Gas hydrate-related proxies inferred from multidisciplinary investigations in the Indian offshore areas

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The presence of gas hydrates along the Indian continental margins has been speculated by earlier workers based on the identification of Bottom Simulating Reflection (BSR) on the multichannel seismic reflection records and computed gas hydrate stability zone thickness map. The BSR alone is inadequate to infer gas hydrates as suggested by drilling results elsewhere. Therefore, to understand the subsurface distribution of gas hydrates along the continental margins of India, multidisciplinary investigations have been undertaken. The observed geophysical anomalies (BSRs, pockmarks, gas upthrust zones, vents, blanking zones, etc.) in association with the geochemical (sulphate reduction trend and increase in methane flux with core depth) and microbiological proxy indicators (sulphate and nitrate-reducing bacteria, and fermenters) favour the presence of gas hydrates in some of the Indian offshore regions.

**Keywords:** Barium front, bottom simulating reflection, gas hydrates, Indian continental margins.

GAS hydrates are white, crystalline, ice-like substances comprised of a methane molecule surrounded by a cage of water molecules. They are formed at low temperature and high pressure in marine sediments under the constraint of a continuous supply of methane gas, either from the surrounding sedimentary column or deeper substrata.¹ The hydrates are mostly methane-rich, but are sometimes associated with ethane, propane, butane, carbon dioxide and hydrogen sulphide. Presence of gas hydrates in marine sediments is inferred by the identification of an anomalous seismic reflection known as the Bottom Simulating Reflection (BSR), a manifestation of negative polarity compressional (P)-wave mimicking the seafloor reflection on the Multi-Channel Seismic (MCS) reflection records. This reflection coincides with the base of the gas hydrate stability zone (GHSZ), wherein gas hydrates are stable.²

The National Institute of Oceanography (NIO), Goa generated the GHSZ thickness map³ using the concept of Miles.⁴ A similar exercise has been carried out by Hanumantha Rao et al.⁵, independently. The GHSZ is derived mainly from the phase equilibrium curve for methane and pure sea water system, hydrothermal profile of the water column, seafloor temperature, bathymetry and geothermal gradient. The origin of methane within the marine sediments is either biogenic/thermogenic or mixed-mode. Biogenic methane can be formed if the sedimentation rate is >30 m/Myr (or 3 cm/kyr) and Total Organic Carbon (TOC)⁶ content exceeds 0.5% (ref. 6).

First indication of the presence of gas hydrates in the Indian offshore dates back to 1985, with the identification of the BSR⁷ on the MCS data acquired by ONGC in the Andaman offshore. A thorough study of the MCS data acquired by the oil industry and NIO indicates the presence of BSR-like features in the offshore areas of Saurashtra and Goa, West Coast of India, Krishna-Godavari (KG) and Mahanadi, East Coast of India and the Andaman Sea. The qualitative distribution map of the probable occurrence of gas hydrates along the Indian continental margins highlights the significance of deep-water zones for thorough investigations with new techniques (Figure 1)⁸.

Presence of gas hydrates below the seafloor at specific locales has been established worldwide by drilling. It is interesting to note that some areas such as the Blake Ridge and Nankai Trough, which are associated with strong BSRs, yielded minimum saturated methane hydrates on drilling. On the other hand, the areas devoid of BSRs on drilling show the presence of gas hydrates.⁹ Therefore, absence of a BSR does not indicate that the area is devoid of methane hydrate or free gas, which suggests that total dependence on the BSRs may severely constrain the findings of gas hydrates. An attempt has been therefore made in the present study to infer some of the geophysical, geological, geochemical and microbiological proxy indicators under the seismic constraints (BSRs) for the occurrence of gas hydrates below the seafloor, since the drilling activity is prohibitively expensive.

**Data**

Multidisciplinary oceanography data (8900 km² of swath bathymetry, 5500 km of echosounding, magnetic and
gravity, 1150 km of high resolution chirp sonar and deep tow digital side scan sonar, and 1450 km of sub-bottom profiler data, besides 95 gravity cores of ~5 m length) have been acquired on-board research vessels ORV Sagar Kanya and AA Sidorenko in the offshore areas of central-west and east coast of India during 2002–03 to infer geophysical, geochemical and microbiological proxy indicators related to gas hydrates under the National Gas Hydrate Programme. Large volume of multi-channel seismic reflection data (acquired by the oil industry and NIO) was examined for the presence of BSRs following the criteria of polarity reversals, velocity inversion, blanking above and below the BSR, and cross-cutting of the geological horizons. The sediment sub-samples obtained from the gravity cores were analysed for geochemical anomalies (sulphate reduction, methane enrichment and chloride depletion) and microbiological proxies (sulphate- and nitrate-reducing bacteria and fermenters), and some of the results are presented here.

Results and discussion

Geophysical anomalies

Gas hydrate provinces mapped earlier are seen associated with gas escape features such as pockmarks, vents, gas upthrusts, gas saturated sediments, mud volcanoes, etc. in addition to the BSRs. MCS records depict the presence of BSR-like anomalous reflections in the Saurashtra, Goa, KG, Mahanadi and Andaman offshore areas (Figure 2). Most of the BSRs inferred from the seismic sections along the eastern offshore satisfy the criteria of mimicking the seafloor, polarity reversal and cross-cutting of the lithological layers, while the BSRs inferred off Goa are devoid of the characteristic cross-cutting. The study area in Goa offshore lies relatively at greater depths and the seafloor is devoid of appreciable gradients resulting in the parallel nature of subsurface seismic horizons, whereas in the KG offshore the study area lies in shallow depths and the seafloor exhibits steep gradients. Though the conditions for the formation of gas hydrates in both these offshore areas are conducive, the contrasting geomorphology of the seafloor appears to constrain the manifestation of cross-cutting of BSRs with the geological horizons. These BSR-like reflections occur between 200 and 400 mbsf in the western and eastern offshore areas, whereas they occur ~600 mbsf in the Andaman Sea. The sedimentation rates in the Arabian Sea vary between 3.5 and 5.2 cm/kyr. Based on these rates, the tentative age of the gas hydrate-bearing sediments is inferred as Pliocene. High sedimentation rates (20–40 cm/kyr) in the Bay of Bengal indicate the occurrence of gas hydrates in the Pliocene sediments.
In the Andaman Sea, the sedimentation rate of ~8 cm/kyr implies that the inferred BSRs cross-cut the Upper to Middle Miocene strata and broadly follow the seafloor topography. Some of the inferred BSRs (seismic data acquired by NIO and ONGC) in Goa offshore region have been classified into strong, weak and possible/moderate based on the fulfillment of various criteria and reflection characteristics. Whereas BSRs observed in the eastern offshore (KG and Mahanadi basins) and Andaman Sea are distinct (courtesy: oil majors). The conspicuous nature of the BSRs is probably due to the higher concentrations of free gas below the GHSZ. Mallik et al. have carried out prestack Genetic Algorithm (GA) inversion of seismic data in the Andaman Sea and observed velocity inversion, which is attributed to the presence of free gas below the BSR.

The multi-frequency chirp sonar and the 3.5 kHz subbottom profiler records show 40–60 m penetration below the seafloor in the KG offshore (Figure 3 a). These records depict the presence of blanking zones, vents, gas upthrusts, plumes, pockmarks, mud lumps, mud volcanoes and submarine diapirs. The sub-bottom reflectors are seen to be affected by gas masking in some records. Discontinuity of sub-bottom reflectors is commonly seen associated with gas masking features. The deep tow digital side scan sonar records depict the presence of pockmarks and shadow zones on the seafloor (Figure 3 b). Most of these gas escape features are due to the fluid/gas expulsion from the sub-bottom layers. Arabian Gulf, Gulf of Mexico, Barent Sea, Gulf of Cadiz, China Sea and Alaska are some of the best-known examples with intense pockmarks and gas escape features associated with gas hydrates. Results of the geophysical data analysis prompted the study of non-geophysical proxies such as sulphate reduction, methane enrichment and microbiological anomalies in order to substantiate the presence of gas hydrates in these two offshore regions.

**Geochemical proxies**

The important geochemical proxies generally investigated are SO$_4^{2-}$ and Cl$^-$ concentrations from pore water and methane flux from gas chemistry. In the present study, all the cores collected in the Goa and KG offshore were analysed for the above proxy indicators.

Geochemical analysis in Goa offshore revealed that the sediments are mostly calcareous. The TOC content is ~0.7 wt%. CaCO$_3$ content is ~60–70%, indicating high biological productivity in the area. There is no appreciable variation in Cl$^-$ concentration (540 ± 20 mM) in most of the cores, with core depth. However, at a few locations a decreased trend up to 282 mM is noticed. The SO$_4^{2-}$ concentration in general, decreases from 28 to 13 mM from top to bottom sediments with a low reduction rate. Methane concentration increases with core depth from 2 to 14 nM. An enrichment of the methane flux though in nanomoles at the core bottom, is observed at most locations.

In the KG offshore, the sediments are mostly silty-clay. In general, the TOC content is >1.6 wt%. Low concentration
of CaCO₃ (~29%) has been attributed to high influx of terrigenous materials coupled with turbidites. There is no appreciable variation in the Cl⁻ concentration (~540 mM) in most of the cores. SO₄²⁻ concentration decreases from 28 to 2 mM with core depth in general. Methane concentration is seen increasing towards core depth from 2 to 20 nM. However, at one location (AAS-4 GC 7), methane flux of >158 nM is observed at the core bottom. Interestingly, the SO₄²⁻ concentration attains minimum at this location, indicating a total anoxic condition. Plots depicting the typical variations of CaCO₃, TOC, Cl⁻, SO₄²⁻ and CH₄ with core depth in Goa and KG offshore are shown in Figure 4.

A preliminary study of the geochemical data, particularly in the KG offshore (water depth 450–1700 m), indicates methane enrichment and SO₄²⁻ reduction trends with core depth at several locations. These trends suggest the prevalence of anaerobic environment at shallow depths. In Goa offshore the study area lies between water depths of 2500 and 3200 m, and the TOC is relatively lower. The rate of sedimentation is significantly lower than in the eastern offshore. The increasing trend of methane and the decreasing trend of SO₄²⁻ with core depth indicate the likely prevalence of anaerobic conditions at deeper levels in Goa offshore.

**Chloride anomaly as an indicator of gas hydrate in sediments:** Lower chlorinity of pore water is considered as one of the most common indirect geochemical proxy indicators of gas hydrates in sediments when deep cores are drilled²⁰. On destabilization of gas hydrates, the elevated chloride concentrations get diluted with the release of pure water back into the pore space, causing freshening. In the present study (Figure 4), the observed gentle depletion trend of Cl⁻ perhaps indicates the ongoing process of freshening due to the destabilization of gas hydrates at deeper levels. Long cores (>30 m) would facilitate identification of various geological and geochemical proxies with confidence.
Sulfate-methane interface as an indicator of gas hydrate in sediments: The sulphate concentration decreases with increasing sediment depth, since sulphate is used as an oxidant by a consortium of microbes, which breakdown the sedimentary organic matter within the sulphate reduction zone. At the base of this zone, sulphate is consumed in a process of anaerobic methane oxidation. On extrapolation of the observed decreasing trend in sulphate concentration to zero, as suggested by Borowski et al., the sulphate minimum is found to occur within 4–8 mbsf in the
KG offshore and 8–32 mbsf in Goa offshore. Below the sulphate reduction zone, bacterial methane is generated by CO₂ reduction and acetate fermentation. The Sulphate-methane interface (SMI) occurs as a boundary between the sulphate reduction and methanogenesis zones, and relatively active methanogenesis occurs in marine sediments with >0.5% TOC content. Further, the relation between sulphate gradient, methane flux and gas hydrates has been established by Borowski et al., and it is suggested that shallow SMI may be useful to predict the gas hydrate occurrence at depth.

**Barium front as a proxy indicator for gas hydrate in sediments:** Elevated Ba concentrations have been used as one of the important proxies by Dickens in understanding the distribution and occurrence of gas hydrates. The solubility of barite is low in deep ocean waters. Thus in the sediment/pore water systems even with minor concentrations of dissolved SO₄²⁻, most labile Ba exists in barite with only small amounts of Ba⁴⁺. However, when SO₄²⁻ is depleted in the pore waters, the solubility of barite increases greatly and dissolved Ba⁴⁺ concentration rises by several orders of magnitude causing the Ba front. Variation in sedimentary Ba can be related to the evolution of pore water sulphate and during sediment burial, barite moves downwards from sulphate-rich zone (top) to sulfate-depleted zone (bottom) and dissolves. In turn, dissolved Ba diffuses upward and reprecipitates as barite. In systems where upward Ba⁴⁺ diffusion exceeds downward barite burial, the Ba cycle results in a barium front, a short interval of high labile Ba concentrations immediately above the depth of SO₄²⁻ depletion.

Enrichment of Ba from 70 to 380 ppm (nearly 5 to 6 times) is observed with core depth at a few locations around GC7 where high methane flux and SO₄²⁻ reduction are observed in KG offshore (Figure 5). The elevated ‘Ba’ concentrations at the bottom sediments suggest the barium front phenomenon as explained above. This observed Ba front serves as another proxy indicator for the presence of methane gas below the sulphate reduction zone. The observed trends of methane enrichment, sulphate reduction, Cl⁻ depletion and SMI with depth in conjecture with Ba front can be used as proxy indicators for the occurrence of gas hydrates below the seafloor.

XRD and SEM studies of the sediment samples indicate the presence of authigenic carbonates (calcite, Mg-calcite, aragonite and dolomite). δ¹³C analysis of calcite reveals a strong depletion in δ¹³C with values less than 50%, suggesting that the microbial communities may have induced calcite precipitation through microbial methane oxidation as in the case of carbonates formed elsewhere. Occurrence of authigenic carbonates within the core indicates the supply of methane gas in the subsurface sediments.

Rapid sedimentation of 20–40 cm/kyr has been reported in the eastern offshore, which appears to facilitate the preservation of buried carbon in the marine sediments. Mixed mode of origin (both bacterial and thermogenic) for the methane gas has been attributed in the eastern offshore from the lower ratio values of methane to the combination of ethane and propane obtained from gas analysis. On the other hand, low sedimentation rate of 3.5–5.2 cm/kyr has been inferred in the Goa offshore based on oxygen isotope studies, which may have constrained carbon accumulation. The tectonic setting and reactivation of the faults and other geodynamic processes appear to control the geological environment and the formation of gas hydrates. According to Gornitz and Fung, surface sediments rich in TOC (>1%) are favourable locales for predicting the occurrence of gas hydrates. However, Borowski et al. cautioned that the relation between organic matter, methane production and occurrence of gas hydrates is not straightforward. In light of the above observations, the inferred proxies on the Goa and KG offshore need further confirmation by a study of long cores.

**Microbiological proxies**

The carbon components (methanol, acetate, formate, monomethylamine, etc.) are formed from organic matter by bacterial processes that degrade complex biopolymers into simple molecules. Further, these components are converted to methane through the process of anaerobic mineralization by a consortia of bacteria and microbese. Microbiological studies revealed the presence of sulphate reducing bacteria SRB_r (reducers) and SRB_f (fermenters) in appreciable quantities in the bottom layers of the core, probably suggesting availability of methane from the subsurface layers and an ongoing process of methanogenesis. Sulphate reduction and methane enrichment as mentioned earlier, endorse the abundance of methane at the core depth.
Conclusion

The BSRs observed in the KG and Andaman offshore suggest high probability of gas hydrate occurrence due to their characteristic nature. The BSRs inferred in Goa offshore though devoid of cross-cutting, cannot be ignored without further investigations.

The deep tow digital side scan sonar and chirp sonar data depict the presence of gas escape features such as pockmarks, vents, gas upthrusts, plumes, mud volcanoes/diapirs, etc. in KG offshore.

Non-geophysical proxies derived from the analysis of 5 m long sediment cores, such as chloride depletion, sulphate reduction, methane enrichment and abundance of sulphate reducing bacteria and fermenters with depth depict the presence of methane, which provides an indirect clue to the occurrence of gas hydrates at greater depths.

The extrapolated SMI and observed Bu front phenomena in conjuncture with the above geochemical proxies can be used as good indicators for the likely occurrence of gas hydrates below the seafloor in the KG offshore.

Integration of geophysical, geological, geochemical and microbiological data suggests that both Goa and KG offshore are promising prospect areas for gas hydrate exploration. Sediment cores longer than 30 m and high resolution seismic reflection (sparker) data will facilitate the demarcation of prospective locales of gas hydrates occurrence.

15. NIO, Bottom simulating reflections on the western continental margin of India (inferred from the seismic reflection data available with NIO) for GAIL (India) Limited, NIO-CON/399, 1999.

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