

EUG XI



Symposium CC11

Clathrates, Climate, and Carbon Budget (B): Sub-Sea Floor Methane Deposits on the Margins of Europe, Arctic to Caspian: Seafloor Carbon Fluxes via Methane

Convenors

John Woodside
Euan Nisbet

CC11 Clathrates, Climate, and Carbon Budget (B)

Wednesday PO Session

CC11 : WEpo01 : PO Hydrocarbon Leakage and Gas Hydrate along the California Continental Margin

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Hydrocarbon gases, mainly methane, seep from three primary localities offshore California: (1) the Santa Barbara basin, (2) in and around Monterey Bay, and (3) the Eel River basin.

Hydrocarbon seeps at Coal Oil Point (Santa Barbara basin) include oil and gas resulting from advection of fluids upward through a breached anticline hosting an oil and gas reservoir. The main area of venting occurs in water depths less than 100 m and results in seafloor mounds saturated with oil. Hydrocarbon gases are rich in non-methane components and retain an unmistakable thermogenic signature. Gas hydrate does not appear on the seabed because the stability field for its formation is not present at these depths. However, gas hydrate may be present in deeper waters within the Santa Barbara basin.

Samples from four geographically and tectonically discrete cold seeps within the Monterey Bay National Marine Sanctuary were analyzed for their hydrocarbon content. The sediments contain gaseous hydrocarbons and carbon dioxide, as well as high molecular weight aliphatic and aromatic hydrocarbons. The latter hydrocarbons are derived from petroleum, modern marine and terrigenous sources. Of particular interest is the cold-seep site at Clamfield, which is characterized by the presence of thermogenic hydrocarbons (including oil) that can likely be correlated to oil-saturated strata exposed at Majors Creek near Davenport, California. Gas hydrate has never been recovered from any site in and around Monterey Bay, nor has gas been observed actively venting from any cold seep site. Gas hydrate may occur at greater depths within the cold-seep hydrocarbon system but has not been sampled.

The Eel River basin is the only known locality offshore California that hosts cold seeps, active methane vents, and gas hydrate. Nearby, onshore, there are numerous oil and gas seeps, and the area has produced minor quantities of light petroleum. The gases from offshore seeps and from gas hydrate are dry, indicating a microbial methane source, but trace amounts of thermogenic gases are present at both offshore seeps and in gas hydrate. Collectively, the carbon isotope composition of methane from gas hydrate varies between -69 to -59 parts per thousand, values typical of microbially-sourced methane. In contrast, the carbon isotopic compositions of gaseous methane in onshore and offshore seeps range from -53‰ to -31‰ and suggest mainly thermal sources. Gases from all three occurrences, onshore seeps, offshore seeps, and gas hydrate, apparently share ethane from a common source as suggested by similar carbon isotopic compositions. The combined molecular and isotopic compositions suggest that a mixture of thermogenic and microbial gases are escaping at the sea floor, and that the thermal component is similar in both offshore and onshore gas occurrences.

CC11 : WEpo02 : PO Gas-Hydrate-Prone Areas of the Ocean and Gas Hydrate Accumulations

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Investigations which were conducted in the Vserossiyskiy Nauchno-Issledovatel'skiy Institut Okeanologii resulted in conclusion about the major role of gas-containing fluids in submarine gas hydrate formation. Consequently, potential gas hydrate-bearing sea-basins have to be characterized by geological environment that would be favorable for filtration processes. On the other hand, the sources of the gas and conditions for gas generation have to exist. The third necessary condition is favorable temperature and pressure.

In terms of geological conditions, the potential gas hydrate areas have to occur within the limits of the basins with thick sedimentary cover or have to be confined to the areas characterized by the high rates of Cenozoic sedimentation or to

be located within the zones of subduction and accretional complexes. In many cases they have to be associated with oil and gas basins.

To estimate the area of gas hydrate prone regions in the ocean, the forecast map at 1:15 000 000 scale was compiled. This map exhibits all known occurrences of gas hydrates: accumulations discovered by core sampling and by deep-sea drilling, areas where seismic indications of gas hydrates were revealed, sites where indirect indications of gas hydrates were determined. The main content of the map are regions where formation of gas hydrate accumulations is possible by geological and PT conditions. Total area of these regions accounts for some 35.7 mln.sq.km, that is 10% of the area of all oceans, of which 12.3% falls on the Arctic offshore, 19.7% - on the Antarctic, 38.2% - on the Atlantic Ocean, 15.4% - on the Pacific Ocean, and 14.4% - on the Indian Ocean.

Analysis of all known gas hydrate occurrences has shown that there are two main types of gas hydrate accumulations: those associated with fluid discharge areas, which form near sea floor and are controlled by fluid conductors (mud volcanoes, diapirs, faults), and those which are not associated with concentrated fluid flow (occurred at significant subbottom depth), but also controlled by fluid migration. The last conclusion is confirmed by the results of deep-sea drilling which revealed spatial association of these accumulations to zones of freshening pore water and to relatively coarse-grain sediments.

The results of our studies demonstrated that the form and dimensions of the accumulations, associated with fluid discharge areas and distribution of the hydrate content within their limits are determined by concentrated flow of gas-containing fluids and diffusion-halo. Gas hydrate accumulation of the Blake Outer Ridge, the largest among known ones, is associated with ascending flow of fresh gas-saturated water which is controlled by the ridge structure itself, and gas hydrate distribution along the section is defined by lithological features both of bands and of individual interlayers.

The work was supported by the Russian Foundation for Basic Research (Grant No.99-05-64247).

Thursday AM Session

CC11 : THam02 : G1 Clathrates on the Margins of Europe: Is there a Danger of Release in Global Warming?

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Clathrate deposits occur around the margins of Europe. They are present in the Black Sea, Mediterranean, Atlantic margin, and Arctic Ocean. Amounts of methane stored in these deposits are large. Although there is much evidence for seepage of methane at present, there is little recent (post 1900) evidence for major releases, except in the Caspian, Black Sea, and perhaps the eastern Mediterranean. Seepage of methane occurs in variable (and still unquantified) amounts from seafloor seeps and vents as well as from mud volcanoes and, in the eastern Mediterranean at least, brine pools. Isotopic measurement of CH₄ in air arriving at Mace Head, Ireland, shows no obvious evidence of major clathrate release of methane in the mid-late 1990s, though sampling is infrequent. It is possible that sea-level rise in post-glacial time has stabilised deposits; however, in the eastern Mediterranean, bottom water temperature rise could destabilise thin patches of clathrates there. Moreover, large submarine megaslumps do occur at intervals, especially in the late Glacial/early Holocene low-stand of sea level, and it may be that over the next few centuries warming may eventually further destabilise clathrates, promoting slumping and release of CH₄ to the atmosphere. Arctic permafrost clathrates on land (as opposed to marine clathrates) occur at shallow level and may be vulnerable 100-500 years after warming. As Arctic air may warm significantly, this source could become a source of feedback to global warming.

CC11 : THam03 : G1 Effects of Gas Hydrate on Oceanic Methane Transport

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Various scenarios exist that relate gas hydrate destabilization to climate. Most of these mechanisms depend on the methane carbon transfer from the geologic reservoirs to the ocean and atmosphere. The fraction of methane released at the seafloor that might reach the atmosphere is determined by a series of transport and consumption mechanisms within the ocean. These include the rise and dissolution rates of buoyant hydrates and gas bubbles both within and out of the hydrate stability field, the advective transport of dissolved methane, the thickness of the well ventilated upper ocean layer, and the time scale of microbial oxidation within the water column. A series of experiments, which address some of these processes, were conducted using MBARIs ROV-technology.

Buoyant chunks of natural hydrates were released from 780 m depth at Hydrate Ridge, Oregon, by churning the seafloor with the ROV-arm and then followed upwards through the water column. Hydrate rise and shrinking rates were monitored. These data provide approximate dissolution rates and allow the minimal size of a hydrate chunk required to reach the sea surface to be estimated. The size change of individual crystals indicates that some hydrate dissolution occurred within the hydrate stability field. Faster size decrease and vigorous degassing was observed above the hydrate stability field. Bubbles, formed during decomposition, will usually rise less than 100 m before complete dissolution. Hydrate pieces with an initial diameter of 10 cm or more are likely to reach the sea surface.

Experiments were conducted to establish whether the dissolution rate of methane bubbles within the hydrate stability field is decreased by the formation of a hydrate skin. Both hydrate forming and non-hydrate forming gases were released from the ROV at various water depths below and above the hydrate stability boundary in Monterey Bay, California. Argon was used as the non-hydrate forming reference gas because it has similar solubility and diffu-

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sivity to methane. Different behavior of methane and argon bubbles within the hydrate stability field suggest that hydrate skins form on methane bubbles and can significantly slow down the speed of dissolution and increase the lifetime of the gas bubble. The time elapsed between the release of a methane bubble and the onset of hydrate formation is currently unpredictable. The initial behavior (i.e. pre-hydrate skin) is similar for both gases. Both floating hydrates and skin-protected bubbles are mechanisms which enhance methane transport through the hydrate stability field. The significance of these processes within the ocean-atmosphere system will be discussed.

CC11 : THam04 : G1 Seep Bubble Layer Deposition due to Sharp Bubble Dissolution

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In addition to their potential global and local environmental impact, natural marine hydrocarbon seeps create a unique bio-geochemical and fluid dynamical environment. Many of these unique seep conditions result from the presence of bubbles. Bubbles exchange gas with the surrounding water, accelerate the fluid, introduce turbulence, and transport oils and particles. Predicting the fraction of released methane, an important greenhouse gas, that is transported to the sea surface and released to the atmosphere depends strongly upon the environmental parameters, and the size distribution of bubbles produced. Bubble size can be divided into three size categories, small bubbles that dissolve, large bubbles that grow until they become unstable and break up, and intermediate bubbles that neither grow nor dissolve. These size ranges depend upon ambient conditions, i.e., depth, temperature, dissolved gas concentrations. Numerical simulations show that the ratio of final radius, r , to initial radius decreases very sharply for $r < 0.05$ mm. In one simulation for bubbles from 70 m depth, this ratio for a 0.1-mm bubble was 100%, for a 0.02 mm bubble it was 10%. If the size spectrum of bubbles produced at a seep is narrow and extends below the 100% survival size, it is likely that many of the bubbles will dissolve in a narrow depth layer. And importantly, when bubbles dissolve, they also deposit materials collected from the water (bacteria, oil, or sediment) at that depth.

Seeps can be classified as continuous or pulsing. While pulsing plumes produce a wide size range of bubbles due to large bubble break-up, continuous plumes produce a narrow size range of bubbles. Thus for continuous plumes, if the bubbles dissolve, they will likely all dissolve in a narrow range of depths. Using video and sonar images from the North Sea, simulations were performed on seep bubble transport, and bubble dissolution layer depths calculated. These were then compared with sonar and visual observations. Sensitivity analyses were also conducted to various environmental parameters.

CC11 : THam05 : G1 Monochromatic Sound Waves Recorded Offshore Ecuador: Possible Evidence of Methane Release

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The northern Ecuador-southern Colombia zone is recognized as a zone of high primary productivity, inferring gas hydrates in oceanic sediments. In this area, the Nazca plate underthrusts the south-American continent. This area experienced 4 historical large ($M > 8$) subduction earthquakes with associated tsunamis. During spring 1998, we conducted an offshore-onshore passive seismic experiment, using 15 3-components digital Ocean Bottom Seismometers (OBSs) in order to better control the local seismicity. Air-gun shots were used to compute the OBS's locations and orientations. During this 3 weeks experiment, we recorded strong monochromatic sound-waves. For some stations, those waves occurred more than 30% of the time. Other previous experiments and other later experiments in the same area, using the same equipments, do not show this type of signals, thus excluding instrumental noise.

The signal characteristics is as follows: Stable frequency of ~ 6 Hz, with large variations in amplitude (1 to 10 000) and duration (10 seconds to 10 hours). The monochromatic signal excludes a biological origin. - Emergent signal begins and ends, - Random occurrence from station to station, thus excluding distant sound-source (Talandier & Okal, 1996) - No correlation with earth tides or sea tides, - Source location, using goniometric methods when possible (i.e. when the signal is recorded on several stations), shows random location of local sources.

Sea-floor gas emissions have recently attracted the attention of the scientific community for their potential to increase the atmospheric concentration of green-house gases (CH_4 and CO_2). Although significant advance is being made in describing sea-floor gas seeps, the impact on global climate remains unknown and methods for quantifying fluxes from large areas of the sea-floor are lacking. Gas release or/and resonant behavior of saturated porous media, could possibly explain the recorded signals and if confirmed, this could open a new method in monitoring sea-floor gas seepage.

Talandier J & Okal EA, *BSSA*, **86#5**, 1529-1544, (1996).

CC11 : THam08 : G1 Gas Venting, Fluid Flow and Gas Hydrate Formation in Slope Sediments off Sakhalin, Sea of Okhotsk

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Pore water and geochemical sediment data indicate active diagenesis at the mid-slope area (Obzhirov flare) off northern Sakhalin. Here, fine-grained sediments composed of riverine particles and biogenic opal are accumulated at high rates. Two types of pore water profiles were found in this area. The first type is characterized by high dissolved ammonia, phosphate, bromide and iodide concentrations rapidly increasing with sediment depth. The second type shows a pronounced depletion in dissolved nutrients in the upper sediment layers (0-3 m depth) and a rapid increase in deeper layers. An early diagenesis model was developed and applied to simulate the first type of pore water profiles and the corresponding profile of particulate organic carbon. The model revealed that the increase of nutrients is due to the in-situ degradation of organic matter. The model also predicts that gas hydrate formation should start at depth of 15-20 m below the sediment surface where sufficient methane is build up to precipitate these methane-bearing solids. Another transport reaction model was applied to the second pore water type. Here, the model implies that downward advection of fluids and the penetration of nutrient-depleted bottom water into the surface sediments causes the observed distribution. Thin layers of gas hydrate were found at the interface between the upper depleted and the lower enriched layer at about 3 m below the sediment surface. The combined evidence suggests that gas bubbles rise to the surface to produce the observed gashydrates and to induce downward advection because the voids at depth previously filled with methane gas are refilled with water from above. The rate of this non-steady state process was constrained by fitting the model to the observed pore water profiles.

CC11 : THam09 : G1 A Methane Plume in the Water Column at Westspitsbergen Shelf: Of Ancient Origin but Influencing the Modern Carbon Cycle ?

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On cruises ARK-XIV and ARK-XVI of RV "Polarstern" in summers 1998 and 2000, respectively, methane anomalies were detected on the continental shelf off Westspitsbergen. Between 76° and 79° N, water samples were collected with the aid of Niskin bottles mounted on a rosette sampler on full depth vertical profiles on the shelf, and down to 1000 m water depth on the continental slope and inside Kongsfjord

and Van Mijenford. Methane was extracted by a vacuum ultrasonic method and concentration was measured gaschromatographically on board ship. For the determination of the stable carbon isotopic composition of methane ($\delta^{13}\text{C}_{\text{CH}_4}$), an aliquot of the gas sample was stored in small glass containers. For measuring the stable carbon isotopic composition of the dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) water samples were filled into glass vials, poisoned with a saturated solution of HgCl_2 , sealed with wax under 4°C air temperature, and kept cool until further treatment. Then on shore, $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{DIC}}$ were determined through continuous flow isotopic ratio analysis techniques (GC-C-IRMS).

The ultimate goal was to calculate the sink and source capacities for a northern high-latitude shelf region and to estimate the balance between the marine methane pathways. The $\delta^{13}\text{C}_{\text{CH}_4}$ values were determined in order to obtain information on genesis and origin of the observed methane anomalies and to further understand the mechanisms and pathways of incorporation of fossil methane into the modern carbon cycle. The $\delta^{13}\text{C}_{\text{DIC}}$ values were used to record the isotopic fractionation resulting from methane oxidation and to figure out whether highly depleted $\delta^{13}\text{C}_{\text{DIC}}$ values are incorporated into biogenic calcite. The latter process would have important implications for paleoclimatic reconstructions based on the isotopic composition of calcareous fossils.

The methane concentrations are up to two orders of magnitude higher than the background concentration level in bottom and intermediate water masses. Although concentrations are decreasing upwards, at the majority of stations the surface water is supersaturated related to the atmospheric methane level, indicating that the continental shelf and fjords off W-Spitsbergen act as a source for atmospheric methane. The methane exchange with the atmosphere is calculated and flux rates are presented. The water column of all of the stations measured on the shelf of Westspitsbergen, in the Kongsfjord, and in Van Mijenford is affected by methane injections from bottom sources. The provenance of these methane enrichments is discussed in relation to yet undetected gas vents on the shelf. The stable carbon isotopic signature of methane indicates thermogenic as well as bacterial origin and contributes to the characterization of different kinds of gas vents. The calculation of isotopic fractionation processes between methane and DIC helps to distinguish between different modifications of the original plume signal due to methane oxidation, mixing and dilution with ambient seawater.

CC11 : THam10 : G1 Gas-Saturated Sediment Accumulations in the Black Sea and their Sonar Investigations

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The Black Sea, one of the largest inland seas in the world lying at the junction between Europe and Asia, is both oceanographically and geologically unique. Off the shelf, the water depth quickly plunges to an average depth of 2 km making it unusually deep for what would normally be termed a marginal sea. Although there is excessive supply of terrigenous sediment input (exceed 100 million tones per annum) in the Black Sea, pelagic sedimentation plays the major role in the deep basin (the total abyssal sedimentation is about 10 cm/k.). These sediments are rich in calcite and organic carbon, the latter showing a high degree of preservation due to anoxia in the waters below 100-150 m. It has been suggested that shelf and slope sediments of high deposition rate are methane sources, whereas the deep basin is methane sink. Methane is geologically (and economically) important for three reasons. First, it is postulated that methane production and migration in sediments may be one cause of massive slope failures, second, methane seeps may indicate the presence at depth of hydrocarbon reservoirs, and third, methane hydrate may be an important source of energy in its own right. In the deep basin mud volcano eruptions are almost certainly formed by breakdown of methane hydrate on a huge scale. Recent studies in marine geology indicate potential geo-resources in the Black Sea.

Methane seeps are a common feature around the basin, and mud volcanoes have been identified. It has been suggested that shelf and slope sediments of high deposition rate are methane sources, whereas the deep basin is methane sink. Methane is geologically (and economically) important for

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three reasons. First, it is postulated that methane production and migration in sediments may be one cause of massive slope failures, second, methane seeps may indicate the presence at depth of hydrocarbon reservoirs, and third, methane hydrate may be an important source of energy in its own right.

The Black Sea is one of the richest waters having immense hydrate accumulations. At the abyssal plain, the sediments contain a high amount of gas in layers that is marked as bright spots, cloudy spots, local disappearance of bedded layers and sometimes masking of the reflectors. The seismic records show another interesting acoustically anomalous reflector as sequence of pockets. These anomalous reflectors were interpreted as being gas (mostly methane) transformed solid gas hydrates, sometimes gas hydrate crystals, and they are often represented by dark strong reflections.

CC11 : THam11 : G1 Marine Gas Seeps and their Indicators – MAGIC

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Natural seabed gas seeps are known to occur throughout the world. They are found in a wide range of water depths and geological environments: from coastal environments to the deep waters of the ocean basins. Associated features include evidence of gas beneath the seabed (seismic features such as bright spots and acoustic turbidity; shallow gas accumulations and gas hydrates), seabed features (pockmarks, mud volcanoes etc.), benthic biological activity ('cold seep communities'), methane-derived carbonates, and gas plumes in the water column (Hovland and Judd, 1988).

MAGIC is an interactive GIS (Geographical Information System) which holds details of published reports of gas seeps and their indicators. It enables the distribution of features to be studied at any user-defined scale, and allows the user to identify and abstract information, and to identify the source document.

MAGIC will be of value in understanding the relationships and interactions between the lithosphere, hydrosphere and atmosphere, a topic currently recognised as of particular importance. It will provide the essential data for a re-evaluation of the significance of natural gas seeps to global methane budgets and the global carbon cycle. Also, the database provides valuable information about the distribution of gas-related geohazards.

Hovland, M & Judd, AG, *Seabed Pockmarks and Seepages: impact on geology, biology and the marine environment*, 293, (1988).

CC11 : THam12 : G1 Hydrocarbon Seeps on Deep Portuguese Margin

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During the TTR10 Cruise in summer 2000 several mud volcanoes were discovered at deep Portuguese margin at the water depths of 2200-3150 m. In seafloor topography, these structures have cone-like shape of tens to hundreds of meters in diameter with an altitude of meters to tens of meters. They are clearly identified on sidescan sonar imagery as high backscattering patches and are also observed on seismic and 3.5 kHz profiles.

Sampling of several of these structures revealed presence of typical mud volcanic breccia, strongly fluidized in most cases. Chemosynthetic fauna was found associated with active vents. Microcrystals of gas hydrate were observed in a core sampled from one of the mud volcanoes (the Bonjardin mud volcano). Presence of gas hydrate is also detected by low-chlorinity anomalies of the pore water.

Most of the cores sampled from the mud volcanoes are noted for abnormal gas content. Methane concentrations measured are up to 10-25 ml/l that is by 3-4 orders of magnitude greater than the background values from hemipelagic sediments of the area. Some cores feature very high concentrations of C₂-C₃ homologues. The C₁/C₂+ ratio varies between 45 to 1. Content of unsaturated hydrocarbons sharply decrease down the sedimentary column is nearly zero in samples with high gas concentrations. The TOC values does not change significantly along the cores, amounting to 0.3-0.5 percent.

All these geochemical characteristics clearly indicate thermogenic nature of the hydrocarbon gas and possibly suggest its relation to deeper oil and gas accumulations.

CC11 : THam13 : G1 Composition of Gas Hydrate-Forming Fluids in the Gulf of Cadiz

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The study areas of mud volcanism located on the Moroccan, Portuguese and Spanish continental margins (Gulf of Cadiz) was investigated in 1999-2000 during the 9-10-th international expeditions on board R/V "Professor Logachev" within the framework of the UNESCO-IOC Training Through Research Programme. A number of mud volcanoes were discovered using multibeam mosaic of Naval Research Laboratory (USA) and data was collected by seismic profiling, ORTECH deep-towed combined sidescan sonar, OKEAN sidescan sonar and 5-kHz subbottom profiler. Gas hydrates have been sampled for the first time with a gravity corer from two of the mud volcanoes in this region (stations AT206 G, 208 G (TTR9), AT238 G (TTR10) 907-910 m water depth, Ginsburg mud volcano; AT246 G (TTR10), 3060 m water depth, Bonjardin mud volcano).

Chemical (elemental) and isotopic analyses of about 170 samples of pore water from mud volcanic sediments were carried out. The results of these analyses testify to considerable variations in chlorinity, the Mg/Cl ratio and the isotopic composition of oxygen and hydrogen in water. Gas hydrate-bearing intervals of sediments recovered from Ginsburg and Bonjardin mud volcanoes is characterized by low chlorinity (to 450 mM and to 415 mM, respectively). We suspect that gas hydrates also occur in sediments from Yuma (980 m water depth) and Carlos Ribeiro (2200 m water depth) mud volcanoes based on the low (relative to ocean water) chlorinity in the pore water. Our data suggest that the chemical composition (chlorinity, Mg/Cl ratio etc.) of the mud volcanoes water is similar to the composition of pore water from pelagic sediments. Based on the chlorinity anomalies, gas hydrate content of Ginsburg and Yuma mud volcanoes sediments was calculated and account for 4-11% and 8-19% by pore space, respectively.

A distinct correlation between the chlorinity (gas hydrate index) and the isotopic composition of the water was revealed. The oxygen gets heavier with decreasing chloride concentration and increasing gas hydrate content, but hydrogen gets lighter in these conditions. This fact is in contrast with the isotopic fractionation during gas hydrate formation and could be a result of sea water and mud volcano water mixture. Mud volcano fluid is probably very high in oxygen (to 35 per mil) and light in hydrogen (to -70 per mil) for Ginsburg-Yuma mud volcanoes system. Water with such isotopic composition has not been described in open literature but theoretically can exist.

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Mazurenko LL, Soloviev VA, Gardner JM, *Abstract book of TTR9 Post Cruise Conference*, 31, (2000).

Mazurenko LL, Soloviev VA, Gardner JM, *Abstract book of VI conference "Gas in marine sediments"*, 97-98, (2000).

CC11 : THam14 : G1 Hydrocarbon Gas Composition and its Distribution in Sediments Related to Cold- Seeps. Summary of Data Obtained during Training Through Research (TTR) Cruises (1995-2000)

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A numerous of hydrocarbon gas samples from pelagic sediments, mud breccia deposits and gas hydrates were collected during six cruises (1995-2000) within the framework of the UNESCO-IOC Training Through Research Programme. During these cruises several areas of active fluid vents and mud volcanoes in the eastern Mediterranean and Black Sea, on the Voring Plateau and on the Moroccan margin were investigated. The composition and distribution of C₁ to C₅ hydrocarbon gases in pelagic sediments, mud volcanic deposits and gas hydrates have been determined for indication of a possible linkage with hydrocarbons that have migrated through zones of weakness from subsurface accumulations. The special interest was straight towards the relationship between individual hydrocarbons and organic matter content along the cores. Following on from the gas measurements three types of hydrocarbon gas mixture were observed. The first type includes basinal cores with background values of hydrocarbon gas concentrations. Unsaturated gases are predominated over those saturated and the good correlation between hydrocarbon gases and total organic carbon (TOC) content is observed. The second type is represented by cores with high concentration of methane while C₂, hydrocarbons, from C₂ through C₄, are present in minor contents. High concentration of C₂, hydrocarbons, from C₂ through C₄ is characterized by the third type of hydrocarbon gas mixture. Types two and three have shown abundance of saturated gases over those unsaturated, and absence of correlation between TOC content and hydrocarbon gas concentration. In some of these cores gas hydrates were recovered. It is worth to be noted, that in some cores, taken from active mud volcanoes or pock marks the unsaturated hydrocarbons, such as ethene and propene, were not detected or presented in very small amounts. This fact allows for speculating that microbiological activity is affected by rather rapid fluid inflow, which probably inhibited the organic matter destruction processes. Therefore, the investigated areas of fluid vents and mud volcanoes demonstrate presence of allochthonous hydrocarbon gases with high input of hydrocarbons associated with hydrocarbon accumulations.

CC11

Clathrates, Climate, and Carbon Budget (B)

Thursday PM Session

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Methane-Related Authigenic Carbonates of Eastern Mediterranean Mud Volcanoes: Sources of Diagenetic Fluids and Role of Micro-Organisms

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Authigenic carbonate crusts formed at seafloor cold seeps are a sink for methane carbon migrating from depth or being released from shallow gas hydrates and possibly contribute in regulating ocean-atmosphere carbon fluxes (Ritger et al., 1987; Matsumoto, 1989). To investigate the geochemical and microbiological processes that induce carbonate crust formation we conducted mineralogical, stable isotope, organic geochemical and phylogenetic studies of carbonate crusts formed on submarine mud volcanoes and brine seep areas of the eastern Mediterranean Sea.

Here crusts form by precipitation of carbonate cements (mainly aragonite and magnesian calcite) in the shallow pore waters of mud volcanic and pelagic sediments. Most of the carbonate cements are depleted in ¹³C (δ¹³C < 20‰ vs PDB) indicating methane as the major source for the carbonate carbon. The crusts show a large range of δ¹⁸O values (1.07 < δ¹⁸O ‰ PDB < 7.08); the highest values are up to 4 ‰ enriched in ¹⁸O compared to expected values for aragonite and magnesian calcite precipitating from modern eastern Mediterranean bottom waters. Precipitation during the Last Glacial Maximum could account for the observed ¹⁸O enrichment, but a synchronous mechanism of formation is needed and massive gas hydrate destabilisation during this period is highly improbable due to the stabilising effect that P/T conditions then had on gas hydrate accumulations of eastern Mediterranean mud volcanoes. Rather, the highest δ¹⁸O of carbonates values could be due to precipitation from modern gas hydrate-derived fluids and/or to the seepage of ¹⁸O-rich relic brines of Messinian age (Aloisi et al., in press).

The organic geochemical and phylogenetic investigations allowed us to assess the microbial processes that lead to carbonate crust precipitation (Aloisi et al., submitted). The assemblages of micro-organisms we identified include methane consuming archaea and sulphate-reducing bacteria which oxidize methane anaerobically increasing pH and carbonate alkalinity and induce carbonate crust formation by producing supersaturation conditions with respect to carbonate minerals. Furthermore, the steep dissolved sulfate gradients produced by microbial sulfate reduction exert an important control on aragonite versus magnesian calcite precipitation.

Our study provides new insight into the processes that lead to the formation of authigenic carbonates at cold seeps. Knowledge of these processes is essential to study ancient methane release events and to constrain present and future methane biogeochemical cycles.

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Spatial Variability in the Anaerobic Methane-Oxidizing Microbial Community in Mediterranean Mud Volcanoes: Evidence from Lipid Biomarkers and Carbon Isotopic Compositions

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Fluxes of methane to and from the atmosphere are influential in moderating earth's climate, potentially over both long (e.g. millions of years) and very short (e.g. instantaneous) time scales due to the strength of methane as a greenhouse gas. Methane has been shown to accumulate in gas hydrates associated with convergent zones, and often cold methane seeps are associated with these gas hydrate accumulations, such as those that occur in mud volcano fields in the eastern Mediterranean Sea. These cold methane seeps stimulate and support a significant biological community, including microbes (archaea and bacteria) as well as macrofauna such as clams, mussels, and tube worms. The biological communities surrounding methane seeps appear to completely scavenge the evolving methane as it exits the sediments, consequently this methane never reaches the atmosphere. Numerous studies have implicated anaerobic methane oxidation as the primary process scavenging methane from cold seeps and incorporating it into organic matter; however, the specific mechanisms and pathways of methane assimilation in these biological communities are poorly understood. The present study investigates possible pathways of methane incorporation into microbial biomass. A number of extremely carbon isotopically depleted biomarkers have been identified which suggest that the process of anaerobic methane oxidation is being mediated primarily by a consortium of archaea and bacteria. Archaeal biomarkers identified include archaeol, hydroxyarchaeol, glycerol dialkyl glycerol tetraethers (GDGT's), and isoprenoid hydrocarbons. Bacterial biomarkers identified include hopanoids (such as diplotene) and fatty acids. The distributions of these compounds vary significantly between different sub-environments, and also within a few centimeters depth in a single core. The distributions and carbon isotopic compositions of these biomarkers suggest that methanogenic archaea are carrying out reverse methanogenesis (methane oxidation) in the sediments surrounding methane cold seeps. In addition, the data suggest that these archaea are directly linked to sulfate reducing and sulfide oxidizing bacteria that are probably creating conditions within the sediments that are favorable for anaerobic methane oxidation.

CC11 : THpm23 : G1

Anaerobic Oxidation of Methane Mediated by a Microbial Consortium above Gas Hydrate

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At the Cascadia convergent margin off the coast of Oregon, discrete methane hydrate layers are exposed at the seafloor, at a water depth of 600-800 m corresponding to the hydrate stability limit. Undisturbed sediment cores were obtained using a video-guided multiple corer during RV SONNE Cruise SO143-2 and SO148-1 in August 1999 and 2000. Integrated over the upper 15 cm, the sulfate reduction rates in the zone of anaerobic oxidation of methane (AOM) are >100 mmol/m²/d and represent some of the highest values ever measured in cold marine sediments. The combination of biomarker studies involving stable isotope analysis and

fluorescence in situ hybridization provides evidence that a structured consortium of archaea and sulfate reducing bacteria (SRB) is responsible for AOM in these and other methane-rich sediments. These symbiotic microorganisms occur in extremely high numbers of 10¹⁰ cells per ml sediment. The methane oxidation rates mediated by these consortia were measured for the first time in parallel to sulfate reduction rates in surface and subsurface zones of methane seeping sediments containing gas hydrates. A large fraction of the methane from dissociating hydrates is converted to CO₂ via anaerobic oxidation with sulfate. New data are presented concerning the distribution, abundance and diversity of the archaea/SRB consortia in methane rich sediments.

CC11 : THpm24 : G1

The Small Sized Benthic Biota in Surficial Marine Gashydrate Sediments

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The effect of methane released from decomposing surficial gashydrates (SGH) on standing stocks and activities of the small sized benthic biota (SSBB), comprising bacteria, fungi, protozoa, and meiobenthic organisms, was studied at about 790 m water depth, at the Hydrate Ridge, Cascadia subduction zone. Extensive bacterial mats of sulfide oxidising *Beggiatoa* sp. and clam fields of *Calyptogena* sp., indicated presence of SGH in the sediment. Vertical and horizontal distribution patterns of the SSBB biomass was derived from DNA and total adenylates sediment assays. Potential bacterial exoenzymatic hydrolytic activity (FDA turnover), which represents a first step and is rate limiting in the degradation of organic matter was measured using fluorescein-di-acetate as substrate. Estimates of the sedimentary chemoautotrophic particulate organic carbon (C_{org}) production were determined by ¹⁴CO₂ uptake incubations in the dark. As input parameter of surface water primary produced C_{org}, inventories of chlorophyll a and pheopigments were determined. The mean SSBB biomass at clam field sediments (765 gcm⁻²) was 3.6 times higher than at the adjacent control sites (213 gcm⁻²). The mean SSBB biomass in bacterial mat sediments (209 gcm⁻²), which were almost devoid of eukaryotic organisms > 31 µm, was comparable to the control sites. Significant correlations between FDA, DNA and plant pigments imply that productivity of the SSBB at SGH sites is only partially uncoupled from the primary production of the surface water. Areal estimates of autotrophic C_{org} production at control sites, bacterial mats and clam fields were 6, 60 and 190 mgCm⁻²d⁻¹ respectively. Based on different models predicting vertical POC fluxes from primary production and water depth, these autotrophic C_{org} productions account for 5 - 17, 35 - 68, and 63 - 87% of the bulk C_{org} provided at the respective sites (sum of allochthonous C_{org} input through the water column and sedimentary autotrophic C_{org} production). At SGH sites sedimentary inventories of plant pigments were about half times lower than at the control sites. We suggest, that this is due to enhanced degradation of phytodetritally associated organic matter. The resulting low molecular weight organic carbon compounds might stimulate and fuel sulfate reduction, providing sulfide for the autotrophic C_{org} production in SGH sediments. A microbial consortium of sulfate reducing bacteria and methane consuming archaea apparently mediates anaerobic methane oxidation in SGH sediments. Through this syntrophic consortium the cycling of gas hydrate derived carbon might be linked with the cycling of allochthonous C_{org}.

CC11 : THpm25 : G1

Anaerobic Methane Oxidation in Euxinic Waters of the Black Sea is Mediated by Archaea

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The release of methane from oceanic gas hydrates is thought to contribute to the global greenhouse effect (Hansen et al., 2000) and has been suggested to have induced some of the largest global climate changes in Earth's history (Dickens et al., 1995; Hesselbo et al., 2000). The identification of sources and sinks of methane in the marine environment are thus of critical importance. The

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Black Sea is the largest euxinic basin in the world and its sediments are an important source for methane: the annual methane flux formed in the sediments is estimated to be 2.9×10^{11} mol methane (Reeburgh et al., 1991). However, only ca. 1% of this flux reaches the atmosphere due to oxidation in the water column. Almost all methane (99.9%) is oxidized anaerobically in the euxinic part of the water column (Reeburgh et al., 1991). Apparently anaerobic methane oxidation in the euxinic part of the water column is responsible for the low emission of methane from the Black Sea into the atmosphere but the organisms responsible for this process are presently unknown.

To investigate the organisms involved in this process we collected suspended particulate matter (SPM) collected at the oxic and euxinic zones and surface sediments from the Black Sea. They were analyzed for archaeal membrane lipids and their stable carbon isotopic compositions were determined. Specific archaeal-derived compounds (biphytanes with 0-2 cyclopentane rings) derived from SPM collected from the euxinic waters showed a significant depletion in ^{13}C (up to -59‰ for the monocyclic biphytane) in contrast to those from oxic SPM or sediments. This depletion was coupled to a significant increase in the relative concentration of the monocyclic biphytane, indicating a specific contribution of anaerobic archaea using a ^{13}C -depleted source of carbon in the euxinic water column of the Black Sea. These observations are analogous to the situation at cold methane seeps and destabilizing hydrates-containing sediments where the largest part of the methane is oxidized anaerobically by archaea in a consortium with sulfate-reducing bacteria (Pancost et al., 2000; Hinrichs et al., 1999).

Our result provide the first evidence that archaea, probably in consortium with sulfate reducing bacteria, are responsible for the efficient removal of methane in euxinic Black Sea waters. The lack of ^{13}C -depleted archaeal compounds in surface sediments suggest that, despite their important role in the biogeochemical cycling of methane, the responsible organisms are present in relatively low abundance in the water column and leave no characteristic fingerprint in the sedimentary record. This may perhaps explain the paradox that, despite the massive methane release proposed to have triggered global change during the Palaeocene/Eocene boundary and Toarcian anoxic event, so far no molecular fossils indicative of widespread methane oxidation have been reported in sediments deposited during these events.

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The influence of the pressure and temperature history on the gas-hydrate distribution in laboratory sediments is being investigated. Current research and observations of recovered samples indicate that hydrates form a variety of fabrics within the sediment and that this distribution of hydrate is a significant factor in hydrate stability, (Malone 1985; Ivanov et al 1998). Pressure vessels are being developed to enable laboratory quantification of the effect of such fabrics. Current investigations are concentrating on developing techniques for the growth of significant quantities of hydrates within sediments under controlled conditions. The physical properties of these hydrate/sediment assemblages will then be studied. Preliminary experiments have succeeded in forming stable CO_2 hydrates in sandy sediments, which serve as a useful step towards experiments with methane hydrates in the future.

Downhole geophysical logs of sediment-hydrates reveal anomalous values for seismic wave velocities and density due possibly to the increased shear rigidity of the sediment, (Goldberg and Saito 1998). Recently developed slope instability analyses undertaken in passive continental margins have been based upon the simulation of earthquake wave propagation through effective stress-controlled geophysical property models. The inclusion of sediment hydrate into these ground models significantly alters the geophysical property profile of the soil column. This in turn has a dramatic effect on the amplification of earthquake waves travelling through this column from the basement to the seabed, and thus the stability of the seabed in areas of potential hydrocarbon development.

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CC11 : THpm26 : G1 Gas-Hydrate Sediment Properties in Improved Ground Models for Slope Instability Evaluations

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The bulk of global organic carbon is stored in methane hydrates below the ocean floor. These ice-like solids can be formed within sediments from 'cages' of water molecules enclosing gas molecules and are only stable at high pressures and low temperatures. Recent work suggests that destabilisation of these sediment-hydrates could trigger catastrophic slope failures on ocean margins, (Max and Dillon 1998; Mienert et al 1998). The liberation of 'greenhouse' gases during destabilisation may also have devastating effects on global thermohaline circulation.