Interrelation of Global Climate and the Response of Oceanic Hydrate Accumulations

Progress Report

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NOTE: *In the previous year, LBNL staff completed all tasks and exhausted the corresponding budget by the end of the fiscal year (September 30) regardless of the time when full funding became available. In light of the realities of Continuing Resolution (CR) in the last few years, and following instructions from DOE Headquarters (Edith Allison), work on the various tasks in this project is (by design) not scheduled to be completed at the end of the 2009 Fiscal Year, but at a later date (December 31, 2009). This project end date is expected to provide sufficient time for Fiscal Year 2010 CR funds to reach LBNL before the FY2009 funds are exhausted, thus preventing disruptions, and allowing seamless project operation and continuation into the next fiscal year.*

Task Progress

Task 09-1: Completion of the Reactive Transport Enhancements to POP

Ocean modelers at LANL have made significant strides in the development of marine methane cycle simulation capabilities for POP. Arctic patch clathrate destabilizations were introduced into the code for multiple sites along the continental slope, consistent with known geography of the gas hydrate stability zone and its evolution during the upcoming period of global warming. Fluxes introduced into the POP model were set at upper-limit values taken from 1-D simulations performed in Tasks 08-3 and 09-3. Early runs were conducted in an inert tracer mode in order to bracket atmospheric release from surface waters of the Arctic Ocean. Then, a full biogeochemical oxidation scheme was implemented such that molecular oxygen is consumed within the POP ecodynamics module while dissolved inorganic carbon is added to the water column with attendant affects on seawater acidity. Methane uptake rates were set to match decay patterns observed for large, preexisting sources to the shelf zone including seeps and mud volcanoes. However, early results are indicating that the primary methanotrophic consumers may be limited in some areas by availability of the standard nutrients or else by the trace metals iron and copper. LANL biogeochemists are in the process of developing a full set of subroutines for the representation of methane microbial ecology in the water column. Bubble rise and methane plume buoyancy effects are currently implemented, and are parameterized such that all additions are made to the deepest grid level overlying an emission zone. Sensitivity tests will be conducted to determine whether more extensive penetration is required.

The results indicate that even localized hydrate-driven releases—those that may not have global-scale impact—can still greatly affect the chemistry of wide swaths of the oceans and have serious ecological consequences. Two papers on the formulation of the model and the first model results are about to be submitted.

In preparation:

1. Elliott, S.M., Maltrud, M., Reagan, M.T., Moridis, G.J., Cameron-Smith, P.J., "Marine Methane Cycle Simulations for the Period of Early Global Warming," *J. Geophysical Res. Biogeo*.
2. Elliott, S.M., Maltrud, M., Reagan, M.T., Moridis, G.J., Cameron-Smith, P.J., "Geochemical Fate and Effects of Methane from Arctic Marine Clathrates," *Geophysical Research Letters*.

These papers review the scientific background of ocean methane processes (derived from diverse sources), describe a new synthesis of knowledge about methane and methanotrophs in the water column, and present the first examples of the modeling of methane injection into a biologically active ocean environment (including simulation "spinup," testing, and forward simulation of releases). The results show that that in different localities any of the major oxidants/nutrients specific to the methanotrophic metabolism may turn out to be limiting: oxygen, nitrate, copper or iron. These resource limitations may hinder the ability of microorganisms to consume the released methane, such that previous assumptions in the literature about "99% consumption" of all methane (derived from observations of established methane seep systems at Coal Oil Point and Cascadia) may be incorrect. To the extent that some constituents of seawater are greatly depleted, geochemistry of the column is clearly altered, other organisms will not have the material available to use, and as such even localized releases may have severe ecological consequences.

Task 09-2: Completion of Code Integration and Testing

Work on this task is in progress and on schedule. The reduction of TOUGH+HYDRATE to a modular subroutine accessible to the POP ocean code has been completed, and the new structure is undergoing testing at LBNL for final incorporation into the POP model. Mat Maltrud from the LANL team traveled to LBL in October 2008 to assist in code integration.

The coupled use of TOUGH+HYDRATE and C.CANDI determined that the ability of sediment biogeochemical processes to mitigate methane release is highly limited, and that large-scale oxidation-reduction of methane to stable carbonates can only occur under a narrow set of conditions. Under the most favorable conditions for AOM (which may be considered unrealistic), over 90% of the methane escapes into the water column. For instances of large gaseous methane fluxes (as seen in the 1-D simulations for all scenarios), the vast majority of methane appears to escape the sediments before processes in the narrow AOM zone affect gas composition, and as such the sequestration of hydrate-derived methane as solid carbonate is unlikely to occur in short-term, high flux release scenarios. These results were presented at the AGU Fall Meeting 2008, and a paper summarizing the results is about to be submitted.

In preparation:

3. Reagan, M.T and Moridis, G.J., “Biological Mitigation of Methane Release from Dissociating Gas Hydrates,” for *Geo-Marine Lett.*

This publication, using C.CANDI coupled to TOUGH+HYDRATE, highlights the limited relevance of sediment biological processes for the types of releases expected to occur due to climate change. It suggests that the focus of methane chemistry must be in the water column, as 1-D and 2-D subseafloor simulations show that methane will enter the ocean primarily in the gas phase.

Task 09-3: Completion of Studies of Greenhouse Gas Releases at the Ocean Floor on Limited Spatial Scales

Work on this task is in progress and on schedule. First, LBNL completed the 1-D studies of hydrate dissociation under various conditions of depth, temperature, rate of warming, sediment permeability, and sea level change. The results of this work have been published in the *Journal of Geophysical Research*. The simulation work has been expanded to large-scale 2-D simulation of dissociating hydrates along the arctic continental margin, with the efforts focused on simulating the system discovered in October 2008 by Westbrook and colleagues off Spitsbergen. The results show that the observed releases could be driven by dissociating hydrate alone, and the results also show the emergence of methane gas plumes at the seafloor at the landward limit of the receding GHSZ—a result that closely resembles the system observed by Westbrook. A conference paper on these simulations and a letter to *Geophysical Research Letters* have been published. A full-length paper on the Spitsbergen system, including multiple temperature scenarios and sensitivity analysis, will be submitted to the *Journal of Geophysical Research* shortly. The simulation methodology is being expanded to study other locations and hydrate configurations around the arctic continental shelf, including simulations to assess the geomechanical consequences of hydrate dissociation on slope stability.

Published:

4. Reagan, M.T. and G.J. Moridis, “The dynamic response of oceanic hydrate deposits to ocean temperature change,” LBNL-01026E, *J. Geophys. Res. Oceans*, **113**, C12023, doi:10.1029/2008JC004938, 2008.

This paper describes the complete capabilities of the 1-D sediment column model, and the response of hydrates at various depths and temperatures with varying sediment properties, initial saturations, and ocean-depth variations.

5. Reagan, M.T. and Moridis, G.J., “Large-Scale Simulation of Oceanic Gas Hydrate Dissociation in Response to Climate Change,” *Geophys. Res. Lett.*, **36**, L23612, doi:10.1029/2009GL041332, 2009.

6. Reagan, M.T, Moridis, G.J., and K. Zhang, “Large-Scale Simulation of Oceanic Gas

Hydrate Dissociation in Response to Climate Change," Proceedings, TOUGH Symposium 2009, Lawrence Berkeley National Laboratory, 14-16 Sept. 2009.

These publications present the first large-scale (5 km x 300 m; 300,000 gridblocks at high resolution) simulation of hydrate dissociation, focusing on the Spitsbergen system. The results show that the Spitsbergen observations are entirely consistent with a hydrate source, and that shallow hydrates alone can account for such a release.

Papers #4-#6 are freely available online at:

http://esdtools.lbl.gov/info/hydrate-publications/climate/

In preparation:

7. Reagan, M.T. and Moridis, G.J., "Oceanic Gas Hydrate Dissociation Along the Arctic Continental Slope" for *J. Geophys. Res. Oceans*.

Task 09-4: Assessment of Global Hydrate Inventory and its Spatial Distribution

Work on this task is in progress and on schedule. The observed methane releases and resulting simulations mentioned in Task 09-3 strengthen the hypothesis that arctic hydrates are the key to understanding the potential for hydrate-derived methane release. Using the GEBCO database of global ocean bathymetry, LBNL, with assistance from LANL, is generating an areal map of seafloor zones that fall within with the gas hydrate stability zone (GHSZ). 1-D simulations of the sediment column will be used to directly calculate the GHSZ thickness of selected locations within the most "promising" hydrate-stable regions, and also to assess the stability of any hydrates that might exist within those regions. These assessments are also being used to perform the additional 2-D large-scale simulations described in Task 09-3.

Task 09-5: Communications and Technology Transfer

Activities in this task are in progress and on schedule. The six papers published, in press, or submitted are listed above. In addition, the work performed in this project and the published papers have been highlighted in prominent articles in the scientific press:

8. "The Hydrate Hazard," *Nature Reports Climate Change*, **3**, 14, doi:10.1038/climate.2009.11 (February 2009).
9. "A Sleeping Giant?" *Nature Reports Climate Change*, doi:10.1038/climate.2009.24 (April 2009).
10. "Greenhouse Gas Leaking from the Arctic Ocean Floor," *Environmental Science and Technology*, doi:10.1021/es9026387 (September 2009).

These news/feature articles reference paper #4 (Reagan and Moridis, 2008) and place in it the context of the larger field of methane-climate research.

The following presentations have been made regarding the work performed in the previous tasks:

(a) "Oceanic Gas Hydrate Dissociation In Response To Climate Change And The Fate Of Hydrate-Derived Methane," (poster), AGU Fall Meeting 2008, San Francisco, CA, 15-19 December 2008.

(b) "Regional Simulation of Oceanic Gas Hydrate Dissociation in Response to Climate Change," (poster) TOUGH Symposium 2009, Berkeley, CA, 14 September 2009.

(c) "Large-Scale Simulation of Oceanic Gas Hydrate Dissociation in Response to Climate Change," AGU Fall Meeting 2009, San Francisco, CA, 14-18 December 2009.

Additionally, G. Moridis was a keynote speaker at the 2009 Goldschmidt Conference, Davos, Switzerland, 21-26 June 2009, where he presented the following paper:

(d) "Interrelationship of dissociating oceanic hydrates and global climate: Methane hydrate response to rising water temperatures," (Keynote) 2009 Goldschidt Conference, Davos, Switzerland, 21-26 June 2009.

This is the top international conference on geochemistry, participation is by invitation only, and being invited as a keynote speaker is a rare honor.

Task 09-6: Using PhyloChip analysis to determine microbial community composition and structure of marine water and microbial mats surrounding methane seeps

Work on this task is nearly complete, and on schedule. Using the PhyloChip, 39 samples of methanotrophic microbial mats, grown in-situ on the seafloor, were analyzed in concert with the Valentine lab at UCSB. These mats were collected after being grown on modular plates at the sea floor in a methane seep at the Coal Oil Point seep field located off Goleta CA. The samples were incubated with methane containing a pure 13C label. After 3-7 days of incubation the mat samples were harvested and the DNA purified. The purified DNA was fractionated by density using a cesium chloride gradient and the resulting fractions collected individually. Both heavy fractions and light fractions from different time points, along with control samples were received at LBL and further processed for PhyloChip analysis. The enriched DNA samples contained far less diversity and richness compared to other samples, suggesting that we may be tracking carbon flow into the broader microbial community in addition to identifying the primary consumers of methane. We investigated the relationships between sulfate reduction rates (SRR) and energy flux (Ef) and bacterial abundance/richness across steep geochemical sediment gradients at two sampling locations. Significant, positive relationships between SRR/energy flux and bacterial abundance/richness estimates were found, suggesting that species-energy theory extends to bacteria community patterns within anaerobic sediments A second set of samples ("hb" samples) also came from the microbial mats, but tracked the natural shifts in isotopic composition that reflect the changing patterns of methane consumption. These samples are still being analyzed. A third set of samples came from sediments of defined methane concentration, and were used to develop the methodology for processing DNA from organic-rich saline sediment samples (all the "SS" samples).

These samples yielded high level of phylotype richness in proportion to metabolic rates and provided the needed method development. A fourth set of samples came from deep suboxic waters where elevated rates of methanotrophy were concurrently measured (all “MH” samples). The analyses on these samples are ongoing as publications are being prepared describing the controls on methanotrophy in these environments (which will be used to test hypotheses about the composition of the microbial community).