1. INTRODUCTION

1.1 Introduction

Methane is an important green house gas, which plays a vital role in driving the global warming, having a well documented record of centennial to millennial scale variability in the polar ice as well as marine archives (Shine et al., 1990; Lorius et al., 1990; Brook et al., 1996). The source of methane in atmosphere could be bacterial decomposition of organic matter in wetlands or deep-sea environment (Barnes and Goldberg, 1976; Warford et al., 1979) or could be destabilizing gas hydrates due to change in the thermohaline circulation and sea floor erosion (Katz et al., 1999; Kennett et al., 2000; Holbrook et al., 2002). Gas hydrates are accumulated in areas where organic production or flux is very high and pressure-temperature conditions are conducive. In recent years, the regions rich in gas hydrates or methane seeps have attracted the attention of marine geologists and ecologists, marine biologists, paleoceanographers to understand the impact of methane or cold seeps on benthic fauna. Because of economic potential of gas hydrates as future energy resource, several oil companies have started studying gas hydrate deposits using geochemical, geological and geophysical tools. The present study examines the relationship between benthic foraminifera, organic matter and methane fluxes in the late Neogene (last ~7 Ma) sediments of the Blake Ridge, northwest (NW) Atlantic Ocean using benthic foraminiferal assemblages (biofacies) and total organic carbon content.

Gas hydrates are naturally occurring solid ice like crystalline structure composed of water molecule and short chain hydrocarbon like methane, and are also known as gas clathrates (Claypool and Kaplan, 1974; Sloan, 1990). The formation of natural gas hydrates require low temperature (≤ 12 °C), high pressure (≥ 2.6 MPa), high organic carbon content of sediments (2.0% to 3.5%) and water depths between 300 and 1000 meters (Claypool and Kaplan, 1974; Sloan, 1990; Istomin and Yakushev, 1992; Kvenvolden, 1993, 1998; Malone, 1994; Ginsburg and Soloviev, 1997; Fehn et al., 2000). Gas hydrates may contribute huge amount of methane to the atmosphere due to disintegration (Sloan, 1990; Kvenvolden, 1998). There are three gas hydrates structures found in nature viz. I, II and H. Among these structure I is the most common one.

1.2 Origin of gas hydrates

The methane formed in gas hydrates may be biogenic (Claypool and Kaplan, 1974) or thermogenic (Hyndman and Davis, 1992) in origin. Biogenic methane is formed from bacterial decomposition of sedimentary organic matter (SOM) in low temperature and anaerobic conditions at shallow depths (Paull et al., 1994). On the contrary, if the SOM breaks at high temperature (>80-120 °C) to produce primary and secondary thermogenic gases which contain less methane and more short chain hydrocarbons like ethane, propane, butane etc., then it becomes thermogenic in origin. Gas hydrates formed from biogenic hydrocarbon contain 99% pure methane. The gas thus produced from deep beneath oceanic sediments enters into gas hydrate stability zone (GHSZ) and forms gas hydrates while the free gas persists beneath it. In addition to the above factors, porosity of sediments, salinity and composition of sea water also affect gas hydrate formation. They may form as cement, veins, lenses or isolated nodules in the sediments. Gas hydrates are mainly found on land in Permafrost regions (onshore) and in the oceanic sediments of the continental margins (offshore). These are also found in deep lakes, inland seas, Arctic localities associated with petroleum accumulations, etc. (Shipley et al., 1979; Kvenvolden, 1990, 1998; MacDonald, 1990). In permafrost regions gas hydrates exist at depths ranging from 130 to 2000 m whereas in continental margins they may occur in oceanic water depth greater than 500 m (Kvenvolden, 1998).



Figure 1.1: Distribution of gas hydrates around the world (Source: Makogon et al., 2007)

The number of observed (through core study and direct sampling) and inferred (through geophysical investigations, geochemical and geological evidences) gas hydrate reserves are 77 (Ginsburg and Soloviev, 1998; Kvenvolden, 1998; Maslin, 2004). Around 220 gas hydrate reservoirs have been found till date and they are distributed throughout the world with concentration as follows: Pacific Ocean-33, Atlantic Ocean-21, Indian Ocean-4, Arctic region-5, Antarctic region-4, Lakes-2 reserves and the continental (permafrost) regions-8 reserves (Fig. 1.1).

1.3 Gas hydrates in the Indian Ocean

Two extensive gas hydrate deposits along the eastern and western continental margins of India are subdivided into seven gas hydrate rich zones using BSRs (Gupta et al., 1998; Kuldeep et al., 1998; Veerayya et al., 1998; Subrahmanium et al., 1999; Gupta, 2003; Fig. 1.2). In 1996, Petroleum Ministry of the Government of India, formed the



National Gas Hydrate Programme (NGHP, Kelkar et al., 1996) to evolve a core group for the investigation and production of gas hydrates from the Indian continental shelf (within the Exclusive Economic Zone) in collaboration with the Gas Authority of India Limited (GAIL), Oil and Natural Gas Corporation (ONGC), Oil India Limited (OIL), Directorate General of Hydrocarbons (DGH), National Geophysical Research Institute (NGRI) and

Figure 1.2: Map showing Indian Gas Hydrate zones. (Source: Collet, USGS)

National Institute of Oceanography (NIO), Goa. Exploration has been in progress since 1997 under NGHP, and the Research and development (R&D) drillship "JOIDES Resolution" carried out an extensive R&D cruise in four selected areas during the year 2006. The four

promising areas were identified as (i) Krishna-Godavari (ii) Kerala-Konkan (iii) Mahanadi basin, and (iv) Andaman offshore through the joint efforts of national and international cooperation (Fig. 1.2).

1.4 Use of benthic foraminifera from gas hydrate zones: A literature review

Before dwelling upon the details of the present study, a systematic review of previous significant studies in and around the study area is required. To achieve this goal, thematic approach of reviewing literatures has been adapted. Microfossil studies have served geology in a big way and this continues to fulfill their promise in the interpretation of paleobiogeography, paleoecology, morphology, evolutionary processes and the origin of new groups and ground plans (Lipps, 1981). Since benthic and planktic foraminifera have long been recognized as paleoceanographic and paleoclimatic marker, with numerous literatures are available about them. Stable oxygen isotope values also being an important tool for paleoclimatic reconstruction, have been analyzed extensively by several workers.

Investigation of Gas Hydrates, apart from other proxies like geophysical seismic surveys that produce BSRs due to change in acoustic velocity at the interface of base of gas hydrate and free gas, geochemical studies (chlorine and iodine content of pore water, total organic carbon, dissolve inorganic carbon), etc. and benthic foraminifera are other important tools to study methane fluxes and seep zones. In this study, I have used benthic foraminiferal assemblages to identify intervals of methane fluxes and paleoceanographic evolution of Ocean Drilling Program (ODP) Holes 991A, 995A and 995B, Leg 164, Blake Ridge, NW Atlantic during the late Neogene.

The Blake Ridge is a well established gas hydrate field which provides ample opportunities to understand methane formation and to identify intervals of methane eruptions using various proxies during the Neogene. Benthic foraminifera are an important component of the marine community and are sensitive to environmental changes. The potential of benthic foraminifera has long been recognized in marine paleoenvironmental studies. They are abundant and diverse in modern oceans where they occur from coastal settings to deep-sea environments. They occupy perched epibenthic to deep infaunal microhabitats and utilize a variety of trophic mechanisms.

Benthic foraminifera have extraordinary power of adaptation and are able to survive and proliferate in a wide range of marine environments, including extreme ecosystems, such as oligotrophic abyssal plains (Coull et al., 1977) or hydrothermal vents (Sen Gupta and Aharon, 1994) as well as deep-sea trenches (Akimoto et al., 2001). Studies of dead and living benthic foraminifera have shown that distribution patterns are closely tied to the organic carbon flux and organic carbon content of the sediment (Mackensen et al., 1985; Caralp, 1984, 1989; Van der Zwaan et al., 1990; Gupta and Srinivasan, 1992; Jorissen et al., 1992; Gooday, 1993; Fariduddin and Loubere, 1997; Schmiedl et al., 1997; De Stigter et al., 1998; Gupta and Thomas, 1999; 2003; Gupta et al., 2004; Singh and Gupta, 2004). Other studies have demonstrated the sensitivity of the biofacies composition to changes in oxygen levels of the bottom water and pore-water oxygenation (Corliss, 1985; Hermelin and Shimmield, 1990; Corliss and Emerson, 1990; Bernhard and Reimers, 1991; Moodley and Hess, 1992; SenGupta and Machain-Castillo, 1993; Gooday, 1994; Loubere, 1996; Jannink et al., 1998). Dickens et al. (1997) described direct measurement of *in situ* methane quantities in a huge gas hydrate reservoir present in Blake Ridge.

Hydrocarbon seepage is indicated here by the presence of methanotrophic bivalves and white bacterial mats, and by present day formation of gas hydrates (Panieri and Sen Gupta, 2008) from Blake Ridge hydrate mound. Seep environments, in general, support infaunal calcareous benthic foraminifera with rare agglutinated forms (Panieri and Sen Gupta, 2008; Panieri et al., 2009) as well as miliolids. Panieri and Sen Gupta (2008) related the paucity of agglutinated foraminifera at Blake Ridge hydrate mound seeps to oxygen depletion caused by the presence of methane or sulfide in pore and bottom water. It is generally believed that agglutinated forms are less tolerant of dysoxia/microxia than calcareous ones (Levin, 2003). Miliolids are generally considered to be indicative of cool, high oxygen, low and pulsed organic food supply and good carbonate preservation (Linke and Lutze, 1993; Gupta and Thomas, 1999).

Researchers have increased their interest to understand association of benthic foraminifera to methane rich environments and relation between benthic foraminifera and gas hydrates sequence. The methane seepages from gas hydrate or methane rich settings are quit common, as reported the continental margin off Peru and clues to ancient methane releases (Wefer et al., 1994). Recent benthic foraminiferal assemblages from the cold seep communities were observed by Akimoto et al. (1994). Foraminiferal colonization of hydrocarbon-seep bacterial mats and underlying sediments were reported by Sen Gupta et al. (1997) at Gulf of Mexico slope whereas Rathburn et al. (2000) described benthic foraminiferal species associated with cold methane seeps on the northern California margin (based on ecology and stable isotopic composition of benthic foraminifera). Important studies of species assemblages, abundance and ultra structure of living foraminifera identified them as an indicator of methane-rich environments from a study of modern methane seeps in Santa Barbara Channel, California (Bernhard et al., 2001; Hill et al., 2003).

Extensive studies have been carried out by many workers in different gas hydrate locations like Gulf of California (Keigwin, 2002), Hydrate Ridge, Oregon (Torres et al., 2003; Hill et al., 2004a; Cannariato and Stott, 2004), Santa Barbara Channel (Kennett et al., 2000; Hinrichs et al., 2003; Hill et al., 2003, 2004b); western North Pacific (Uchida et al., 2004), Rockall Trough (Panieri, 2005), Sea of Okhotsk (Sahling et al., 2003), Miocene limestone of Italy (Barbieri and Panieri, 2004) and Papua Gulf (de Garidel-Thoron et al., 2004). Some of the important recent studies are focused on Blake Ridge, northwest Atlantic (Katz et al., 1999; Dillon et al., 2001; Holbrook et al., 2002; Robinson et al., 2004). These methane fluxes are identified mainly using the highly negative carbon isotopic excursions of benthic and planktic foraminifera, total organic carbon (Wefer et al., 1994; Dickens et al., 1995; Katz et al., 1999; Kennett et al., 2000; Rathburn et al., 2000; Torres et al., 2003; Hill et al., 2003, 2004a,b), presence of chemosynthetic bacteria and biota (Hinrichs et al., 2003; Van Dover et al., 2003), reflection seismic profiles (Dillon et al., 2001; Holbrook et al., 2003), etc.

Recent studies suggest that, in general benthic foraminiferal distribution is limited by a combination of food availability and oxygenation (Sen Gupta and Machin-Castillo, 1993; Jorissen et al., 1995; Gooday, 2003). However, in areas where oxygen content of bottom waters is not a limiting factor, the amount of organic flux to the sea floor mainly governs the occurrence of benthic species in the sediments (Van der Zwaan et al., 1999; Friedrich and Hemleben, 2007).

Numerous species of benthic foraminifera have been found in different methane rich marine settings and have proved to be good indicator of methane releases (e.g., Wefer et al., 1994; Sen Gupta et al., 1997; Rathburn et al., 2000; Hill et al., 2003). Some species prefer to feed on rich bacterial food sources at methane seeps showing their potential as indicators of methane release in the geological record. Certain methane loving taxa include species of Bolivina, Bulimina, Cassidulina, Chilostomella, Epistominella, Gavelinopsis, Globobulimina, Nonionella, Stainforthia, Trifarina and Uvigerina which can withstand such stressful conditions (Sen Gupta and Aharon, 1994; Wefer et al., 1994; Sen Gupta et al., 1997; Rathburn et al., 2000; Bernhard et al., 2001; Torres et al., 2003; Hill et al., 2003, 2004a; Robinson et al., 2004; Panieri, 2005). In view of recent studies confirming lack of endemic species in methane settings of the Blake Ridge (Panieri and Sen Gupta, 2008; Lobegeier and Sen Gupta, 2008), this study is focused to examine benthic foraminiferal population from methane rich environments of the Blake Ridge to understand if certain species of benthic foraminifera can be classified as methane loving, although our attempt is largely aimed at understanding paleoceanographic changes in the Blake Ridge region.

1.5 Aims and Objectives

The late Miocene record of benthic foraminifera from Holes 991A, 995A and 995B was generated to understand paleoceanographic evolution of the NW Atlantic Ocean. The recent benthic foraminiferal fauna from different holes at Blake Ridge were examined to understand a relation between benthic foraminifera in methane rich environments. Following are the main objectives of this study:

- ✓ To document deep-sea benthic foraminifera from Holes 991A, 995A and 995B, Leg 164, Blake Ridge during the late Neogene.
- To identify intervals of high organic carbon in marine sediments of the Blake Ridge using benthic foraminiferal assemblages and total organic carbon (TOC) and their relation with Deep Western Boundary Undercurrent (DWBUC) during the late Neogene.

- ✓ To understand the role of deep water circulation in the North Atlantic like North Atlantic Deep Water (NADW) in benthic faunal distribution at Blake Ridge.
- ✓ To understand the relation between certain species/groups of benthic foraminifera (e.g., agglutinated, miliolid, high organic species) and methane seeps at Blake Ridge during the late Neogene.

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