

GAS HYDRATE AND OCEAN DRILLING PROGRAM LEG 164

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Abstract

Leg 164 of the Ocean Drilling Program (ODP) was devoted to investigating the amount and *in situ* characteristics of natural gas hydrates stored in marine sediments. Three sites (penetration depths of 700 to 750 m) were drilled on the Blake Ridge, an area characterized by prominent bottom simulating reflectors and simple geology. Here gas hydrates typically occur in a zone 200 to 450 meters below the sea floor. Based on interstitial geochemistry, well-logging, and vertical seismic profiling data, gas hydrates occupy 1-8% of the sedimentary section in this zone and are mostly finely disseminated. However, gas hydrate veins and nodules also occur. Samples of gas generated from decomposition of the gas hydrate nodules are ~99% methane and 1% carbon dioxide. Free gas, similar in composition, is also prevalent throughout a few hundred-meter-thick zone below the gas hydrate-bearing zone. Extrapolations based on the regional geophysical data indicate that ~35 Gt of methane are stored in gas hydrate on the Blake Ridge.

Introduction

Gas hydrates are a solid phase composed of water and low-molecular weight gases (predominantly methane), which form under conditions of low temperature, high pressure, and adequate gas concentrations (Sloan, 1990): conditions that are common in the upper few hundred meters of rapidly-accumulating marine sediments (Kvenvolden, 1995). Although gas hydrates may be a common phase in the shallow geobiosphere, they are unstable under normal surface conditions, and thus surprisingly little is known about them in natural settings.

Enormous volumes of natural gas may be associated with sediments containing gas hydrate. Estimates suggest that there are 10^3 to 10^4 Gt (Gt = 10^{15} gm) of carbon stored in gas hydrates, an amount which rivals the estimated size of all other fossil fuel deposits (Kvenvolden, 1988). Moreover, there may be considerable volumes of dissolved methane in pore fluids and free gas trapped beneath gas hydrate-bearing zones. However, at present we know too little about the distribution and abundance of natural gas hydrates to be confident about these global estimates.

Gas hydrates are believed to be common because seismic reflection data have indicated their presence in every ocean basin (Kvenvolden, 1993). Prominent reflectors in seismic reflection profiles, called bottom simulating reflectors (BSRs), are frequently

associated with gas hydrate-bearing sediment. The BSR roughly parallels the sea floor but in places cuts across sediment bedding planes, thus clearly distinguishing itself as an acoustic response to a diagenetic change rather than a depositional horizon. The BSR is believed to represent the base of the gas hydrate stability, which typically occurs between about 200 and 600 meters below the sea floor (mbsf) on continental rises.

Importance of Gas Hydrates

The resource potential of marine gas hydrate deposits is currently unknown. Specialized technologies to economically produce gas hydrates have not been developed. However, the possibility that enormous volumes of natural gas may be contained within gas hydrate reservoirs requires that gas-hydrate-bearing deposits be considered as future development targets.

Gas hydrates may effect the physical properties of continental margin sediments, strengthening the sediments above, and weakening sediments at and below the base of gas hydrate stability. One explanation for some of the major slumps on continental rises relates to sediment instability caused by gas hydrate breakdown (Kayen and Lee (1993). If gas hydrates comprise a significant portion of the volume of continental rise sediments above the base of gas hydrate stability, the mechanical properties of sediments will change dramatically when gas hydrates decompose. Gas hydrates decompose to yield water and (over-pressured?) gas at the base of gas hydrate stability. Sediment instability and failure are likely to be concentrated along this lubricated horizon.

The formation of gas hydrates within sediment pores may significantly alter the mechanical properties and diagenetic history of the sediment in a number of ways: 1) the pore volume will be decreased by authigenic mineral (hydrate and carbonate) formation; 2) the addition of gas hydrate will also change the mechanical and physical properties of the sediments; and 3) hydrate formation and decomposition will alter the porosity and permeability of the sediments and thus influence fluid migration patterns.

The stability of continental rise gas hydrates will be affected by changes in hydrostatic pressure associated with substantial sea level changes, and by bottom water temperature changes. If the rate of methane escape from these geologic reservoirs to the ocean-atmosphere system is sensitive to sea floor pressure and temperature, episodic venting of

methane could result in global carbon isotope shifts or climate changes (via the addition of greenhouse gases) (Paull et al., 1990; Dickens et al., 1995).

ODP Leg 164

ODP Leg 164 took place on the Blake Ridge, which is an area where gas hydrates appear to be especially extensive. Sites 994, 995, and 997 were drilled to 700-750 mbsf within the same stratigraphic units (Paull, Matsumoto, Wallace et al., 1996). The Sites form a 10-km-long transect which extends from the ridge flank where there is no BSR, to the ridge crest where a very strong BSR exists. The holes extended through the base of gas hydrate stability (~450 mbsf) and 250 to 300 m into the underlying sediments. Because of the ephemeral nature of gas hydrates, emphasis was placed on proxy sampling and down-hole tool measurements that allowed reconstruction of the *in situ* conditions associated with the gas hydrates.

The stratigraphic sequence is composed of lithologically homogeneous, nannofossil-rich clays and claystones. Inter-site and down-hole variation in sediment physical properties and lithology was minimal. The lithologic similarity allows the distribution of gas hydrate and the origins of the BSR (~ 450 mbsf) to be studied without considering lithologic factors. The sediments typically contain between 0.5 to 1.5% organic carbon, enough to generate significant quantities of microbial methane.

The cored sediments were very gassy and experienced vigorous expansion during recovery. Sediments frequently extruded from the liners as the cores arrived on deck. Sediment recovery between ~190 and 480 mbsf tended to be low (averaging ~50%). The gas is predominately methane (~99%) with secondary amounts of carbon dioxide, and only trace amounts of ethane and other hydrocarbon gases. The methane to ethane ratios (>1,000) and isotopic ratios ($\delta^{13}\text{C}$ of methane <-60 ‰ PDB) indicate that the gas is largely of microbial origin.

Recovered gas hydrate occurred as nodules and veins. One >30-cm-thick horizon of massive gas hydrate was recovered. Decomposing gas hydrates yielded gas that was ~99% methane and 1% carbon dioxide. Gas-to-water ratios of these hydrate samples ranged from 130 to 160, confirming that these hydrates were probably Structure I methane gas hydrates (Sloan, 1990). However, most of the most commonly observed hydrate occurrences were associated with thin (~1 mm) veins of white hydrate, that could be seen on the surfaces of quickly-opened cores.

Measurements of interstitial-water chloride concentrations from high-resolution sampling provided quantitative estimates of the amount of *in situ* gas hydrate. During gas hydrate formation, water

and methane removal leave residual pore waters increasingly saline. Over time, locally elevated chloride concentrations associated with gas hydrate formation diffuse away. When gas hydrates in sediments decompose during drilling and core recovery, they release water and gas back into the pore space, freshening the pore waters. Pore water profiles from Sites 994, 995, and 997 show a progressive freshening to depths of ~200 mbsf. From 200 mbsf to the depth of the BSR (~450 mbsf) pore water chloride concentrations are highly variable and characterized by local, anomalously fresh values. Beneath 450 mbsf chloride values are nearly constant. Departures from base line chloride values can be used to calculate that gas hydrate amounts. The calculated amounts of gas hydrate that decomposed in individual samples was quite variable, but most samples had 1-2% gas hydrate and the calculated values range up to 14% within the zone from 200-450 mbsf.

A full suite of logs was run at each of these sites. Well-logs show distinct zones of higher velocity and electrical resistivity that are coincident with zones where chloride anomalies indicate the presence of gas hydrates. Shipboard physical property data (e.g., porosity, grain density, water content, etc.) do not explain these variations. Thus, it is inferred that the log parameters are related to properties that are lost during core recovery (e.g., free gas and gas hydrate). Calculations of the amount of gas hydrate needed to produce these offsets are consistent with predictions from the chloride data. Below 450 mbsf, sediment velocities that are equal to or less than sea water (1500 m/sec), indicating the presence of free gas.

A pressure core sampler (PCS) was used with unprecedented success (Dickens et al., 1997). The device takes a small sediment core (42 mm diameter, up to 0.86 m long) from the bottom of the bore hole and seals the core into a pressure housing so that recovery occurs under *in situ* pressure. Thus, PCS cores contain all their original gases until they are opened to the atmosphere. Some samples produced 15 liters of methane per each liter of sediment in the cores. Such observations make it easy to understand why the other cores expanded so dramatically during recovery. Gas volumes captured by the PCS often grossly exceeded the concentration needed for gas saturation, given the size of the recovered core. Above the base of gas hydrate stability, the excess gas was presumably supplied from dissociation of gas hydrates that would have occupied up to 8% of the sediment volume. The excess gas that was captured at and beneath the base of gas hydrate stability demonstrates that free gas is associated with the BSR and occurs intermittently throughout the sedimentary section below. In fact, the volume of free gas trapped in sediments beneath the base of gas hydrate stability rivals the amounts stored as gas

hydrate. Dickens et al. used the amounts of gas measured at these sites and the known regional distribution of the BSR (Dillon and Paull, 1983) to estimate that there is approximately 35 Gt of methane carbon is stored in the Blake Ridge.

The velocity structure of the sediments and the precise depth of the BSR were determined with vertical seismic reflection profiles (Holbrook et al., 1996). The velocities of sediments overlying the BSR did not exceed 1850 m/sec, consistent with the presence of a few percent gas hydrate. However, velocities as low as 1400 m/sec were measured beneath the BSR at Site 997, indicating the presence of free gas.

Summary

The results of ODP leg 164 indicate that Blake Ridge sediments contain significant amounts of methane stored both as gas hydrate, and as free gas below the base of gas hydrate stability. Gas hydrates occupy 1-8% of the sediment volume in a zone ~250 meters thick on the Blake Ridge. Site 994 without a BSR also contains nearly as much gas hydrate as those sites with a BSR. Apparently the BSR in this area occurs when gas saturation is achieved at the base of the gas hydrate stability field. The volume of free gas that occurs beneath the base of gas hydrate stability in this region rivals the amounts stored in the overlying section.

Acknowledgments

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