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Fumigation of agricultural soils prior to planting row crops constitutes the largest anthropogenic source of methyl bromide (MeBr) to the atmosphere. Typically, more than 60% of the MeBr added is lost to the atmosphere during the 5-6 day fumigation period. The remainder is oxidized by bacteria or otherwise degraded in the soil. In experiments using washed cells of methylotrophic bacteria isolated from agricultural soil (strain IMB-1), oxidation of MeBr, methyl chloride (MeCl) and methyl iodide to CO₂ resulted in large (up to 70‰) fractionation of stable carbon isotopes (Miller, et al. 2001). By contrast, fractionation measured in field soils using both in situ techniques and bottle incubations with MeBr was less than 35‰. This discrepancy was initially attributed to the large transportation losses that occur without isotopic fractionation during field fumigation. However, this rationale cannot explain why bottle incubations with soil resulted in lower fractionation factors than incubations with bacterial cultures.

We conducted additional laboratory bottle experiments to examine the biological and chemical controls of carbon isotope fractionation during degradation of MeBr and MeCl by soils and bacteria. Soils were collected from a strawberry field in Santa Cruz County, California within two weeks of the start of each experiment. The rate of removal of methyl halides from the headspace was greatest during incubations at soil moisture contents around 8%. Increasing the amount of soil and hence native bacteria in each bottle minimized the lag in uptake by up to several days. No lag was observed during incubations of soils with added IMB-1. Stable isotope fractionation factors were similar for degradation by live soil and live soil with added IMB-1. Heat-killed controls of cell cultures showed little uptake (<10% over 5 days) and no isotope fractionation. Heat-killed soil controls, by contrast, demonstrated significant loss of MeBr (20-30%) with isotope fractionation factors comparable to live soil. Loss of MeCl during the same time was lower (<10%) however isotope fractionation was comparable to live soil.

Our results indicate that bacterial oxidation in soil rapidly consumes methyl halides but only partly controls the fractionation of carbon isotopes. Two chemical processes also act to remove MeBr in soil, hydrolysis and nucleophilic exchange with Cl⁻, both of which result in fractionation of carbon isotopes. Hydrolysis does not remove MeCl. It seems likely that fractionation in soil could result from a combination of biological and chemical processes, but since they all have sizeable fractionation factors associated with the removal of methyl halides, the relative rate of each process may not be as important as the total amount of methyl halide degraded. Attempts to constrain our understanding of atmospheric methyl halide budgets using stable isotope signatures of sources and sinks will have to rely on this type of information regarding the net isotopic impact of methyl halide uptake by soils.

Miller, L.G., Kalin, R.M., McCauley, S.E., Hamilton, J.T.G., Harper, D.B., Millet, D.B., Oremland, R.S., and Goldstein, A.H. (2001) Large carbon isotope fractionation associated with oxidation of methyl halides by methylotrophic bacteria, PNAS, vol. 98, 5833-5837.

B12A-0115 1330h POSTER

Simulating the interannual variability of the ¹³C isotope signature of the atmospheric CO₂ concentration with an integrated soil-vegetation-atmosphere-transfer and carbon cycle model

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Interannual variations of the global mean atmospheric concentrations of ¹²CO₂ and ¹³CO₂ largely reflect climate induced year-to-year imbalances of the carbon fluxes from the different global carbon reservoirs and, thus, their climate sensitivity. We employ the apparent interannual variation of the global terrestrial carbon fluxes as inferred from inversion studies of the atmospheric CO₂ concentration to evaluate simulations with the integrated soil-vegetation-atmosphere-transfer and carbon cycle model SCS. The model, driven by satellite observations and meteorology, is designed to be employed as a land surface parameterization within an atmospheric general circulation model. In addition it simulates complete cycling of ¹²C and ¹³C through the terrestrial biosphere using ecophysiological approaches. For the simulations on a global 1x1 degree grid reported here, the model was forced with NDVI data from satellite observations and ECMWF reanalysis data for the time period 1983-1993. We discuss the climate sensitivities of the various modeled carbon transfers and identify the most important fluxes on the interannual time scale. Furthermore we examine the isotope fluxes, the climate induced changes in ¹³C discrimination of C₃ photosynthesis and the variability of the isotopic signature from resulting from carbon cycling in ecosystems dominated by C₃ or C₄ plants. Inversion approaches to the determination of terrestrial and oceanic carbon sinks depend partially on assumptions about the isotope signature of the fluxes. We use our results to evaluate the sensitivity of those inversion based estimates of the terrestrial and oceanic carbon sinks on the isotopic signatures of the fluxes.

B12B MC: Hall D Monday 1330h

Geomicrobiology and Biogeochemistry of Gas Hydrate Systems I (joint with A, OS)

Presiding: C Zhang, University of Missouri; B D Lanolli, Univ of California

B12B-0116 1330h POSTER

Sulfate Profiles and Barium Fronts in Sediment on the Blake Ridge: Present and Past Depths of Anaerobic Methane Oxidation Above a Large Gas Hydrate Reservoir

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Ocean Drilling Program (ODP) Sites 994, 995, and 997 were drilled into a large gas hydrate deposit on the crest of the Blake Ridge (southeast U.S. margin) where upward CH₄ fluxes (F_{Out}) quantitatively consume pore water SO₄²⁻ over a narrow interval of sediment through anaerobic methane oxidation. High-resolution pore water SO₄²⁻ and sediment Ba profiles have been constructed at these sites to assess present and past depths of the SMI and (F_{Out}). Pore water SO₄²⁻ profiles are linear with zero SO₄²⁻ concentration occurring at 21.4, 21.6, and 22.8 mbsf at holes 994A, 995A and 997A, respectively. Using steady state solutions to diffusion equations with appropriate parameters, the steep SO₄²⁻ gradients support upward CH₄ fluxes between 7.2 and 8.6 mol/m²ky at present-day, with the range primarily reflecting different approaches for incorporating porosity. Taking into account the generally decreasing porosity with depth and the high clay content of the sediment, the best estimates for F_{Out} are 7.9, 7.6 and 7.2 mol CH₄/m²ky at sites 994, 995 and 997, respectively. However, non-steady state solutions to diffusion equations show that the SO₄²⁻ gradients do not imply steady state conditions. Elevated Ba concentrations (530-1410 ppm) exist in sediment between 18.23 and 20.65, between 17.31 and 20.31, between 19.40 and 21.80, and between 19.58 and 21.91 mbsf at holes 994A, 994C, 995A, and 997A, respectively. These Ba fronts coincide with highs in bulk sediment Ba/Al (to 0.025) and are caused by Ba cycling just above time averaged depths of the SMI. Because the Ba fronts lie immediately above the present-day depths of pore water SO₄²⁻ depletion, because the Ba fronts contain substantial Ba, and because no other Ba fronts are found in the upper 25 m at the three sites, the depth of the SMI beneath the seafloor has been nearly constant for considerable time (>18,000 years). Thus, CH₄ fluxes can be determined through SO₄²⁻ gradients and steady state solutions to diffusion equations. More importantly, F_{Out} through the crest of the Blake Ridge has not varied significantly across major changes in sea level and hydrostatic pressure.

URL: <http://www.elsevier.nl/80/inca/publications/store/2/1/2/>

B12B-0117 1330h POSTER

Biogeologic Control of Methane—Implications for Global Climate Change

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Methane, the most simple of organic molecules, is perhaps the most complex in terms of its role in the exogenic global organic carbon cycle. Sources of methane at the earth's surface are both biologic and geologic, with activities of humankind adding to the mix of sources. Of particular interest currently is methane from geological sources in the surface and shallow lithosphere. The amount of geological methane is enormous (likely exceeding 10 million metric tons of carbon as methane) with much of it stored in the form of methane hydrate. Methane hydrate, being both a sink and source of methane, is a major reservoir that acts to control the amount of methane that leaks from the lithosphere into the hydrosphere/atmosphere system. A second major controlling factor is methane oxidation, both anaerobic and aerobic, which converts leaking methane to carbon dioxide. Anaerobic methane oxidation is carried out by a consortia of archaea and bacteria, whereas, aerobic oxidation results from methanotrophy. Thus methane-hydrate storage and methane oxidation in sediment and water operate in concert to limit the amount of methane that escapes from the lithosphere/hydrosphere into the atmosphere. These controls have implications for global climate change because the storage and conversion of geological methane strongly limit the amount of methane that ever reaches the atmosphere where its greenhouse-gas properties could be effective. Only when the rates of methane oxidation cannot keep up with the rates of methane release from storage, can methane reach the atmosphere and become a factor in global climate change.

B12B-0118 1330h POSTER

Dissolution Rates of Synthetic Methane Hydrate and Carbon Dioxide Hydrate in Undersaturated Seawater at 1000m depth

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Dissolution of synthetic methane and carbon dioxide hydrates was monitored after their transport to the ocean floor at 1000m depth. Cylindrical test specimens were initially grown in the laboratory by combining either cold, pressurized methane gas or pressurized liquid CO₂ with sieved granular water ice, then heating the reactants through the H₂O melting point. Samples were then hydrostatically compacted to near-zero porosity, with resulting geometry of approximately 2.5 cm in diameter by 3-4 cm in length. Two samples each of methane and carbon dioxide hydrate were placed in a custom-made sample display rack having individual compartments for each sample with a transparent polycarbonate front window, and side and back walls of a flexible fine-mesh screen that permitted seawater flow around the hydrates. The sample rack was then transferred to the ocean in a stainless steel transport vessel pressurized with 10 MPa methane using the (ROV) Ventana.

On the seafloor, the sample display rack was removed from the pressure vessel and secured in a stand attached to an autonomous underwater video recorder system using a time-programmable Hi8 video recorder. The samples were continuously monitored for 2.30 h using Ventanas HDTV camera system, then followed by 20.75 h observation with the autonomous Hi8 time-lapse camera system (15 s every 0.25 h), and additional 3.33 h HDTV observation at the end of the experiment. Loss of volume and dissolution rates of the hydrates were derived from the measurement of the change of the projected diameter of the individual samples over time.

During the first 2.30 h, the diameter of the two CO₂ hydrates decreased from 22 mm to 15 and 13 mm, respectively. Diameter loss followed a generally linear trend of 0.94 and 1.20 μm/sec, corresponding to a dissolution rate of 13 to 17 mole CO₂/m²h. Similar short-term oscillations about this linear trend were observed on both samples, suggesting a link to bottom current velocity. The CH₄ hydrates dissolved much more slowly, with a diameter loss rate of 0.09 to 0.097 μm/sec, corresponding to 1.2 to 1.4 mole CH₄/m²h.

The ratio of the dissolution rates of the CO₂ and CH₄ hydrates can be readily explained using a diffusive sublayer model for gas hydrate dissolution. Given the similarity of the diffusion coefficients of methane and CO₂, the ratio of their dissolution rates should be given by the ratio of their solubilities under the ambient P,T-conditions. We calculated the solubilities of methane and CO₂ in the presence of hydrates using the Redlich-Kwong-Soave equation-of-state and the gas-hydrate model of van der Waals and Plateeuw and derive a ratio of the solubilities of 10.5, which is in close agreement with our hypothesis.

The fast dissolution rate of CO₂-hydrate is comparable to the rate of dissolution of liquid CO₂, which implies that gas hydrate formation has no major consequences for the residence time of CO₂ in a "deep-sea lake" CO₂-sequestration scenario. The dissolution of several mm methane hydrate per day in undersaturated seawater implies that long-term survival of seafloor hydrate outcrops observed today must be sustained by hydrate regrowth. Changes in the appearances of such outcrops on sites visited over time could be explained simply by dissolution, without the assumption of changes in bottom temperatures or detachment of buoyant solid hydrate structures.

B12B-0119 1330h POSTER

Fatty Acids and Stable Carbon Isotopes of a Sulfate-Reducing Bacterium: Implications for Carbon Cycling in Organic-Rich Marine Sediments

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Sulfate-reducing bacteria have characteristic lipid biomarkers, which help delineate carbon cycling pathways under sulfate-reducing conditions. This is especially important for marine sediments because of the predominance of sulfate reduction in such environments. Little research has been done to determine carbon isotope fractionations associated with lipid biomarkers of known sulfate-reducing bacteria. We examined the fatty acid compositions and their carbon isotope ratios of *Desulfovibrio desulfuricans* G-20 using lactate, pyruvate, or formate as the electron donor and sulfate as the electron acceptor. No CO₂ or HCO₃⁻ was added during experimentation. G-20 grew well with lactate and pyruvate but only marginally, if at all, with formate. Diagnostic fatty acids of iso- and anteiso-15:0 and 17:0 were higher in formate and lactate cultures (5-17%) than in pyruvate cultures (2.5-5.0%). Carbon isotope fractionation of these and other fatty acids against total biomass was similar under lactate (-10.7 to -15.1‰) and pyruvate (-9.9 to -15.7‰) conditions, which may be due to the fact that no carbon splitting occurs during lactate degradation to pyruvate (DeNiro and Epstein, 1977). The fractionation was much smaller (0.1 to -8.21‰) under formate conditions, suggesting that a different biosynthetic pathway may be utilized by G-20 when it is incubated with this substrate or it is carbon limited. The results indicate that carbon isotopes of lipid biomarkers may provide insight into metabolic pathways and have implications of carbon cycling by sulfate-reducing bacteria in hydrocarbon-rich environments where the bacteria can grow on different organic substrates.

URL: <http://web.missouri.edu/~geosccz/research.html>

B12B-0120 1330h POSTER

Sulfur Cycling in Mud Volcanoes Along the Crimean Peninsula, Black Sea

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Recent sediment sampling (Leg 1, TTR-11 Cruise, R/V Professor Logachev, July-August 2001) in the north-central Black Sea was undertaken to characterize bacterial sulfur cycling associated with the abundant hydrocarbon vents in the region and, more specifically, with the products and pathways of anaerobic methane oxidation. Gravity cores and box cores from proximal and distal locations relative to specific vents revealed a complex and spatially varying array of sediment types ranging from mud breccias and enigmatic, homogeneous mud flows along the flanks of the volcanoes to both coherent and disrupted sections of the classic Unit 1-2-3 late Pleistocene-Holocene sequence in the deep Black Sea. Gas hydrates and/or carbonate crusts were also recovered at many localities. In order to track the sulfur cycle and specifically link bacterially mediated oxidation-reduction reactions and mineral precipitation to methane cycling, a detailed characterization of pore-water and solid-phase constituents was initiated. These efforts are emphasizing the concentrations and S-isotope relationships of dissolved sulfate and sulfide, iron monosulfide and pyrite, and organic sulfur fractions. The oxygen isotope trend for dissolved sulfate will also be tracked. All of these analyses will benefit from high-resolution sampling across the subsurface maximum in bacterial sulfate reduction rate and the corresponding maximum in methane oxidation marking the interface between upward migration of methane and downward diffusion of seawater sulfate. Additional analyses include (1) quantification of the reactive Fe reservoir as it relates to sources and sinks in the S cycle and (2) collaborative microbiology with an emphasis on 16S rRNA PCR approaches and lipid biomarkers.

Among other objectives, the goal of this research is to contrast the sulfur geochemical baseline that is well established for "typical" late Pleistocene-Holocene deposits of the abyssal Black Sea, including a recent model for the ubiquitous muddy turbidites, with patterns associated with the high fluxes of methane and other hydrocarbon gases via the mud volcanoes. Ultimately, the impact of the gas seeps on the basin-scale sediment and water-column chemistries of the Black Sea will be explored, as will comparisons between models for Black Sea mud volcanoes and those developed from other marine settings.

B12B-0121 1330h POSTER

Coupled modeling of gas hydrate formation and anaerobic methane oxidation in near-surface sediments at Hydrate Ridge

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A comprehensive one-dimensional transport-reaction model (C. CANDI) was modified to investigate the formation of near-surface methane gas hydrates through ascending methane-bearing fluids at the sea floor of the southern summit of Hydrate Ridge, Cascadia Margin. A considerable salinity increase was observed 120 cm below the sediment-surface. A hydrate layer was almost unaffected from sampling and the adjacent sediment visually dry and fragmented. The piece of hydrate was removed immediately from the sediment before dissociation could commence. Samples separated in that way showed chloride concentrations up to 800 mM, a salt-enrichment of about 1.5 times the seawater salinity. Corresponding δ¹⁸O and δD profiles indicate that chloride anomalies certainly originated from hydrate formation.

The enhanced diagenetic model C.CANDI was applied to pore water chloride and sulfate profiles using steady state as well as non-steady state approaches to simulate the response of gas hydrate formation to varying fluid-flow rates and time. Upward fluid flow rates of 20 cm/yr, as determined by the model, are sufficient to account for the pore water sulfate profiles that arise from methane oxidation. The potential maximum concentration of dissolved methane in interstitial water in the presence of gas hydrate is given by thermodynamic considerations. The general trend of the measured chloride concentrations can be described by a source function for hydrate that produces significant quantities of gas hydrate at 120 cm sediment depth, the lower model boundary. Integrated hydrate formation rates of 10²-10³ mol m⁻² h⁻¹ were determined by the non-steady state modeling approach. These rates are about 10 times smaller than values reported from hydrate formation from water solution in the laboratory and several orders of magnitude larger than values calculated for Blake Ridge sediments (ODP 997).

B12B-0122 1330h POSTER

Tracing Viable Bacteria in Wadden Sea Sediments Using Phospholipid Analysis

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Lipid analysis is a commonly used tool for chemotaxonomical characterization of bacterial strains. In particular, phospholipids - determined as polar lipid fatty acids (PLFA) - have proven to be appropriate biomarkers for viable bacterial cells. In this study the lipid content of different bacterial isolates from an intertidal mudflat (Wadden Sea, NW Germany) was investigated. To identify the phospholipids present in the isolated bacteria, fractionated lipid extracts were studied using HPLC-ESI-MS and -MS-MS. This technique gives information on types of phospholipids and their corresponding fatty acid substituents. It could be shown by cluster analyses that the combined information of phospholipid types and corresponding fatty acids allows a better differentiation of bacterial groups than fatty acid patterns determined after whole cell hydrolysis. Sedimentary microbial communities were studied by an interdisciplinary approach using microbiological as well as geochemical techniques. Characteristic phospholipids were traced in the sediment cores (0-70 cm) in order to estimate the relative contributions of different bacterial groups to the sedimentary microbial communities. Seasonal variations of environmental parameters (temperature, sulfate concentrations, oxygen availability etc.) and their influence on the microbial communities were studied.

B12B-0123 1330h POSTER

Constraints of Microbial Production from Physical Models of Hydrate Formation

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We develop a numerical model to describe the physical processes that govern the volume and distribution of gas hydrate in marine sediments. We consider the environment of a deep continental margin where sedimentation adds organic material to the region of hydrate stability. Conversion of the organic material to methane by bacteria promotes hydrate formation and depletes the supply of organic carbon. We derive mass balance equations for the volume of hydrate and gas bubbles in the sediments and account for the changing concentration of dissolved methane and salts in the pore fluid. A biological component is incorporated in the model to allow the relationship between the biological communities and physical processes that govern hydrate formation to be studied. The effects of sediment compaction and the associated fluid flow are explicitly modeled. Allowances for deeper sources of fluid are also described, though we focus on the case of an idealized passive margin where carbon is input solely through sedimentation. The numerical calculations indicate that the key parameters in this model are the rate of sedimentation, the quantity and quality of the organic material, and a rate constant that characterizes the vigor of biological productivity. Model predictions for conditions that are representative of the Blake Ridge are compared with observations from Ocean Drilling Program Leg 164. We obtain a very good match to the observed chlorinity profile, including the region below the stability zone, without invoking any extraneous sources of freshening. We also predict that hydrate is unlikely to occupy more than 7% of the pore volume, in good agreement with observed estimates. Model predictions confirm that in situ microbial production provides a sufficient methane source for hydrate formation at these locales. Methane production is confined to the uppermost sediments where a high rate of carbon conversion (nominally 0.012 nmol mL⁻¹ per day) quickly degrades the available stock of metabolizable carbon.

B12B-0124 1330h POSTER

Environmental influences on cold seep communities

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Symbioses involving sulfide-oxidizing bacteria and various metazoan phyla dominate invertebrate assemblages at cold seeps worldwide. The predominant species found living at cold seeps in Monterey Bay are the vesicomyid clams *Calyptogena kilmari* and *C. pacifica*. Based on physiological measurements, it appears that the presence and distribution of these clams can reliably provide information about the sulfide, and perhaps oxygen, conditions of the sediment pore fluids. The growth and survival of these clams depend directly upon the productivity of their chemoautotrophic endosymbionts, which is fueled by the oxidation of sulfide. For this reason, sulfide and oxygen availability are thought to constrain symbiont and host production. Here we describe research concerning the productivity of the two common clam species in relation to environmental parameters. In addition, we investigated the phylogenetic relationships of these two species and their sister taxa, *V. lepta* and *V. gigas*, from populations occurring from the San Clemente Basin to the Victoria Island Margin. Divergence within these two lineages appears to be influenced by depth, larval dispersal, and environmental stability. Discovery of new seeps within Monterey Bay will also be discussed.

B12B-0125 1330h POSTER

Geochemical and Biological Implications of Anaerobic Methane Oxidation Associated with Gas Hydrates in the Gulf of Mexico

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An integrated lipid biomarker-carbon isotope approach reveals new insight to microbial methane oxidation in the Gulf of Mexico gas hydrate system. Hydrate-bearing and hydrate-free sediments were collected from the Gulf slope using a research submersible. Phospholipid fatty acids suggest that bacterial biomass is enhanced by up to 30-fold in gas hydrate-bearing sediment compared to hydrate-free sediment. Archaeal lipids are also abundant in hydrate-bearing sediment but only present in trace abundance in hydrate-free sediment. These results suggest that populations of Bacteria and Archaea are enriched at gas hydrate deposits in comparison to the normal marine sediment. In hydrate-bearing sediment, lipid biomarkers indicative of sulfate-reducing bacteria have $\delta^{13}\text{C}$ values ranging from -48‰ to -70‰ and archaeal lipids indicative of methanogens have $\delta^{13}\text{C}$ values ranging from -74.9‰ to -99.3‰ . These results suggest that sulfate-reducing bacteria and methanogens are involved in the oxidation of methane and contribute to increases in microbial biomass in gas hydrate samples. In the hydrate-free sample, fatty acid biomarkers have $\delta^{13}\text{C}$ values ranging from -27.6‰ to -39.6‰ , indicating that crude oil (average about -27‰) and/or terrestrial organic carbon (average about -20‰) are the likely carbon sources. Our results provide convincing evidence that sulfate-reducing bacteria and methanogens play an important role in anaerobic methane oxidation in the Gulf of Mexico gas hydrates. The coupled activities of methane-oxidizing and sulfate-reducing bacteria in the presence of hydrocarbons result in sequestration of carbon as massive accumulations of authigenic carbonate rock, thus impacting models of climate change based on carbon budgets. URL: <http://web.missouri.edu/~geoscscz/research.html>

B12B-0126 1330h POSTER

Methane-Derived Hydrogen in Lipids Produced by Aerobic Methanotrophs

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Combined hydrogen- and carbon-isotopic analyses of methane often provide important clues about its origin. Unfortunately, methane is not preserved in the geologic record so these analyses can only examine trapped or actively produced methane. The lipids of microorganisms that consume methane potentially record its isotopic composition, and are accessible throughout most of the geologic record. Those lipids therefore represent a potential means for examining the characteristics of methane released into the oceans over geologic history. We have examined the hydrogen-isotopic relationships between methane and lipids in the aerobic methanotroph *Methylococcus capsulatus* using cultures in which the D/H ratio of supplied water and methane were controlled independently. Resulting δD values were measured for a range of fatty acids, sterols, and hopanols using isotope-ratio-monitoring gas chromatography/mass spectrometry. We estimate that $31 \pm 2\%$ of hydrogen in every lipid we examined is derived from methane, regardless of whether cultures were harvested in exponential or stationary phase. The biochemical pathways responsible for the transfer of hydrogen from methane to lipids are not fully understood. Isotope fractionation associated with the utilization of methane (i.e., $\alpha_{\text{lipid/methane}}$) averages 0.986 for fatty acids and 0.789 for isoprenoid lipids. For water, fractionation ($\alpha_{\text{lipid/water}}$) averages 0.938 for fatty acids and 0.831 for isoprenoid lipids. Given typical δD values for seawater (0) and thermogenic dry methane (-150‰), fatty acids from *M. capsulatus* should have δD values near -95‰ , and isoprenoids should have δD values near -215‰ . Using $\delta\text{D}_{\text{methane}} = -300\text{‰}$, a value near the lower limit of those for biogenic methanes, we predict δD values for methanotroph fatty acids and isoprenoid lipids of -140 and -260‰ , respectively. It appears possible that D/H measurements of lipids from methanotrophic bacteria will provide useful hydrogen-isotopic information about methane that has been entirely consumed.

B12B-0127 1330h POSTER

The FISH-SIMS Approach: Isotopic Imprints of Methane in Diverse Microbial Assemblages

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One of the more important biogeochemical processes influencing carbon turnover in continental margin environments and cold seeps is the anaerobic oxidation of methane (AOM). Although there is convincing biogeochemical evidence for archaeal/sulfate-reducer cooperative involvement in AOM, methane-consuming anaerobic microorganisms have eluded identification until only very recently. Parallel phylogenetic gene surveys and isotopic determination of lipid biomarkers in methane-rich seep sediments suggested that diverse archaeal and bacterial assemblages are involved in AOM. Specifically, a novel clade of Archaea related to known methanogens (ANME-1 group), as well as microorganisms affiliated with the Methanosarcinales (ANME-2 group) and their syntrophic sulfate-reducing bacterial partner affiliated with the Desulfosarcina, have been

identified as likely candidate methane-oxidizing microorganisms. Both 16S rDNA and lipid analyses provide only circumstantial evidence linking these specific groups to AOM, however, because they are based on bulk analyses of whole sediments, rather than on the level of single microorganisms.

In this study, we provide the first concrete evidence directly linking two distinct groups of Archaea, the uncultured consortium archaeal ANME-2/ bacterial Desulfosarcina spp. and the archaeal ANME-1 to methane consumption in anoxic marine sediments. Using a novel approach combining fluorescent in situ hybridization (FISH) and secondary ion mass spectrometry (SIMS), we identified aggregations of ANME-2/ Desulfosarcina and single cells and aggregates of ANME-1 from methane seep sediments and directly determined the carbon stable isotopic composition for the individual cells and cell aggregates. Both archaeal groups ANME-1 and ANME-2 displayed isotopic signatures suggestive of methane assimilation, with extreme ^{13}C depletion (down to 97 per mil). In comparison, the carbon isotopic composition of microorganisms from the same sample not targeted with either the archaeal ANME-1 or ANME-2 specific rRNA probe sets had ^{13}C values averaging 30 per mil. Interestingly, large bacterial filaments resembling sulfide-oxidizing Beggiatoa were slightly more depleted in ^{13}C (approx. -50 per mil), and may signify ecosystem-wide incorporation of methane-derived endproducts. The combined application of FISH and SIMS serves as a new useful tool in geomicrobiology for deciphering the metabolic function of environmental microorganisms in situ.

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Bacterial Utilization of Gas Hydrate and Inhibition of Crystallization in Chemosynthetic Communities, Northwestern Gulf of Mexico

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The spatial association of structure II gas hydrate with lush chemosynthetic communities of tubeworms and other organisms in the upper slope of the Gulf of Mexico is obvious. Several sites in the Green Canyon area are characterized by moderate flux of oil-related gas (methane through pentanes, carbon dioxide) and crude oil, derived from the subsurface petroleum system. Most venting gas bypasses hydrate-rich sediments, as shown by large gas plumes that enter the water column and create natural oil slicks. This low conversion rate is also demonstrated by molecular properties of venting gas that is only slightly depleted in hydrate-forming hydrocarbons. Sea floor experiments suggest crystal nucleation on available mineral particles is a limiting factor. Gas hydrate crystallized from venting gas shows isotopic fractionation consistent with selective bacterial oxidation of methane (heavy carbon and hydrogen) and concomitant production of carbon dioxide (light carbon). Natural gas hydrate is frequently permeable and porous with large internal surface area, offering a favorable substrate for bacterial utilization. Abundant free gas occurs in sediment of chemosynthetic communities even though crystallization of the hydrate is favored thermodynamically. Bacterial oxidation of free hydrocarbon gas and reduction of sulfate occur in sediment at the periphery of buried gas hydrate. No gas hydrate is observed to crystallize on living bacterial mats, tubeworms, or bivalves immersed in gas bubble trains. This observation suggests that the surface chemistry of living organisms in chemosynthetic communities inhibits crystallization of gas hydrate, possibly an adaptive trait to the environment.