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The Strain Path Method (SPM) is used to predict the initial undrained pore pressure response upon insertion of the Davis-Villinger Temperature/Pressure Probe (DVTP-P) and Fugro McClelland's tapered piezoprobe. Uncoupled-isotropic consolidation is assumed and the coefficient of consolidation is estimated from excess pore pressure dissipation. The modeled response to insertion in normally consolidated Boston Blue Clay (BBC) includes the following. The initial excess pore pressure at the port is 3.3 times the in situ vertical effective stress for the DVTP-P, whereas for a piezoprobe, it is 2.4 times the in situ vertical stress. Dissipation of the piezoprobe is much faster than that of a DVTP-P in the early stages due to the much narrower tip of the piezoprobe. The time to achieve 50% dissipation, t_{50} , for the DVTP-P is 2.6 times that for the piezoprobe. Nevertheless, the piezoprobe dissipation is retarded by the arrival of a pore pressure front from above tapered section, which forms a platform on the dissipation curve. The DVTP-P and the piezoprobe were deployed in the Ocean Drilling Program (ODP) on ODP Leg 204 at approximately 53 mbsf in the same lithology, but in an adjacent borehole. The in situ pore pressure (9.55MPa) can be estimated accurately within 0.5 hours at this site by comparing the dissipated pore pressures measured at pressure ports of the piezoprobe and DVTP-P (Two-Point Intersection Method), which is approximately the hydrostatic pressure (9.53MPa). The peak excess pore pressures of the DVTP-P and piezoprobe are 3.0 and 2.2 times the in situ vertical effective stress, respectively. t_{50} of the DVTP-P is approximately 2.5 times that of the piezoprobe. The results show very good agreement between the predicted and measured dissipation curves for both the piezoprobe and the DVTP-P. The coefficient of consolidation is estimated to be 8×10^{-7} m²/s.

OS52C MCC: 3000 Friday 1340h

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

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

OS52C-01 1340h

Gas hydrate distribution and its relationship to free-gas sources within southern Hydrate Ridge: Results from recent seismic experiments

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In August and September, 2002, we conducted a two-ship seismic experiment with the R/V Ewing and the D/V Resolution in coordination with Ocean Drilling Program Leg 204 on Hydrate Ridge, offshore Oregon. We acquired three types of vertical seismic profiles, (zero-offset, constant offset, and walkaway VSP) at four drill sites, and ocean bottom seismometer refraction and seismic reflection data across southern Hydrate Ridge using a high-resolution seismic acquisition system. At Site 1247, which lies near the summit of southern Hydrate Ridge, the constant offset VSP records have two arrivals interpreted as primary-to-shear wave conversions from horizons 46 and 109 m below seafloor, 79 and 16 m above the bottom simulation reflection (BSR) respectively. These events correlate with the top of two hydrate intervals observed in cores and inferred from pore fluid geochemistry. The deeper event also correlates with a seismic reflection, which is discordant with local stratigraphy, and is interpreted as a reflection from the top of the hydrate layer. Both VSP and seismic reflection observations are evidence for a regional hydrate layer that extends at least 250 m around the borehole and directly above the intersection of an inferred free-gas source horizon and the BSR. Seismic p-wave velocities were also measured from the high-resolution seismic reflection data to infer hydrate concentrations within the hydrate stability zone. Preliminary results show that north of the summit of southern Hydrate Ridge, near Sites 1244, 1245, and 1246, seismic velocities are notably higher

on the flanks of the ridge than at the ridge crest (1700 m/s between the seafloor and BSR on the flanks vs. 1580 m/s in the equivalent interval on the crest). At the summit of southern Hydrate Ridge, near Sites 1249 and 1250, velocities are locally high (1680 m/s in the interval between the seafloor and BSR at the summit vs. 1580 m/s in adjacent, equivalent intervals). VSP and seismic interval velocity data are consistent with hydrate accumulations above the intersection of the inferred free gas source horizons and the BSR.

OS52C-02 1400h

Why Gas Hydrate Is Where It Is At Hydrate Ridge: The Story From Infrared Images

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A detailed analysis of infrared (IR) images from Ocean Drilling Program (ODP) Leg 204 to southern Hydrate Ridge, combined with core based observations of structure and lithology indicates that lithology plays a stronger role in influencing hydrate distribution at the ridge crest and western flank sites than on the lower eastern flanks and slope basin of southern Hydrate Ridge. Core based observations of silt layers and structural features from five sites representing the three major environments at southern Hydrate Ridge, the ridge crest, the ridge flanks, and the eastern slope basin, were documented in detail. These features were then correlated to the locations of negative temperature anomalies, indicative of decomposing gas hydrate, identified in IR images of the cores. The silt layers are typically <0.5 cm thick, laterally discontinuous, and compose <3% of the total sedimentary section in the gas hydrate stability zone (GHSZ). Structural indicators in the cores, though rare, typically consisted of shear bands and small offset faults (<1 cm). IR data at sites 1245, 1246, and 1250, on the western flank, high on the eastern flank, and ridge crest respectively, indicate that 40 to 60% of the temperature anomalies occur within the documented silt layers, yet show little correlation to structural features. The correlation between gas hydrate and silt layers is weaker at sites 1244 and 1251 where anywhere from 0 to 25% of the anomalies correlate with silt layers. Silt composes <1% of the sedimentary section at these sites east of the ridge crest. While counterintuitive at first glance, as lithology was expected to play a larger role in controlling gas hydrate distribution in the eastern slope basin than at any other site cored, these results, when placed in the regional geologic context for Hydrate Ridge should not be unexpected. Uplift and erosion of the summit and western slope of Hydrate Ridge has exposed previously deposited turbidite sequences with silty basal layers. These turbidites are sampled within 30 m of the seafloor at sites 1245, 1246, and 1250, well within the GHSZ. At sites 1244 and 1251, however, this sequence of frequent turbidite layers occurs deeper in the stratigraphic section. As a result, lithology exerts a lesser control at the core scale at sites 1244 and 1251, than at sites 1245, 1246, and 1251. It should also be noted that the steeply dipping faults and fractures likely to control fluid flow through the ridge are difficult to sample. Thus the gas hydrate imaged during the leg may be biased towards that located in sub-horizontal silt layers.

OS52C-03 1415h INVITED

Controls on Regional Gas Hydrate Occurrence at Southern Hydrate Ridge (ODP Leg 204)-Geochemical Evidence

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Ocean Drilling Program Leg 204 on southern Hydrate Ridge found concentrated gas hydrate (20-40% of pore volume) only in shallow (0-30 m) sediments over a limited area (0.3 x 0.5 km) at the summit of the Ridge, just above seismically imaged gas migration pathways. Although summit gas hydrates are dominated by microbial methane ($\delta^{13}\text{C} = -65$ permil), the hydrates contain thermogenic ethane ($\delta^{13}\text{C} = -34$ permil) and sediments cored within the migration conduits contain elevated amounts of C2-C6 hydrocarbons having carbon isotopic compositions indicating hydrocarbon origin at temperatures on the order of 120-140 deg C. At sites away from the summit of southern Hydrate Ridge, gas hydrate occurrence is more limited, with average contents on the order 1-3% of pore volume. Non-summit sites have no significant input of migrated thermogenic hydrocarbons to the hydrate stability zone. However, intense microbial activity results in relatively steep (1.6 to 3.6 mM/m) methane concentration gradients, and a top of gas hydrate occurrence marked by distinctive hydrocarbon fractionation (ethane depletion, propane enrichment) in the dissolved gas geochemistry. Ethane in shallow sediments is isotopically light ($\delta^{13}\text{C} = -52$ permil) and probably related to microbial acetogenesis and carboxyl group reduction. Formation of Structure I methane hydrate involves a fourfold ethane-enrichment in the hydrate relative to the dissolved gas phase, and results in a net transfer of ethane from the pore water to the sediment. Steep porosity gradients result in the burial velocity of sediment being greater than that of pore water with respect to the sediment-seawater interface. Downward sediment velocity is even greater relative to the base of gas hydrate stability, which is shoaling due to tectonic uplift concurrent with sedimentation. Decomposition of ethane-enriched gas hydrate upon subsidence beneath the stability zone results in transfer of ethane from the sediment back to dissolved gas/free gas phases, and produces large shifts in C1/C2 ratio. Carbon isotopic composition of dissolved inorganic carbon indicates that anaerobic methane oxidation is an important process mainly in the summit region. At most non-summit sites, rapid burial apparently limits the amount of methane diffusing upward to the sulfate reduction zone.

OS52C-04 1435h

Sources of gas hydrates: ¹²⁹I results from Blake Ridge, Nankai Trough, Peru Margin and Hydrate Ridge

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The presence of the cosmogenic isotope ¹²⁹I ($T_{1/2} = 15.7$ Myr) allows the dating of iodine in pore waters associated with gas hydrates. Since iodine is closely associated with organic material, ¹²⁹I / I ratios give information on the age of the source material of iodine and, by association, of the methane found in gas hydrate occurrences. The first application of this type was carried out at Blake Ridge (ODP 164; Fehn et al., 2000), followed by a study of the Nankai area (Fehn et al., 2003). We compare here the earlier results to new data from the Peru Margin (ODP 201) and Hydrate Ridge (ODP 204). All of the results obtained show that stable iodine in sediment pore waters associated with gas hydrates is enriched 500-fold (Nankai) to 5000-fold (Hydrate Ridge) over seawater, indicating derivation from organic sources. The high concentration of iodine in the pore waters allows preparation of targets for AMS determinations from the small quantities (3 to 10 mL) typical for individual pore water samples. All ¹²⁹I / I ratios measured in the two new investigations indicate ages older than the host sediments, confirming findings from Blake Ridge and Nankai that iodine (and methane) is predominantly not derived from local sources. In contrast to Blake Ridge, however, ratios in the other three areas show considerable variation. In Nankai and Peru Margin, a clear decrease in ratio (and increase in age) with increasing depth is discernable, pointing to mixing between a deep, old and

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 $^{129}\text{I}/\text{I}$ ratios. The lowest ratios found in all four areas are consistently below 200×10^{-15} , corresponding to minimum ages of 45 Ma. $^{129}\text{I}/\text{I}$ 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

Properties 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 ± 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 (*Methanococcus 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 20-30 mbsf. 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 CH₄ reside in gas hydrate, dissolved gas and free gas bubbles in marine sediment. Global carbon cycle models and paleoenvironmental studies habitually neglect this CH₄, 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 CH₄ 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 SO₄ reduction, and holds large amounts of CH₄ fairly well dispersed in pore space surrounded by very fresh waters greatly enriched in I but only moderately enriched in PO₄ and ammonia. By contrast, the gas hydrate zone at the Peru Trench site lies beneath a relatively thin interval of SO₄ reduction, and holds relatively low amounts of CH₄ in moderately fresh waters moderately enriched in I but greatly enriched in PO₄ 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 CH₄ 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.