a shallow, young source. The situation is more complex at Hydrate Ridge, where in several sites maxima in iodine concentrations were found at depths between 100 and 200 m, associated with relatively high ^{129}I /I ratios. The lowest ratios found in all four areas are consistently below $200x10^{-15}$, corresponding to minimum ages of 45 Ma. ^{129}I /I ratios found for iodine in pore waters associated with gas hydrates indicate that old organic sources are an important source for iodine (and probably also of methane) in gas hydrates deposits, but that addition of locally derived iodine is visible in some cases. Fehn et al., Science 289, 2332-2335, 2000; Fehn et al., Geology 31, 521-524, 2003

OS52C-05 1450h INVITED

Properies of sea Floor Hydrates From Hydrate Ridge/Cascadia Margin

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Near-surface methane hydrates are well known from southern and northern summits at Hydrate Ridge. Fabric analyses of such samples indicate that at least parts of the hydrate are formed from free methane gas. Free gas migrates upwards through the sediment column and is also indicated by gas bubbles emanating at the seafloor. These bubbles form plumes in the water column. In most cases pure white hydrate occurs here in layers millimeters to several decimeters thick. On a macroscopic scale the fabric varies from highly porous, with pore diameters of up to several cm, to massive with no visible pores. Bulk densities range from 0.35-0.75 g cm-3 and are inversely correlated with the pore volume, which ranged from 10 - 70 vol percent. A total end-member density of pure natural methane hydrate of 0.79 $\pm$0.13 g cm-3 is estimated differing considerably from the theoretical value of 0.91 g cm-3. The low bulk density and the porous fabric result from the formation of hydrate from bubbles of methane. Our CT investigations on samples obtained by autoclave coring technology show that at least parts of the pores within pure hydrate layers are filled by free gas in situ, which additionally lowers the material density in its natural environment. Low densities create high positive buoyancy as well as low acoustic velocity of hydrate-rich sediments. Strong buoyancy facilitates the rapid transfer of solid methane hydrates from the seafloor to the atmosphere by hydrate floats, and hence affects the greenhouse gas budget. Furthermore, the low acoustic velocity affects the subsurface distribution as well as the thickness of hydrated strata estimated from seismic velocities and hence the estimate of the amount of hydrate stored in off-shore sedimentary formations.

OS52C-06 1505h INVITED

Geomicrobiology and Methanogenesis in Accretionary Complexes

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As elsewhere in subsurface environments, microbes are known to colonize the sediments of accretionary margins. In fact, much of the methane present in hydrates along continental margins originates from microbial activity. However, models to predict hydrate distribution or the amount of methane in the sediments lack reliable values for in situ microbial methane production rates. Our studies of hydrate-bearing sediments focus first on the molecular identification of the microbes present and then on estimating realistic methanogenic rates to be used in these models. 16S rDNA extracted from deep marine sediments, then sequenced, and compared to known sequences indicates the presence of diverse bacterial and archaeal lineages. In one example, the Nankai Trough, *Archaea* (both Crenarchaeota and Euryarchaeota) and *Bacteria* (e.g., Proteobacteria, Actinobacteria, green non-sulfur) were detected at various depths above, within, and below the hydrate stability zone. Often methanogens cannot be detected using molecular approaches in accretionary sediments, but at least one methanogen (*Methanoculleus submarinus*) has been isolated from deep sediments that contain hydrates. Although culture-based enrichments for methanogens often yield evidence of methanogenic activity methanogenic rates derived from these studies are likely several orders of magnitude higher than the rates that are possible under in situ conditions. By combining data on methanogen numbers at various depths and realistic methanogenesis rates obtained from starved methanogens we hope to determine the productivity of methanogens on a volumetric basis for the sediments. These data will be used in models that predict hydrate distribution and formation rates in marine sediments.

OS52C-07 1525h

Migration of the Base of the Hydrate Zone Tracked by Rock Magnetism

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Previous studies have indicated that the presence of gas hydrate produces responses in the authigenic magnetic mineralogy which can be readily distinguished by the methods of rock magnetism. An index based on the Day plot of domain state has proven particularly useful in delineating hydrate occurrence. Recent ODP Legs 201 and 204 have provided the opportunity to test the broad applicability of the rock magnetic proxy for hydrate. Growth of the metastable sulfide mineral greigite in its single-domain size range is stimulated where disseminated hydrate occupies a high proportion of pore spaces. Greigite production apparently results from extracellular reduction of iron derived from iron silicates. Preservation of the metastable greigite, without further reduction to pyrite, seems to be a characteristic feature of the hydrate zone. Disseminated hydrate at Peru Margin Site 1230 from Leg 201 is present in an upper unit of Pleistocene to Holocene diatomaceous mud, but is comparatively rare in the low porosity, consolidated accretionary wedge sediments of Miocene age that occur below a hiatus at 200 meters below seafloor. Bacterial counts mirror this decreased abundance of hydrate below the hiatus: so do the rock magnetic proxies. Leg 204 sites from South Hydrate Ridge similarly show a rock magnetic response to the presence of hydrate, and what appears to be the rock magnetic signature of the base of the hydrate zone; however, this occurs about 30 m below the modern base of hydrate stability, marked by a BSR. Our suggested explanation is a rapid upward migration of the thermally-controlled base of hydrate stability resulting from a warming of bottom-water at the close of the last glacial. This result confirms and extends the Leg 146 results from the Vancouver Island Margin (Site 889), and North Hydrate Ridge (Site 892); water depth appears to have controlled the amount of bottom-water warming experienced by each site, suggesting a control from intermediate water bodies on the shelf.

OS52D MCC: 3000 Friday 1600h

Gas Hydrates in Accretionary Complexes III *(joint with A, B, PP, T, C, GC)*

Presiding: **A M Trehu,** Oregon State University**; J E Johnson,** Oregon State University

OS52D-01 1600h

Constraints on Gas Hydrate Dynamics at the Southern Summit of Hydrate Ridge Based on Dissolved Chloride Data

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At the summit of Hydrate Ridge (ODP Sites 1249 and 1250), pore fluids are highly enriched in dissolved chloride (up to 1360 mM) in a zone that extends from the near the sediment surface (1 mbsf) to depths of 20-30mbsf. The presence of this brine indicates that gas hydrate formation here must be very recent and rapid. Below 30 mbsf, high chloride brines give way to chloride values near seawater concentrations with even lower chloride anomalies superimposed on baseline values. Fresher chloride anomalies represent intervals where gas hydrate has dissociated during sediment recovery. The low chloride values observed below 30 mbsf, and similar anomalies observed at sites drilled in a nearby basin and on the flanks of Hydrate Ridge, can be used to estimate the gas hydrate concentration in these sediments. The observed chloride enrichment at Site 1249 can be reproduced by a one dimensional, non-steady state, transport-reaction model only if methane transport occurs in the gas phase; i.e. the observed chloride enrichment cannot be generated exclusively from transport of methane dissolved in the pore fluids. Model best fits to measured chloride values require an enhanced rate of methane transfer from the gas phase in near-surface sediments, possibly due to enhanced bubble formation. Transport of methane as free gas within the GHSZ is consistent with geophysical observations at this site. The gas hydrate currently present at the Hydrate Ridge summit could have been generated in less than 1,000 years if we allow for enhanced transfer rates of methane gas near the seafloor, and 5,000 years if the gas dissolution rate remains constant with depth. Such high values highlight the dynamic nature of this system. In comparison, gas hydrate present in the deeper sediments of Site 1249, at other sites on Hydrate Ridge, and other locations where no positive chloride anomalies are observed, must be significantly older than 40,000 years.

OS52D-02 1615h INVITED

Carbon Cycling in Gas Hydrate Systems and Consideration of the Time Domain

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Enormous amounts of microbial CH_4 reside in gas hydrate, dissolved gas and free gas bubbles in marine sediment. Global carbon cycle models and paleoenvironmental studies habitually neglect this CH_4, although its distribution clearly depends on carbon fluxes to and from the ocean, and external conditions, especially temperature. As we begin to appropriately connect this large, dynamic seafloor CH_4 cycle into broad Earth systems science, we are faced with some major conceptual problems, including how amounts, distributions, and fluxes from selected boreholes can be extrapolated globally. Well-reasoned commentary on this issue has led to the prevailing idea of typical gas hydrate systems on passive (low fluid flux) and active (high fluid flux) margins. The Ocean Drilling Program has now targeted three locations explicitly to characterize the amount, distribution and biogeochemical cycling in marine gas hydrate systems: Blake Ridge (passive), Hydrate Ridge (active), and Peru Trench (active). Although much work remains, in situ gas profiles and detailed pore water concentration profiles of many species have now been generated at all three locations. The gas hydrate zone at the Blake Ridge lies beneath a relatively thick interval of SO_4 reduction, and holds large amounts of CH_4 fairly well dispersed in pore space surrounded by very fresh waters greatly enriched in I but only moderately enriched in PO_4 and ammonia. By contrast, the gas hydrate zone at the Peru Trench site lies beneath a relatively thin interval of SO_4 reduction, and holds relatively low amounts of CH_4 in moderately fresh waters moderately enriched in I but greatly enriched in PO_4 and ammonia. Amounts and distribution of gas and pore water species at Hydrate Ridge lie somewhere between, although the most striking generalization is the variability in all components across this area. Our most basic conclusion from this emerging data is that we must move beyond classifying gas hydrate systems on physical differences alone and include the time domain. Blake Ridge represents an old, contracting system (where current CH_4 outputs exceed inputs) with low, generally unfocused fluid flow. The Peru Trench represents a younger, growing system with moderate, generally unfocused fluid flow. Hydrate Ridge represents a growing system with highly variable fluid flow.

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OS52D-03 1630h

Biogeochemical Investigations of Methane Seepage, Hydrate Ridge, OR.

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During July, 2002 we conducted a series of biogeochemical studies at the southern summit of Hydrate Ridge, OR. Using the DSV Alvin we collected sediment push cores from 2 distinct types of seep environments (clam beds and microbial mats) and from control sites (bare sediment). Samples from each setting were analyzed for the depth distributions of microbial abundance, most probable number counts for methanogenic archaea, volatile organic acids, dissolved organic carbon (including δ^{13}C), total organic carbon (including δ^{13}C and Δ^{14}C), sulfate, alkalinity (including δ^{13}C-DIC), δ^{13}C-CH_4, as well as the distribution of bacterial and archaeal 16S rDNA genes. These distributions provide the basis for a comparative analysis of the distinct seep environments and of biogeochemical controls on methane hydrate. Primary production in the seeps appears to be driven by anaerobic methane oxidation in the sediments and sulfide oxidation at the sediment-water interface. However, results indicate distinctive microbial habitats in the different seep settings. Results further indicate a vigorous, secondary microbial community living off the wastes of the primary producers. High levels (up to 4%) of ^{13}C-depleted ($\sim$-45$^{o}/_{oo}$) organic carbon in the seeps and high C:N ratios (as high as 50:1) indicate a buildup of CH_4-derived organic carbon, and raise the possibility of nitrogen limitation impacting seep communities.

OS52D-04 1645h

Holocene Earthquakes, Gas Hydrates, and an 11,000 Year Record of Slope Failures at Hydrate Ridge, Cascadia Margin

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Hydrate Ridge Basin-West (HRB-W) is an isolated slope basin located down slope of the well-studied gas hydrate-bearing Hydrate Ridge structure on the lower slope of the Cascadia accretionary wedge. Swath bathymetry and deep-towed sidescan sonar imagery indicate the western flank of Hydrate Ridge is dissected by a large submarine canyon, which serves as the major pathway for slope failure sediment transport into the basin. In June of 2002, we collected two piston and companion trigger cores and a kasten core from the stratigraphy preserved in HRB-W to obtain the Holocene record of slope failures (turbidites/debris flows) derived from Hydrate Ridge. Comparison of this record with the margin-wide earthquake triggered turbidite record (Goldfinger et al., 2003) will help determine (1) if earthquakes are the dominant mechanism for triggering slope failures along portions of the margin bearing gas hydrate and if so, the potential role they might play in destabilizing seafloor and subseafloor gas hydrates and/or (2) if the presence of gas hydrate weakens the sediment sufficiently to cause repeated slope failure, independent of earthquake shaking. The recovered cores reveal a good record of Holocene turbidites across the slope basin floor. We have identified and correlated the five records within the basin, by detailed lithologic description, high resolution magnetic susceptibility and gamma density logging, core x-rays and digital photos, 210Pb analyses of core tops, and radiocarbon dating of individual events. We are currently running XRD analyses to determine the potential differences in clay mineralogy between hemipelagic and turbidite tail clays to better aid us in the interpretation of the exact number of individual turbidites preserved in our cores (as there are 3 tightly spaced sets of turbidites that may be individual events triggered separately in time or amalgamated turbidites triggered at the same time and deposited together). If we assume they are amalgamated events, then 20 turbidites have been deposited within the last 11,102 years B.P., yielding an ave. recurrence of 555 years, very close to the average recurrence (564 years) of earthquake triggered turbidites across the northern Cascadia margin over the same time interval. Continued radiocarbon dating of the individual turbidites and resolution of the tightly spaced portions of the record will test whether or not this initial interpretation remains valid, however, we are encouraged by these early results.

OS52D-05 1700h

Innovations in Sampling Pore Fluids From Deep-Sea Hydrate Sites

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We have developed a sea-floor probe capable of collecting and returning undecompressed pore water samples at in situ pressures for determination of dissolved gas concentrations and isotopic values in deep-sea sediments. In the summer of 2003, we tested this instrument in sediments containing gas hydrates off Vancouver Island, Cascadia Margin from ROPOS (a remotely operated vehicle) and in the Gulf of Mexico from Johnson-Sea-Link I (a manned submersible). Sediment push cores were collected alongside the probe to compare methane concentrations and stable carbon isotope compositions in decompressed samples vs. in situ samples obtained by probe. When sufficient gas was available, ethane and propane concentrations and isotopes were also compared. Preliminary data show maximum concentrations of dissolved methane to be 5mM at the Cascadia Margin Fish Boat site (850m water depth) and 12mM in the Gulf of Mexico Bush Hill hydrate site (550m water depth). Methane concentrations were, on average, five times as high in probe samples as in the cores. Carbon isotopic values show a thermogenic input and oxidative effects approaching the sediment-water interface at both sites. This novel data set will provide information that is critical to the understanding of the in situ processes and environmental conditions controlling gas hydrate occurrences in sediments.

OS52D-06 1715h

Thermogenic and Biogenic Gas Hydrates on the Northern Cascadia Margin: A Molecular, Isotopic and Geochemical Comparison

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A seafloor survey of Barkley Canyon, located off the coast of Vancouver Island, was conducted in August 2002. This survey revealed massive outcrops of gas hydrates exposed as large slabs (6-8m in length) and thinly sedimented mounds (2-3m high). Molecular and isotopic analyses of gas hydrates collected at this site suggested a thermogenic gas source, which was corroborated by observation of hydrocarbons seeping from the seafloor. Methane δ^{13}C values from disassociated hydrates collected from Barkley canyon during this and a subsequent survey ranged from -43.0 to -56.9 per mil. Additionally, all hydrate samples contained substantial quantities of C_2-C_5 hydrocarbons. This hydrocarbon distribution is similar to that of thermogenic hydrates collected in the Gulf of Mexico, which have been classified by Sassen and MacDonald (1994) as Structure II hydrate. Sediment pore water enrichment of 2-methylbutane (isopentane), a hydrocarbon excluded from the lattice of Structure II hydrate, provides further evidence for the occurrence of Structure II hydrate at Barkley canyon. Despite clear evidence of a thermogenic gas source for Barkley Canyon hydrates, relatively light δ^{13}C values (e.g., -56.9 per mil) and higher percentages of methane in some samples suggested additional contribution from a biogenic source. Vertical advection of pore water containing high concentrations of biogenic methane is common along the Cascadia Margin accretionary prism (e.g., Hydrate Ridge). Alternatively, localized methanogenesis could be the source of the biogenic methane. To illustrate the spatial heterogeneity of this region region and identify the source of the biogenic methane, gas hydrate composition and geochemical data from pore water collected at a nearby ($\sim$50 km) biogenic site (Bullseye Vent) will be compared to data from Barkley Canyon.

OS52D-07 1730h

Southern Ritchie Banks, Hikurangi Margin, New Zealand - Similarities to Hydrate Ridge?

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The Hikurangi Margin offshore New Zealand's East Coast is predicted to contain large quantities of gas hydrates, based on the observation of wide-spread bottom simulating reflections (BSRs). The Hikurangi Plateau, a large igneous province populated by seamounts, is being subducted at this margin beneath the New Zealand continent. Subducting seamounts disrupt the margin and may underlie Ritchie Banks, a series of prominent outer-margin highs. We present results from three seismic lines across the Southern high of Ritchie Banks. BSRs are visible on the flanks of Southern Ritchie Banks clearly suggesting the presence of gas hydrates. At the crest, we were able to identify gas conduits that extend close to the seafloor. Depending on bottom water temperature, most of the crest is predicted to be within the methane hydrate stability zone. We therefore predict gas hydrates to be present above the gas conduits. One of the gas conduits is located beneath the projected location of a gas plume that has been identified previously in the water column, suggesting venting of gas through the gas hydrate stability zone. Southern Ritchie Banks displays similarities to Hydrate Ridge. Both ridges appear to be uplifted and form large-scale structures of fluid flow focusing. Water depths are similar and both ridges exhibit gas venting. Structural similarities include landward dipping layers at the seaward flanks of both ridges. We observe high seafloor reflectivity at the crest of Southern Ritchie Banks, perhaps indicative of carbonate cementation or even gas hydrate outcrops, similar to Hydrate Ridge. Our observations suggest that Southern Ritchie Banks may contain a very "active" gas hydrate system.

OS52D-08 1745h

A Possible Origin of the Gas Hydrate in Southwest Taiwan Offshore Area

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The southwest Taiwan locate at the eastward subduction zone of the Eurasian plate, which is currently converging with the Philippine Sea plate at a rate of several few centimeters per year. The geological setting of this region is characterized by the appearance of thick accreted sediments up to several kilometers, numerous submarine canyons, active faults, and mud diapirs/volcanoes. The origin of mud diapir/volcano is probably related to the plate convergence. During the tectonic processes, the organic matters were "cooked" thermogenically and biogenically to produce the natural gases, and possibly the oil in the sediment. Beneath the seafloor, if the natural gases were at the appropriate temperature and pressure condition, they would become the gas hydrate, and preserved in the top sediment layers. The formation of gas hydrate is situated under the water depth at about 300 to 3000 meters in this region. In the seismic profiles, the Bottom Simulation Reflector (BSR) probably represents the boundary between the solid-state and gas-state natural gas. The BSR is also regarded as an important marker as an existence of gas hydrate. It is extensively distributed in the continental margin off southwest Taiwan, but unstable, especially along the active fault zones. The natural gas as well as the mud and hydraulic fluid in the deep sediment are pushed into the surface layer. In order to investigate the relationship between mud diapir and gas hydrate, we conduct the geophysical and geological methods: using a 38/150 kHz high-frequency echo sounder system to guide and select the sites for mud diapirs, and take 1-3 m gravity core samples. We, then, adopt an up-side-down "headspace" tin-can technique to preserve the gases, and use a gas chromatography to analyze its contents. Oil companies commonly use the method. The first result shows that the existence of methane, ethane, propane and possible other higher hydrocarbon contents in the core samples. The methane is the most abundant gas, up to 1859 parts per million in volume (ppm); the others are not significant, probably due to a leaking in the sampling and transportation. We have reduced the "headspace" in order to preserve more concentrated gases in the second attempt, and the result shows similar. Nonetheless, our results suggest that the gases are probably a mixture of thermogenic and biogenic origin. Due to the existence of higher hydrocarbon contents, we believe that the thermogenic gases are produced in the deep source sediments, while the shallow biogenic methane is mixing with them in the top sediment. In the mud diapir/volcano area, the contents of natural gases are usually higher than that in a flat seafloor. As several high gas values have been founded in the near shore area (e.g., 1604 ppm of C1 plus C2 and C3 found at a water depth of 23 m), we suggest that the 300-3000 m gas hydrate zone is probably in a dynamic balance of which the deep gases are continuously migrating to the BSR and the free gases are being evaporating from this zone. Our data illustrate the potential existence of natural gases in this region; however, we cannot quantify the reserve at this time. Further investigations with a long core and better-improved techniques are needed.