Final Technical Report on: Controls on Gas Hydrate Formation and Dissociation, Gulf of Mexico: In Situ Field Study with Laboratory Characterizations of Exposed and Buried Gas Hydrates

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Abstract

The main objectives of the project were to monitor, characterize, and quantify *in situ* the rates of formation and dissociation of methane hydrates at and near the seafloor in the northern Gulf of Mexico, with a focus on the Bush Hill seafloor hydrate mound; to record the linkages between physical and chemical parameters of the deposits over the course of one year, by emphasizing the response of the hydrate mound to temperature and chemical perturbations; and to document the seafloor and water column environmental impacts of hydrate formation and dissociation.

For these, monitoring the dynamics of gas hydrate formation and dissociation was required. The objectives were achieved by an integrated field and laboratory scientific study, particularly by monitoring *in situ* formation and dissociation of the outcropping gas hydrate mound and of the associated gas-rich sediments. In addition to monitoring with the MOSQUITOs, fluid flow rates and temperature, continuously sampling *in situ* pore fluids for the chemistry, and imaging the hydrate mound, pore fluids from cores, peepers and gas hydrate samples from the mound were as well sampled and analyzed for chemical and isotopic compositions. In order to determine the impact of gas hydrate dissociation and/or methane venting across the seafloor on the ocean and atmosphere, the overlying seawater was sampled and thoroughly analyzed chemically and for methane C isotope ratios.

At Bush hill the pore fluid chemistry varies significantly over short distances as well as within some of the specific sites monitored for 440 days, and gas venting is primarily focused. The pore fluid chemistry in the tub-warm and mussel shell fields clearly documented active gas hydrate and authigenic carbonate formation during the monitoring period. The advecting fluid is depleted in sulfate, Ca Mg, and Sr and is rich in methane; at the main vent sites the fluid is methane supersaturated, thus bubble plumes form. The subsurface hydrology exhibits both up-flow and down-flow of fluid at rates that range between 0.5 to 214 cm/yr and 2-162 cm/yr, respectively. The fluid flow system at the mound and background sites are coupled having opposite polarities that oscillate episodically between 14 days to ~4 months. Stability calculations suggest that despite bottom water temperature fluctuations, of up to ~3 °C, the Bush Hill gas hydrate mound is presently stable, as also corroborated by the time-lapse video camera images that did not detect change in the gas hydrate mound. As long as methane (and other hydrocarbon) continues advecting at the observed rates the mound would remain stable.

The _^{13}C-DIC data suggest that crude oil instead of methane serves as the primary electron-donor and metabolic substrate for anaerobic sulfate reduction. The oil-dominated environment at Bush Hill shields some of the methane bubbles from being oxidized both anaerobically in the sediment and aerobically in the water column. Consequently, the methane flux across the seafloor is higher at Bush hill than at non-oil rich seafloor gas hydrate regions, such as at Hydrate Ridge, Cascadia. The methane flux across the ocean/atmosphere interface is as well higher. Modeling the methane flux across this interface at three bubble plumes provides values that range from 180-2000 _mol/m^2 day; extrapolating it over the Gulf of Mexico basin utilizing satellite data is in progress.

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Introduction

Seafloor occurrences of gas hydrate are especially prominent and the Gulf of Mexico, at Bush Hill (GC 185) (e.g. Macdonald et al., 1994), the focus site of this research project. The occurrence of methane hydrate at or near the seafloor indicates active upward advection of methane-rich fluids or methane gas. The seafloor and shallow buried gas hydrates are the most vulnerable to global warming. The environmental impact of release of large quantities of methane into the ocean and atmosphere could have important societal and microbiological consequences.

Hydrate dissociation poses risks to drilling and seafloor stability as well as to the local seafloor environment, and possibly to global climate. As the hydrate system begins to dissociate, the resulting volume and density change in the sediment may initiate local destabilization of the continental slope and result in a major submarine landslide that could be accompanied by rapid massive release of methane to the ocean and possibly the atmosphere. The potential for slope instability could have serious economic implications for offshore drilling platforms and cabling operations. It could also seriously affect the overlying water mass and local fisheries by consuming the dissolved oxygen of the entrained seawater. This project was thus designed to provide a more in-depth understanding of the responses of seafloor hydrates to natural chemical and thermal perturbations.

Much of our understanding of the kinetics of gas hydrate behavior comes from laboratory studies on certain types of synthetic gas hydrates (e.g., structure I). At Bush Hill, however, gas hydrate structure II dominates (e.g. MacDonald et al., 1994; Sassen et al., 1998). Even for Structure I, data on the kinetics of natural gas hydrate formation and dissociation in the marine environment are lacking and the major and minor physical and chemical controls have not been monitored.

Bush Hill (lease block GC 185) in the northern Gulf of Mexico (27^{o}47.5’N and 91^{o}30.5’W) is a fault-related seep at ~ 570 m water depth (Figure 1) at the top of a ~500 m wide, ~40 m high topographic high (MacDonald et al., 2003). The Bush Hill site contains a persistent 2-3 m wide and ~ 0.65 m high gas hydrate mound, only moderately covered by sediment, with gas hydrate outcropping at its flanks (Vardaro et al., 2005). The study area also contains several gas vents situated within and adjacent to the hydrate mound that continuously emit methane and other hydrocarbons to the water column. The methane in the gas hydrates outcropping at the seafloor is dominantly thermogenic in origin (based on the methane _^{13}C values), and the hydrates are mainly structure-II type (Brooks et al., 1984; Sassen et al., 1999). The annual mean bottom water temperature ranges from 7.5 to 8.0 ^{o}C (MacDonald et al., 2005), and the hydrostatic pressure is ~5400 kPa. At this pressure, the stability temperature for a structure-II gas hydrate is approximately 14.5 ^{o}C and the stability temperature for a structure-I gas hydrate is 8.1^{o}C computed using the CSMHYD program of Sloan (1998) for a pore water salinity of 36, suggesting the gas hydrates at Bush Hill are near the P-T conditions at the three-phase stability boundary. Hence, in contrast to gas hydrates buried tens to hundreds of meters below the sediment-water interface, the gas hydrates at Bush Hill are particularly vulnerable to changes in bottom water temperature, subsurface hydrology, and methane flux.

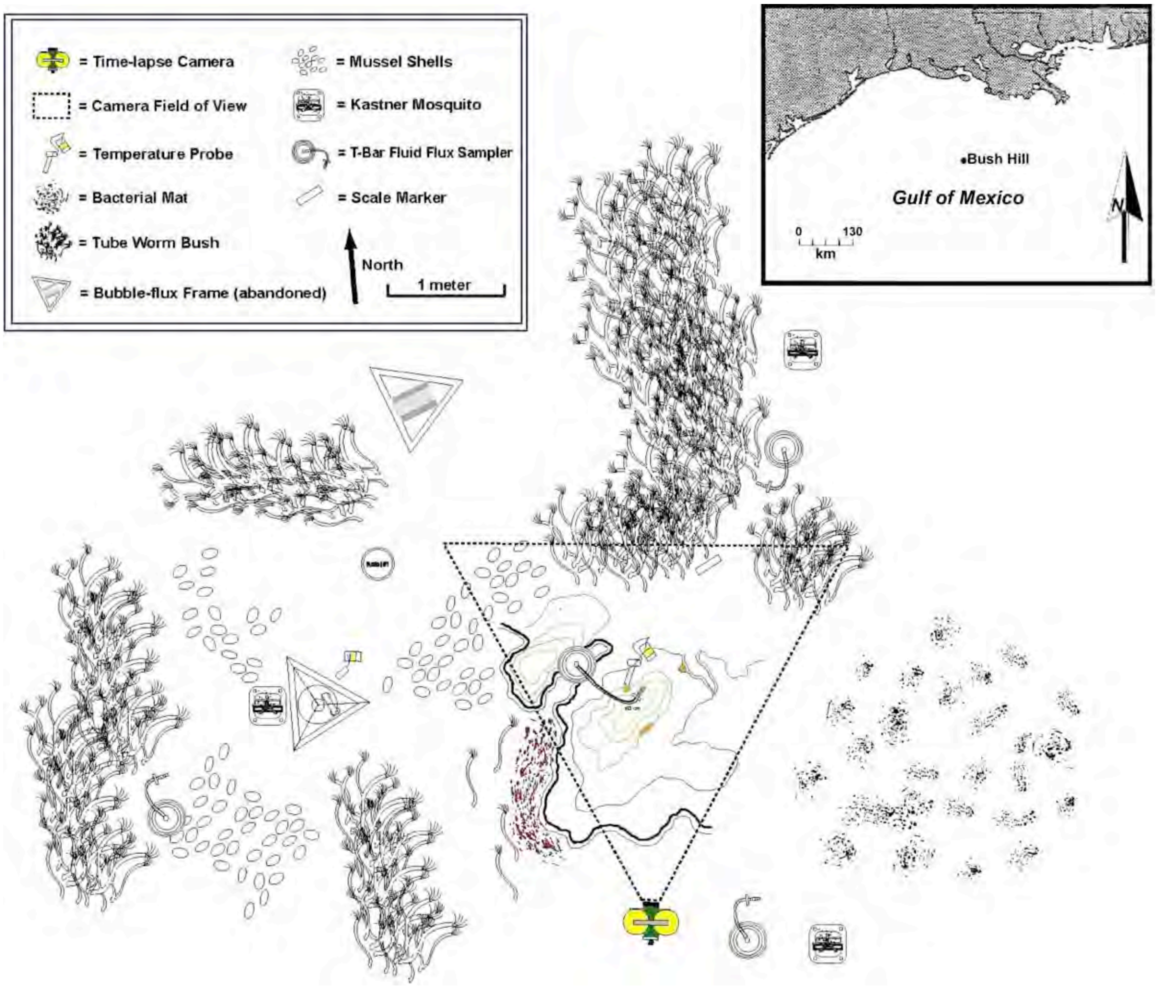


Figure 1. Schematic of camera deployment site at Bush Hill (GC 185, see inset map at top right) as it appeared in June 2002, made using photo-mosaics assembled from video footage of submersible overflights. The MOSQUITOs are also shown. The gas hydrate mound has an irregular shape and about 50cm of relief. All of the equipment shown, except for the bubble-flux meter platforms, has since been recovered.

The gas hydrate mound at Bush Hill has been observed to change size and shape in less than a year, with lobes intermittently breaking off, releasing methane and exposing fresh gas hydrate. Furthermore, spontaneous gas expulsion episodes at vents around the mound were recorded when bottom water temperatures exceeded 8 ^{o}C. (MacDonald et al., 1994). Those results were confirmed by Roberts et al. (1999) who observed a doubling of the outflow rate at a seafloor methane vent in response to a 1 ^{o}C increase in temperature. Despite these short term variations in the flux of gas bubbles emitted from nearby vents corresponding to small-scale temperature fluctuations, the gas hydrate mounds at Bush Hill have persisted at the same locations for >12 years (MacDonald et al., 1994). The Bush Hill (GC 185) hydrate mound site has been studied extensively for

some time (e.g. MacDonald et al., 1994; Sassen et al., 1998; Aharon and Fu, 2000; and references therein).
To this date, only a few long-term measurements of *in situ* temperature and fluid flux have been made at GC 185 (Tryon and Brown, 2004; MacDonald et al., 2005), nor has the impact of the methane advection into the water column and possibly into the atmosphere been documented before. This prompted us (Miriam Kastner, Scripps Institution of Oceanography, and Ian MacDonald, (Texas A&M University, Corpus Christi) to propose a project to provide this missing information.

This combined scientific field monitoring and laboratory project focused on documenting the present system that maintains the Bush Hill seafloor hydrate mound in the northern Gulf of Mexico (GOM). The main objective was to determine the physical and chemical effects of *in situ* environmental perturbations on seafloor gas hydrate stability at the Bush Hill gas hydrate mound and vicinity. For this project focused on the following: What is the subsurface hydrology; what are the methane and solute fluxes at the hydrate mound, in the vicinity and at a “background” site; how much of the methane escapes across the seafloor into bottom water; how much of the methane gets oxidized in the water column, thus how much escapes into the atmosphere? The strategies to achieve the objective and address these questions were: (1) to recover push cores as close to the mound as possible and in the vicinity at sites colonized by chemosynthetic tube worms, mussels, and bacterial mats, as well as regionally; (2) to analyzed the pore fluids from the cores and from peepers for methane, major, and minor component concentrations, and for methane and Dissolved Inorganic Carbon (DIC) C-isotope ratios; (3) to obtain water column samples from plumes and regionally and analyze them for methane concentrations and _^{13}C values; (4) to deploy flux meters, MOSQUITOs were with *Johnson Sea –Link* at critical sites for long-term continuous monitoring of fluid chemistry, methane fluxes, and seafloor temperatures. Three MOSQUITO samplers adjacent to the Bush Hill hydrate mound were deployed, one each in a mussel field, a bacterial mat, and a tubeworm field. The fourth MOSQUITO was positioned a short distance southwest of the mound to record baseline background conditions; (5) to recover gas hydrate cores from the mound by drilling, and analyze them for chemical and isotopic compositions; and (6) To continuously hourly image the gas hydrate mound with a time-lapse video camera assembly.

The project consisted of two field expeditions having the acronym GHOST.The submersible *Johnson Sea-Link* was used to emplace and retrieve the flux meters, peepers, and a video camera instruments and to collect gas hydrate, water column, sediment, and pore fluid samples. All the samples underwent extensive laboratory analyses.

The results of (1) the comprehensive long-term measurements of fluid chemistry, fluid flux, and temperature, and their time dependent variations and subsequent impact on gas hydrate stability at Bush Hill between June 2002 and August 2003, and of (2) the seafloor and water column environmental impacts of gas hydrate formation and dissociation, as well as dynamic fluid flow over the course of ~15 months using a new long-term continuous, three-dimensional fluid flow meter/chemical sampler called the MOSQUITO are presented below.

Experimental

The experimental approach consisted of both established and newly designed and constructed methodologies, as described below. Figure 1 is a schematic map of the Bush Hill (GC 185) main field area, showing the deployment locations of the various field monitoring instruments used in this project.

Sediment Core Recovery and Subsampling:

Sediments were recovered with push cores near and immediately adjacent to the Bush Hill gas hydrate mound, as well as regionally, to document “background” properties. At each sediment sampling site triplicate push cores were recovered: 1) for sediment characterization, 2) for pore fluid chemistry, and 3) for dissolved methane concentration and isotope analyses. The cores were stored in a cold room under anaerobic conditions prior to and during processing.

Pore fluid and Water Column Analyses:

Geochemical analyses were performed on pore fluids from sediment push cores at Bush Hill and on water column samples at and near the main Bush Hill plume. Pore fluid samples from the cores and CTD water samples were analyzed for the depth distributions of dissolved methane, salinity, Cl, Ca, Mg, pH, alkalinity, sulfide, and sulfate concentrations, and for DIC and methane _^{13}C values. The spatial and depth distribution of pore fluid solute concentrations provide information on the subsurface hydrology, and on solute fluxes across the sediment-water interface.

Pore fluids were recovered by centrifuging subsections of the push cores at *in situ* temperature and under anaerobic conditions. The samples were immediately analyzed, shipboard, for salinity, alkalinity, pH, and sulfide and sulfate concentrations, and the remaining pore fluid was sub-sampled into different aliquots that were individually pretreated, depending on the component, and appropriately stored for shore-based, major, minor, and trace element concentration, as well as for isotope analyses. For most solutes the pore fluids were analyzed by ICP-OES or ICP-MS. Chloride concentration was determined by titration with $AgNO_3$, and sulfate concentration was also determined by Ion Chromatography (IC). For methane and other hydrocarbon analyses the pore fluid samples, as well as the water column samples were stored in serum bottles poisoned with mercuric chloride. Concentrations of hydrocarbons were measured by gas chromatography and the _^{13}C-CH_4 -and-DIC were determined by mass spectrometry. The flux meter data were analyzed for the above components and for the degree of the dye dilution, used to determine fluid flow rates.

In situ pore fluids were recovered from peepers inserted into the sediment adjacent to the push core locations, as well as in transient bubble plumes near the gas hydrate mound. The chemical and isotopic analyses followed the above described procedures.

MOSQUITOs:

Gas hydrate outcrops on the seafloor at the Bush Hill hydrocarbon seep sites, in the northern Gulf of Mexico, provide an ideal location to monitor the response of shallow gas hydrates to temperature, biochemical, and hydrological perturbations. Four newly designed fluid flux meters were deployed for 440 days at Bush Hill, to determine how fluid fluxes and composition simultaneously influence gas hydrate stability and to quantify the associated methane fluxes out of the sediment column. The MOSQUITO flux meters are capable of continuously measuring fluid flow rates and sampling pore fluid chemistry at multiple depths below the seafloor in three dimensions, as well as monitoring bottom water temperature.

The innovative, newly modified for the project MOSQUITOs) were built for time series concentrations, fluid-flow rates, and temperature data. The MOSQUITO operates using the principles of osmotic pumping (Jannasch et al., 2004) and tracer dilution. The tracer (fluorescein) time-series was determined on a scanning fluorimeter. The novel design is shown in Figure 2 before deployment and on the seafloor. The MOSQUITO allows one to continuously monitor, in three-dimensions, for months to years, both vertical and horizontal fluid flow in sediments, and to obtain an accurate record of the fluid chemistry (Solomon et al., 2005, 2006). Temperature probes attached to the MOSQUITOs recorded the bottom water temperature for 440 days. These temperature recorders were deployed as a supplement to a specially designed temperature probe that simultaneously recorded temperature in the water, sediment, and gas hydrate over 350 days.

Gas Hydrate Samples:

Core samples of gas hydrates exposed on the seafloor were successfully recovered for the first time with a newly designed hydrate corer, a manipulator-operated drill with a 6-inch detachable core bit, shown in Figures 3 and 4. The challenge with hydrate sampling is not only with coring, but also to transport the hydrates to the laboratory with minimum disturbance and contamination. The hydrate was placed in a specially designed hydrate recovery pressure chamber prior to being hauled to the surface (Figure 3A). The insulated recovery chamber preserves the sample at 90 percent of the bottom pressure and over 95 percent of the bottom temperatures. Shipboard, in a cold room, the core was photographed and sliced into sections, shown in Figures 3C, and 3D, and preserved in liquid nitrogen for shore-based chemical and isotopic analyses. The gas hydrate composition was analyzed by gas chromatography, and the methane C-isotopic composition by mass spectrometry.

Observing the Gas Hydrate Mound Habitat and Thermistor Probes:

A time-lapse video camera assembly was designed and constructed; then it was installed on the seafloor near the Bush Hill hydrate mound. This digital camera, shown in Figure 4 recorded one still image every six hours for three months in 2001 and one month (July) in 2002, and every two hours for a month in June 2002, to image the growth or dissociation of the Bush Hill hydrate mound. It was also equipped with a synoptic temperature recorder mentioned above (Figure 4A).

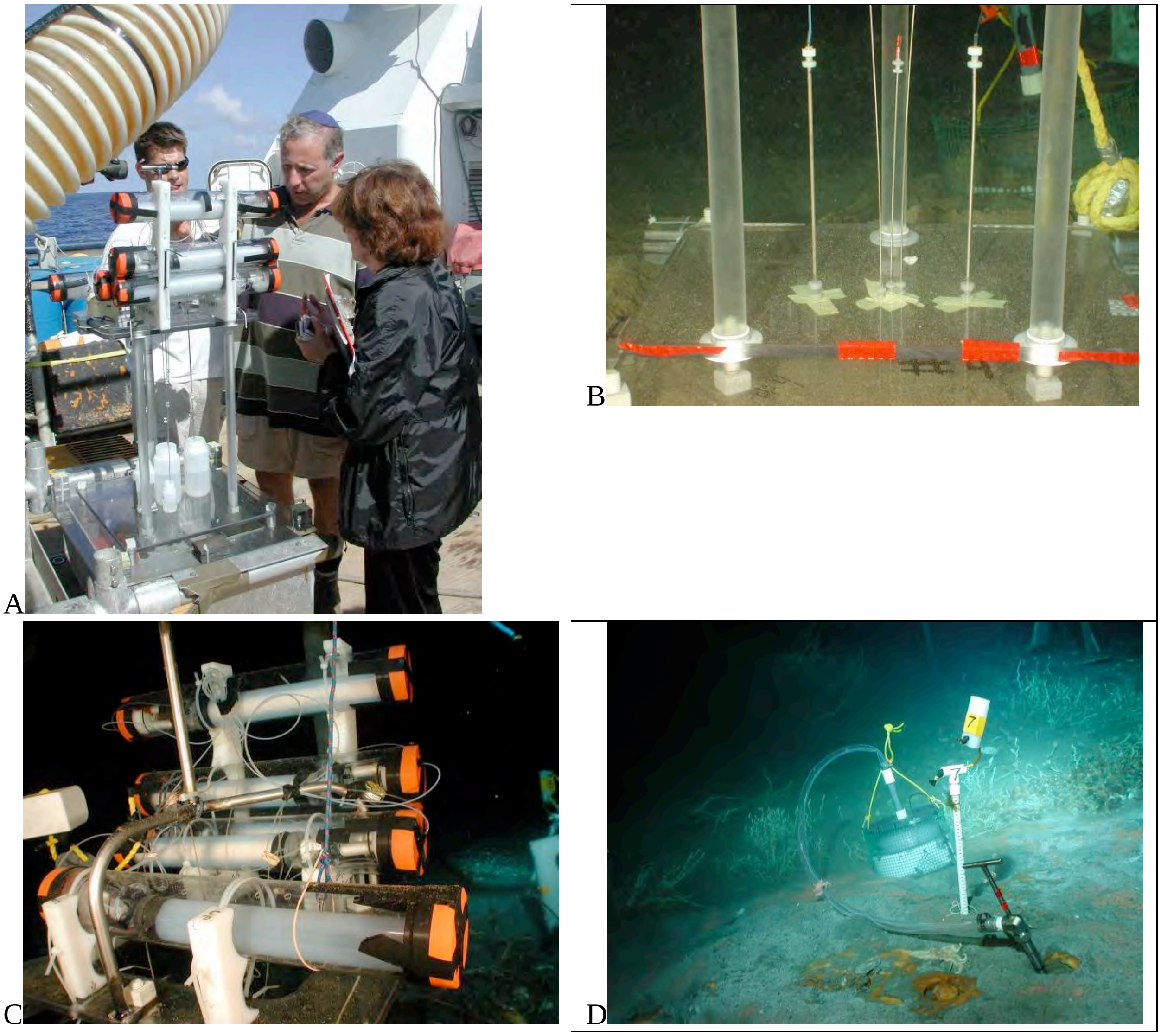


Figure 2. Flux measurement methodology: A) MOSOQUITO prepared for deployment by *Sea Link* submarine. B) MOSQUITO sampling Ti capillary needles prior to insertion into sediment. C) Osmo-pump and sample collection cores. D) White tee-bar probe in middle-ground of hydrate mound is thermistor probe.

Water Column Sampling and Gas Vent Detecting:

Water column samples were obtained by two methods: (1) with Nisken bottle on a CTD. The water samples were immediately stored in serum bottles for shore-based methane concentration and C-isotope ratio analyses. (2) From within the main bubble plumes with the submersible *Johnson Sea-Link* by drawing water through a hose into the submarine into serum bottles as the submersible was slowly ascending to the surface. Gas plumes from natural seeps were also examined and data collected by 100 and 384 kHz side-scan sonar which was operated from a submarine near the seafloor. Side-scan sonar bubble plumes at Bush Hill, GC 234, and GB 425 are shown in Figure 5.

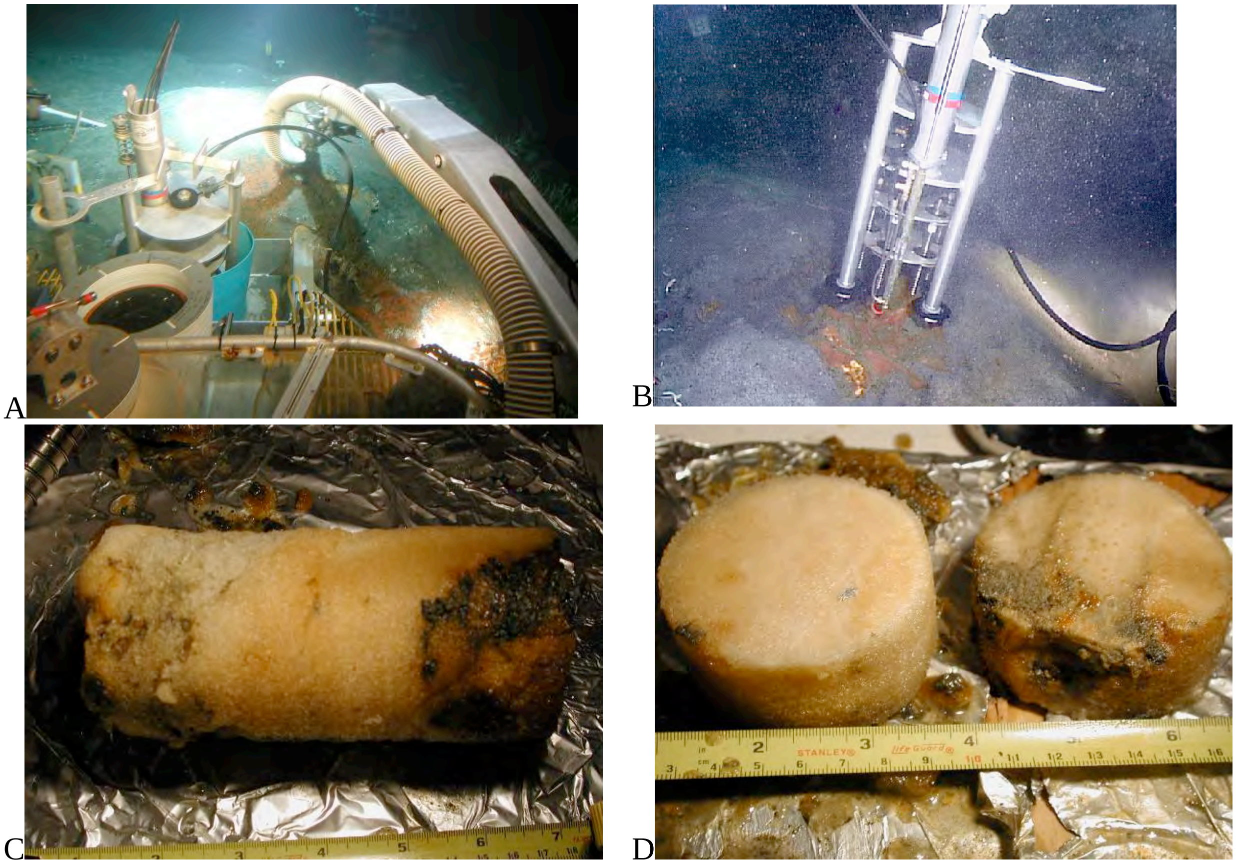


Figure 3. Hydrate recovery methology: A) Recovery chamber in open position. B) Hydrate drill collecting core on hydrate mound. C) Preserved core on surface. D) Cores sectioned for storage in liquid nitrogen.

Results and Discussion

Pore Fluid Samples:

Twenty-seven push cores were collected during the first cruise, providing a wealth of information about the chemistry near-seafloor gas hydrates. Of particular interest is how the formation of hydrates changes the porosity and integrity of the sediment. They also provide a record of initial *in-situ* sediment-pore fluid chemistry. Pore fluids from the cores were sampled and sectioned in the cold room aboard the ship. Using standard wet chemistry techniques, the fluids were immediately analyzed for salinity, alkalinity, pH, and ammonium, and sulfide was precipitated. The remaining fluids were stored for later shore-based analyses.

The pore fluid chemistry at Bush Hill varies significantly over short distances, which is manifested at the seafloor by sharp interfaces between benthic biological communities. Not surprisingly, the transient bubble plumes and the bacterial mats show the most modified pore water chemistry. Ca and SO_4 concentrations measured in the peepers and push cores from the bubble plumes and bacterial mats decrease dramatically with depth.

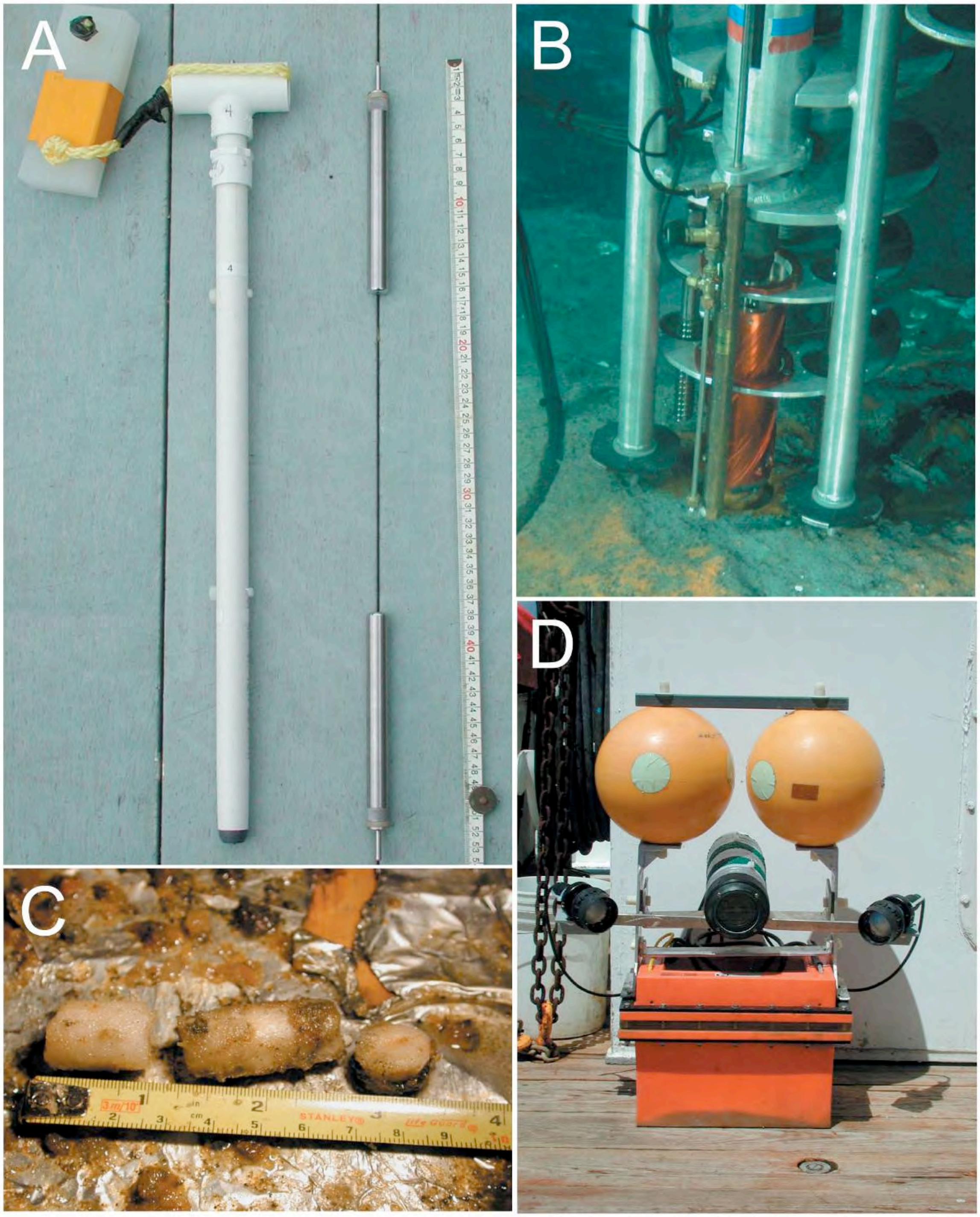


Figure 4. Application of hydrate drill for measuring thermal properties of gas hydrate. A) Thermistor probes (2) were deployed in a PVC wand. B) Small-diameter holes were drilled in gas hydrate mound. C) Hydrate was recovered for analysis. D) A time lapse camera was used to monitor setting during deployment.

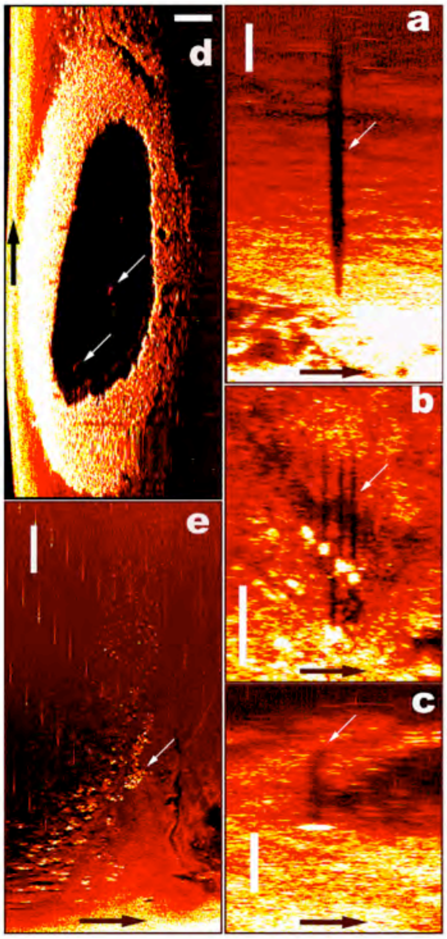
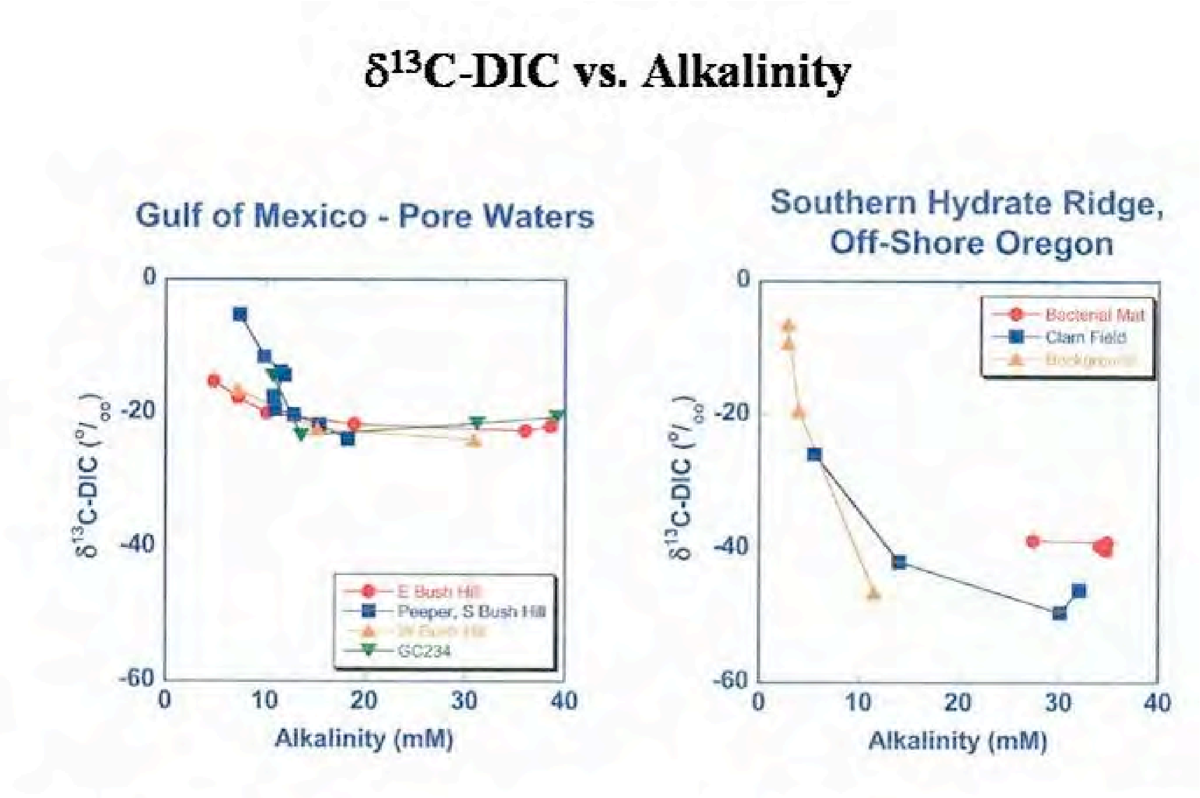


Figure 5. Side-scan sonar images of bubble plumes with white 5 meter scalebars and black arrows indicating the direction of the submersible. A) one of the GC234 bubble streams. B) Three bubble streams northeast of Bush Hill mound with arrow pointing to the plume depicted as low backscatter on the side-scan record. C) One of the steams at Bush Hill. D) The Brine Pool at GC233 with arrows pointing to areas of high backscatter. E) Bubble stream at GB425 with arrow indicating bubbles depicted as high backscatter

Sulfate is almost completely depleted by 12 cmbsf near the most active CH_4 vent at the mussel shell field, and SO_4 concentrations are ~ 2mM at 14 cmbsf within the bacterial mats and associated transient bubble plumes; as a result, alkalinity increases to ~15 times seawater concentration, indicating active microbial reduction of SO_4 to sulfide, causing *in-situ* precipitation of Ca (and some Mg) authigenic carbonates within these two mound environments, as manifested in the Ca, Mg, and Sr concentration profiles. Some of the sulfide precipitates as Fe sulfides. Chloride concentrations indicate *in situ* methane hydrate formation at and adjacent to the main Bush Hill methane seep. High chlorinities in the pore fluids are localized in specific horizons of active hydrate formation, are not pervasive throughout the concentration-depth profiles, thus, do not suggest that brines are controlling the stability of the Bush Hill hydrate mound. In contrast, within the tubeworm and mussel shell fields, and background site, Ca concentrations are near seawater throughout the depth profile, while sulfate concentrations are only slightly below seawater concentration and alkalinity is only moderately above seawater value.

In the vicinity of the main Bush Hill plume, the pore fluid chemistry indicates regional sulfate reduction that is particularly intense in and near active vents; the intensity is manifested by the spatial distribution of benthic chemosynthetic communities, and *in situ* methane hydrate and authigenic carbonate formation near the sediment-water interface.



$2\,CH_2O + SO_4^{2-} \longrightarrow H_2S + 2HCO_3^-$

$CH_4 + SO_4^{2-} \longrightarrow HS^- + HCO_3^- + H_2O$

Figure 6. A comparison between _^{13}C-DIC values versus alkalinity in pore fluids at Bush Hill and GC234, Gulf of Mexico and Southern Hydrate Ridge, off-shore Oregon, indicating that different sulfate reduction reactions are responsible for the observed differences at the two regions.

The pore fluid data indicate that although sulfate reduction is regionally pervasive, upward advection of methane (plus other hydrocarbons) is mostly focused at and in the vicinity of the hydrate mound; the intensity and frequency of focused methane advection sites increases toward the hydrate mound. This is manifested in the very high alkalinity concentrations, > 40 mM at and near the mound, and the negative _^{13}C-DIC values, shown in Figure 6, a cross plot of _^{13}C-DIC (‰) versus alkalinity (mM). An identical regime pattern was observed at GC234 (Figure 6). Most interesting is the observation that unlike at typical cold seep sites associated with methane hydrate, for example at Hydrate Ridge, Cascadia, where _^{13}C-DIC values are extremely negative, (between -20 to -50‰), more negative than the organic matter C isotope values, at Bush Hill (and GC 234) even at methane seeps where the pore fluid sulfate concentration is reduced at or near the seafloor, the minimum negative _^{13}C-DIC values observed are -21 to -22‰ (Figure 6). The very negative _^{13}C-DIC values at Hydrate Ridge, indicate anaerobic sulfate reduction by methane oxidation, and the considerably less negative values at Bush Hill (and GC234), indicate that crude oil serves as the primary electron-donor and metabolic substrate for anaerobic sulfate reduction.

Time-Series Data from the MOSQUITOs:

The fluids recovered from the MOSQUITO Teflon coils were analyzed chemically and isotopically at a resolution of 1-2 days; these data were used for fluid flow rate and solute flux calculations.

Three of the MOSQUITOS were deployed within 3 m of the gas hydrate mound, adjacent to transient gas vents, in mussel shells, a tubeworm field, and in bacterial mats (Figure 1). The fourth fluid flux meter was placed >50 m away from the gas hydrate outcrop to monitor background conditions.

The peepers and push cores only provide a one-dimensional depth profile of pore fluid chemistry and do not render any information on how the pore fluid composition evolves with time. The MOSQUITOs, however, sample three-dimensional depth profiles of pore fluid chemistry, as well as a time-series of the pore fluid composition. The MOSQUITO deployed at ~1.0 m from the most active bubble plume in the mussel shells, sampled low Ca (~ 3mM) and SO_4 concentrations for the duration of the deployment period (440 days) (Figure 7), further supporting very active SO_4 reduction and alkalinity production, and subsequent authigenic carbonate precipitation. The MOSQUITOs deployed at the background site and within the bacterial mats sampled Ca and SO_4 concentrations near seawater value for the duration of the deployment period, whereas the MOSQUITO deployed in the tubeworm field sampled formation fluid with low Ca and SO_4 concentrations during the last ~140 days of the deployment (Figure 7).

When gas hydrate forms, water molecules are removed from the surrounding pore water excluding dissolved ions, thus increasing the pore water salinity. When gas hydrate dissociates, the surrounding pore water becomes fresher due to the release of pure water from the clathrate structure. The MOSQUITO deployed in the mussel field sampled Cl concentrations above bottom water value for the duration of the deployment period (Figure 7), indicating steady-state formation of gas hydrate below the mussel field associated with the main gas vent at Bush Hill. The background site MOSQUITO also sampled elevated Cl concentrations during the first half of the deployment period associated with upward fluid advection (Figure 7). Most striking are the abrupt Cl maxima recorded in the time-series collected by the tubeworm field MOSQUITO. The tubeworm field Cl concentrations increased abruptly to ~6% higher than seawater (on Sept. 23, 2002), coincident with a change in the polarity of fluid flow at the mound sites, from strong downward fluid flow over the first 140 days to upward fluid advection (shown in Figure 8). The second Cl maximum, of 3.6% higher than seawater

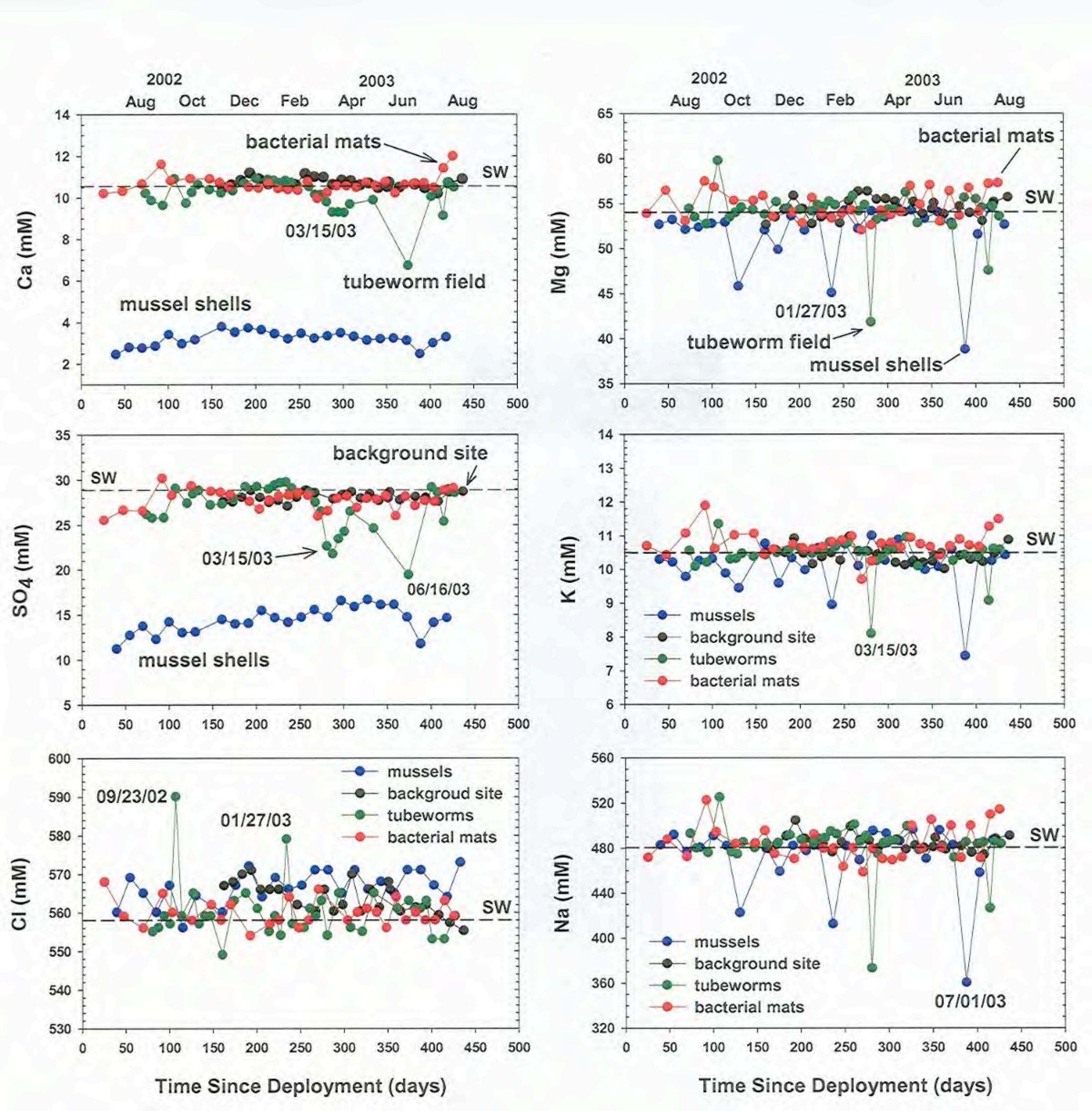


Figure 7. Plots of Ca, Mg, SO4, K, Na, and Cl versus time since deployment for each of the MOSQUITOs. Depth of Ti capillary sampling in the mussel shell field was 14.5 cmbsf in the tubeworm field 14 cmbsf; in the bacterial mats field 20 cmbs, and at the background site 25 cmbsf. Dashed line on each plot signifies seawater concentration.

concentration (on Jan. 27, 2003), as well coincides with a fluid pulsing event manifested by sharp decreases in Mg, Na, and K concentrations in the mussel shells (Figure 7). The sharp decreases in Mg, K, and Na coincident with higher Cl concentrations, suggest an event of rapid fluid expulsion of a deeper-sourced fluid, also advecting CH_4 and heavier hydrocarbons, thus, providing conditions suitable for rapid gas hydrate formation. Chloride concentrations sampled by the bacterial mat MOSQUITO were seawater concentration throughout the 430-day deployment.

A strong link between episodic fluid expulsion adjacent to the main gas vent and oil oxidation in the tubeworm field demonstrates that lateral fluid advection occurs at shallow depths at Bush Hill, and may be one of the reasons why some of the benthic biological communities can survive far away from focused fluid and gas discharge sites.

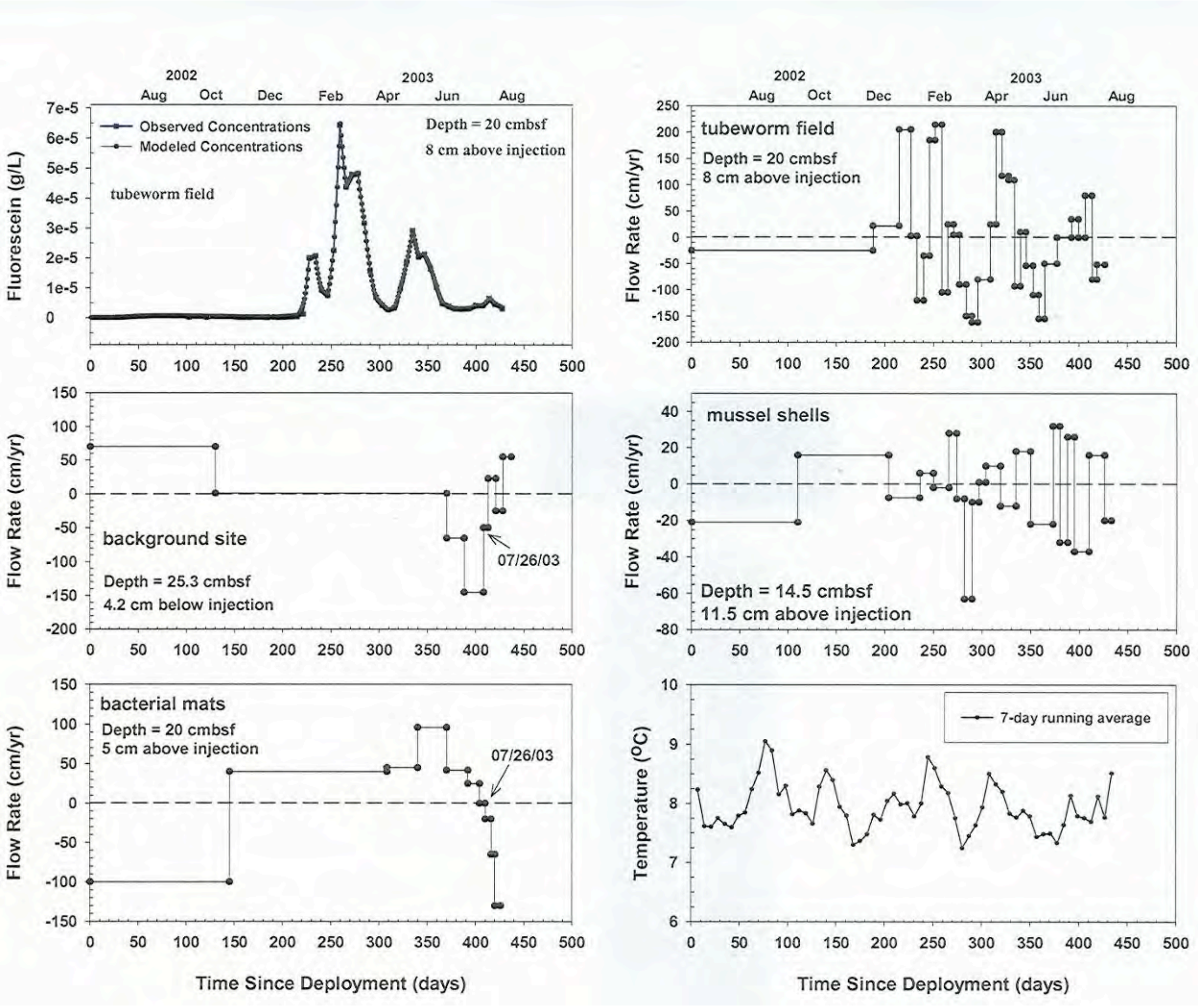


Figure 8. Fluid flow rate versus time for each of the MOSQUITOs. Upper left plot shows tracer concentrations from the solute transport model (Weinstein et al., in press). Bottom right plot shows a 7-day running average of bottom water temperatures at the gas hydrate mound over 430 days of deployment.

The subsurface hydrology of the hydrate mound is complex with both up-flow and down-flow occurring within each of the sub-environments (Figure 8). Upward flow rates ranged from 0.5 – 214 cm/yr and downward flow rates ranged from 2 to 162 cm/yr. Fluid flow rates were the highest in the tubeworm field and the background site (Figure 8). Flow rates are most variable in the northern mound sites, tubeworm and mussel fields, and less variable in the bacterial mats and the background site.

Fluid flow polarity oscillates at periods ranging from 14 days to 4 months and is coupled (but at opposite directions) between the mound sites and the background site, where periods of downward flow at the mound sites correspond to upward flow at the background site. Results from the long-term continuous monitoring of fluid chemistry and fluid flow rates, shown in Figures 7 and 8, indicate that gas hydrate actively formed within the mussel shell and tubeworm fields during a long period of ebullition of methane at the focused vent located adjacent to the gas hydrate mound, despite the significant bottom water temperature fluctuations from 6.86 to 9.63 ^{o}C. Modeled upward CH_4 fluxes range from 0.89 mol/m^{2}yr in the mussel shell field to 5.51 x 10^7 mol/m^{2}yr at the focused gas vent adjacent to the mound; this vent keeps the gas hydrate deposit stable and supports the long-term accumulation of gas hydrate at Bush Hill. The significant methane flux combined with negligible anaerobic oxidation of methane within the sediment column, (δ^{13}C-DIC between –5 and –23.8 ‰), suggests the Bush Hill seep and other hydrocarbon seeps in the northern Gulf of Mexico may be important natural sources of methane to the ocean and atmosphere.

The long-term fluid flow rate time-series thus exhibits three principle features: (1) downward flow at the three mound sites (mussel shells, tubeworm field, and bacterial mats) coupled to outward fluid flow at the background site during the first 130 days of the deployment; (2) higher frequency flow reversals in the tubeworm and mussel fields for about 10 months (October 2002 to July 2003), but net outward fluid flow, contemporaneous with outward fluid flow in the bacterial mats coupled to very low flow rates at the background site; (3) downward fluid flow in the bacterial mats coupled to outward fluid flow at the background site during the last two months (July to August 2003). The observed long periods between flow reversals (~14 days to 4 months) suggest episodic gas venting, rather than tidal forcing or initiation by local salt tectonics. The higher frequency oscillations (~14 days) seen in the middle of the time-series are similar to those observed at Hydrate Ridge (Tryon et al., 1999; 2002), however the longer period flow fluctuations (~ 4 months fluid inflow, ~9 months fluid outflow) have not been sampled to date. The conceptual model for the underlying physical mechanisms for the high frequency and low frequency fluid flow oscillations resulting from episodic gas venting discussed below is a modified version of the models presented in Tryon et al. (1999; 2002) and Flemings et al. (2003).

Based on this model, as well as previous models (Tryon et al., 1999; 2002), there are long-period (~130 day) episodes of gas venting that provide a steady-focused flux of CH_4 and heavier hydrocarbons. During the ~9-month period between these events there are higher frequency pulsing events that advect residual methane to shallower depths overprinted on a steady upward fluid flow regime that may be advecting dissolved CH_4 from depth. Because most of the gas hydrate at Bush Hill is Structure II hydrate, the P-T condition for gas hydrate dissociation (~14.5 ^{o}C) is never met, thus stability is primarily a function of CH_4 supply. During the low frequency gas venting episodes, Cl concentrations increase abruptly in the tubeworm field and Cl concentrations are above seawater value in the mussel shell field over the duration of the MOSQUITO deployment, indicating that the gas hydrate mound receives an ample supply of methane by high-volume focused gas venting followed by a more diffuse CH_4 flux to keep the gas hydrates within the stability field. This interpretation is corroborated by the slight increase in overall size of the gas hydrate mound and number of gas hydrate-filled crevices on the flanks and margins of the mound observed between July 2001 and July 2002 by Vardaro et al. (2005). The rapid increase in the flux of gas bubbles at vents adjacent to the gas hydrate mound due to 1 ^{o}C temperature changes reported by

MacDonald et al.(1994) and Roberts et al. (2001) may simply be the manifestation of the high frequency pulsing events observed in the MOSQUITO fluid chemistry and flow rate time-series. Overall, these data indicate that the Bush Hill gas hydrate deposit is stable despite the variable bottom water temperature regime, and is currently a fixed component of the seep environment. It has been in its current location for >12 years (MacDonald et al., 1994) and kinetic models suggest it has been accumulating for 10,000 years (Chen and Cathles, 2003).

Gas Hydrate Samples:

Samples of gas hydrates exposed on the seafloor were collected during the first cruise with a special hydraulic drill that successfully recovered gas hydrate cores; one of the cores before and after sectioning is shown in Figure 3. The newly designed hydrate corer, being able to collect gas hydrate near *in-situ* temperature and pressure, was a key part of the program. The hydrate cores were placed in the specially designed hydrate recovery pressure chamber prior to being hauled to the surface. The oil drops associated with the gas hydrate are giving the gas hydrate the yellow-brown color, seen in Figure 3. Some of the hydrate was dissociated shipboard in a pressure vessel and the rest was sliced and stored in liquid nitrogen for shore-based analyses. The chemistry of the pristine gas from the shipboard dissociated gas hydrate piece was analyzed for hydrocarbons, H_2S, and CO_2 concentrations. The chemical compositions and of the gas hydrate and of gas samples obtained from the associated bubble plumes are compared in Figure 9. The gas hydrate fractionates the original gas composition; it is depleted in methane and CO_2 and enriched in ethane, propane, and H_2S relative to the residual gas samples in the bubble plumes. The gas hydrate core was also analyzed for CFC composition. The presence of CFC in the gas hydrate core provides an age boundary of less than ~30 years.

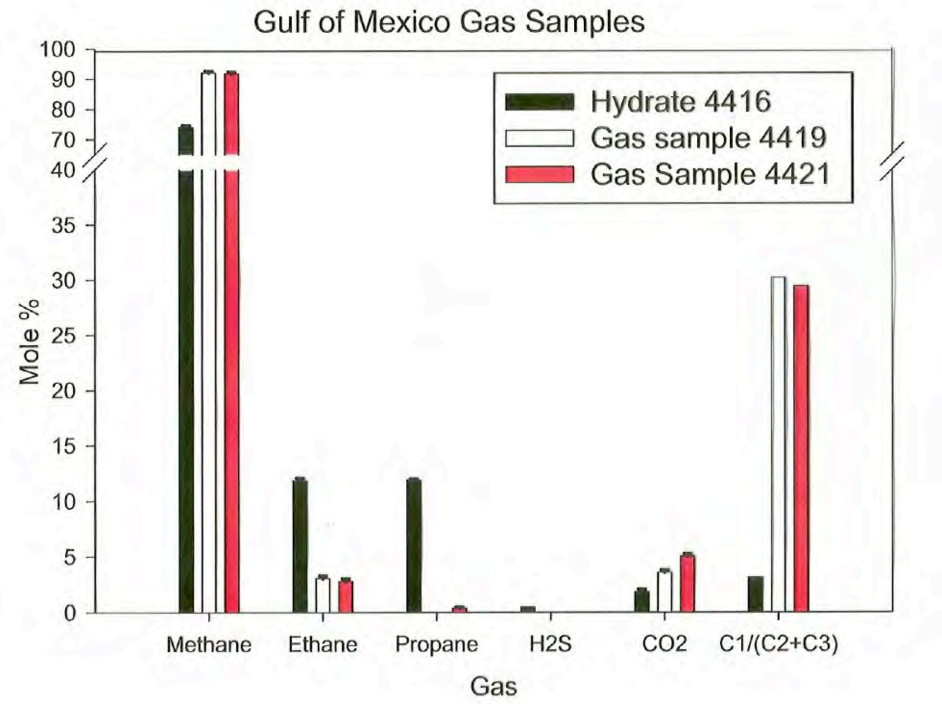


Figure 9. Gas chemistry of gas hydrates and gas samples from bubble plumes at Bush Hill. Note the preferential fractionation of ethane, propane, and H_2S into the gas hydrate structure.

Observing Gas Hydrate Habitat and Thermistor Probes:
The video image records from a time-lapse video camera assembly installed on the seafloor augmented the hydrologic program at GC185.

The newly designed time-lapse video camera, shown in Figure 4, was used to monitor potential growth in a hydrate mound. It provided a unique opportunity to study the short-term response of gas hydrate to changing temperature, water circulation, potential growth in a hydrate mound, and morphology during growth. As mentioned above, temperature probes were as well in place for the entire experiment. The data reported in Vardaro et al. (2005) provide for the first time a record of benthic processes at gas hydrate mounds. Sediment re-suspension and redistribution were regular occurrences during the deployment periods. By digitally analyzing the luminosity of the water column above the mound and plotting the results over time, the turbidity at the site was quantified. A significant diurnal pattern can be seen in both luminosity and temperature records, indicating a possible tidal or inertial component to deep-sea currents in this area. Contrary to expectations, there was no major change in shape or size of the gas hydrate outcrop at this site within the time frame of this study (Figure 10). This indicates that this particular mound is more stable than suggested by laboratory studies and prior *in situ* observations. The stable topography of the gas hydrate mound combined with high chemosynthetic bacteria activity and sediment turnover appears to focus benthic predatory activity in the mound area. The frequency and recurrence of sediment re-suspension indicates that short-term change in the depth and distribution of surface sediments is a feature of the benthic regime at the site.

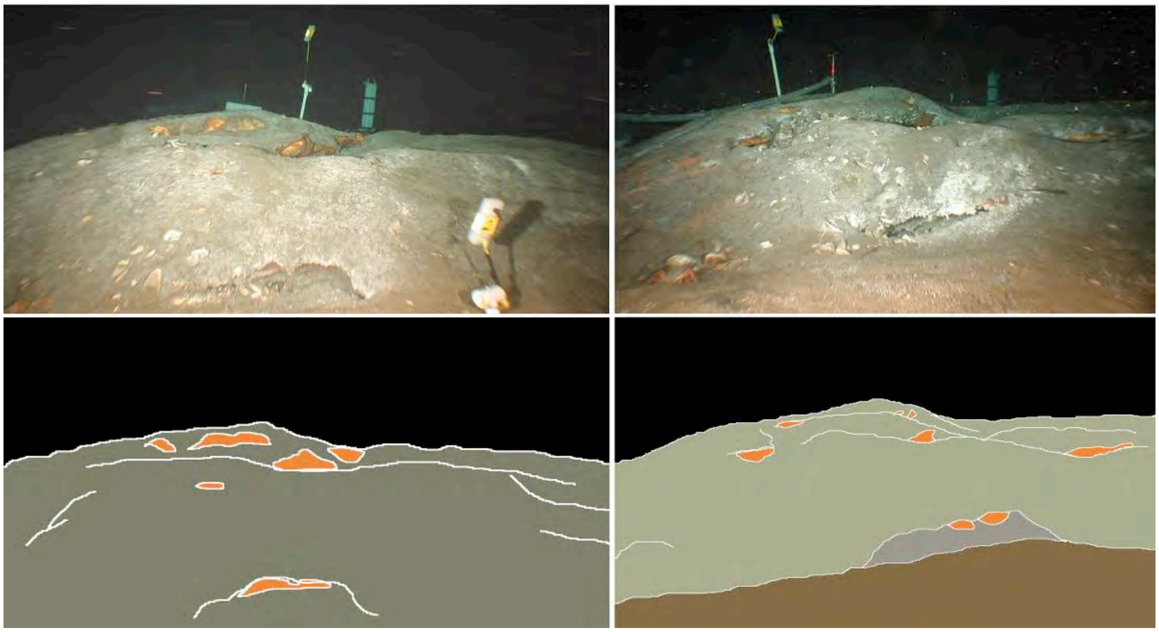


Figure 10. Time-lapse photographs taken just after the first camera deployment (top left) and at the end of the second deployment (top right) exhibit very few changes, aside from a slight shift to the southwest in camera placement. The gas hydrate mound has the same shape and exhibits only a slight change in elevation. The undercut area in the foreground has widened and deepened slightly, and the sediment cap covering the mound has been redistributed to cover some hydrate and expose other patches.

Thermistor Probes and Thermal Time-series Data from the Gas Hydrate Mound:

Ambient temperature is a critical factor determining the stability of gas hydrate deposits on continental margins. To study this process directly under varying conditions, a monitoring array comprising a time-lapse camera (Figure 10) and *in-situ* temperature probes (Figure 4A) was deployed at the Bush Hill hydrocarbon seep associated with the exposed seafloor gas hydrate mound, at 570m water depth. The temperature probes were constructed with one autonomous thermistor at each end of a 50-cm PVC wand and recorded temperatures with precision of better than 0.1 °C at 30-min intervals over 327 days. One probe was implanted with a tight seal into a drill-hole about 7 cm deep in the top of the gas hydrate mound. The second was inserted about 50 cm deep into the adjacent sediments. For each probe, the top thermistor recorded the ambient water temperature while the bottom thermistor synoptically recorded the internal temperature of the hydrate or sediment. The bottom water temperatures ranged from 6.64 to 9.73°C with a mean of 7.90°C and standard deviation of 0.437 (Figure 11). Photographic results showed no dramatic changes in the size, shape, or gas venting from the mound. By comparing the temperatures recorded at the tips of the probes with the synoptic water temperature, the thermal diffusivity for the gas hydrate deposit was estimated to be 2.57 to 3.00 cm^{2} h^{-1} and was 6.36 to 10.82 cm^{2}h^{-1} for the sediments at the sites where temperatures were recorded. The diffusivity measured in gas hydrate is lower than that measured under laboratory conditions. Stability of gas hydrate in this setting is not likely to be affected by short-term changes in bottom water temperature within the range observed. This result (MacDonald et al. 2005; Solomon et al., 2006)) indicates that the thermal regime of gas hydrate is much less subject to variation than that of the water column. This preserves gas hydrate from frequent decomposition due to high frequency temperature events.

Water Column Samples:

Water column profile samples were successfully acquired using a Nisken bottle rosette sampler. Nine high-resolution profiles, including those from a gas-plume and from background sites were collected for comprehensive solute and dissolved gas analyses, including CFC. Deep samples help to document the chemical effects of gas venting on seawater chemistry. Samples from shallower depths document if and how much methane is presently reaching the atmosphere at Bush Hill. The CFC data in the water column indicated that the apparent age of the bottom water is ~30 years. The CFC present in the water column was detected in the hydrate core from the top of the mound.

Water column methane concentration and isotope data show that at the main plume methane concentrations are high, and even in the uppermost 5 meters of the water column seawater is considerably supersaturated (150-200 times) with respect to methane, hence, methane escapes into the atmosphere. Away from the plume, methane concentrations decrease rapidly and the significant enrichment in the _^{13}C-CH_4 values along isopycnals away from the plume, from the methane source, are indicative of aerobic methane oxidation (methanotrophy) that is extensive and widespread, especially at depths where dissolved methane concentrations are highest, following the reaction:

$$\mathbf{CH_4 + 2O_2 \;\lozenge\; CO_2 + 2H_2O}$$

The _^{13}C-CH_4 value in the methane plumes range from -44 to -47‰ at Bush Hill. Along the isopycnals _^{13}C values up to -27‰ were observed. Preliminary calculations suggest that 80 to maximum 90% of the methane flux across the sediment-water interface is aerobically oxidized in the water column and responsible for the less negative _^{13}C-DIC values.

Bottom water _^{13}C- DIC values are considerably more negative than the ‘background’ value near methane cold seeps, where methane concentrations are also high. The benthic foraminifera that form $CaCO_3$ in such a bottom water environment may record the more negative C isotopic signatures. Assuming no diagenesis, such benthic foraminifera may be used for mapping paleo methane seeps.

Detecting Gas Vents in the Water Column and on the Sea Surface:
Methane is the most abundant trace gas in the atmosphere (mixing ratio ~1.8 ppm; residence time ~9 years), and is an important greenhouse gas with a global warming potential ~20 times greater than an equivalent amount of carbon dioxide. The global oceanic source of methane to the atmosphere has been estimated at 5-50 Tg/yr, which is 0.8 to 8% of all natural sources of CH_4 (~ 600 Tg/yr). The large uncertainty in the magnitude of the oceanic source strength emphasizes the importance of better understanding the temporal and spatial variations of the marine methane emissions. Methane is produced within oceanic sediments and is transported into the water column as dissolved gas by diffusion through the sediments and/or as bubbles advecting at methane seeps. Anaerobic oxidation of methane (AOM) is an important CH_4 removal process in diffusion-dominated sediment systems. In such systems most to all of the methane is consumed before it reaches the water column. In advective methane seeps, however, methane advection rates are higher than rates of methane oxidation through sulfate reduction, especially in oil-rich environments like Bush Hill, and significant quantities of CH_4 can enter the ocean system. Methane that escapes the sediments and enters the water column is further subject to oxidation by aerobic methanotrophs. The amount that is oxidized in the water column depends on the bubble rise velocity and whether the bubbles are coated with a surfactant.

During the two research expeditions in the Gulf of Mexico (June 2002 and August 2003), methane concentrations were measured within the water column by a novel experiment that captured bubble plume samples with an ascending submersible; three active methane plumes, at Bush Hill, GC 234, and GB 425, were sampled from the seafloor to the sea-surface. Water column CH_4 concentrations measured within the plumes are extremely high (surface waters are up to 500 times supersaturated), and results from these experiments indicate that the CH_4 flux out of the sediments is on the order of 20 cm/s. Because the flux rates are high and the bubbles are coated with oil, little to none of the CH_4 in these plumes is oxidized within the sediments and overlying water column. These results are unique, because most water column experiments utilized CTD casts for sampling, which because of currents, only meander through these relatively narrow plumes at best, therefore inadequately sampling these bubble plumes, thus possibly overestimating the amount of methane being oxidized in the water column.

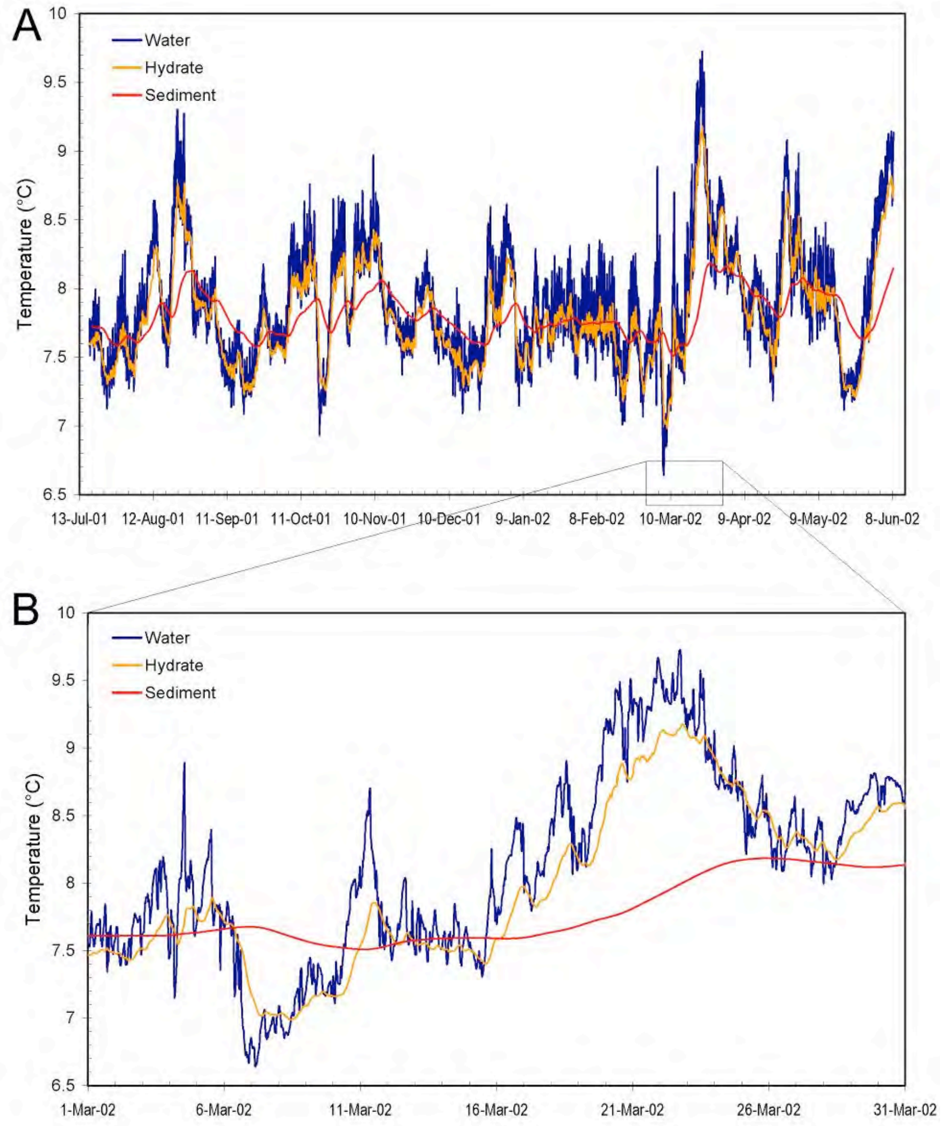


Figure 11. A) The probe recorded temperature time-series up to 350 days. B) Detail shows how the thermal conductivity of the hydrate (yellow) and the sediment (red) retard propagation of the thermal signal from the water column into the sediment.

Methane fluxes from the surface ocean (mixed layer) to the atmosphere at the three seep sites in the Gulf of Mexico have been computed using air-sea gas exchange models presented in Wannikof (1992) and Wannikof and McGillis (1999). Wind speed data collected at nearby stations from the National Data Buoy Center were used as inputs to the Gas transfer coefficient equations. Methane fluxes range from 180 to 2000 μmol/m^2 day, with the highest fluxes occurring at Bush Hill and GB 425.

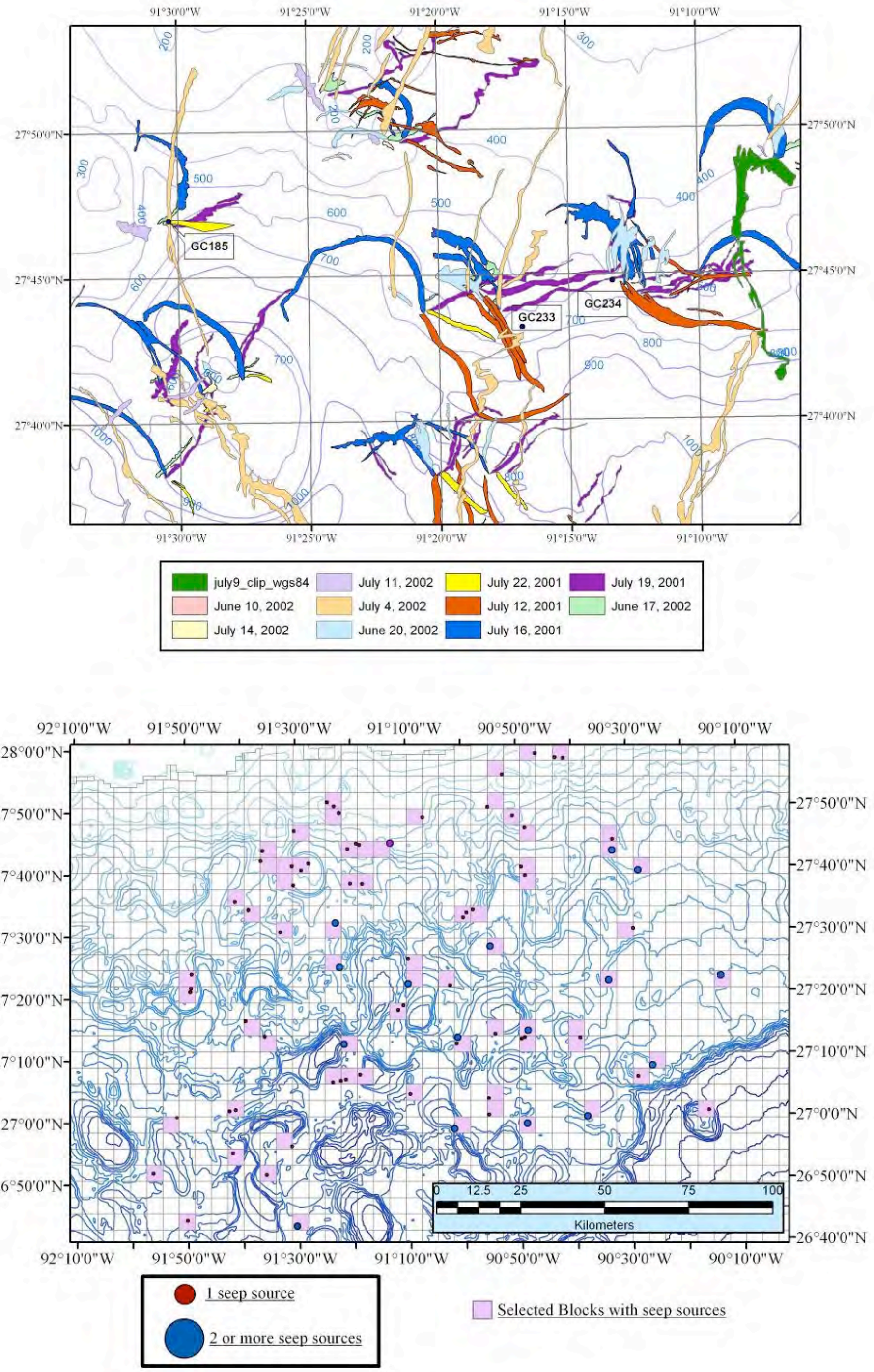


Figure 12. Results of satellite remote sensing over gas hydrate seeps. A) Multiple scenes of RADARSAT data show persistent targets associated with locations where hydrate sampling and *in-situ* measurements were conducted. B) Summary figure showing locations where gas hydrate probably occurs in the surface sediments.

The areas affected by seepage where gas hydrate is found are often on the order of a square kilometer or more, as noted during exploration of the sites with submarines.

Typically, gas and oil escape into the water from discrete vents within larger seep site. Side scan sonar, and satellite remote sensing (Figure 12) were used to detect the locations where escaping gas reaches the sea surface to carefully determine the number of gas vents at a “typical” seep (De Beukelaer et al., 2003).

Gas plumes from natural seeps were examined in data collected by 100 and 384 kHz side-scan sonar, operated from a submarine near the seafloor, by 20 kHz chirp profiler, which was operated from a surface ship, and by Synthetic Aperture Radar (SAR) images from the RADARSAT Satellite. Gas plumes from rapidly venting mud volcanoes and from shallow deposits of gas hydrate were compared. Gas bubbles venting from mud volcanoes lacked oily contaminants and produced high backscatter on the side-scan sonar records, but were difficult to detect with the chirp profiler. Bubbles from hydrate deposits were oily, produced low backscatter on the side-scan sonar records, and generated clear chirp signatures extending from the seafloor to the near surface. Radarsat SAR images (Figure 12) verified presence of surface oil slicks over hydrate deposits, but not over mud volcanoes.

The main objective of our attempts to quantify CH_4 flux into the atmosphere at Bush Hill and vicinity and extrapolate it over the entire Gulf of Mexico basin was to asses the contribution of this oceanic basin methane source to the atmosphere. If significant, it would be important to conduct similar studies at other regions with active methane seeps and natural oil, such as the Sea of Okhotsk, Black Sea, and Caspian Sea, in order to better constrain/quantify the flux of oceanic methane to the atmosphere.

Conclusions

The Bush Hill pore fluid chemistry varies significantly over short distances and gas venting is primarily focused, as reflected by sharp interfaces between distinct benthic biological communities.

Pore fluid chemistry indicates regional sulfate reduction (and carbonate formation) that is particularly intense in and near active vents. The intensity is manifested by the spatial distribution of chemosynthetic communities and seafloor gas hydrate.

Active gas hydrate formation in the tubeworm and mussel shell fields during the monitoring period (440 days) was documented by the time-series fluid chemical data.

In addition to widespread vertical fluid advection, the existence of lateral advection was also documented. This may explain why some benthic biological communities survive away from the active vents.

The subsurface hydrology is complex with both up-flow and down-flow occurring within each of the sub-environments; up-flow ranged from 0.5 to 214 cm/yr and down-flow from 2-162 cm/yr.

Fluid flow polarity oscillates at periods of 14 days to 4 months and is coupled between the mound sites and background site.

The gas hydrate preferentially fractionates ethane, propane, and H_2S into its structure, thus, the residual vent gas composition differs from that of the original gas.

At bush Hill the seafloor gas hydrate mound is presently stable despite bottom water temperature fluctuations. It has been observed in its current position for >12 years and benthic models suggest that it has been accumulating for 10,000 years.

Based on _^{13}C-DIC anaerobic oil oxidation at Bush Hill instead of anaerobic methane oxidation is the dominant sulfate reducing reaction in the sub-seafloor, therefore much of the methane is transported across the seafloor into the water column; most of it is venting through faults.

Methane concentrations in surface waters above plumes are highly supersaturated 200-500 times the equilibrium value.

Aerobic oxidation of methane (methanotrophy) consumes about 80% to maximum 90% of the methane.

Water column DIC is depleted in ^{13}C. Minimum bottom water _^{13}C-DIC value observed is -3.63‰.

Above and near the bubble plumes _^{13}C-DIC values in surface waters are as well slightly negative (0.06 to -0.16‰, PDB).

Based on methane supersaturation, air-sea exchange, wind speed, and mixed-layer average depth, methane flux into the atmosphere at three vent sites was modeled; the fluxes obtained range from 100-2000 _mol/m^2 per day. This result allows further calculations of basin-wide methane flux into the atmosphere, using satellite data for the number of methane plumes, and assuming that these data are regionally representative.

Leifer and MacDonald used the rate and size of bubbles at seeps and the number of seeps observed via satellites to estimate the methane flux to the atmosphere in the Gulf of Mexico. They concluded that ~0.5 Tg/year methane escapes to the atmosphere in the Gulf of Mexico.

It is suggested that although supersaturation of methane in surface waters is a persistent feature of most ocean waters, it is considerably enhanced in continental margins, in particular in regions of oil and gas seeps, and gas hydrates, as in the Gulf of Mexico.

The present day relationships between regional tectonics and hydrology at margins, and sea-air methane exchange, thus the global magnitude of methane flux from surface water continental margins to the atmosphere, are as yet undetermined. Data acquired during this project at the Gulf of Mexico provide an important step forward to answering this question.

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Acronyms and Abbreviations

AOM (Anaerobic oxidation of methane)
CFC (Chlorofluorocarbon)
cmbsf (centimeters below seafloor)
CTD (Conductivity, Temperature and Depth sensor)
DIC (Dissolved Inorganic Carbon)
GHOST (Gas Hydrate Observation, Sampling, and Tracer Study)
GOM (Gulf of Mexico)
IC (Ion Chromatography)
ICP-MS (Inductively Coupled Plasma Mass Spectrometry)
ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy)
mM (Millimolar)
MOSQUITO (Multiple Orifice sampler and Quantitative Injection Tracer Observer)
PBD (Pee Dee Belemnite)
SAR Synthetic Aperture Radar
Tg (teragram)