Interrelation of Global Climate and the Response of Oceanic Hydrate Accumulations

Final Report

Date: July 15, 2013
Period: October 1, 2008 – June 30, 2013
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1. Goal of this report

This report will summarize previously reported or published results concerning the behavior of hydrates subjected to warming, highlighting contributing and mitigating factors relating to the possibility of rapid climate feedbacks. We will thus assess various scenarios and possibilities for the relationship between climate and hydrates: i.e., the likelihood of a "clathrate gun" event and the mechanisms required for it to occur. The intent of the report is to highlight the most important research results generated during the four-year term of the project, and to report on the completion of proposed task. Please see the referenced papers for additional information at a higher level of detail.

2. Abstract

It has been postulated that methane from oceanic hydrates may have a significant role in future climate, but the behavior of contemporary oceanic methane hydrate deposits subjected to rapid temperature changes has only recently been investigated. Field investigations have discovered substantial methane gas plumes exiting the seafloor at depths corresponding to the upper limit of a receding gas hydrate stability zone, suggesting the possible warming-driven dissociation of shallow hydrate deposits and raising the question of whether these releases may increase and become more common in the future. Previous work in this project has established that such methane release is strongly regulated by coupled thermo-hydrological-transport processes in the sediments and coupled biogeochemical processes in the water column. In this task report, we discuss the research to date, highlighting the factors that increase or decrease the risk of runaway feedbacks due to climate-driven methane release from the seafloor. The results show that the methane release is likely to be confined to a narrow region of high dissociation susceptibility, defined mainly by depth and temperature, and that any release will be relatively uniform and controlled, rather than explosive. However, coupled ocean simulations indicate that released quantities can be biogeochemically and climatologically significant, as they are similar in magnitude and distribution to the estimated methane release quantities derived from earlier sensitivity studies that suggest significant chemical changes in the water column and significant changes in atmospheric chemistry. This assessment indicates that there are several enhancing and mitigating factors that are still not fully quantified, but even if all positive enhancements are considered, a century-scale injection of methane powerful enough to cause large climate forcing is highly unlikely. However, as warming continues into subsequent centuries, it is likely that much of the methane carbon in shallow hydrates will eventually enter the water column, with significant biogeochemical and possibly significant long-term climate impacts. The project has generated five publications and has received extensive publicity and recognition.

3. Project Summary

Models and Methods

The TOUGH+HYDRATE code (Moridis et al., 2008) used in this study describes multiphase flow and transport in hydrate-bearing geologic media. It includes coupled mass and energy transport within porous and fractured media, and also describes the full phase behavior of water, methane, solid hydrate, ice, and inhibitors (i.e. salts). This code was used in previous studies of hydrate dissociation in oceanic sediments (Reagan & Moridis, 2007). The global ocean simulations are based on a one degree resolution, global Parallel Ocean Program (POP), part of the Community Earth System Model (CESM), a fully-coupled, global climate model that provides state-of-the-art computer simulations of past, present, and future climate states (Gent et al., 2011).

Summary of Results

The Clathrate Gun Hypothesis focused on large-scale, rapid release of methane from seafloor hydrates in quantities large enough to 1) result in widespread injection of methane into the atmosphere, and 2) cause rapid warming feedbacks. Our research has strongly suggested that the release of methane from hydrates is actually likely to be:

1) Regional, rather than global
2) Persistent or gradual, rather than explosive
3) Limited by the magnitude of warming expected in the near term, from pre-industrial times through 2100
4) Mitigated by a number of factors in the sediments, including:
    a. Limits to the rate at which heat can be transported through sediments via conduction and advection
    b. The endothermic nature of hydrate dissociation
    c. Slow transport of methane in the sediments without overpressure driving flow, including the retention of a large fraction of the methane in the short term
5) Mitigated by factors in the water column, including:
    a. Oxidation by methanotrophs
    b. Transport into deep water (guaranteeing complete oxidation) through Arctic polar currents that feed the deeper ocean
    c. The limited set of circumstances under which bubble plumes or other fast transport pathways to the atmosphere can form.
6) Significant as an climate forcing only in cases of rapid release directly to the atmosphere

However, the research also indicates that:

1) Significant quantities of methane can still be released from hydrates as a result of predicted ocean warming scenarios
2) Methane will continued to be released over many centuries, even if warming stops
3) Long-term prospects are for continued and significant ocean warming, further extending the time of potential release
4) These quantities are likely to be globally significant, even if feedbacks are not triggered
5) The biochemical consequences of the released methane in the water column are an issue of real concern, and this issue has not been quantitatively addressed before

6) Resource limitations may hinder methane consumption, and the consumed resources may upset other aspects of ocean biology
7) Releases of methane into the atmosphere below the threshold for fast radiative feedbacks may still have chemical consequences in the troposphere and stratosphere.

4. Task Completion Reports

What follows is a summary of project tasks and a brief description of the work performed. For years 1 & 2, we roughly followed a fiscal-year-based schedule. For later years, the reality of Continuing Resolution resulted in funding arrival at varying times throughout the year. Therefore, from 2008 through 2013, we highlight four project years representing four funding allocations matched to the original proposal schedule.

Year 1 (FY08-09):

Task 08-1: Assessing and Quantifying Global Warming Scenarios: The LANL team used data from IPCC projection (the A1B "mid-range" scenario) to assess the potential temperature change at five locations: the Barents Sea, the Bering Sea, the Gulf of Mexico, Blake Ridge (North Atlantic), and the Sea of Okhotsk. The results show localized temperature variations between 1 and 5 ^{o}C are highly variable, but account for variations in seafloor topography and are valid at multiple depths in each zone. These temperature results are currently being used as inputs for the simulations of Task 08-3, and will form the basis for all future studies.

Tasks 08-2 and 08-5: Coupling of the TOUGH+HYDRATE, C. CANDI and TOUGHREACT Codes; and Code Integration: Forward-coupling of TOUGH+HYDRATE and C.CANDI produced the first results that assess the potential of biochemical mitigation and the fate of hydrate-derived methane released through ocean warming (Reagan et al., 2008). The results indicate that known biogeochemistry of the sub-seafloor (as measured in contemporary active venting sites such as Cascadia/Hydrate Ridge) is capable of fully oxidizing released methane in the aqueous phase for the release scenarios proposed, however, much of the gaseous methane is likely to escape the sediment and enter the water column.

Task 08-3: Studies of Greenhouse Gas Releases at the Ocean Floor on Limited Spatial Scales: Using the temperature profiles derived from Task 08-1 and the enhanced TOUGH+HYDRATE of Task 08-2, the LBNL team performed 1-D hydrate dissociation and methane release simulations involving the new, extended set of locations and temperature-change scenarios. These simulations formed the basis of the next step in the project—coupling, for the first time, hydrate release to ocean water column processes (described with Task 08-4).

Task 08-4: Reactive Transport Enhancements to POP: The LANL team has implemented baseline simulations of the background marine methane cycle onto which hydrate-derived methane fluxes can be superimposed. Standard, global 1^{o}-resolution (latitude/longitude) ocean circulation models with complete nutrient ecodynamics have been supplemented with background seabed fluid flow inputs, central-ocean microbial methane consumption and production, and sea to air transfer mechanisms. This model accounts for biological consumption of methane leading to a loss of dissolved molecular oxygen, plus the production of dissolved inorganic carbon (CO_2, bicarbonate, and carbonates), and will be accompanied by computations of changes to the local pH. The new release model of Task 08-3 and the enhanced circulation model of Task 08-4 are implemented such that they will provide the first ever assessment of how rapid hydrate dissociation affects the ocean ecosystem, and completes the first step in quantifying the global consequences.

Task 08-6: Communications, Reporting and Technology Transfer: Despite late initiation of the project for FY08 (May/June 2008), the LBNL team submitted one journal article incorporating some early results from this project (Reagan and Moridis, 2008) and this article has been accepted for publication. We presented initial chemistry-coupling results at the 2008 6th International Conference on Gas Hydrates (Reagan et al., 2008). A status report was presented to a NETL program review panel in August 2008.

Year 2 (FY 09-10):

Task 09-1: Completion of the Reactive Transport Enhancements to POP: Ocean modelers at LANL developed 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. Results indicated 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. These results indicated 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 were about to be submitted (published later). These papers reviewed the scientific background of ocean methane processes (derived from diverse sources), described a new synthesis of knowledge about methane and methanotrophs in the water column, and presented 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 showed 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: The reduction of TOUGH+HYDRATE to a sub-code more easily accessible to the POP ocean code was been completed, and the new structure was undergoing testing at LBNL. Mathew 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.

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 were published in the *Journal of Geophysical Research* (Reagan & Moridis, 2008). This paper described 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. The simulation work was 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. This was one of the first uses of the MPI-parallel pTOUGH+ code, running on up to 128 processors. 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* has been published (Reagan et al., 2009; Reagan & Moridis, 2009). A full-length paper on the Spitsbergen system, including multiple temperature scenarios and sensitivity analysis, was submitted to the *Journal of Geophysical Research* (published later). These publications presented 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. Additionally, George Moridis was invited as a keynote speaker at the 2009 Goldschmidt 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 09-4: Assessment of Global Hydrate Inventory and its Spatial Distribution: 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, generated an areal map of seafloor zones that fall within with the gas hydrate stability zone (GHSZ). 1-D simulations of the sediment column were 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 were also used to perform the additional 2-D large-scale simulations described in Task 09-3.

Task 09-6: Using PhyloChip analysis to determine microbial community composition and structure of marine water and microbial mats surrounding methane seeps: 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). A paper on this work is currently in review.

Year 3 (FY 10-11, with some carryover into FY 12):

Task 10-1: Expansion to Medium-Scale, Fully-Coupled Simulations of Releases of Hydrate-Originating Greenhouse Gases: The ocean model component of the team analyzed results from the introduction of LBNL 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 oxidized the methane in large part. This process depleted oxygen and lowered pH in poorly ventilated deepwater masses, and depleted nutrients such as the trace metals and nitrogen in many locations. Reagent restrictions thus may allow the undersea gas distributions to expand and approach the atmosphere, where methane could acts as a greenhouse forcing. For aqueous release (full dissolution of the methane), much of the effluent, however, remained 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 remained a large uncertainty at this point in the project (as plumes would transport addition methane into the mixed layer), so adding bubble-plume parameterizations to POP continued.

These outcomes were described in a paper published in *Geophysical Research Letters* in 2010, and also as a longer exposition recently published in the *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 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.

The original paper published in *JGR* stated that, although the methane had significant effects in the water column, less than 1% was likely to enter the atmosphere through the ocean-atmospheric interface. Reanalysis of the data found a significant error in the data processing used in the paper, and in fact, 60% of an inert "tracer" methane could be expected to find its way into the atmosphere within 30 years. An erratum was submitted to, and accepted by, *JGR*, and is now attached to the original paper. This change does not change any of the core conclusions of the paper except the "1%" upper limit, and suggests that even without bubble-plume dynamics, methane can reach the atmosphere. However, as the previous analysis was stopped after the "tracer" methane was assessed (since the tracer case was seen as an upper limit for release), additional runs were begun to give a realistic treatment of ocean-atmosphere transfer of CH_4 and CO_2. As part of Task 10-2 further coupled ocean-chemistry simulations were being performed to re-assess the magnitude of methane release for a system with water-column chemistry and resource limitations.

In Task 10-1, the sediment simulation work was expanded to 1-D and 2-D simulations of dissociating hydrates along the arctic continental margin, with the efforts beginning with the system discovered by Westbrook and colleagues off Spitsbergen. The simulations represented other areas of interest, including the Sea of Okhotsk, Beaufort Sea, the New Zealand margin, etc. Results in each case showed 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 full-length paper on the behavior of sloping systems under arctic conditions, including multiple temperature scenarios, slope angles, sediment properties, and a sensitivity analysis, was later published in the *Journal of Geophysical Research*.

The increased stability of sII hydrates (common on the Gulf of Mexico seafloor) was 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. However, these simulations were also used as part of the DOE investigation into the Macondo well disaster (flow-rate group), and the final report was honored with a DOE Secretary's Award for Achievement in October 2011.

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. The preliminary results were presented at the 2010 AGU Fall Meeting. A similar assessment was later performed for the Beaufort Sea and for the overall Arctic Ocean basin.

Task 10-2: Global Scale Simulations of Hydrate Dissociation and Global Climate: Work on this task consumed the better part of two project years, with data mining, conversion of climate-model data to TOUGH+ inputs, and construction of various scenarios involving a tremendous amount of custom programming and new simulation runs. The basin- and region-scale models are were scaled up to larger assessments. As a first step, the regional assessments were being combined to deliver a net global source term of methane, tied to predetermined temperature trends (i.e. IPCC A1B warming values, with uniform $\Delta T = +1$ °C and +5 °C changes at all depths bracketing the limits of the analysis). Using ETOPO2 bathymetry data, we established a depth-temperature-ΔT map of the oceans that can used to seed the 1-D TOUGH+HYDRATE model of dissociation and methane release. 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.

Initial results for the basin-scale 1-D integrations were promising, and shed new light on the potential for methane release. At the local 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 matched 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 was performed for the Beaufort Sea, and the combined results were presented at the 2011 Arctic Technology Conference.

Using a 4-min grid, the entire Arctic Ocean basin bathymetry was mapped, and 1-D column simulations were performed (at 25 m to 50 m depth intervals) for each depth, initial temperature, and at various values of ΔT. As seen in the Beaufort and Okhotsk results presented at AGU (but at much higher resolution), the region of potential hydrate dissociation and significant resultant methane flux was confined to a narrow “bathtub ring” of sensitivity—mainly deposits in water depths from 320 m down to about 450 m, with deeper hydrates not likely to release large amounts of methane unless temperature changes continue for many centuries and propagate deep into the water column. However, despite this limitation, the quantities of methane suggested by this integration are still at the same order-of-magnitude as the assumed patch fluxes selected for the POP+chemistry simulations. Therefore, it suggests that the hypoxia and anoxia scenarios previously described could indeed occur through the dissociation of sparse, continental slope hydrates (if such hydrates exist uniformly at even sparse saturations). A paper describing this Arctic-scale integration was published in the proceedings of the 2011 International Conference on Gas Hydrates, and presented at ICGH 7 in July 2011.

Year 4 (some FY12-FY13):

After resumption of funding in June 2013, the final tasks were tackled.

Task 1: Project Management Plan: Completed.

Task 2: Global Scale Simulations of the Interrelation Between Hydrate Dissociation and Global Climate, and

Task 3: Testing of the Clathrate Gun Hypothesis:

This task takes the Arctic Ocean assessments from the previous task and expanded the scope to a global set of calculations, using not only fixed estimates of ΔT, but calculating directly from global climate model results for seafloor temperatures under various climate forcing scenarios. This task and the following task provide a quantitative estimate of the hazards of climate-related hydrate dissociation. The coupled global climate simulation runs perturbed by these hydrate releases are still ongoing, as they are multi-month/yearlong runs tied into schedules unrelated to this project, including IPCC report deadlines.

As in previous studies, we performed 1-D column simulations of disperse, low-saturation deposits from a water depth of 300 m, above the top of the likely GHSZ for any non-permafrost-associated hydrates, down to a water depth of 1000 m. Initial seafloor temperatures are taken from the bottom (seafloor) gridblocks of the CESM/POP model—thus T and P vary with depth and location. We use a uniform initial hydrate saturation of 3% reflecting the high end of the estimated global average saturation for stratigraphic deposits (Reagan & Moridis, 2008). This, of course, is an assumption that all regions that allow stable hydrate actually contain stable hydrate, and as such we are calculating upper limits for hydrate dissociation and methane release. A detailed description of the column-simulation methodology, the sourcing of the common parameters, parametric sensitivity studies, and justification of assumptions can be found in Reagan & Moridis (2008).

We calculate potential methane fluxes at the seafloor using the RCP8.5 (radiative forcing of 8.5 W/m^2 by 2100), one of the more strongly forced climate change scenarios (van Vuuren et al., 2011) that has recently received greater attention as a possible viable outcome. After 2100, the temperature is held constant (as predicting temperature change beyond this point becomes increasingly speculative), and the system is allowed to find a new equilibrium. We also use the "Historical" dataset, a set of climate simulations used to "hindcast" the period from 1855-2010, to establish the potential location of stable hydrates in the pre-warming ocean. We remove from the integration CESM/POP gridblocks where 1) shallow hydrate could not have existed prior to 1855, 2) climate simulations show no temperature increase by 2100, and 3) hydrates are deep enough that the largest temperature changes indicated in the RCP8.5 scenario ($\Delta T = + 6^\circ C$ for locations remaining after criteria 1 and 2 are applied) would not cause hydrate dissociation at the top of the column (i.e., the seafloor remains within the GHSZ). We use the ETOPO2 database [USDC, 2006] to convert the longitude and latitude of each CESM/POP gridblock to an accurate value for seafloor depth. We use a coarse integration discretization in depth and temperature for this initial study, grouping initial temperatures and ΔTs into 1˚ bins, and depths into 50 m bins. While this may "smooth out" some of the z/T dependences, previous studies [Reagan et al., 2011b] lead us to expect that only a few depth zones with similar average fluxes will play a role.

The "Historical" results show that the bulk of the seafloor that 1) could have had shallow hydrates and 2) could have climate-sensitive hydrates is located in the polar regions, with the currently poorly understood Antarctic continental slope having quite a bit of potential hydrate in addition to the better-understood (and often studied) Arctic basin. The temperature changes since 1855 to the present, however, are small compared to previous 1-D release studies, suggesting little release of methane should be underway. For the strong RCP8.5 scenario, we have a strong bias towards polar regions for the location of climate-sensitive hydrates. This is in close agreement to the assumptions made earlier in the study, where we chose to focus on Arctic systems. By areal percentage, the bulk of the climate-sensitive hydrates (based on the RCP8.5 scenario) exist in high northern latitudes regions, moreso than even in Antarctic waters. In the right panel, we see that shallow hydrates in the 300 m – 600 m range make up the bulk of sensitive hydrates, with hydrates deeper than 1000 m not expected to be affected. As a result, we do not expect the global-scale integrations to differ drastically from the estimated temperature scenarios studied in early work on this project (Reagan et al., 2011).

We then integrate the depth-temperature driven sediment column releases, forced by the RCP8.5 derived temperature changes at the seafloor, and integrate across the coarse depth, temperature, and 1-degree spatial grid to estimates methane flux into the water column as driven directly by the CESM climate model. the global integration for the RCP 8.5 scenario gives an estimate of 0.25×10^{15} mol (4,000 Tg) CH_4. Despite the coarseness of these initial simulations, this is within the magnitude range computed in the hypothetical scenarios. The estimated global flux peaks at $t = +93$ yr at 5.1×10^{12} mol/yr (82 Tg/yr). Combined with the strong weighting of the releases in the Arctic basin (as well as Okhotsk), the previously assessed biogeochemical consequences (oxygen depletion, pH increases, and possible stressing of the water column biogeochemical “filter”) hold for the global-scale assessment. Furthermore, colleagues at LLNL have reported that methane releases into the atmosphere of order 100 Tg/yr, localized around the Arctic basin, are significant enough to be a small but noticeable contributor to warming, though not necessarily a runaway feedback mechanism (unpublished research, personal communication). Related work has also shown the possibility that methane releases potentially lead to increased surface ozone (at levels equal to urban smog at some locations) and decreased stratospheric ozone (due to chemical pathways that lead to increased stratospheric cloud formation). Therefore this first global assessment maintains the potential significance of hydrate-derived methane to global climate, suggesting further investigation of climate and ecological consequences is warranted.

As a net assessment, the overall analysis suggests limits to the direct climate impact of hydrates, at least as a fast positive feedback or “global disaster scenario.” However, the research performed during this project has led to new insights about other aspects of hydrates and global climate. Even if rapid feedbacks do not occur, the biochemical and chemical consequences to the oceans and atmosphere demand further investigation, and in the long term, the vast quantities of carbon stored as shallow hydrates are likely to find their way into the oceans and atmosphere though some combination of the above-mentioned mechanisms. Therefore the reality is likely to be between the methane-driven climate shocks of Kennett and colleagues (2000) and the long-term view of hydrates as only another long-term contributor to total CO_2 in the atmosphere (Archer, 2007).

Even if not catastrophic in magnitude, the methane fluxes shown here are still within the range of potential climate sensitivity, such that recent developments in bubble-plume modeling and nutrient-limitation effects in the water-column biochemical filter will factor into fully understanding the range of climate impacts potentially driven by hydrates. In addition, understanding how climate-sensitive hydrates couple to other methane-transport problems—i.e., how the formation and dissociation of hydrates on the margin may regulate the transport of methane from other, deeper sources (Thatcher et al., 2013)—will be necessary, as this study focused only on hydrate-driven feedbacks by themselves.

At the time of this report, coupled climate/ocean models (which proceed on multi-month to multi-year schedules) continue to generate results. This report will be updated as new data arrives, although the key insights in Sections 1-4 will hold even if the range of possible outcomes is narrowed. Follow-on studies need to examine longer time horizons, as warming penetrates to deeper and deeper waters (as presumed) a thicker “bathtub ring” of sensitivity is likely to be affected. As the time window expands, the likelihood of large-scale hydrate dissociation increases, even if rates are constrained. Future work in this area also needs to include field studies and direct observation of shallow hydrate systems, which may confirm the predicted scarcity of climate-driven methane release at the current time and also provide better data to constrain subseafloor, ocean, and atmospheric models used to predict future behavior.

Two publications are currently in preparation:

1. Scott Elliott, “Systems Model Representation of Ocean Bubble Plumes Over Decomposing Arctic Clathrates”
2. Matthew Reagan, “Geological and Thermodynamic Constraints on the Release of Hydrate-Derived Methane in Response to Climate Change”

Communications and Technology Transfer

The project resulted in 5 peer-reviewed publication (with two more in preparation), 4 conference publications, and 31 presentations. Additional publications and presentations are in preparation.

The project generated the following peer-reviewed publications:

1. Reagan, M.T., Moridis, G.J. “The dynamic response of oceanic hydrate deposits to ocean temperature change,” LBNL-01026E, *J. Geophys. Res. Oceans*, **113**, C12023, doi:10.1029/2008JC004938, 2008.
2. Reagan, M.T., Moridis, G.J., “Large-Scale Simulation of Oceanic Gas Hydrate Dissociation in Response to Climate Change,” LBNL-2908E, *Geophys. Res. Lett*., **36**, L23612, doi:10.1029/2009GL041332, 2009.
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4. 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,” LBNL-4239E, *J. Geophysical Res. Biogeo*., **116**, G01010, 2011.
5. Reagan, M.T., Moridis, G.J., Elliott, S.M., and Maltrud, M., “Contributions of Oceanic Gas Hydrate Dissociation to the Formation of Arctic Ocean Methane Plumes,” *J. Geophys. Res. Oceans*, **116**, C09014, doi: 10.1029/2011JC007189, 2011.

The project resulted in the following conference publications:

6. Reagan, M.T., Moridis, G.J., Elliott, S.M., Maltrud, M., and Cameron-Smith, P.J., “Basin-Scale Assessment of Gas Hydrate Dissociation in Response to Climate Change,” *Proc.* 7th International Conference on Gas Hydrates, Edinburgh, Scotland, UK, 17-21 July 2011.
7. Reagan, M.T., Moridis, G.J., Elliott, S.M., and Maltrud, M., “Simulation of Arctic Gas Hydrate Dissociation in Response to Climate Change: Basin-Scale Assessment,” OTC 22153, *Proc.* 2011 Arctic Technology Conference, Houston, Texas, USA, 7–9 February 2011.
8. Reagan, M.T, Moridis, G.J., and K. Zhang, “Large-Scale Simulation of Oceanic Gas Hydrate Dissociation in Response to Climate Change,” *Proc*. TOUGH Symposium 2009, Lawrence Berkeley National Laboratory, 14-16 Sept. 2009.

9. Reagan, M.T, Moridis, G.J., Zhang, K., “Modeling of Gas Hydrate Instability and Methane Release in Response to Climate Change,” LBNL-00712E, *Proc.* of the 6th International Conference on Gas Hydrates, Vancouver, BC, July 6-10, 2008.

The project resulted in the following presentations:

Invited Presentations:

1. Reagan, M., “The Response of Marine Clathrates to Climate Change: Beyond the "Clathrate Gun," Climate Sensitivity on Decadal to Century Timescales: Implications for Civilization, Aspen Global Change Institute, Aspen, CO, 24 May 2012.
2. Reagan, M., “Simulation of Arctic Gas Hydrate Dissociation in Response to Climate Change: Basin-Scale Assessments” USGS/DOE Climate-Hydrates Research Workshop, Boston, MA, 15-16 March 2011.
3. Elliott, S., “Arctic marine methane cycle simulations for the period of global warming”, USGS/DOE Climate-Hydrates Research Workshop, Boston, MA, 15-16 March 2011.
4. Reagan, M., “Climate Change and the Response of Oceanic Hydrate Accumulations,” European Geosciences Union General Assembly, Vienna, Austria, 7 May 2010.
5. Reagan, M., “Arctic Methane, Hydrates, and Global Climate,” DOE Laboratory Energy R&D Working Group (LERDWG) Meeting, Washington, DC, 17 Feb 2010.
6. Moridis, G., “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.
7. Elliott, S., “Ocean to atmosphere exchange of short lived forcing agents in the Community Earth System Model”, Scripps Institute of Oceanography, June 2012.
8. Elliott, S., “Ocean to atmosphere exchange of short lived forcing agents in the Community Earth System Model”, Pacific Northwest National Laboratory, May 2013.

Other presentations:

9. Reagan, M., “Consequences of Hydrate Dissociation in Response to Climate Change,” (poster) 2nd Gordon Research Conference on Natural Gas Hydrates, Ventura, CA, 18-23 March 2012.
10. Elliott, S., “Biogenic forcing agents in the climate system”, 2011 Program in Interdisciplinary Biological and Biomedical Sciences, U. of New Mexico, Albuquerque, NM, summer 2011.
11. Elliott, S., “Biogenic forcing agents in the climate system”, Graduate level class in Global Change, Biology Department, U. of New Mexico, Albuquerque NM, summer 2011.
12. Elliott, S., Ibid. on title, Chemistry Department, New Mexico Institute of Mining and Technology, summer 2012.
13. Maltrud, M., “Global ocean methane cycle simulations in the Community Earth System Model”, NCAR Biogeochemistry Working Group Meeting, Boulder CO, Winter 2012.
14. Reagan, M., “Basin-Scale Assessment of Hydrate Dissociation in Response to Climate Change,” 7B.2, 7th International Conference on Gas Hydrates, Edinburgh, UK, 18-22 July 2011.

15. Elliott, S., "Arctic Marine Biogeochemistry Modeling", 2011 IARC Summer School, U. of Alaska, Fairbanks, 23 May – 4 June, 2011.
16. Reagan, M., "Advanced Computation in Energy Science," LBNL Advisory Board Meeting—Early Career Panel, 29 March 2011.
17. Elliott, S., "Trace Greenhouse Gases and Sea Ice", NCAR Polar Climate Working Group Meeting, Boulder, CO, 28 Feb – 1 March 2011.
18. Reagan, M., "Simulation of Arctic Gas Hydrate Dissociation in Response to Climate Change: Basin-Scale Assessment," OTC 22153, 2011 Arctic Technology Conference, Houston, Texas, USA, 7–9 February 2011.
19. Reagan, M., "Basin-Scale Simulation of Oceanic Gas Hydrate Dissociation in Response to Climate Change," AGU Fall Meeting 2010, San Francisco, CA, 13-17 December 2010.
20. Elliott, S., "Arctic marine methane cycle simulations for the period of global warming", AGU Fall Meeting 2010, 13-17 Dec 2010.
21. Reagan, M., "Oceanic Hydrates, Methane, Ocean Chemistry, and Climate," Gordon Research Conference on Natural Gas Hydrates, Colby College, Waterville, ME, 6-10 June 2010.
22. Reagan, M., "Arctic Methane, Hydrates, and Global Climate," Environmental and Energy Technology Division Seminar, 17 March 2010.
23. Reagan, M., "Climate Change and the Response of Oceanic Hydrate Accumulations," ESD Town Hall, February 2010.
24. Reagan, M., "Interrelation of Global Climate and the Response of Oceanic Hydrate Accumulations," NETL Methane Hydrates Program Symposium, Atlanta, GA, 25-29 January 2010.
25. Reagan, M., "Large-Scale Simulation of Oceanic Gas Hydrate Dissociation in Response to Climate Change," AGU Fall Meeting 2009, San Francisco, CA, 14-18 December 2009.
26. Elliott, S., "Arctic Marine Methane Cycle Simulations for the Period of Global Warming," AGU Fall Meeting 2009, San Francisco, CA, 14-18 December 2009.
27. Reagan, M., "Regional Simulation of Oceanic Gas Hydrate Dissociation in Response to Climate Change," (poster) TOUGH Symposium 2009, Berkeley, CA, 14 September 2009.
28. Reagan, M., "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.
29. Reagan, M., "Modeling Of Oceanic Gas Hydrate Instability And Methane Release In Response To Climate Change**,"** (poster) 6th International Conference on Gas Hydrates, Vancouver, BC, 6-10 July 2008.
30. Reagan, M., "Dynamic Response Of Oceanic Hydrate Deposits To Ocean Temperature Change," USGS Methane and Climate Symposium, MIT, Cambridge, MA, 25-26 February 2008.
31. Reagan, M., "Oceanic Gas Hydrate Instability And Dissociation In Response To Climate Change" AGU Fall Meeting 2007, San Francisco, CA, 9-14 December 2007.

Work under this project was honored with the following award:

- LANL "Top 10 science & technology developments of 2010" (Scott Elliott and Mathew Maltrud) for work on methane and ocean oxygen limitations.

The project resulted in the following features and publicity:

1. "As Climate Changes, Methane Trapped Under Arctic Ocean Could Bubble to the Surface," *Today at Berkeley Lab,* May 5, 2011.
2. "'Arctic Armageddon' Needs More Science, Less Hype," *Science*, 329, 5992, 620-621, doi: 10.1126/science.329.5992.620, 2010.
3. "Dissociation of Oceanic Hydrates in Response to Climate Change and the Biogeochemical Consequences," *Fire in the Ice*, DOE Methane Hydrates Program, 2010.
4. "Getting to the Bottom of Methane," (Radio segment) NPR's *Living On Earth*, March 12, 2010.
5. "Defusing the Methane Greenhouse Time Bomb," *Scientific American News*, February 5, 2010.
6. "A Sleeping Giant?" *Nature Reports Climate Change,* doi:10.1038/climate.2009.24 (April 2009).
7. "The Hydrate Hazard," *Nature Reports Climate Change*, **3**, 14, doi:10.1038/climate.2009.11, February 2009.

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Reagan, M.T. and G.J. Moridis, (2007) "Oceanic Gas Hydrate Instability and Dissociation Under Climate Change Scenarios," LBNL-62999, *Geophys. Res. Lett.*, **34**, L22709, doi: 10.1029/2007GL031671.

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Reagan, M.T., Moridis, G.J., Elliott, S.M., Maltrud, M., Cameron-Smith, P.J., (2011b). Basin-Scale Assessment of Gas Hydrate Dissociation in Response to Climate Change, *Proc*. 7th International Conference on Gas Hydrates, Edinburgh, Scotland, UK, 17-21 July 2011.

Reagan, M.T., Moridis, G.J. (2008), Dynamic response of oceanic hydrate deposits to ocean temperature change, *J. Geophys. Res*., *113*, C12023, doi:10.1029/2008JC004938.

Reagan, M.T, Moridis, G.J., Zhang, K., (2008) Modeling of Gas Hydrate Instability and Methane Release in Response to Climate Change, *Proc.* of the 6th International Conference on Gas Hydrates, Vancouver, BC, July 6-10, 2008.

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