

Interrelation of Global Climate and the Response of Oceanic Hydrate Accumulations

Year-End Progress Report

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NOTE: *In previous years, LBNL staff attempted to complete all tasks and exhaust the corresponding budget by the end of the fiscal year regardless of the time when full funding became available. In light of our experience with Continuing Resolutions (CR), and expecting such funding delays in the near future, we are carefully moderating spending on this project to insure available funding into early 2011.*

Task Progress

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

(Finished at the end of 2009/beginning of 2010) The team at LANL developed a marine methane cycle simulation capability within POP. 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. Results using this code are discussed below.

Task 09-2: Completion of Code Integration and Testing

(Finished at the end of 2009/beginning of 2010) 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. This suggested that the focus of methane chemistry must be in the water column.

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

Task 10-1: Expansion to Medium-Scale, Fully-Coupled Simulations of Releases of Hydrate-Originating Greenhouse Gases

The ocean model component of our team has analyzed results from the introduction of LBL sediment interface fluxes into the Parallel Ocean Program (POP). Fully dynamic chemistry-transport simulations were conducted representing intense

methane release into the Arctic regime during the period of early global warming. Marine methane consuming bacteria will oxidize the molecule in large part. This process has the potential to deplete oxygen and raise pH in poorly ventilated deepwater masses, and to deplete nutrients such as the trace metals and nitrogen in many locations. Reagent restrictions may allow the undersea gas distributions to expand and approach the atmosphere, where methane acts as an ultra-strong greenhouse forcer. For aqueous release (full dissolution of the methane), much of the effluent, however, remains below the ocean mixed layer while circuiting the central Arctic and then subducting into the abyssal Atlantic. The portion of methane rising from sea floor as bubbles remains a large uncertainty (as plumes would transport additional methane into the mixed layer), so adding bubble-plume parameterizations to POP is underway.

These outcomes were described in a paper recently published in *Geophysical Research Letters*, and also as a longer exposition currently in press at the parent publication *Journal of Geophysical Research*. 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 models of methane injection into a biologically active ocean environment. The results show 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) are incorrect. The geochemistry of the water 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. These papers should be important early contributions to the growing area of methane and the environment.

Published/In Press:

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.*, doi: 10.1029/2010JG001300, in press, 2010.
2. Elliott, S.M., Reagan, M.T., Moridis, G.J., Cameron-Smith, P.J., “Geochemistry of Clathrate-Derived Methane in Arctic Ocean Waters,” LBNL-3389E, *Geophys. Res. Lett.*, 37, L12607, doi:10.1029/2010GL043369, 2010.

In Task 10-1, the simulation work was expanded to large-scale 2-D simulation of dissociating hydrates along the arctic continental margin, with the efforts beginning with the system discovered by Westbrook and colleagues off Spitsbergen. Current and ongoing simulations represent other areas of interest, including the Sea of Okhotsk, Beaufort Sea, the New Zealand margin, and locations in the Gulf of Mexico. Results in each case show that methane can be released in gaseous form, driven by dissociating hydrate alone, for systems with sufficient permeability (typically 1 mD or greater) and capillary properties that allow gas migration via buoyancy. The results also show the emergence of a narrow zone 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, strengthening the possible connection between the plumes and hydrates. A conference paper and a letter to *Geophysical Research Letters*, both addressing the Spitsbergen system, were published in 2009. A full-length paper on the behavior of sloping systems under arctic conditions, including multiple temperature scenarios, slope angles, sediment properties, and a sensitivity analysis, has been submitted to the *Journal of Geophysical Research*.

The increased stability of sII hydrates (common on the Gulf of Mexico seafloor) has been assessed using the CSMGem physical properties package, indicating that such hydrates may be more stable than initially assumed when a mixture of gases (methane, ethane, propane) is considered, suggesting a possible mitigating factor for the climate-related dissociation of high-saturation hydrates associated with thermogenic methane reservoirs. However, this mitigation seems unique to the massive hydrate deposits present on the floor of the Gulf of Mexico, and does not apply to the more extensive sparse biogenic, stratigraphic hydrates found throughout the world ocean.

At the basin scale, hydrates in the Sea of Okhotsk, categorized by depth, temperature, and likely concentration, were assessed for the first time using coarse point-by-point simulation, and the total potential release was integrated from local results. The potential fluxes calculated by this assessment closely match the Okhotsk point-flux assumed in the global POP simulations, strengthening our preliminary conclusion that hydrate dissociation and methane release could lead to local biochemical effects, even if the net global greenhouse gas contribution is not significant. The Okhotsk simulations also indicated that only a small fraction (< 1%) of the existing hydrates in the basin are subject to dissociation from ocean warming, but that the methane flux from even this limited, controlled dissociation is significant. These preliminary results were presented at the 2010 AGU Fall Meeting. A similar assessment is underway for the Beaufort Sea and for the overall Arctic Ocean basin. The LBNL team is working directly with the LANL team to assess the ocean biogeochemical effects of each of these new scenarios on a basin/regional scale (Task 10-2).

Submitted:

3. Reagan, M.T., Moridis, G.J., Elliott, S.M., Maltrud, M., “Contribution of Oceanic Gas Hydrate Dissociation to the Formation of Arctic Ocean Methane Plumes” for *J. Geophys. Res. Oceans*.

Task 10-2: Global Scale Simulations of Hydrate Dissociation and Global Climate

Work on this task is progressing and on schedule. The basin- and region-scale models are being scaled up to larger assessments. As a first step, the regional assessments are being combined to deliver a net global source term of methane, tied to predetermined temperature trends (i.e. IPCC A1B warming values). Using POP bathymetry data, we are establishing a coarse depth-temperature- ΔT map of the oceans that can be used to seed the 1-D TOUGH+HYDRATE model of dissociation and methane release. The resultant fluxes

can be fed into a new POP simulation of short term methane transport and biochemical response. This will allow a “one-way” coupling on a global scale to determine the short-term (century-scale) effect of hydrate dissociation and methane release. At this point, new parameterizations for bubble plume behavior are being incorporated into POP, such that the next set of POP simulations will inject methane into the water column at multiple levels, with simulations running at higher resolution than Task 10-1.

Also, the Earth Sciences Division at LBNL has recently developed an extensive climate research program through the creation of a new climate department. This program involves climate scientists at several national laboratories and universities, including members of the LANL team and experts on the chemistry of methane in the atmosphere. As a result, we are beginning to leverage this close association such that the latest version of CCSM and its upcoming successor, CESM 1.0, will be available for use in future coupled global-scale simulations, including novel methane chemistry, forcings, and feedbacks previously not available.

Task 10-3: Communications and Technology Transfer

Activities in this task are in progress and on schedule. The three papers published/submitted are listed above. In addition, the work performed in this project has gained significant attention, and once again has been highlighted in the scientific press:

1. “Getting to the Bottom of Methane,” *NPR’s Living On Earth*, March 12, 2010.
2. “‘Arctic Armageddon’ Needs More Science, Less Hype,” *Science*, 329, 5992, 620-621, doi: 10.1126/science.329.5992.620.
3. Reagan, M.T., Moridis, G.J., Elliott, S.M., Maltrud, M., “Dissociation of Oceanic Hydrates in Response to Climate Change and the Biogeochemical Consequences,” *Fire in the Ice*, DOE Methane Hydrates Program.

The following presentations have been made in 2010 regarding the work performed in the previous tasks:

1. “Basin-Scale Assessment of Hydrate Dissociation in Response to Climate Change,” OS43B-08, AGU Fall Meeting 2010, 13-17 Dec 2010.
2. “Oceanic Hydrates, Methane, Ocean Chemistry, and Climate,” Gordon Research Conference on Natural Gas Hydrates, Colby College, Waterville, ME, 6-10 June 2010.
3. “Arctic Methane, Hydrates, and Global Climate,” (invited) DOE Laboratory Energy R&D Working Group Meeting, Washington, DC, 17 Feb 2010.
4. “Interrelation of Global Climate and the Response of Oceanic Hydrate Accumulations,” NETL Methane Hydrates Program Symposium, Atlanta, GA, 25-29

January 2010.

This work has also been highlighted in internal seminars at LBNL:

1. “Arctic Methane, Hydrates, and Global Climate,” Environmental and Energy Technology Division Seminar, 17 March 2010.
2. “Climate Change and the Response of Oceanic Hydrate Accumulations,” ESD Town Hall, February 2010.