# Gas Hydrate Systems at Hydrate Ridge: Results from ODP Leg 204

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Abstract: We report and discuss molecular and isotopic properties of hydrate-bound gases from 55 samples and void gases from 494 samples collected during Ocean Drilling Program (ODP) Leg 204 at Hydrate Ridge offshore Oregon. Gas hydrates appear to crystallize in sediments from two end-member gas sources (deep allochthonous and in situ) as mixtures of different proportions. In an area of high gas flux at the Southern Summit of the ridge (Sites 1248-1250), shallow (0-40 meters below the seafloor (mbsf)) gas hydrates are composed of mainly allochthonous mixed microbial and thermogenic methane and a small portion of thermogenic C2+ gases, which migrated vertically and laterally from as deep as 2-2.5 km depths. In contrast, deep (50-105 mbsf) gas hydrates at the Southern Summit (Sites 1248 and 1250) and on the flanks of the ridge (Sites 1244-1247) crystallize mainly from microbial methane and ethane generated dominantly in situ. A small contribution of allochthonous gas may also be present at sites where geologic and tectonic settings favor vertical gas migration from greater depth (e.g., Site 1244).

#### 1. Introduction

Natural marine gas hydrates contain large amount of methane and are considered as an important component of the global carbon cycle (Dickens, 2001) and a potential energy source 2002). Geophysical (Milkov Sassen, and evidence such as Bottom Simulating Reflectors (BSRs) and strong seafloor acoustic reflectivities are commonly used to infer the distribution of gas hydrates on continental margins (Kvenvolden and Lorenson, 2001; Sager et al., 2003; Johnson et al., 2003). However, samples are essential to gas hydrate ground-truth geophysical observation, understand the origin of this mineral, visualize the migration of hydrate-forming fluids, and constrain mechanisms of gas hydrate formation near the seafloor and in deep sediments. The lack of extensive and comprehensive direct measurements of molecular and isotopic properties of hydrate-bound gases sometimes result in controversial views on the origin of gas in gas hydrate systems such as the Blake Ridge (Davie and Buffett, 2003).

ODP Leg 204 addressed gas hydrate distribution and origin at Hydrate Ridge offshore Oregon (Milkov et al., 2003). More gas hydrate samples were recovered and analyzed on Leg 204 (55 samples from 0-105 mbsf) than during all previous DSDP-ODP Legs. In this paper, we present and discuss the molecular and isotopic properties of hydrate-bound and void gases. These data are used to infer the origin of gas hydrates, relate gas hydrate occurrences to fluid flow regimes that prevail in the studied area; and develop an integrated model of gas hydrate crystallization at the Southern Summit of Hydrate Ridge.

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## 2. Methods and Materials

hydrate was Gas recovered from the sediments, cleaned, and fully decomposed inside a 20 cm<sup>3</sup> syringe. Although significant effort was made to collect as many gas hydrate samples as possible, many sediment intervals with cold spots were preserved in liquid nitrogen immediately after recovery and not made available for analysis. A total of 55 gas hydrate samples were obtained and analyzed. Gas voids form in the core liner upon transfer to surface conditions (Paull and Ussler, 2001) when the concentration of dissolved C1 exceeds 10-20 mM (Trehu et al, 2003). The voids were sampled by puncturing the plastic core liner with a steel penetration tool connected through a valve to a syringe. A total of 494 gas voids were sampled and analyzed on Leg 204 (Trehu et al, 2003). Average gas void frequency for Leg 204 was one void per every ~6 m of recovered sediments, with much greater frequency within the GHSZ.

#### 3. Results and discussion

#### 3.1. Shallow Gas Hydrate

Shallow gas hydrates at the Southern Summit characterized by higher gas flux at the seafloor (Sites 1248-1250) are relatively enriched in  $C_{24}$  gases. They crystallize predominantly from hydrocarbon gases likely generated as deep as 2-2.5 km below the seafloor along permeable conduits such as Horizon A. Although the hydrate-bound gas is largely microbial  $C_1$ , included  $C_{24}$  gases are mainly thermogenic in origin. The enrichment of  $C_3$  in some of the gas hydrate samples may suggest that small amounts of sII gas hydrates are mixed as crystal intergrowths with largely sI gas hydrates in the shallow sediments.

## 3.2. Deep Gas Hydrate

Deep gas hydrates at Southern Summit (Sites 1248-1250) and in the surrounding lower gas flux area (Sites 1244-1247) contain only  $C_1$ ,  $CO_2$  and minor  $C_2$  and thus are characterized by sI. They crystallize mainly from in situ generated microbial gas, although some gas hydrates near the Southern Summit and in faulted areas of Sites 1244 and 1245 may contain a minor fraction of thermogenic gas migrated from greater depth.

## 3.3. Gas Transport

It appears that gas is supplied from Horizon A through self-created permeable pathways as

sealing destroys the overpressured gas capacity of overlaying muds. Gas hydrate distribution and concentration within the sediments is controlled by 1) thermodynamic conditions and local solubility of gas favoring nucleation and growth of gas hydrate and wider lateral diffusion of gas in relatively shallow sediments; 2) trapping of free gas below the seafloor gas hydrate cap and refocusing it along relatively permeable horizons; 3) local structural setting that favors lateral migration of hydrocarbons to the crest of the summit (anticline).

## 4. Summary

A large number of molecular and isotopic analyses on void and hydrate-bound gases from Hydrate Ridge (ODP Leg 204) allow us to constrain the origin of natural gases and their mixing during the migration through the sediment section along specific pathways.

Several discussed issues remain unresolved and should be addressed in future research. For example, it is not clear why less thermogenic C2+ gas is present at Site 1250 located closer to the assumed main migration conduit relative to the more distant Site 1249. Heterogeneity of relative permeability in sediments in 3D space may explain this observation, and in-depth sedimentological and structural studies are needed to better understand fluid migration within the Southern Summit. The proposed gas migration mechanism from Horizon A into the shallow sediments should be validated. Timing and dynamics of gas migration and gas hydrate formation with respect to structural development of Hydrate Ridge and the underlying accretionary complex are not addressed here and are an important direction of future 3D basin modeling efforts.

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