

**GAS HYDRATES IN THREE INDIAN OCEAN REGIONS, A
COMPARATIVE STUDY OF OCCURRENCE AND SUBSURFACE
HYDROLOGY**

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ABSTRACT

To establish the structural and lithological controls on gas hydrate distribution and to assess the potential energy resource and environmental hazards in the Indian Ocean, non-pressurized and pressurized cores were recovered from the Krishna-Godavari (K-G) and Mahanadi Basins offshore east India, and from an Andaman Sea site. The pore fluids were analyzed for: salinity, Cl⁻, sulfate, sulfide, carbonate alkalinity, Ca²⁺, Mg²⁺, Sr²⁺, K⁺, Na⁺, Ba²⁺, and Li⁺ concentrations, $\delta^{13}\text{C-DIC}$, $\delta^{18}\text{O}$, D/H, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios; together with infra-red imaging they provided important constraints on the presence and distribution of gas hydrates, thus on the subsurface hydrology. Evidence for methane hydrate was obtained at each of the sites. Only in the K-G Basin, between the sulfate-methane transition zone (SMT) depth and ~80 mbsf, higher than seawater chloride concentrations are observed; below this zone to the depth of the base of the gas hydrate zone (BGHSZ), chloride concentrations and salinity are lower than seawater value. In the Andaman Sea and Mahanadi Basin, only lower than seawater chloride concentrations are observed, and the shallowest gas hydrates occur at 100-200 m below the sulfate-methane transition zone (SMT) and extend to the depth of the BGHSZ. In the K-G Basin, the highest methane hydrate concentrations are associated with fracture zones in clay-rich sediments and/or in some coarser grained horizons. In the Andaman Sea, however, they are primarily associated with volcanic ash horizons. Assuming dilution by water released from dissociated methane hydrate, chloride and salinity anomalies suggest pore volume occupancies on the order of <1% to a maximum of ~61% at two sites (10, 21) in the K-G Basin and <1% to a maximum of ~76% at the Andaman Sea site. Overall, the percent pore volume occupancies based on pressure core methane concentrations and the chloride concentrations in conventional cores are similar.

Variations in sulfate gradients were observed with the steepest gradient having the SMT at 8 mbsf in the K-G Basin and the deepest SMT at ~25 mbsf at the Andaman Sea site. The extreme negative $\delta^{13}\text{C}$ values of the dissolved inorganic carbon (DIC), ranging from -38‰ to -47‰ at the SMT at some of the sites, indicate that anaerobic oxidation of methane (AOM) is an important reaction responsible for sulfate reduction at these sites. At several sites in the K-G Basin, however, the $\delta^{13}\text{C-DIC}$ values indicate that organic matter oxidation is the dominant reaction.

Keywords: gas hydrates, pore fluids, Cl⁻ concentration, sulfate-methane transition zone, dissolved inorganic carbon

INTRODUCTION

The 2006 Indian Ocean Gas Hydrate Program, (NGHP) aimed to investigate the controls on the geologic occurrence and characteristics of gas hydrates off-shore India in order to eventually assess the possibility of exploiting gas hydrates as a potential energy source. The amount of gas hydrate accumulation in the ocean is enormous; estimates vary from 2,500 to 10,000 gigatons (Milkov, 2003 [1]; Kvenvolden, 1988 [2], respectively).

Following extensive geologic and geophysical explorations, two distinct geologic settings in the passive margin of east India, in the Krishna-Godavari (K-G) and Mahanadi Basins, and one in the Andaman convergent margin, were targeted for deep drilling and coring (Figure 1); both conventional and pressure cores were obtained for

shipboard and shore-based analyses. The logging while drilling (LWD) results guided the coring and sampling in the three distinct geologic regions. Nine sites were cored in the K-G Basin, 2 in the Mahanadi Basin, and one in the Andaman Sea. At both the K-G and Mahanadi Basins sedimentation rates are high and are dominated by river input of clay-rich sediments with well-defined sand horizons (Collet et al., 2008 [3]). The sediments at the convergent margin site in the Andaman Sea primarily consist of nannofossil ooze with numerous volcanic ash layers and minor terrigenous input (Collet et al., 2008 [3]). Pore fluids were extracted and analyzed for a large range of chemical components and isotope ratios. Geochemical analyses provide key information about the origin of pore fluids at the cored sites. The chloride ion is conservative at low to

moderate temperatures, and can help detect fluid-sediment

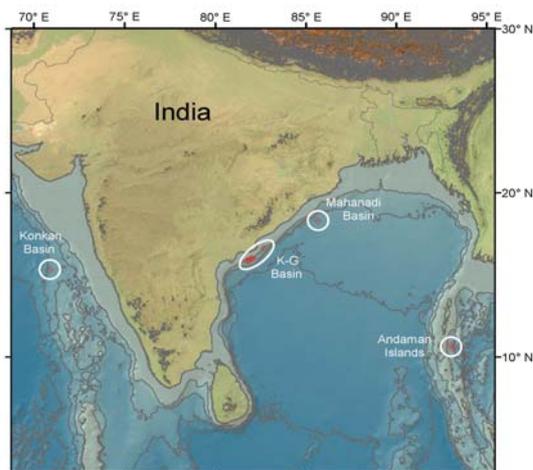


Figure 1. Schematic map of coring locations

processes such as gas hydrate dissociation or mineral hydration-dehydration reactions. Key objectives of the NGHP geochemical program were (1) to document the pore-fluid chemical and isotopic compositions at each of the drill sites in order to determine the geologic controls on the formation and occurrence of gas hydrate; (2) to establish the depth, spatial distribution, and concentration of gas hydrates and their relation to lithology and other physical properties; (3) to identify the nature of the microbial reactions responsible for gas generation *in situ* and methane fluxes at the sulfate-methane transition zone; and (4) to determine the subsurface hydrology and the geologic controls on fluid migration. A special important objective of the NGHP expedition is to test gas hydrate formation models especially for concentrated occurrences, such as at Site 10 in the K-G Basin, having a 130 m thick fracture controlled gas hydrate occurrence. In the K-G Basin the occurrence of gas hydrate appears to be closely associated with large scale structural features; it is a fracture-controlled gas hydrate occurrence. In the Andaman Sea, the lithology is the main control on the gas hydrate distribution; the gas hydrate is mostly concentrated in the numerous volcanic ash layers. In the Mahanadi

Basin, gas hydrate is disseminated in the sediment pore spaces. Some disseminated gas hydrate is present at most sites cored.

METHODS

The main components analyzed in the pore fluids were salinity, Cl^- , sulfate, sulfide, carbonate alkalinity, Ca^{2+} , Mg^{2+} , Sr^{2+} , K^+ , Na^+ , Ba^{2+} , Li^+ , and silica concentrations, $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC), $\delta^{18}\text{O}$ values, D/H and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Pore fluid samples were taken routinely following a predetermined scheme. In cores in which gas hydrate was present, additional samples were identified and selected using infrared images of the cores. After careful cleaning to remove outside layers of sediment possibly contaminated with seawater used in drilling fluids, the sediment sample was placed in titanium squeezers and subjected to pressures ranging from 800 to 40,000 lbs. In addition, pressure cores were sub-sampled after they were degassed for methane concentration; this sub-sampling was guided by X-rays of the cores taken before and after degassing, which indicated the spatial distribution of gas hydrate. The pore fluids derived from squeezing were filtered and analyzed shipboard for salinity by refractometry, for chloride, bromide, and sulfate concentrations by ion chromatography, and for alkalinity by the Gran-titration. The upper sections of the cores were analyzed at high resolution for sulfate concentrations to determine the sulfate gradient and depth of the sulfate-to-methane transition zone. Sulfide was captured by precipitation with $\text{Cd}(\text{NO}_3)_2$ for shore-based analysis. Following the alkalinity and sulfate analyses, the remaining volume of the squeezed pore fluids was subdivided for shore-based analyses of major and trace element concentrations and for $\delta^{13}\text{C}$ -DIC, $\delta^{18}\text{O}$, D/H, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Precisions for salinity, alkalinity, sulfate, major and minor element concentration data ranged between 1-3%.

RESULTS AND DISCUSSION

Because of the conservative nature of chloride at low to moderate fluid-rock interactions, pore fluid Cl^- concentration profiles of conventional cores provide the best information on the distribution of gas hydrates in sediments. Gas hydrate formation incorporates water molecules into the gas hydrate structure and the dissolved ions in seawater are excluded, increasing their concentrations (and the

salinity) in the associated pore fluid. In most cases, the rate of *in situ* gas hydrate formation, hence of ion exclusion, is considerably slower than the rate of diffusion of the excluded ions, therefore, over long periods the pore fluid's chloride and excluded ion concentrations do not exceed the adjacent pore fluid concentrations. In such cases when non-pressurized cores are retrieved, because gas hydrate stability depends on pressure and temperature, gas concentration, and pore fluid chemistry, (Sloan and Koh, 2008 [4]) gas hydrates decompose in the cores and dilute the chloride (and other ions) concentration of the pore fluids. In such closed systems mass balance calculations can provide the amount of gas hydrate that dissociated; assuming that the background chloride concentration can be established. If, however, the kinetics of gas hydrate formation exceeds the rate of diffusion (or mixing with other fluids) elevated chloride concentration and salinity will be observed. Transport of methane as a free gas phase was invoked to explain the higher than seawater Cl^- and salinity pore fluids observed at the summit of Hydrate Ridge, Cascadia (Torres et al., 2004 [5]; Liu and Fleming, 2007 [6]). In the K-G Basin sites with higher than seawater chloride concentration, however, no free methane gas phase was observed (Collet et al., 2008 [3]). The formation of high Cl^- concentrations by mixing with brines (e.g. Ruppel et al., 2005 [7]; Kastner et al., 2008 [8]) as in the Gulf of Mexico is as well not applicable to the NGHP study regions.

Based on infra-red (IR) imaging and diagnostic geochemical signatures, in particular chloride concentration, the presence of gas hydrates at all sites cored was indicated. In most cases the occurrence of gas hydrate was manifested by lower than seawater chloride concentrations. Based on the Cl^- concentration profile, the highest methane hydrate concentrations occur in the K-G Basin. The mode of occurrence varies from fracture filling in fine grained sediments, nodules, lenses, and layers. Some disseminated methane hydrate is present as well. Figure 2 shows the two extreme occurrences in the K-G Basin; at Site 7 only minor amounts of disseminated methane hydrate are present having maximum concentrations near the base of the gas hydrate stability zone (GHSZ) that coincides with the bottom simulating reflector (BSR). The highest concentrations of methane hydrate occur at Sites 10 and 21. The maximum concentrations occur

between ~25 to ~80 mbsf, but gas hydrates are also present to the depth of the BGHSZ at ~160 mbsf; hence, a ~125 m thick layer with methane hydrate from ~1% to 61% pore volume occupancy and an average concentration of gas hydrate of approximately 30% pore volume occupancy is present at these sites. Most interesting is the occurrence of higher than seawater chloride concentrations, primarily between ~25 and ~80 mbsf, suggesting rapid formation of methane hydrate at the maximum concentration depth interval. The origin of this high salinity horizon in the absence of a methane gas phase is being modeled.

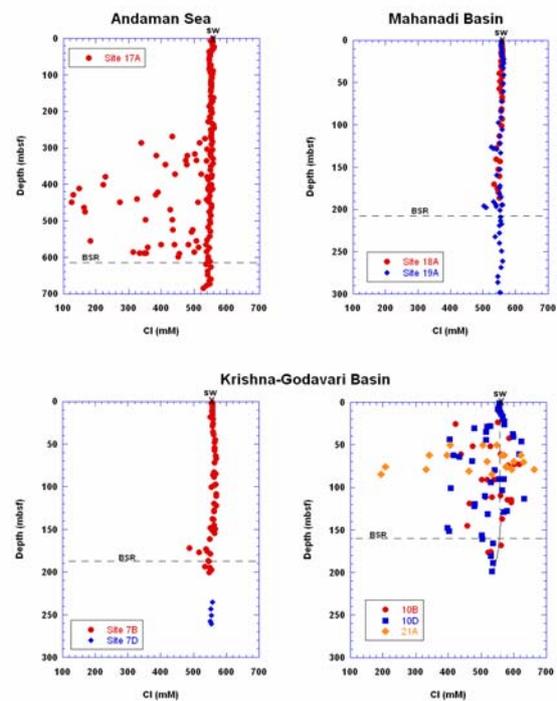


Figure 2. Representative chloride depth profiles at three regions cored

In the Mahanadi Basin although present, methane hydrate is not abundant at Sites 18 and 19 (Figure 2), but is present in a disseminated mode, with a maximum occurrence just above the BGHSZ. In the Andaman Sea, because of the very low geothermal gradient, the BGHSZ is at ~600 mbsf, the deepest recorded so far. Gas hydrate is rather abundant, below ~270 mbsf ranging from ~1% to 76% with an average of ~15-20% pore volume occupancy from ~270 to 600 mbsf (Figure 2). In addition to some disseminated gas hydrate, the

distribution of most of the methane hydrate is lithologically controlled, concentrated in volcanic ash layers.

Formation of gas hydrate accumulations depends on the adequate supply of hydrocarbon gas. At the three regions cored the gas hydrates are primarily methane hydrates and the origin of the methane is biogenic (Tom Lorenson, personal communication). When the main electron source for sulfate reduction is anaerobic oxidation of methane that is supplied from depth, the methane flux, apparent rate of sulfate reduction, and the depth of the SMT are proportional (Borowski et al., 1996 [9]). Dissolved sulfate reduction is, however, also linked to organic matter oxidation. The relationship between the amount of sulfate reduction and the amount and carbon isotopic composition of the DIC can indicate the nature of the oxidation reaction responsible for sulfate reduction. The former reaction produces one mole of bicarbonate per mole of sulfate reduced, and the latter reaction produces two moles of bicarbonate per mole of sulfate reduced. Thus, the proportion of bicarbonate produced and sulfate reduced, and the $\delta^{13}\text{C}$ -DIC provide information on the dominant process governing the oxidation of dissolved sulfate (Claypool and Kaplan, 1974 [10]). Biogenic methane $\delta^{13}\text{C}$ values on average range from -60 to -80‰ (PDB) and sediment organic matter $\delta^{13}\text{C}$ is about -20 to -25‰. Analysis of the contribution of the two processes is thus possible from the measured $\delta^{13}\text{C}$ -DIC values and from the relation between alkalinity production and sulfate reduction. At the SMT depth where sulfate concentrations are approaching zero, alkalinities are at their maximum values.

On the basis of the $\delta^{13}\text{C}$ -DIC data, and alkalinity production versus sulfate reduction data at all sites, AOM is the more important reaction responsible for sulfate reduction at the Andaman Sea site, the two Mahanadi Basin sites and at a third of the sites at the K-G Basin, whereas at ~60% of the sites in the K-G Basin organic matter oxidation is the primary reaction responsible for sulfate reduction.

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