atmosphere in near future.

Indian Gas hydrate deposits

Study of gas hydrate in the Indian offshore regions particularly in the Andaman region started in the mid-nineties

(Chopra, 1985). Presence of BSR in the both the eastern and western offshore region within the Bay of Bengal and Arabian Sea (Krishna-Godavari Basin, Mahanadi Basin, Kerala-Konkan Basin, offshore Saurashtra) and Andaman region indicate accumulation of gas hydrate within the sediments (Kelkar *et al.*, 1996; Verrayya *et al.*, 1998; Rao *et al.*, 2001). Later during 1996, Ministry of Petroleum and Natural Resources constituted a committee under the aegis of National Gas Hydrate Program (NGHP) for the exploration of gas hydrate along the vast continental margins of India. Organizations like Directorate General of Hydrocarbons (DGH), Oil and Natural Gas Corporations (ONGC), Oil India Limited (OIL), Gas Authority of India Limited (GAIL), National Institute of Oceanography (NIO), National Geophysical Research Institute (NGRI), National Institute of Ocean Technology (NIOT), etc. are involved for gas hydrate exploration. On the basis of the recommendations of the NGHP committee, drilling was done on 4 Legs, 39 Holes, 21 Sites in three phases along the Kerala-Konkan, Mahanadi, Krishna-Godavari and Andaman Basins during 2006 (Collett *et al.*, 2008a). Direct drilling as well as different proxies showed that Andaman convergent margin (Microbial/thermogenic methane), Mahanadi Basin (Microbial/thermogenic methane) and Krishna-Godavari Basin (Microbial methane) contain gas hydrate deposits among which Krishna-Godavari basin has the richest gas hydrate deposits in the world yet documented (Collett *et al.*, 2008b). However, Kerala-Konkan zone is devoid of gas hydrate accumulation. Estimation done by NGHP to quantify the amount of methane stored in the Indian continental margins is about 1894 trillion cubic meters. Till date several studies has been carried out on Indian gas hydrate deposits. Most of these studies were targeted using seismic and geochemical data mainly on the Krishna-Godavari and Mahanadi basins to understand the distribution, saturation and quantification of gas hydrate as well as stability zone of the gas hydrates (Kocherla *et al.*, 2006; Dewangan *et al.*, 2007; Mazumder *et al.*, 2009; Sain *et al.*, 2011, Shankar and Riedel, 2011). The study of Dewangan *et al.* (2010) shows that signature of paleo-fluid/gas migration in terms of methane or sulfidic fluids are there associated with structures such as acoustic voids, acoustic chimney and acoustic turbid layers. Carbon isotopic studies on cold seep biota (ranging in between -41 to -52‰) performed in the Krishna-Godavari Basin which indicates that methane in this zone is originated by anaerobic bacterial degradation of organic matter (Mazumder *et al.*, 2009). However, foraminiferal study from these zones is still awaited.

CONCLUSIONS

Gas hydrates have attracted us to consider them as an alternative resource of energy in future as the natural resources are fast depleting. There are vast unexplored gas hydrate reservoirs trapped in marine sediments, which require multifaceted extensive efforts to bring them into the world energy balance. Though exploitation of gas hydrate started in the permafrost regions, economic exploitation of submarine gas hydrates still remains a problem. However, with developing technologies in future gas hydrate will prove to be good resource to meet energy requirements of the world. Since India has very limited petroleum reserves, efforts should be intensified to look for alternative energy sources like gas hydrates. Government laboratories and agencies have recently intensified their efforts to explore gas hydrates in Indian offshore waters.

On the other hand, recent trends in global warming also warn us about the future concentration of methane in the atmosphere. Melting of ice sheets in Arctic region may contribute huge methane to the atmosphere by the dissociation of permafrost gas hydrates. On the other hand, rising sea level related to global warming also may shift the gas hydrate stability zone through which significant amount of marine methane might drift into atmosphere. Thus, methane can be a major driving force in near future owing to its increased concentration as well as huge green house effect as experienced during PETM. Successful exploitation of gas hydrate may help us to control methane flux. This methane can be used as energy resource and by-product carbon dioxide may be trapped by carbon sequestration methods which will help us to keep the Earth green.

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