NIGEC -Final Progress Report

Sampling the Marine Gas-Hydrate Reservoir: Assessing the Methane Inventory, Internal Dynamics, and Potential of Methane Discharges to the Atmosphere.

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The status of the pore water and sediment core analysis of the surface sediments that overlie a major gas-hydrate field on the Carolina Continental Rise and Blake Ridge is reported here. Funding from NIGEC's southern regional center provided support for a cruise of the RV Cape Hatteras in September 1992 (CH-11-92) on which 20 piston cores were taken. However, over the last 18 months we have had the opportunity to collect an additional 35 piston cores in this region, in part through the assistance of another DOE funded project that is being run by the USGS. At this date, we have pore water data from 55 piston cores which gives us both a regional and a site-specific insight into the processes in this region (figure 1). It is our intention to combine the results of all these cores to arrive at a unified understanding of the processes acting on the continental margin which influence gas-hydrate formation and distribution. Some of the highlights of this work are outlined below and some of accomplishments of this project to-date are outlined.

No gas-hydrates were sampled in any of these piston cores, almost all of which were collected over sediments that are known to contain strong Bottom Simulating Reflectors in geophysical data. However, two cores on the Blake Ridge yielded moderate amounts of methane gas. These cores penetrated the zone of zero sulfate and into the region where microbial sulfate reduction should occur. Shipboard gas-chromatographs showed that the pore fluids contained up to ~1% methane by volume, but no significant concentration of higher molecular weight hydrocarbons were measured. Carbon isotopic measurements from this methane ($\delta^{13}\text{C} = -98 \text{ ‰ PDB}$) suggest that the gas is microbial in origin, however the deuterium isotope values of this gas are surprisingly heavy ($\delta\text{D} = -118 \text{ ‰ SMOW}$) compared with the range of published deuterium values in methane samples. One explanation of these heavy δD values is that the methane that was captured at the base of these cores was not produced locally but

Figure 1. Locations of piston core samples collected and analyzed as part of the NIGEC supported project to investigate the influence of gas hydrates in continental rise sediments. Most of these cores are about 10 meters in length and have had intensive pore water analyses, carbonate percent, organic carbon percent, and lithologic description. Plotting symbols indicate cruise on which samples collected: diamonds - CH-11-91, circles - CH-15-92, squares - CH-31-93.

at greater depths and at higher temperatures and has subsequently migrated toward the surface.

A carbonate-cemented layer containing abundant shell debris was encountered 3 meters down piston core CH-11-1992 #12. The occurrence of an extensively carbonate-cemented horizon containing abundant mollusc shell hash within fine grained clastic sediments is surprising. Some of these shell pieces look like mussel shells that are commonly associated with modern chemosynthetic communities. 3.5 kHz seismic reflection data and other cores from the area indicates that this horizon corresponds with the sole of a slide that occurred in the late Pleistocene. The importance of methane in the generation of these layers is indicated by $\delta^{13}\text{C}$ values for the carbonate in these cemented sediments that are as light as -40.8 ‰ PDB and $\delta^{13}\text{C}$ values of disseminated organic carbon in bulk sediments that are as light as -35.86 ‰ PDB. This preliminary data suggests that a methane seep occurred in this area during the late Pleistocene.

Dating of unconformities that have been identified in these cores is still on-going, however, the preliminary results indicate that unconformities are more common in the Pleistocene than the Holocene sequences. We are still evaluating this data as to its potential significance with respect to slump occurrences and its potential relationship with gas hydrate decomposition during the sealevel lowstand associated with the last ice age.

We have completed measurements of the chloride, sulfate, carbonate, organic carbon, and major element geochemical profiles on 48 of these cores. These data have allowed us to assess the potential of microbial production in the sediment column in this region as a mechanism for gas-hydrate formation. The conclusions of this effort indicate that the source of methane that is required to form any substantial amount of gas-hydrate in this region must involve migration and concentration of gas recycling rather than in situ production in a closed system. This argument is summarized in the attached preprint (Paull et al., in press).

A few cores show distinct increases in the concentration of pore water chloride with depth (Figure 2). The existence of these chloride gradients is very exciting because they may indicate that ion exclusion is occurring and that chloride gradients have the potential to predict the extent of gas-hydrate development nearby. Ion exclusion occurs during gas-hydrate formation by the removal of water and dissolved gas from the interstitial fluids by the growing

Figure 2. Plot of all the interstitial chloride concentrations that were measured from samples collected on the Carolina Rise and Blake Plateau versus depth. The lines indicate the some of the more distinct gradients that were measured in individual cores.

gas-hydrates. Dissolved salts are excluded from the gas-hydrate, enriching the remaining pore fluid. Chloride is of particular interest because it is not affected by biochemical processes occurring within the sediment, thus it behaves as a passive tracer. Interstitial pore fluid salinities may become increasingly salty if there is an extensive amount of gas-hydrate formation without pore water advection. We are still assessing whether the gradients we have measured are in fact related to gas-hydrate development at depth or to other sources of salt. We are also refining the theory of the using salt exclusion models to predict the extent of gas-hydrate development at depth.

Large variations in the rate of sulfate depletion with depth occur in these cores (Figure 3). Because these sulfate gradients are usually linear with depth, we can use these data to predict the depth where the sulfate concentrations reaches zero. Predicted depths of zero sulfate vary from 11 meters to over 80 meters, however, the cause of this variation are unknown. Sulfate reduction rate is an indicator of microbial activity and typically sulfate is consumed before methanogenesis can begin. Thus, the zero sulfate depth is an indicator of where microbial methane production starts and a

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qualitative indicator of the relative extent of microbial activity. We are still determining whether the variations in the predicted depth of zero sulfate is driven by major variations in the amounts of organic carbon, or the age of the sediments within individual cores. No obvious sedimentological explanation is available at this time. We are also considering these data in light of the possibility that pore water circulation cells are present on the margin.

Carbon-14 age versus depth measurement has been obtained on 16 cores from the region (Figure 4). These data provide information on the sedimentological aspects of the Quaternary cover on top of the gas-hydrated sediments. These data clearly indicate that the age of the sediment is not controlling the concentration of the sulfate in the sediment (Figure 5).

Figure 4. Plot of carbon-14 age from samples collected on the Carolina Rise and Blake Plateau versus depth. The lines indicate the age gradients that were measured in individual cores.

Figure 5. Plot of carbon-14 age from samples collected on the Carolina Rise and Blake Plateau versus the sulfate concentration in at the same level.

Products:

Dissertations and Thesis:

The pore water data will form the core of Mr. Walter Borowski's Ph.D dissertation which we anticipate will be done in early 1995.

Sediment lithologies will be the topic of Mr. William Buellow's M.S. thesis. Anticipated completion is January 1994.

ODP Drilling Proposal:

Data collected in this project has been used as part of the site survey data that is required to have hole drilled by the Ocean Drilling Program. As a result, a proposal for into gas hydrated sediments has been included into the Prospectus drilling in 1995.

Manuscripts:

Paull, C. K., Ussler, W. III, and Borowski, W., 199-, Sources of biogenic gas to form gas-hydrates: In situ production or gas recycling on the Carolina Continental Rise - Blake Ridge area?, New York Academy of Sciences, International Conference on Natural Gas Hydrates, June 20-24, 1993, (in press) 15 p.

Ussler, W., and Paull, C. K., 199-, Effects of ion exclusion in gas hydrate cemented strata, (in preparation) 24 p.

Paull, C.K., von Herzen, R., Borowski, W., Ussler, W., III, Dillon, W. P., Speiss, F., and Holbrook, S., 199-, Atlantic margin shale diapirs, Where is the salt?, in prep.

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