

EUG XI



Symposium CC09

Clathrates, Climate, and Carbon Budget (A):
Accumulation and Destabilisation of
Natural Gas Hydrate Systems:
Dynamic Carbon Reservoirs at the
Earth's Surface

Convenors

Marc de Batist
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CC09 Clathrates, Climate, and Carbon Budget (A)

Wednesday PM Session

CC09 : WEpm25 : G1 Global Implications of Natural Methane Hydrate

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Natural methane hydrate is found in the shallow geosphere within 2,000 m of the solid surface, mainly in two discrete geographic regions: outer continental margins of all oceans and in polar regions with continuous permafrost. The potential amount of methane in natural methane hydrate is very large, estimated to be about 10 teratonnes (10^{19} g) of methane carbon. Thus, on earth there is a huge, shallow reservoir of methane in the solid form of methane hydrate, which is in a metastable state, responding to changes in temperature and pressure.

The compound, methane, is an important energy fuel and a potent greenhouse gas. These same properties apply to hydrate methane, resulting in speculation concerning the use of methane hydrate as a potential energy resource and the role of methane hydrate as an environmental factor in near-surface geological processes. The possible energy and environmental aspects of methane hydrate may be globally interrelated. For example, wherever methane hydrate occurs, its presence has profound effects on the physical and chemical properties of the near-surface sediment in which it resides. There is a likely connection between gas hydrate and submarine slope stability. Submarine slope failure caused by gas-hydrate destabilization will release methane into the ocean/atmosphere system. The released methane alters the chemistry of this system, resulting, in the extreme, to possible global climate change, if the methane and its oxidized derivative, carbon dioxide, actually reach the atmosphere to act as greenhouse gases. Numerous near-surface phenomena and properties, such as chemical and biochemical oxidation, thermal conductivity, and heat-transfer, however, buffer methane-hydrate-induced global change. Therefore, methane hydrate may be more of a modulator of global environmental change rather than an agent of change. Nevertheless, development of ideas and technology to exploit methane hydrate as an energy resource must be done in concert with understanding the role of methane hydrate in near-surface processes, because one could have dramatic effects on the other.

CC09 : WEpm26 : G1 Multi-Component Ocean Bottom Cable Data in Gas Hydrate Investigations

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In order to understand the importance of natural gas hydrates within the shallow geosphere and their potential release of large volumes of methane to the atmosphere, it is necessary to obtain reliable information about concentration and distribution of hydrates and associated free gas beneath the sea floor. Seismic methods seem to be the most promising approach for indirect detection and quantification of hydrates. Estimation of hydrate concentration from seismic velocities will, however depend strongly on the micro-scale hydrate distribution in the sediment pore space. If the hydrate forms at grain contacts it may act as a cementing agent and stiffen the sediment framework, and both V_p and V_s will increase dramatically when hydrate occupies only a few percent of the pore space. If the hydrate is formed in the pore space away from grain contacts, increasing hydrate content is assumed to have less effect on the seismic velocities. Shear wave reflections have the potential for remotely discriminating whether the hydrate cements grain contacts or not. In order to test what information P-S converted waves can provide about gas-hydrate bearing sediments and associated free gas, a 4 km long 4-component sea-bottom line was acquired by PGS Reservoir where a well-defined BSR is identified on conventional multi-channel P-wave seismic from the Storegga Slide area. This data set is the first 2-dimensional shear-wave line over a gas-hydrate related BSR. Strong reflections on the PS section show that S-waves are

converted within the whole sediment column. Converted S-waves will occur at horizons where there is a contrast in shear modulus or in density, which (1) may occur at the interface between sediment layers, and (2) possibly be due to gas hydrate forming at grain contacts. Since the BSR has a different dip than the sediment layers in this area, converted S-waves that are due to gas hydrates can be separated from events caused by sediment interfaces. Results from detailed interpretation to investigate the potential for using converted waves in detection and quantification of gas hydrates and associated free gas will be presented and compared with results from 2D and amplitude-versus-angle modelling.

CC09 : WEpm27 : G1 Multi-Frequency Seismic Study of the Gas Hydrate Accumulations in Lake Baikal, Siberia

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Recently, the presence of methane hydrates has been evidenced in Lake Baikal, Siberia, by means of seismic profiling, deep drilling and shallow coring. This is, up to now, the only reported occurrence of gas hydrates in a confined fresh-water basin.

In this presentation, we discuss the frequency-dependent acoustic characteristics of the hydrate-bearing sediments, using 5 different types of reflection seismic data encompassing frequencies from 10 to 1000 Hz. On low-frequency airgun-array data, the base of the hydrate stability zone (HSZ) is observed as a single, high-amplitude, inverse-polarity reflection that often crosscuts the local stratigraphy. Amplitude and continuity of the BSR decrease or even disappear on higher-frequency data. On medium- to high-frequency data (e.g. watergun) the base of the HSZ is no longer expressed as a single reflector, but rather as a facies change between enhanced reflections below and blanked reflections above. The increasing reflection amplitude of the BSR with increasing offset (AVO-analysis), the high reflection coefficient of the BSR (~40% of lake floor reflection) and the presence of enhanced reflections beneath the BSR suggest the presence of free gas below the HSZ. The observation of some enhanced reflections extending into the HSZ could even indicate that free gas may co-exist with hydrates within the HSZ. Blanking of the reflection amplitudes above the BSR is variable. Instantaneous frequency analyses reveal a low-frequency shadow beneath the BSR.

We also collected lake-bottom reflection/refraction data, using GEOMAR's "Ocean-Bottom Hydrophones". Several profiles were recorded with a medium-resolution single airgun with sufficient energy to penetrate below the HSZ. The velocity information obtained from these measurements shows a distinct low-velocity layer below the base of the HSZ. Above, several higher-velocity layers are recognised. Modelling of interval velocities in this zone indicate hydrate presence of 5 to 8% of pore volume.

We also acquired new medium-frequency, single-channel airgun data at the BDP-1997 site (Baikal Drilling Project), providing the first acoustic images from this location. Hydrates (10% pore volume) were retrieved from 121 and 160 m sub-bottom depth, but still about 200 m above the base of the local hydrate stability field. Remarkably, the seismic data at the drilling site show no indications for the presence of hydrates at the hydrate-recovery depths (no acoustic blanking, no BSR). These results were used to roughly estimate the amount of carbon stored in the Lake Baikal hydrate reservoirs, showing that most probably they do not form a potential future energy resource.

CC09 : WEpm28 : G1 High Resolution Seismic Images of Near Sea-Floor Gas Hydrate Occurrences and Fluid/Gas Migration Zones within the Hydrate Stability Zone

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In many cases the presence of gas hydrates is assumed where bottom simulating reflectors (BSR) were identified in low frequency seismic records, indicating an acoustic impedance decrease due to free or dissolved gas beneath the base of probably massive hydrate layers. Whereas the deeper limit of the hydrate stability zone is most pronounced in conventional seismic data, the structural framework and the distribution of hydrates, gas and fluids within the hydrate stability zone are much more difficult to image and the relationship between hydrate concentration, pore pressure and the effect of fluid movement to seismic signatures within the stability zone is still a matter of research and difficult to analyse.

From recent cruises to the southwest African and Cascadia continental margins (R/V Meteor M47/3 and R/V Sonne SO 149 and SO 111) examples are shown where different seismic systems spanning a frequency range from <100 Hz through >4000 Hz are combined to study near-surface sedimentary sequences at multiple scales. Digital echosounder data and multichannel seismic data with a small volume watergun and a GI Gun were collected simultaneously to identify pathways for methane supply to surface, details of vent sites and their sea floor expressions, characteristics of near-surface hydrate occurrences as well as the fine structure of BSRs.

Besides the structural images, which also become more detailed with increasing frequency, seismic amplitudes turned out to be most sensitive for detecting fluid and/or gas migration zones. Columnar acoustic blanking zones may be attributed to higher porosities, the lack of compaction or a structural disturbance. Carbonate concretions as indicator for continuous supply of methane to the sea floor, were imaged as flat, high amplitude horizons in digital echosounder data. Their mapping provided relationships to local venting at fault zones. High amplitude layers were observed also within the hydrate stability zone in digital echosounder data at shallow depth of several tens of meters. Derived from their spatial distribution, they seem to indicate either the upper limit of gas hydrates or horizons of lateral hydrate growth initiated from local methane supply structures. In all cases, small scale sediment tectonics from accretion at an active margin or slumping on a passive margin were probably the most likely causes for anomalous surface features, which are best imaged in sedimentary environments with uniform layering.

CC09 : WEpm29 : G1 New Seismic Reflection Data from the Blake Ridge Hydrate Province, SE U.S. Margin: Implications for Gas Dynamics and Methane Expulsion

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The Blake Ridge, offshore South Carolina, U.S. East Coast, constitutes a premier natural laboratory for the study of gas hydrate dynamics, because of its lithological homogeneity, tectonic simplicity, and wealth of existing hydrate studies, including ODP Leg 164. In September-October 2000, we acquired new seismic reflection and refraction data on the Blake Ridge for the purpose of quantifying the regional and local 3D structure of this large methane hydrate province. Three data types were acquired: (1) A 3D data set over a 250-sq-km area using a 4-km-long streamer; (2) Long-offset (6 km), high-fold (80) 2D regional reflection data;

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and (3) three-component ocean-bottom seismometer data specifically targeting P-to-S converted waves. The Blake Ridge as imaged on our new data is seen to be a highly dynamic region in which hydrate and gas distribution is governed by the complex interplay of sedimentation, erosion, methanogenesis, and gas migration. The data show clear cross-stratal reflections within the hydrate stability zone that likely come from layers of highly concentrated hydrate. These reflections occur on the northeast (eroding) flank of the ridge and are likely 'paleo-BSRs' left behind when erosional events lowered the BSR, thus freezing free gas into hydrate. Evidence for dynamic gas incursions into the hydrate stability zone (HSZ) comes in the form of vertical chimneys that appear to disrupt strata both beneath and above the BSR. In addition, strong evidence for gas expulsion into the ocean/atmosphere system exists beneath the Blake Ridge 'collapse' structure, which has formerly been interpreted as a structural collapse and large-scale sediment blow-out. Our new data show clearly that the 'collapse' is not a structural collapse, but rather a construct of large-scale sediment waves formed entirely by deposition and erosion. Indeed, the new data show similar features farther north on the ridge crest that also appear to be associated with a lack of free gas and weak or absent BSR. We suggest that stratal boundaries between sediment wave packages act as high-permeability pathways along which methane escapes into the ocean; the driving force for methane expulsion is likely overpressure generated by the high deposition rate of the sediment waves. Thus sediment waves on contourite drift deposits may be inherently 'leaky' reservoirs of methane hydrate.

CC09 : WEpm32 : G1 Short-Lived Mud Volcanism and Cold Seeps Caused by Dissociation of Gas Hydrates in Lake Baikal

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Four cold seeps are studied in Lake Baikal's South Basin using side scan sonar in combination with detailed bathymetry, measurements of near-bottom water properties, and selected seismic profiles. The cold seeps occur at the crest of a fault block in the hanging wall of a large normal fault (the Posolsky fault), at a waterdepth of 1340 m to 1420 m. They were named Bolshoy (large), Stari (old), Malenki (small), and Malyutka (very small). The seeps at the lake floor are identified on side scan sonar and echosounding data and interpreted as flat-topped (craters, e.g. Malenki) and/or conical-shaped mud volcanoes (e.g. Bolshoy). Each vent is characterized by a near-bottom acoustic anomaly in the water column. Measurements of near-bottom water properties indicate a negative oxygen anomaly and a small but consistent positive temperature anomaly but no difference in salinity. The expelled fluids appear to be not much different from the lake water and most likely originate from shallow depth, probably from gas hydrate dissociation between 300 m and 150 m below the lake floor.

Combination with subsurface data from seismic profiles shows that the seeps occur where the base of gas hydrate layer (BGH) is irregular and shallowing rapidly towards the vent sites. Coincident with the shallowing BGH, positive heat flow anomalies occur. Local dissociation of gas hydrates from the base to the top is attributed to a pulse of hydrothermal heat flow along an active fault segment. Volumetric expansion associated to hydrate dissociation probably caused a high-pressure compartment bounded at the top by the elevated BGH. From the top of the dome-shaped BGH a vertical feeder pipe extends to the mud volcano at the lake floor, disrupting the horizontally stratified seismic facies. The mud volcanism seems to be short-lived, as is illustrated by the Bolshoy mud volcano that seems to be in a final phase of mud extrusion despite its recent initiation. The mud volcanoes and cold seeps are interpreted to be an example of a vigorous gas and fluid expulsion caused by gas hydrate dissociation due to a hydrothermal event. The duration of fluid and mud expulsion is limited by the amount of hydrate, by the duration of the hydrothermal pulse, or by the time needed for a new

equilibrium to be installed. This mechanism may be an explanation for traces of short-lived mud volcanism in other gas hydrate areas in a tectonically active setting.

CC09 : WEpm33 : G1 Methane-Hydrate Dissociation in the Lorca Basin (SE Spain) during the Mediterranean Messinian Salinity Crisis

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The Tortonian marls which were deposited in the Lorca basin (SE Spain) prior to the Messinian Tripoli Formation represent a rather homogeneous unit of some 1000 meters in thickness whose duration was probably more than 2 Myr (Rouchy et al., 1998). They contain discontinuous levels of indurated nodules and massive layers up to a few meters thick diagenetic dolomite. The oxygen and carbon isotopic compositions of these dolomites indicate that the carbonate diagenesis occurred mostly in ¹³C-rich and ¹⁸O-rich to ¹⁸O-poor solutions. The vertical distributions of the δ values of these dolomites are interpreted as the result of the past occurrence of gas-hydrate reservoirs where the methane source probably originated from the organic-rich marls. We postulate that the gas-hydrates contained in the Tortonian marls were destabilized during the water level drops related to the Messinian. The large amounts of methane released by the gas-hydrates dissociation were further oxidized as CO₂ during bacterial sulfate reduction; this process may have contributed to the partial to total replacement of the gypsum layers intercalated in the Tripoli Formation by diagenetic carbonates which are characterized by negative δ^{13} C values. Associated sedimentary structures include numerous syn-sedimentary deformations and brecciation which are the expression of important sedimentary instabilities, which could have been generated during the gas-hydrates decomposition.

Rouchy JM et al, *Sed. Geol.*, **121**, 23-55, (1998).

CC09 : WEpm34 : G1 Variability of Benthic Flux and Discharge Rates at Vent Sites Determined by In Situ Instruments

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A decade of research in the Cascadia accretionary complex has documented active venting of fluids and gases, prolific benthic chemosynthetic communities and the extensive accumulation of gas hydrate at the seafloor. Recent studies as part of the international TECFLUX program on Hydrate Ridge demonstrate that this site is an ideal laboratory for the understanding of gas hydrate dynamics and free gas expulsion. Spatial and temporal variability of bottom currents and temperature, fluid discharge, gas venting, energy and biogeochemical fluxes were recently documented using a great variety of seafloor instrumentation. These included ship-borne video-guided landers and observatories as well as video systems deployed by ROV. Measurements were conducted from hours to weeks at localities around active regions of fluid and gas venting. Results indicate, not unexpectedly, that fluid flux rates vary by many orders of magnitude spatially, due to the heterogeneity in fluid expulsion and underlying conduit patterns around vent sites. Methane released from gas hydrates induces changes of transportation rates and affects degradation rates of organic matter by the benthic communities. Seeps appear as a complex system with vertical and horizontal shifts in the relative dominance of chemoautotrophic and heterotrophic processes with increasing distance away

from the seep. A surprising discovery was the temporal variability of free gas venting and aqueous flux rates. In situ measurements reveal that orders of magnitude in variability occurs at the highest aqueous flux rate sites, with episodes of reduced flow and even flow reversals. A short-period variability appears to correlate with tidally induced flow oscillations. Significantly, superimposed on the oscillations were fluctuations that lasted over periods of several days to weeks or longer. These temporal changes give a unique insight into the complex dynamics behind the hydrates and gas venting and must be understood before mechanisms responsible for hydrate formation/destruction can be defined.

CC09 : WEpm35 : G1 Gas Hydrates in Surface Sediments of the Northern Congo Fan- Geochemical and Microbiological Characterization of the Top of the Gas Hydrate Stability Zone

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During cruise M47/3 of RV Meteor in June/July 2000 gas hydrates have been found at and close to the sediment surface on the Northern Congo Fan. Besides a mud volcano site in the North Atlantic this is the only passive continental margin location where gas hydrates have been recovered directly from the sediment surface. Two gravity cores were retrieved from this hydrate site. In one of these cores gas hydrates occurred below 4 m sediment depth, with the second gravity corer gas hydrates were recovered directly from the sediment surface.

The gas hydrates are associated with a pockmark which represents a common feature in the study area. Measurements of methane in the water column revealed elevated concentrations close to the sediment surface. The fact that these methane concentrations are significantly higher than background methane levels in bottom and deep waters suggests that there is a supply of methane from the sediment. We discuss whether the transport of methane into the overlying bottom water occurs via diffusion and/or advection from destabilizing gas hydrates or in relation with active fluid migration.

We present data for a sediment core which contained massive pieces of gas hydrate below a sediment depth of 4 m and give an estimation of the amount of gas hydrates present in these sediments. Concentration profiles of various pore water constituents allow the geochemical characterization of the transitional interval from hydrate-bearing sediments to the upper sulfate-containing zone of the sediment. Microbiological investigations have revealed the occurrence of aggregates of archaea surrounded by sulfate-reducing bacteria which have been recently identified (Boetius et al., 2000) in sediments of the Cascadia convergent margin. These consortia are most likely mediating the anaerobic oxidation of methane by sulfate.

Boetius A, Ravenschlag K, Schubert CJ, Rickert D, Widdel F, Giesecke A, Amann R, Jörgensen BB, Witte U & Pfannkuche O, *Nature*, **407**, 623-626, (2000).

CC09 : WEpm36 : G1 Pore-Water Anomalies of Submarine Hydrate Zones – Progress Made during the Past Decade

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The most important new contributions to the study of natural gas hydrates in the past decade have come from findings of the Ocean Drilling Program (ODP), notably legs 112, 141, 146, and 164, to a lesser extent legs 131 and 160. Leg 164 in particular was dedicated to gas-hydrate drilling in the classical Blake Ridge gas-hydrate field in the West Atlantic in an unprecedented multidisciplinary

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research effort (Paull et al., 1996, 2000). The most important progress of hydrochemical studies related to gas hydrates has been the growing awareness of the significance of diffusion-modulated advective processes shaping the chemical and isotopic pore-water profiles in hydrate zones. This started with qualitative evidence for advective flow obtained before the beginning of the decade from drilling the Peru (Cl- profile of Site 683) and Barbados (Cl- and CH₄-profiles, Site 671) active margins, continued with the Nankai Trough accretionary prism (low chlorinity water in lower part of Site 808) and the Cascadia margin (Cl-, Sr- and oxygen isotope profiles, sites 888-892) and culminated in the quantitative advection-diffusion model of Egeberg & Dickens (1999) for the passive margin setting of Blake Ridge. Advective-flow regimes appear to be different at active and passive margins as there is a tendency for the flow at active margins to be more focussed along landward-dipping thrust planes and faults in the wedge of imbricated thrust sheets that finds expression in the step-pattern of the pore-water profiles. For passive margins, but also for some active margin sites, advection is from sources below the drilled section, either at greater depth in the stratigraphic column (passive margins) or from the décollement zone (active margins).

We have learned that the well-known coupled pore-water anomalies that are ascribed to hydrate dissociation - downward chlorinity decrease combined with $\delta^{18}O$ increase (Hesse & Harrison 1981) - need not occur together in the presence of hydrates because the isotope effect may be overprinted by the effects of other reactions such as volcanic-ash alteration or by advection of low- $\delta^{18}O$ fluids. However, if the anomalies show up, hydrates are present almost invariably (with the exception of advected low-Cl-/high $\delta^{18}O$ waters). Coming to terms with the effects of advection and diffusion has allowed successful modeling of the simpler hydrate-affected pore-water profiles at passive margins. Instrumental for modeling are chlorine isotopes (Hesse et al. 2000) providing an effective tool to assess advection rates. The Egeberg & Dickens model allows estimation of hydrate concentration and distribution in the subsurface, because it separates the effects of advection, diffusion and hydrate dissociation, but critically depends on samples taken under in-situ pressure and temperature conditions. Among different methods to estimate hydrate concentration the geochemical method gives minimum amounts.

Egeberg PK & Dickens GR, *Chem. Geol.*, **153**, 53-97, (1999).
Hesse Ret al, *Proc. Ocean Drilling Progr., Scient. Res.*, **164**, 129-137, (2000).

Hesse, R & Harrison, WE, *Earth Planet. Sci. Lett.*, **55**, 453-462, (1981).

Paull CK et al, *Proc. Ocean Drilling Progr., Initial Repts.*, **164**, 623 pp, (1996).

Paull CK et al, *Proc. Ocean Drilling Progr., Scient. Res.*, **164**, 459 pp, (2000).

CC09 : WEpm37 : G1 In Situ Measurement of the Effect of Methane Hydrate Formation on the Microgeometry of Sediment and Rock

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Knowledge of the interaction of gas hydrates with the host sediment is required for models of hydrate growth, and for interpretation of acoustic signatures. Yet the instability of hydrate during recovery, and the linked resultant changes in the sediments, pore waters, and hydrate itself has made progress difficult. Here we report on the use of nuclear magnetic resonance (NMR) to measure in situ changes in sediment and rock as a result of methane hydrate formation. The experiments took place in Monterey Bay, California at a depth of 1034 m. Hydrate formation from CH₄ gas was induced in samples of porous rock and sand by a modification of the method of Brewer et al. (1). Hydrate was formed in specimens pre-positioned on the sea floor several months before measurement. NMR measurements were made with

a modified version of the well logging tool described by Kleinberg et al. (2). Sample placement and NMR measurements were carried out with ROV technology.

NMR signal amplitude is directly proportional to the volume fraction of liquid water in a porous medium, and the magnetization decay is sensitive to the liquid-water-filled pore size distribution of the porous medium. Laboratory measurements show gas hydrates are invisible to the nuclear magnetic resonance apparatus used in these experiments. Thus by comparing measurements on samples with and without hydrate present, NMR provides pore-scale information on the formation of hydrate. In the present experiments NMR measurements were made on samples containing hydrate. Then the samples were transported above the hydrate stability depth where hydrate volume was assayed by gas production. The samples were returned to the seafloor for repeat measurements, which were in turn compared to laboratory studies.

The mass balance assays showed that only small quantities of hydrate were formed in the samples. Nonetheless NMR measurements demonstrated the high degree of precision with which hydrate saturation can be measured nondestructively and in situ. Laboratory measurements demonstrated the capability of NMR measurements to estimate hydraulic permeability.

(1) Brewer, P.G. et al. (1997) *Geology*, v. 25, 407-410. (2) Kleinberg, R. L. et al. (1992) *J. Mag. Res.*, v. 97, 466-485.

CC09 : WEpm38 : G1 U Isotopes: A Sensitive Tracer for Pore Fluid Signatures in Authigenic Carbonates at Methane Vents

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Authigenic carbonates are widely distributed in the sediments of the Cascadia accretionary complex (Hydrate Ridge) (Kulm and Suess, 1990). They document not only their age, growth rates and the environment of their formation, but also preserve the geochemical signature and variability of the circulating, methane-rich fluids. Therefore, they represent an excellent archive of the temporal and spatial evolution of cold vents.

Layered gas hydrate-carbonates precipitate in soft sediments near the sediment-water interface. Methane-rich gases are most likely released from beneath the bottom simulating reflector (BSR). They intrude into the unconsolidated sediments mostly parallel to the bedding and form porous gas hydrates. In the so-generated secondary pore space layered aragonite precipitates in direct contact with gas hydrate. Aragonite that forms pseudomorphs after bubble structures confirm the close association with gas hydrate (Bohrmann et al., 1998).

From our observations, gas hydrate-carbonates are more abundant on the southern Hydrate Ridge. Their Sr isotope signatures indicate that they precipitated from seawater-dominated fluids. The average ⁸⁷Sr/⁸⁶Sr is 0.709164 (7) which is equivalent to seawater samples from this location.

U isotopes show more variability among the gas hydrate-carbonates and proved to be a sensitive tracer for pore fluid signatures contrary to Sr isotopes. The ²³⁴U/²³⁸U activity ratios of the gas hydrate-carbonates are as high as $\delta^{234}U = 416 \pm 4$, while seawater has a $\delta^{234}U$ of 144 ± 2 . Furthermore, the ²³⁴U/²³⁸U activity ratios lie on a binary mixing line. One endmember is seawater with a known U isotope composition. The second endmember is probably U that originates from porewater where ²³⁴U is enriched due to recoil effects.

U/Th ages for gas hydrate-carbonates from the southern Hydrate Ridge range from $1,700 \pm 60$ to $5,300 \pm 260$ years. One sample from the northern Hydrate Ridge gave an age of $68,900 \pm 1,400$ years. This observation confirms the hypothesis that the northern Hydrate Ridge is already a more evolved fluid venting system, whereas at the southern Hydrate Ridge venting has just started (Tréhu et al., 1999).

Another type of authigenic carbonate that we observed at cold vents of Hydrate Ridge are chemoherm-carbonates. They precipitate not in the sediments but in direct contact with seawater. ⁸⁷Sr/⁸⁶Sr have an average of 0.709152 (7) and the ²³⁴U/²³⁸U activity ratios have an average $\delta^{234}U$ of

153 ± 6 which are isotopic compositions typical for seawater. Focussed fluid flow creates steep, calcareous pinnacles that rise several tens of meters from the seafloor. The aragonites show high porosity and distinct layers of cements - possible indicators for high fluid flow and episodic aragonite precipitation.

U/Th ages of a pinnacle at the southern Hydrate Ridge range from $2,900 \pm 150$ to $10,800 \pm 640$ years. A chemoherm complex southeast of Hydrate Ridge is much older with an age of $268,000 \pm 5,500$ years.

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Wednesday PO Session

CC09 : WEpo01 : PO
Submarine Slope Failure Offshore Norway
Causes Rapid Gas Hydrate Decomposition and
Seafloor Collapse

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Offshore mid-Norway side-scan sonar and reflection seismic data indicate areas of seafloor collapse in close proximity to the northern head scarp of the Storegga Slide. The area involved in the seafloor collapse is 34 km² and the maximum observed collapse depth is 80 m. Reflection seismic data show evidence for laterally confined sediment mobilization and transport at 210 m beneath sea floor. Numerical modeling indicates that this was close to the depth of the base of the hydrate stability zone when the landslide occurred. We conclude that the seafloor collapse is a direct result of gas hydrate decomposition and subsequent gas and fluid escape. Readjustment of the steady-state geotherm deepened the base of the gas hydrate stability zone quickly after the landslide occurred. Thus, gas and fluid escape and associated sea floor collapse in this area are rapid processes.

CC09 : WEpo02 : PO
The Structural Control of the Methane Venting
Area in the Southern Basin of Lake Baikal,
Siberia

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Gas hydrates have been found in the near-bottom sediments within gas venting structures in the southern basin of Lake Baikal. The Baikal basin consists of three subbasins, separated by accommodation zones: the Academician Ridge between the north and central basins, the Selenga Delta Accommodation Zone between the central and south basins. The venting structures are located south of the Posolskiy Bank, which is a basement ridge with a thick sequence of sediments on top, trending NE, oblique to the main border fault. The Posolskiy Bank belongs to the Selenga Delta Accommodation Zone. It is delimited at its south-eastern side by the Posolskiy Fault with a displacement of more than 1000 metres. The venting structures are located close to an ENE trending fault, parallel to the Posolskiy Fault. Besides the fault which is delimiting the venting area at its northern side, and which has a vertical offset of its northern footwall of 25-30 metres, a fault with a vertical offset of its eastern footwall is not more than 5 metres. The venting area corresponds to a zone of local elevation of the lake floor, which is delimited at its northern side by the ENE trending fault and which is gently dipping towards SW in its southern part. It consequently appears as a zone of updoming probably related to a fluid and gas flow from depth, finally disrupted along its northern and eastern sides. The updoming is interpreted as the consequence of the disruption of the deep gas hydrate layer resulting from fluid overpressure. This interpretation is favoured by the regional pattern of the BSR, which shows strong variations in depth over this part of the south Baikal basin: it reaches minimum depths in the venting area and drops abruptly down to significantly larger depths north of the fault delimiting the venting area. The upward migration of the BSR is interpreted as a consequence of a regional fluid flow at depth, resulting in heat transport, consequent upward migration of the gas hydrates stability zone, updoming of the area and finally disruption along a fault zone. The origin of the fluid flow is discussed. Folding structures in the lake sediments along a NW-SE to WNW-ESE trend have been described in different parts of the central and southern basins. These folding structures are assumed to be related to left-lateral strike-slip movements along the eastern side

of the basin. In this assumption, the NE trending fault associated with the venting structures and the spatial alignment of the structures themselves would correspond to the direction of extension associated with the left-lateral strike-slip, whereas the NW oriented direction of compression would correspond to the fluid flow.

CC09 : WEpo03 : PO
Multi-Frequency Acoustic Data (Deeptow,
Surface Towed) on Hydrate Ridge: First Results

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During the SO150 expedition within the HYDGAS project framework on Hydrate Ridge, multi-frequency seismic profiles (sparker, watergun, GI-gun, airgun array, bolt gun) have been recorded with both deep-towed and surface-towed receivers in the immediate vicinity of ODP-site 892 (Leg 146) in order to characterise the acoustic signatures related to gas hydrate and free gas accumulations in the sediments. The data encompasses a total frequency bandwidth from 20 to 1500 Hz. The analogue signal detected by the deep-tow streamer was transmitted via a 8000 m long cable before being digitised in the acquisition unit. The submergence depth was typically 500 m (offsets 850-900 m, vessel's speed about 3 kt). Despite the geometrical corrections inherent to the deep-tow system, advantages of such records over surface-towed data are the improvement of resolution (both lateral and vertical) and enhanced signal/noise ratio, as is evidenced by comparing the simultaneously recorded deep-towed vs. surface-towed acoustics sections. Next to that, data with larger offset can emphasise the presence of shallow gas accumulations (AVO-effect).

At present, data are being analysed in GEOMAR and RCMG. First results indicate that the continuity and reflection amplitude of the BSR is observed to decrease with increasing source frequency, a feature explained in terms of vertical and horizontal resolution. GI-gun data give the best quality records with continuous high-amplitude BSR features in the entire area. On the very-high-frequency sparker profiles, the commonly-expected BSR is often replaced by a series of enhanced reflections, thought to be caused by gas saturation. This suggests that (1) gas migration and accumulation is stratigraphically and lithologically controlled and (2) the BSR as evidenced on lower-frequency data originates at the top of the free gas layer rather than at the base of the hydrate stability zone.

CC09 : WEpo04 : PO
Measured and BSR-Derived Heat Flow in an
Area of Gas Venting in Lake Baikal

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Recently gas venting sites associated with hydrate occurrences and destabilization, have been discovered on the bottom of Lake Baikal. The mapping of local BSR and heat flow variations in that area offered the opportunity to study the measured versus BSR-derived heat flow in detail and in relation with processes of hydrate destabilization. A large-scale BSR-derived heat flow map for the southern and central Baikal (Golmshtok et al., 1997) shows an overall good agreement with the existing probe data, but at individual stations deviations up to 50% occur in both senses. Near the venting sites in the southern Baikal basin strong fluctuations in the BSR depth and heat flow are known to exist. We present new shallow heat flow and BSR data from a small study area including the venting sites. We used the 2 m long GEOS-T thermoprobe for the in-situ measurement

of thermal gradients and conductivities. The BSR derived heat flow values have been calculated assuming a thermal conductivity/depth relationship as described by Golmshtok et al. (1997). The following geothermal features have been recognized: (1) Measured heat flow in the study area averages to 75 mW/m², which is slightly higher compared to the common background heat flow values for Baikal (50-70 mW/m²). At the venting site heat flow increases to a maximum of 110-160 mW/m². The shape of the anomaly is typical for the focused upflow of warm fluids, but the intensity suggests a relatively cold seepage. (2) In general there is a good correlation between the heat flow and changes in BSR depth. However, everywhere along the profiles the measured data is higher compared to the BSR derived heat flow values. (3) Along the venting site the correlation is very good. Measured values vary between 55 to 90 mW/m², and difference with BSR heat flow is only about 5%. (4) Southeast of the venting sites the measured thermal gradient variations correlate better with BSR depth changes than the heat flow. Here, measured heat flow (60-80 mW/m²) is up to 40% larger than estimates from BSR depth. In fact, the BSR-derived heat flow shows a regional low in this area and is most anomalous. The geothermal observations suggest that in the vicinity of the venting sites the thermal conditions in the sediments are disturbed, both near the surface and near the gas hydrate stability zone. The differences outlined between the shallow and BSR derived heat flow are believed to be the result of processes of heat and fluid flow destabilizing the hydrates, and offer a useful tool to constrain the mechanism of these processes.

Golmshtok AYa, Duchkov AD, Hutchinson DR, Khanukaev SB & Elnikov AI, *Russian Geology and Geophysics*, **38**, 1714-1727, (1997).

CC09 : WEpo05 : PO
Effect of Mud Volcano Activity and Gas
Hydrate Formation on Sub-bottom
Temperature Field

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Gas hydrate accumulations associated with submarine mud volcanoes are known in many areas of the ocean. Gas hydrate accumulation in submarine mud volcano Haakon Mosby is the most extensively studied including geothermal measurements. This accumulation has an axial-symmetric structure and is controlled by shape and size of the mud volcano. The formation of the accumulation is conditioned by ascending fluid flow that is the main source of hydrate-forming gas and water (Ginsburg et al., 1999). The central part of the mud volcano is also characterized by significant value of sub-bottom geothermal gradient more than 30°C/m. It can be explained by steady-state filtration of mud fluid. In this case the rate of fluid rise can account for 2.5 m/year. Based on this assumption the steady-state model of the temperature field and gas hydrate stability zone was calculated.

There is in addition a non steady-state discharge of warm mud that spread over the seafloor, eventually flowing down-slope from mud volcano center. This is evident from temperature data measured in the cores from the central part of the mud volcano. The similar sheet-flows of mud has been observed in Gulf of Mexico (MacDonald et al., 2000). Our investigation shows that time of cooling of warm mud layer with thickness of 4 m can reach 30 days for an assumed temperature of 20 deg C of warm mud. In this case the influence of this transient heat pulse on the underlying depth can be close to 10 m. By this is meant that the boundary of gas hydrate stability zone will be changed. Our results suggest that time-dependence of mud discharging should be considered when geothermal modeling of mud volcanoes are used.

Ginsburg GD, Milkov AV, Soloviev VA, Egorov AV, Cherkashev GA, Vogt PR, Crane K, Lorenson TD, Khutorshoy MD, *Geo-Marine Letters*, **19**, 1/2, 57-68, (1999).

MacDonald IR, Buthaman DB, Sager WW, Peccini MB, Guinasso NL, *6th International Conference on Gas in Marine Sediments, Abstracts Book*, 86-88, (2000).

CC09 Clathrates, Climate, and Carbon Budget (A)

CC09 : WEpo06 : PO Gas Hydrate Accumulation Associated with Fluid Discharge Structure in Lake Baikal

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During Russian-Belgian expedition-2000, gas hydrate accumulation was discovered by coring in subsurface sediments within fluid discharge structure of Malenkii (Southern Basin of the Lake Baikal). Gas hydrates have been collected at sub-bottom depths from 16 to 30 cm, and at a water depth up to 1380 m. Hydrates have been documented in 6 of 25 cores recovered in the study area. Based on the chromatography data methane is the dominant hydrate gas (97.4-99.0% by volume). The gas composition is consistent with gas hydrates structure I. The gas hydrate accumulation occur close to faults zone that serve as conduits for fluid migration in the sediments.

A summary of the interstitial water chemical composition data revealed presence of an ascending water flow moving up through the tectonically induced channels and cracks. Chemical and isotopic data suggest that this gas-saturated, relatively mineralized water, advecting on the lake floor is one of the major hydrate-forming components. Visual inspection of the cores revealed the following features: no hydrates or gas release from the sediments have been observed in cores from site close to gas hydrate-bearing point (5-9 m). However, at a distance of 110-150 m from the hydrate-bearing point, two sites with indicators of the gas expansion from the sediments have been recovered. These observations suggest that several small fluid vents exist within the fluid discharge structure of Malenkii. Gas hydrates were found out in one of such fluid vents, in others - gas-containing sediments were observed. Thus, at sufficient fluid saturation by gas, it can be expected that more hydrate-bearing points exist within structure of Malenkii.

The fact that gas hydrates are formed in the fresh water sediments of Lake Baikal with rather low mineralized discharge fluid involved, implies that such wide-spread indication of gas hydrate content as chlorinity of sediment water can not be used. Therefore more attention should be given to the data of the isotopic composition of oxygen and hydrogen of pore water, in particular, for estimation of gas hydrate content in sediments.

The study was supported by the Russian Foundation for Basic Research (grant 99-05-64247) and the Education Ministry (grant 992649 of Program "Russian Universities - Basic Research").

CC09 : WEpo07 : PO Visualization of Fluid Flow at Cold Seep Sites using a Novel 'Schlieren Optic' System

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Discharge of fluids is a widespread phenomenon in a variety of tectonic settings. At cold seep sites chemoautotrophic communities and precipitates of authigenic minerals mark areas of active fluid discharge. The determination of fluid discharge rates and the characterization of fluid flow pattern is a frontier of current research. For these investigations an optic system was developed which visualizes and characterizes the seepage. The so-called 'schlieren optic' is sensitive for heterogeneous water masses comprising fluids with different densities.

The optic system consists of a camera with a time-lapse controller, a LED light source and two spherical mirrors. Light beams running through heterogeneous water masses

will be differently refracted by the escaping fluids since the refraction index of water correlates with its density. Captured by the CCD camera, the discharged fluids are visible as 'schlieren'. To quantify the fluid flow rate, a funnel was integrated in the system to focus the released fluids. If the system is deployed above a suspected vent site the funnel is located directly on the sediment surface. The smaller exhaust port at the top is visible in the video screen. Escaping fluids are channeled through the funnel and are visible as 'schlieren' as long as their density varies from the ambient bottom water. The visible area is approximately 6 cm x 6 cm. Fluids escaping around the funnel are detectable as well. They appear as diffuse background outflow. The videos show immediately if fluids are escaping and whether they are caught in the funnel or not. Image processing allows to estimate the water discharge rate due to the particle velocity.

The optic system has been successfully used during the Tecflux-Expedition on R.V. Sonne cruise SO-148. In this research project the investigation of fluid flow associated with occurrence of near-surface gas hydrate at Hydrates Ridge, Cascadia margin, was of major interest. At this location, at 600-1000 m below sea level, vent fields are associated with methane-charged, low-salinity fluid emissions. Since there is a close relationship between the discharge rate of sulfide-enriched fluids and the occurrence of specific biological communities like bacteria mats and clam fields the highest fluid fluxes were expected in these areas. By using the frame of a TV-guided multiple corer the camera system was deployed at two locations on bacteria mats where a strong fluid flow could be observed and analyzed.

CC09 : WEpo08 : PO Fluid-Escape Features in Potentially Gas Hydrated Sediments

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A variety of fluid-migration related features from shallow faulting, vents, carbonate mounds and possible seafloor collapse can be found north of the Storegga Slide. Their spatial distribution is controlled by the proximal occurrence of geophysically inferred gas-hydrated sediments as well as the structural development. 3D seismic, newly acquired high-resolution seismic profiles and TOBI data image fluid-escape features and hydrated sediments in a cube approach. The gas hydrates seem to have a widespread distribution in the area, however a clear BSR is only visible on the southern part, an area with gas and fluid accumulations in domed structures and several pockmarks on the seabed. In the northern part hydrates are present more patchily. Here, gas and fluid migration processes are related to shallow small-scale faulting and ensuing seabed cracks. Carbonate crust samples taken by submersible investigations are showing light carbon isotopic compositions, indicating methane seepage in the area. Acoustic wipe-out zones, laterally migrating fluids and a weak BSR on the lower slope may indicate the decomposition of gas hydrates. Small fault and chaotic seismic reflection pattern exhibit preceding and maybe ongoing alteration of the surface and subsurface sediment architecture. Consequently it seems to be likely that gas hydrate decomposition could contribute to seafloor collapse.

CC09 : WEpo09 : PO Black Sea Methane Hydrates – How Many are They?

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This paper presents results of quantity evaluation of the Black Sea Methane Hydrate reservoir based on 6x6 minutes longitude - altitude data grid. It starts with calculation of the parameters of Methane Hydrate Stability Zone (MHSZ) and hydrate content evaluated then by different approaches to obtain an estimation tending to reality. The average water depth in the Black Sea from which methane hydrate start to form runs from 620 m to 700 m embracing a prone area of 288,100 km², representing 91% of the deep Black Sea basin. The average thickness of the MHSZ is 303 m with a bulk of sediment running from 85,310 to 100,280 km³. Generalized methods of estimation

set the hydrate content on 75 to 350x10⁹ m³ or about 10 to 50x10¹² m³ of gas methane are trapped within the Black Sea sediments in a form of hydrate. The more realistic approach is to define areas of great prospect for gas hydrate findings based on their spatial distribution, geology of the single area, evidences of shallow gas etc., and then estimate each of them, consider local peculiarities. Based on detail evaluation of mud volcanoes in the Sorokin Trough area, the hydrates connected with fluid escape along mud volcano pipes are estimated by analogy on a total amount of 0.7 km³ pure hydrate, or about 100x10⁹ m³ of methane gas (using a gas expanding factor of 140). The areas of abundance faults and fracture zones are estimated on the basis of the Caucasian area (Tuapse Trough and Shatsky ridge) and may contain about 3.2 km³ of hydrate (450x10⁹ m³ of methane). The hydrates connected with faults complicating diapir structures in the fifth Black Sea mud volcano provinces are also taken in consideration. Hydrates in the Danube deep sea fan are estimated assuming that they are confined mainly to more coarse sediments of channel-levee systems. The very low percentage of hydrate discovering and the fact, that no any BSR is observed there, dramatically reduce the hydrate content to less than 0.01% of MHSZ of the Danube fan, or on about 0.2 km³ of pure hydrate. The bulk of hydrate in the rest Black Sea submarine fans are set on 0.1 km³. Summing the obtained separate values, the total volume of the Black Sea hydrates is evaluated on 4.2 km³, or about 0.6x10¹² m³ of methane gas. Taking in to account the great uncertainty and number of inevitable assumptions made, we suggest that, from 0.1 to 1.0x10¹² m³ of methane are trapped within the Black Sea gas hydrates.

CC09 : WEpo10 : PO Experimental Modeling of Methane Hydrate Formation and Dissociation in Nature

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Recently, during the field activities on Lake Baikal, methane venting sites have been discovered in the southern basin of the lake. The seismic profiles show local disruptions of the gas hydrate layer and channels of gas flow up to the surface. Several craters on the lake floor have been identified by side-scan sonar. Above these craters plumes up to 25 metres above the lake bottom have been observed by echosounding. The nature of these bottom plumes is unknown. They may consist of gas bubbles, but also of gas hydrates forming in the bottom water at the venting when gases cool down in contact with the lake water. As it is known now such gas escapes at the bottom of the natural pools are quite widely spread. Taking into consideration, that this phenomenon concerns formation and dissociation of methane hydrate and problems of natural pool existence, the understanding of this process is of a great importance.

The purpose of this research was to simulate in laboratory the process of gas escape at the bottom of natural pools, and to define the physical-chemical conditions which provide formation of gas hydrates by gas venting. By now the following experimental work has been done.

The precision phase diagram of a system "water - methane - hydrate of methane" has been obtained in the temperature range 2-16°C and in the pressure range of 20-140 bar. The peculiarity of the work is the definition not only of lines of a three-phase equilibrium, but also of lines of formation and dissociation of the methane hydrate.

For more detailed understanding of processes happening after contact of gas and water in nature the data of the processes of methane dissolution in water and of methane hydrate formation have been obtained.

CC09 Clathrates, Climate, and Carbon Budget (A)

CC09 : WEpo11 : PO Effect of Salinity on Hydrate Phase Equilibria in Porous Media

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The huge amounts of hydrates in deep sea sediments represent a potential source of energy as well as a safety hazard to drilling operations. Furthermore, they influence ocean margin stability and global climate changes.

It is generally accepted that small diameter capillary media have an inhibiting effect on hydrate stability. The pore spaces of fine-grained marine sediments can be viewed as such a media. Marine sediments are very complex systems, and in addition to a pore size distribution control on hydrate equilibria, mineral surface properties and the presence of saline water could also play an important role. The large number of factors involved makes it difficult to accurately predict hydrate phase behaviour in marine sediments.

Considering the ever-increasing importance of gas hydrates in sediments, it is crucial to gain a better understanding of their formation and decomposition in porous media. Nevertheless, before hydrate formation and decomposition in complex marine sediment systems can be successfully described, it is necessary to understand the basic interactions between fluids, hydrates and the porous medium. Such information can be obtained by performing experiments in the controlled laboratory environment using well defined porous media and fluids.

The available hydrate equilibrium data in tight porous media are sparse and inconsistent. Recently, we have presented an improved test procedure and subsequent measurements obtained from porous glass beads. In this paper we focus on the effect of saline water on the hydrate equilibria in porous media. Experimental results on gas hydrate equilibria of methane in the presence of inhibited water (representing salinities typical to marine sediments) in porous glass with 251 Å, 128Å, and 82 Å pore sizes are presented.

Finally, a thermodynamic model taking into account the effect of pore size as well as the presence of saline water is constructed. The model, which is based on comprehensive thermodynamics, enables successful prediction of the experimental data. The model can also be used as a tool to simulate, and consequently to gain better understanding of, hydrate equilibria in marine sediments.

