2011857

Gas Hydrates and Authigenic Carbonates: A Comparative Study from the Eastern and Western Continental Margins of India

M. Kocherla and Surabhi Pillai

CSIR-National Institute of Oceanography, Dona Paula, Goa-403004, India

Presenting author, E-mail: kocherla@nio.org

Abstract

We report here the abundant occurrences of authigenic siderite ($FeCO_3$) and high-Mg calcite (HMC) nodules/precipitates from 17 long cores recovered from the Krishna-Godavari Basin (K-G Basin), Bay of Bengal. The cores were collected as part of our gas hydrate exploration program on board R/V Marion Dufresne (MD-161: May, 2007) under various geological environments, including mud diapirs, mass flows, and hemipelagic sediments over a water depth range of 740-2080 m from K-G Basin. Authigenic carbonates are distributed at different depths (5-29 mbsf) within the sediment section ranging from 1 mm to 12 cm in diameter and display irregular shapes and exhibit clear vertical zonation. More than 100 carbonate nodules/precipitates from these cores were investigated for their occurrence, stratigraphic distribution, mineralogy, geochemical and stable isotopic compositions. Bulk mineralogical compositions by X-ray detraction (XRD) revealed that the carbonates are predominantly soft friable siderite nodules with inclusions of strontianite, witherite, cerussite and occasionally high-mg calcite (HMC) at specific sub-surface depths but rarely aragonite or low-Mg calcite (LMC) with trace amounts of pyrites and barites. The $\delta^{13}C$ and $\delta^{18}O$ values for the siderite nodules vary from -35.4 to +6.42 ‰ and -0.1 to 6.1 ‰ VPDB respectively. Whereas for the HMC nodules $\delta^{13}C$ and $\delta^{18}O$ range from -52.42 to -27.8 ‰ and 0.3 to +5.4 ‰ VPDB. Highly depleted carbon isotope ratios of HMC nodules indicate anaerobic oxidation of methane (AOM) as the primary source of bicarbonate ions; on the other hand Rayleigh fractionation of residual pore water bicarbonate is suggested by the enriched carbon isotope ratios of siderite nodules. Different types of carbonate morphologies ranging from finely dispersed crystals to massive nodules and chimneys are the products of two different fluids migration systems of dispersive to diffusive respectively and the occurrence of similar age carbonate deposits associated with methane seepage throughout the K-G Basin indicate a regional supply of methane. Highly depleted carbon isotope ratios of HMC advocate AOM as the primary source of bicarbonate ions and unambiguously indicate that the carbonates are predominantly derived from sedimentary methane via AOM. Distinctive clusters of stable isotope values regardless of mineralogy imply that carbonate precipitates formed in a closed-diagenetic system and suggest that these carbonate nodule are formed in-situ within the sediment column. The carbon source for the formation of authigenic carbonates is attributed in part to the occurrence of gas hydrate and the carbonates were formed from the flow of methane-enriched fluids through fracture network formed as the result of the shale diapirism. Although the presence of gas charged sediments and sub-surface gas-escape features has been inferred from shallow seismic studies and possible occurrence of gas hydrates by BSR's and stable carbon isotope signatures of authigenic carbonates and evaluation of pore-fluid chemistry are not indicative of enhanced methane flux in the region and argue against a precipitation of carbonates due to AOM and refute the possible connection of methane from the shallow gas charged sediments to the observed carbonates or suspected BSR's for or the Western region.

Keywords: Authigenic Carbonates; Gas-hydrates; Eastern Continental Margins of India (ECMI) Western Continental Margin of India (WCMI); Stable carbon isotopes, Stable oxygen isotopes.

Introduction

Methane-derived authigenic carbonates are indirect indicators of high methane flux region (such as gas seepages and pore fluid venting) which are common in areas overlying gas hydrate deposits. Precipitation and consequent preservation of authigenic carbonates is mainly due to increase in pore water bicarbonate (HCO_3^-) ion concentration and anaerobic oxidation of methane (AOM) from gas hydrate system and concomitant sulfate reduction process in the sediment sequence. Authigenic carbonates can also be formed due to degradation of organic matter during early diagenesis. These processes increase pore water alkalinity by the production of bicarbonate (HCO_3^-) thus favouring precipitation of authigenic carbonate minerals in the shallow sub-surface. Determining which of the above two processes is responsible for the authigenic carbonate precipitation is very essential as it provides definite evidence for high methane fluxes either due to localized diagenetic processes or due to the presence of gas hydrates beneath. In marine sediments, methane migrates upward and reacts with sulfate at SMTZ and results in the formation of various authigenic minerals depending on the fluids, gases and composition of the host sediments. The variety of authigenic minerals that are formed in cold seep environments provide diagnostic information on the chemistry of the diagenetic fluids, and therefore their mineralogy, morphology can be used to indicate the magnitude of methane flux and the depth of SMTZ and consequently the presence of underlying methane gas hydrate deposits. In the northern Indian Ocean occurrences of methane-derived authigenic carbonates are reported from the Krishna-Godavari basin, eastern continental margins of India and Makran accretionary prism off Pakistan in the Arabian Sea. Western continental margin is characterized by shallow gas charged sediments and several gas escape features. Geophysical studies in the western continental margin of India revealed the presence mud-diapirs and bottom simulating reflectors (BSRs) & vent-like features representing gas escape features from the sea floor. Recent drilling work carried out on-board JOIDES Resolution Leg-3A confirmed the presence of massive authigenic carbonate nodules/concretions along with more than 100 m thick accumulation of gas hydrates in Krishna-Godavari offshore basin, Bay of Bengal. Since occurrence of authigenic carbonates can help to decipher the source of gas seepages in an area we undertook a comparative study of authigenic carbonates from the both Eastern and Western continental margins of India.

Geological Settings

Eastern Continental Margin of India (ECMI): The study area in the K-G Basin lies in the middle of Eastern continental Margins of India (ECMI) which is a pericratonic rift basin (Rao, 2001) that evolved after the breakup of Gondwanaland around 130 Ma years ago (Powell et al., 1988; Scotese et al., 1988; Ramana et al., 1994). Onshore extension of K-G Basin is ~28,000 km^2 and its offshore extension is ~1, 45,000 km^2 (Ojha and Dubey, 2006). Much of the detrital influx into the K-G Basin is brought by the two major river systems: Krishna and Godavari Rivers. The sediment thickness ranges from 3-5 km in onshore region to ~8 km in the offshore portion of the basin (Prabhakar and Zutshi, 1993; Basti, 2007) with several cycles of deposition, ranging in age from late Carboniferous to Pleistocene. The sediment in the study area consists of silty clay with negligible amount of sand (Kocherla et al., 2006). The dominant clay fraction is montmorillonite with traces of illite and kaolinite.

In the K-G Basin, widespread presence of gas hydrate is manifested in the multi-channel seismic data in the form of bottom simulating reflectors (BSRs). Drilling and coring in the K-G Basin has confirmed the presence of gas hydrate (Collett et al., 2008). Several acoustic features related to fluid and/or gas migration have been reported in the shallow subsurface (Ramana et al., 2007; Ramana et al., 2009; Dewangan et al., 2010) suggesting active migration of methane in the study area. The geological and geochemical analyses of long sediment cores, acquired on-board the R/V *Marion Dufresne*, have confirmed paleo-methane seepage in the study area (Mazumdar et al., 2009). Slumping/sliding of slope sediments, associated with fluid and/or gas migration, has led to mass transport deposits in the K-G offshore basin (Ramprasad et al., 2011). Several bathymetric mounds formed due to shale tectonics are heavily faulted and show acoustic signatures of fluid and/or gas migration through the fault system (Dewangan et al., 2010). The analysis of available geophysical datasets such as multi-channel seismic, high resolution seismic, sub-bottom profiler, and multibeam bathymetry has divided the study area into distinct deposition environments, including mid-slope mini basins, in the north-east and south-west directions, bathymetry mounds, toe-thrust sedimentary ridges, and deep oceanic basin (Ramana et al., 2007; Ramana et al., 2009; Dewangan et al., 2010; Ramprasad et al., 2011). The sediments are nano fossil bearing clays with sand silt beds and terrigenous organic carbon content. The accumulation of total organic carbon (TOC) content of the sediments along ECMI has been enhanced as a consequence of the uplift and erosion of the Himalaya (Meyer and Dickens, 1992). The high sedimentation and the consequent rapid burial in the K-G Basin have resulted in preserving the TOC in the sediments. The environment shows dominance of carbonates mostly siderite, occurring as nodules, crusts, hard grounds and fine grained bands.

Western Continental Margin of India (WCMI): The western continental margin of is a passive margin and characterized by (i) NW-SE trending shelf more than 200 km wide in the north and about 50 km in the south near Cape Comorin, (ii) a straight outer edge limited by 200m isobaths, (iii) a narrow continental slope bounded by 200 and 2000m isobaths, (iv) deep sedimentary basins viz., Western Arabian Basin, Eastern Arabian Basin, Kori-Komorin Basin and Kerala-Konkan Basin and (v) several structural features such as Chagos-Laccadive Ridge, Laxmi Ridge, Pratap Ridge(east of Chagos Laccadive Ridge). Geographically Goa offshore (Eastern Arabian Basin) lies between the eastern end of Laxmi-Laccadive Ridge and the adjacent western continental slope of India (Biswas 1982; Kolla and Coumes 1987; NIO (2005). The depth in this basin ranges from 1800 to 3600m. Approximately 2.9 km thick sediments overlie the basement. The Indus River is the primary source of detrital sediment to this region. Average sedimentation rate in this region is 2-6 cm/ky over last 100 ky (Banakar et al 2005). Sediment cores selected for the present study are shown in Figure1. The study area in the eastern Arabian Sea has oxic bottom waters (2665-3210 m) and overlain by the well-established OMZ in mid-depths (200 to 1500 m) (Parpokari et al 1993). The sediments are characterised by low organic carbon content and abundance of nano fossils/ foram-rich nano-ooze. The inorganic carbon content is diluted by terrigenous input and ocean productivity. The sediments show illite as the dominant clay mineral. Authigenic carbonates are microscopic and inferred as being diagenetic in origin. Few large pyrites and mono sulphides are also observed at bottom depth of 130-190m. The occurrence of gas charged sediments and the presence of BSR's (possible gas hydrate horizons) have been detected along the western continental margin of India based on shallow seismic records (Veerayya et al 1998; Satyavani et al 2005; Ramana et al 2006; Dewangan and Ramprasad 2007).

Samples and Methods

A total of 17 long cores (23-35 m long) were recovered over a water depth range of 740-2080 m (Fig.1) from regions of elevated methane in the K-G Basin from the R/V Marion Dufresne using a Giant Calypso piston corer. A suite of authigenic carbonate nodules/precipitates from the sediment subsamples (5 to 29 mbsf) were isolated and washed with water to remove the salts and then washed in an ultrasonic bath for 15 min and dried and cleaned. Mineralogy, TIC, $CaCO_3$ and stable carbon isotopic compositions have determined for the carbonate precipitates and the results are presented in Table.2. Typical carbonate nodules/precipitates were selected and powdered with an agate mortar and pestle for XRD analysis and stable isotope measurements. Bulk mineralogy of carbonate precipitates was carried out on randomly oriented samples using a Regaku X-ray diffractometer (Ultima-IV). All the carbonate samples were run from 25 to 35 °2θ at 1°/min scan speed using CuKα radiation (λ = 1.541838Å) at the National Institute of Oceanography, Goa India. The $MgCO_3$ (mole %) was calculated using an $MgCO_3$ content (mole %) - d-spacing standard curve in Hardy and Tucker (1988). Dried and disaggregated sediment samples were first examined under the binocular microscope (Nikon, SMZ-1500) and some selected grains/samples were examined under scanning electron microscope (JEOL-JSM 5800 LV1 at the National Institute of Oceanography, Goa India for their morphological studies. Several freshly broken surfaces of the carbonates have been investigated using Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) to understand textural, morphological characteristics and their mutual association. Carbon and oxygen isotope ratios of authigenic carbonate samples were determined with a Thermo Finnigan Delta plus XP continuous flow isotope ratio mass spectrometer attached to a GASBENCH II and equipped with a PAL auto sampler at the National Geophysical Research Institute, Hyderabad, India. The carbon isotope ratios are reported in standard $\delta^{13}C$ formats relative to VPDB standard. A sample reproducibility of 0.1‰ for both carbon and oxygen is reported here.

Results and Discussion

The down-core carbonate size distribution along with carbonate mineralogy shows that mostly carbonate nodules are confined to 5-29 mbsf within the sediment sequence ranging from 1 mm to 12 cm in diameter and display irregular shapes. The average thickness of the carbonate concretions range between 0.2- 12 cm with a minimum being at stations 3,7,13,14,16 and17 (siderites) and maximum at stations 8 and 9 HMC and LMC respectively. The $\delta^{13}C$ and $\delta^{18}O$ values for the siderite nodules vary from -35.4 to +6.42 ‰ and -0.1 to 6.1 ‰ VPDB respectively. Whereas for the HMC nodules $\delta^{13}C$ and $\delta^{18}O$ range from -52.42 to -27.8 ‰ and 0.3 to +5.4 ‰ VPDB. Highly depleted carbon isotope ratios of HMC nodules indicate anaerobic oxidation of methane (AOM) as the primary source of bicarbonate ions and show characteristic finger printing isotopic composition for HMC and Siderites. The AOM is very evident at shallow depths of 5-29mbsf.A possible mechanism for widespread methane seepage in the Krishna-Godavari Basin could be a glacial sea level lowering shifting the bottom of the gas hydrate stability zone into shallower depths followed by gas hydrate decomposition in deeper sediments. This enhanced decomposition of gas hydrates may then generate an increase in methane outflow.

For the Western region the $\delta^{13}C$ values of the authigenic carbonates range between –0.63 and –8.12‰, and is attributed to a contribution of isotopically light CO_2 derived from the oxidation of sedimentary organic matter in the surficial sub-oxic Fe reduction and the bacterial sulphate reduction zone during early diagenesis. The observed CH_4 concentration does not show an appreciable increase with depth indicating that the contribution of CH_4 from the shallow sediments to authigenic carbonate formation is negligible. Although the presence of gas charged sediments and sub-surface gas-escape features in and around the study area has been inferred from shallow seismic studies and possible occurrence of gas hydrates by BSR's, but mineralogy morphology and stable carbon isotope signatures of authigenic carbonates and evaluation of pore-fluid chemistry are not indicative of enhanced methane flux in the region and argue against a precipitation of carbonates due to AOM and refute the possible connection of methane from the shallow gas charged sediments to the observed carbonates or suspected BSR's. The recent drilling carried by JOIDES Resolution (NGHP-Leg1) in the study area rules out the occurrence of BSR's due to gas hydrates and supports our contention. In the present study we report on the occurrence of different types of authigenic carbonates in sedimentary cores from both the Eastern and Western continental margins of India and discuss their origin based on their mineralogy, morphology and stable carbon isotopes signatures.

Conclusions

1. A variety of authigenic carbonates from 17 long cores (23-35 m long) were recovered at numerous locations in K-G Basin in the gas hydrate bearing sediments with wide variety of morphologies, predominantly as nodules followed by chimneys, tubules, bone-like structures, individual slabs, thinly lithified pavements, fine grained carbonate bands micro-nodules and as dispersed crystal aggregates. The carbonate size distribution along with their mineralogy show that they are confined to 5-29 mbsf within the sediment sequence ranging from 1 mm to 12 cm in diameter and display irregular shapes. The average thickness of the carbonate precipitates are minimum at sites 3, 7,13,14,16 and 17 (siderites) and maximum at stations 5 (siderite) 8 (HMC) and 9 (LMC), 12 (siderite) and 15 (siderite) and most of sites with massive carbonate nodules are associated with topographic mounds.
2. Highly depleted isotopic ratios of HMC advocate AOM as the primary source of bicarbonate ions and unambiguously indicate that the carbonates are predominantly derived from sedimentary methane via AOM. The carbon source for the formation of authigenic carbonates is attributed to gas hydrates below and the carbonates were formed from the flow of methane-enriched fluids through fracture network formed because of shale diapirism reported in this region.
3. Different types of carbonate morphologies ranging from finely dispersed crystals to massive nodules and chimneys are the products of two different fluids migration systems of dispersive to diffusive respectively and the widely distributed methane seep carbonates suggest that they are related to similar age throughout the K-G Basin pointing to a large supply of methane and more regional acting mechanism rather than the site specific attributes. The detailed genetic framework is under investigation.
4. Dispersed authigenic carbonates are reported from five sediment cores from Goa offshore region central continental margin of western India between water depths 2665 to 3070 m. Morphological evidences such as euhedral carbonate crystals, slender radiating aragonite crystals and $\delta^{13}C$ values suggest that these carbonates are formed authigenically. The $\delta^{13}C$ values of the authigenic carbonates range between–0.63 and –8.12‰, and is attributed to a contribution of isotopically light CO_2 derived from the oxidation of sedimentary organic matter in the surficial sub-oxic Fe reduction and the bacterial sulphate reduction zone during early diagenesis.
5. Although the presence of gas charged sediments and sub-surface gas-escape features in and around the study area has been inferred from shallow seismic studies and possible occurrence of gas hydrates by BSR's, but mineralogy morphology and stable carbon isotope signatures of authigenic carbonates and evaluation of pore-fluid chemistry are not indicative of enhanced methane flux in the region and argue against a precipitation of carbonates due to AOM and refute the possible connection of methane from the shallow gas charged sediments to the observed carbonates or suspected BSR's. The recent drilling carried by JOIDES Resolution (NGHP-Leg1) in the study area rules out the occurrence of BSR's due to gas hydrates and supports our contention. Further studies are in progress for comprehensive understanding of the process involved.

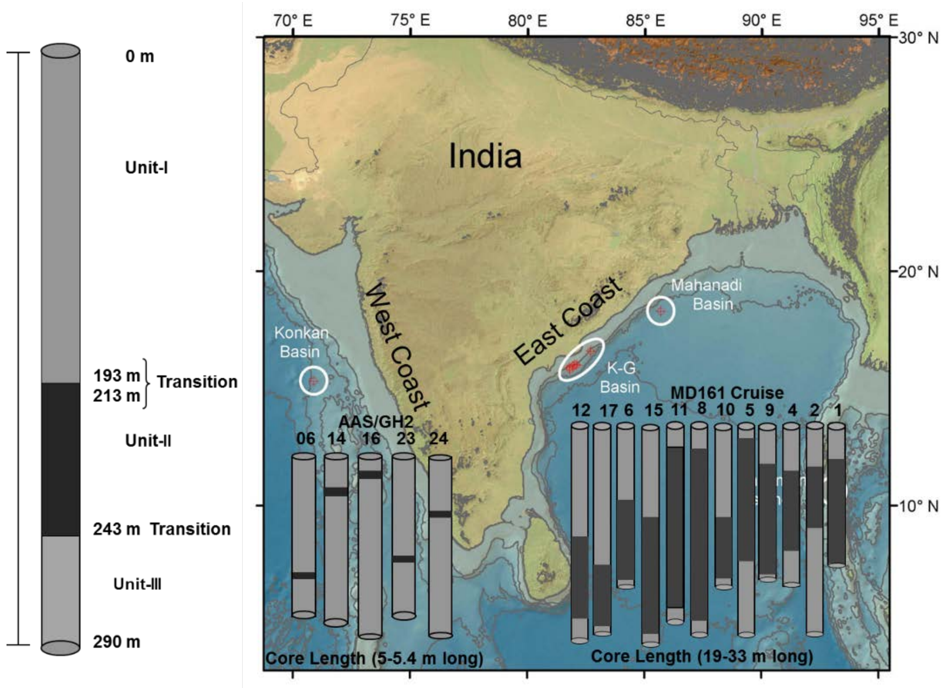

Figure-1. Map showing the core locations in the Eastern and Western Continental margins of India: 5 cores (5 m long from AAS/GH2 cruise and 290 m long ODP core from NGHP-01 Leg-1 and 17 cores (19-33 m long) from MD-161 cruise).

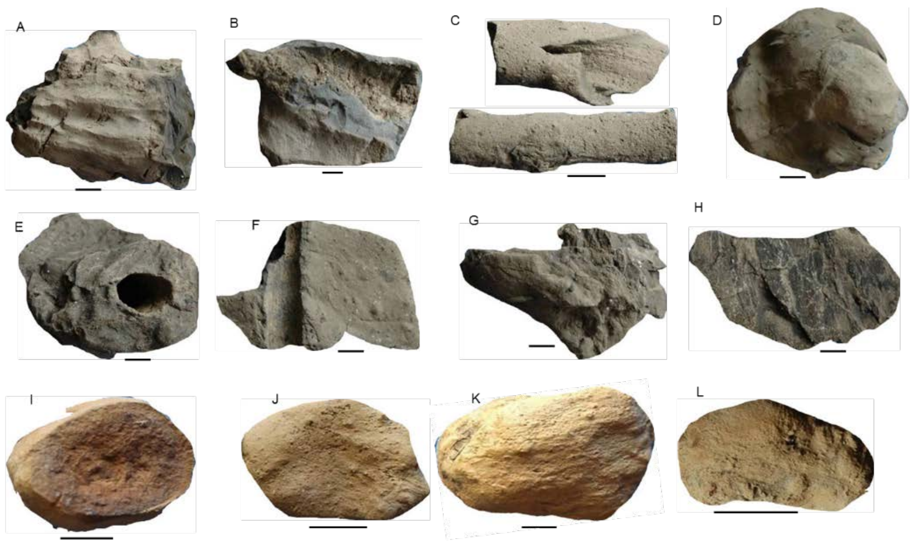

Figure-4. Morphology of authigenic Carbonate concretions: (A) tree trunk-like; (B) Chimney-like structures with conduits; (C) High-Mg calcite tubules with conduits; (D) Massive; (E) Chimney; (F) Slab with conduits (F) Fractured; ((H) Layered; highly lithified siderite nodule; (J, K,) moderately lithified siderites nodules; (L) soft siderite nodule. Scale bar represents 1cm (A-from site 8 at1656

Acknowledgements

We thank Directors of CSIR-NIO, CSIR-NGRI, NCAOR, NIOT and secretary MoES, India, for supporting the study, facilities and permission to publish this work. H. Leau, head of the Oceanography Department, and P. Sangiardi, in charge of on-board operations of IPEV on board *RV Marion Dufresne* (MD-161) is thanked for providing on-board technical support and facilities. The authors also thank T. Ramprasad A. Mazumdar, P. Dewangan, M.J Gonsalves and M. Joao for their valuable inputs. Mr.Girish Prabhu and Mr. Vijay Khedekar are thanked for their help during XRD and SEM operation and data acquisition respectively. This is NIO contribution no XXXX.

References

Banakar, V K., Oba, T., Chodankar, A. R., Kuramoto, T., Yamamoto, M., Minagawa, M., Monsoon related changes in the sea surface productivity and water column denitrification in the Eastern Arabian Sea during the last glacial cycle. Mar. Geol, 219, 99-108.

Bastia., 2007. Geologic settings and petroleum systems of India's east coast offshore basins, Concepts and Applications. Technology Publication, Dehradun, India.

Biswas 1982; Biswas, S.K., Rift basins in the western margin of India and their hydrocarbon prospects. AAPG Bulletin., 66,1497-1513.

Collet T., Riedel, M., Cochran, J., Boswell, R., Presley, J., Kumar P., Sathe, A., Sethi, A., Lall, M. and Sibal, V., 2008. Results of the Indian National Gas Hydrate Program Expedition 01 initial reports, Dir. Gen. of Hydrocarbons, Min. of Pet. and Nat. Gas, New Delhi.

Dewangan, P., Ramprasad, T., Ramana, M.V., Mazumdar, A., Desa, M. and Badesab, F.K., 2010. Seabed morphology and gas venting features in the continental slope region of Krishna-Godavari basin, bay of bengal: Implications in Gas-Hydrate Exploration. Mar. Pet. Geol., 27(7),1628-1641.

Kocherla M., Mazumdar, A., Karisiddaiah, S.M., Borole D.V. and Ramalingeswara Rao., B., 2006. Evidences of methane derived authigenic carbonates from the sediments of the Krishna – Godavari Basin, eastern continental margin of India. Curr. Sci., 91, 318-323.

Kolla, V. and Coumes, F., 1987. Morphology, internal structure, seismic stratigraphy, and sedimentation on the Indus Fan – AAPG Bulletin, 71, 650-677.

Mazumdar A., Dewangan, P., Joa¨o, H. M., Peketi, A., Khosla, V. R., Kocherla, M., Badesab, F. K., Joshi, R. K., Roxanne, P., Ramamurty, P. B., Karisiddaiah., S. M., Patil, D. J., Dayal, A. M., Ramprasad, T., Hawkesworth, C. J. and Avanzinelli, R., 2009. Evidence of paleo–cold seep activity from the Bay of Bengal, offshore India. Geochem. Geophys. Geosys., 10(6),1-15.

Meyers, P. A. and Dickens, G. R., 1992. Accumulations of organic matter in sediments of the Indian Ocean: A synthesis of results from scientific deep sea drilling. In: Duncan, R. A., et al., (eds.) Synthesis of Results From Scientific Drilling in the Indian Ocean, Geophys. Monogr. Ser., 70, 295-309.

Ojha and Dubey., 2006. Gaint hydrocarbon fields of offshore Krishna-Godavari Basin. Petroview 1, published by Directorate General of Hydrocarbons, New Delhi , 26-30.

Powell C.M., Roots, S.R. and Veevers, J.J.,1988. Pre-breakup continental extension in east Gondwanaland and the early opening of the eastern Indian Ocean. Tectonophysics, 155, 261-283.

Prabhakar and Zutshi, 1993. Evolution of southern part of Indian east coast basins. J. Geological Society of India, 41, 215-230.

Ramana, M.V, Ramprasad, T., Desa, M, Sethi, A.K., Sathe, A.V., 2010. Gas hydrate related proxies inferred from multidisciplinary investigations in the India off-shore areas. Curr.Sci.., 91, 183 –189.

Ramana, M.V, Ramprasad, T., Paropkar A.L, Borolei, D.V. Ramalingeswara Rao B., Karisiddaiah, S.M., Desa, M., Kocherla, M., Joao, H.M., Lokabharati .P., Maria-Judith Gonsalves., Pattan, J.N., Khadge, N.H., Prakash Babu, C., Sathe, A.V., Kumar, P., Sethi, A.K., 2009. Multidisciplinary investigations exploring indicators of gas hydrate occurrence in the Krishna–Godavari Basin offshore, east coast of India. Geo-Marine Lett., 29, 25-38.

Ramana, M.V, Ramprasad, T, Kamesh Raju., K.A. and Desa., M 2007. Occurrence of gas hydrates along the continental margins of India, particularly the Krishna-Godavari offshore basin. Int. J. Environ. Stud., 64, 675-693.

Ramana M.V., Nair, R.R., Sarma, K.V.L.N.S., Ramprasad, T., Krishnaa, K.S., Subrahmanyam, V., D'Cruza, M., Subrahmanyam, C., Paul, J., Subrahmanyam, V. D. and Chandra Sekhar, V., 1994. Mesozoic anomalies in the Bay of Bengal. Earth Planet. Sci. Lett., 121,469–475.

Ramprasad, T., Dewangan, P., Ramana, M.V., Mazumdar, A., Karisiddaiah, S.M., Ramya, E.R. and Sriram, G., 2011. Evidence of slumping/sliding in Krishna-Godavari offshore basin due to gas/fluid movements. Mar. Petrol. Geol., 28,1806-1816.

Rao, 2001. Sedimentation, stratigraphy, and petroleum potential of Krishna-Godavari Basin, East Coast of India. AAPG Bulletin, 85, 1623-1643.

Satyavani, N., Thankur, N.K., Arvind Kumar , N., Reddy, S.I., Migration of methane at the diapiric structure of the western continental margin of India- Insights from seismic data. Mar. Geol., 219,19-25.

Scotese C. R., Gahagan, L.M. and Larson, R.L., 1988. Plate tectonic reconstructions of the Cretaceous and Cenozoic ocean basins. Tectonophysics, 155, 27-48

Veerayya, M., Karisiddaiah, S. M., Vora, K. H., Wagle, B. G., Almeida, F., Detection of gas charged sediments and gas hydrate horizons in high resolution seismic profiles from the western continental margin of India. In Gas Hydrates, Relevance to World Margin Stability and Climate (ed Henriet, J. P. and Mienert, J.), Spec. Publ. Geological Society of London., 137, 239–253.