TECHNOLOGY STATUS ASSESSMENT

GAS HYDRATE INSTABILITY IN THE SOUTHEASTERN BERING SEA

CONTRACT NO. DE-FC26-05NT42665

Prepared by

Dr. Lloyd D. Keigwin, Jr. Woods Hole Oceanographic Institute 360 Woods Hole Road Woods Hole, Massachusetts 02543

Prepared for

U.S. Department of Energy National Energy Technology Laboratory 626 Cochrans Mill Road P.O. Box 10940 Pittsburgh, PA 15236-0940

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use world not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade mane, trademark, manufacture, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This Technical Assessment Report was prepared with the support of the U.S. Department of Energy, under Award No. DE-FC26-05NT42665. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author and do not necessarily reflect the views of the DOE.

TECHNOLOGY STATUS ASSESSMENT

Introduction – Current State of Technology

Methane hydrates buried in the seafloor present a large and untapped hydrocarbon resource. The stability of these deposits is a matter of concern because it is possible that developing their energy potential could also promote their dissociation, and the release of free methane to the ocean and atmosphere. The climate impact of large-scale dissociation is unknown. This is not an idle concern because the geological record is rich with examples where the influence of methane on sediments and biota is suspected. In particular, the largest and most sudden climate warming in the last 60 million years (my), the late Paleocene thermal maximum at about 59 ma (milliannum), is thought to have been caused by methane release from the deep ocean to the atmosphere. Although that was in "deep time," the correlation is compelling. In this project, we will investigate the role of methane in late Quaternary (the last 100,000 years (100 kyr)) climate change with a particular emphasis on testing the idea that every few millennia gas hydrates in ocean sediments dissociate and can account for higher atmospheric methane concentrations during climate warming (Kennett et al., 2000; Kennett et al., 2003).

Foraminifera from sediments cored in Santa Barbara Basin contain unusually low δ^{13} C (Kennett et al., 2000). The low δ^{13} C is associated with alternations of laminated and nonlaminated sediments, and paleoceanographic evidence for warming and cooling that was found to correlate precisely with the millennial to centennial climate oscillations documented in the Greenland ice sheet over the past 60 kyr. For every warm episode in Greenland ice, there is a corresponding surface water warming and bottom water warming in the laminated sediments of Santa Barbara Basin. In particular, two laminated intervals in Marine Isotope Stage (MIS) 3 (~25-60 ka) contained planktonic foraminifera with δ^{13} C much lower than open ocean Σ CO₂. One way to account for δ^{13} C events as much as 3 % (permil) below baseline is through oxidation of enough methane ($\delta^{13}C = -$ 60 ‰) in the water column to draw down local δ^{13} C of Σ CO₂. The presence of methane hydrate in Santa Barbara Basin is known from seeps and from the presence of a bottomsimulating reflector, and Hinrichs (2003) identified biomarkers for anaerobic and aerobic methane oxidation in samples from Kennett's core. Thus, Kennett et al. (2000) suggested that during MIS 3 there must have been two processes operating to liberate methane. First, methane was oxidized at the seafloor during bottom water warming. Second, more catastrophic events such as earthquake-driven slumps may have occasionally reduced sediment overburden and led to methane hydrate dissociation (Paull et al. 1996) and lower δ^{13} C in the water column. It should be noted that catastrophic events are not required; there are many examples of seeps and even plumes of methane (Suess et al., 1999; Klaucke et al. 2005) or hydrate emanating from the seafloor at water depths as great as 2165 m (Paull et al., 1995).

Discussion – Project Strategies

This project will investigate the link between methane hydrates and climate in sediments from the southeastern Bering Sea. In summer 2002 Dr. Keigwin (PI for this project) led an oceanographic expedition to the Bering Sea to collect a series of sediment cores for investigation into the late Quaternary ocean and climate history of the region. Sites from the Umnak Plateau region were cored based on evaluation of seismic data published in the U.S. Geological Survey GLORIA Atlas of the U.S. Exclusive Economic Zone, and exact sites were chosen based on the Edgetech chirp sonar system brought aboard and operated by Dr. Neal W. Driscoll of Scripps Institution of Oceanography. Our overriding goal was to find locations with high rates of accumulation and continuous deposition of sediment. The chirp sonar was ideal because of its ability to resolve decimeter-scale features in the upper tens of meters of the seafloor. We sampled most locations with a multicorer (MC) to recover the sediment water interface, a gravity corer (GGC, up to 5 m), and a large diameter (jumbo) piston corer (JPC, up to 20 m).

Umnak Plateau is a classic location for methane hydrate research. It is here that scientists first coined the term BSR (bottom simulating reflector) (Scholl and Hart, 1993). Although presence of a BSR is commonly taken as a sign of methane hydrates, on Umnak Plateau the BSR was found to result from silica diagenesis. Nevertheless, we now know that the absence of a BSR does not mean the absence of methane hydrate (Borowski et al., 1999; Paull, Matsumoto, Wallace et al., 1996), and indeed Deep Sea Drilling Project (DSDP) scientists measured nearly pure methane in the head space of DSDP Site 185 collected from the plateau at 2110 m (Fig. 2; Creager, Scholl, et al., 1973). Offshore of Umnak Plateau in the Aleutian Basin, USGS scientists have mapped extensive seismic features that are thought to indicate the presence of vast stores of methane hydrate (Scholl and Hart, 1993). On the Pacific side of the Aleutians, Elvert et al. (2000) identified anaerobic methane oxidation associated with cold seeps at seafloor depths of nearly 5000 m. Thus, the entire region off southwest Alaska probably has enormous stores of methane hydrate.

Preliminary sampling of Umnak Plateau core 51JPC (~1500 m) for stable isotopes in foraminifera revealed five events of δ^{13} C in MIS 3 as low as -12 ‰, and one of those may correlate with an event in a deeper core. In this project we will develop the stratigraphy and chronology of these and other Umnak Plateau cores from a range of water depths between 700 m and 2000 m. For the first time, the reproducibility of δ^{13} C minima will be tested in multiple cores, and because the cores span a range of water depths we have the potential to develop a three dimensional picture of possible methane hydrate dissociation. Events of low δ^{13} C will be sampled to identify methanotrophy biomarkers and confirm their postulated origin from methane hydrate through compound specific mass spectrometry.

In addition to mass spectrometric measurement of the stable isotope ratios of C and O in foraminifera, standard logging of cores for Gamma Ray attenuation and magnetic susceptibility, and measurement of radiocarbon age, our colleague, Dr. Steve Lund of University of Southern California, will develop high resolution studies of magnetic field behavior in at least one of our cores. This will provide an independent chronology through the resulting history of magnetic susceptibility, declination and paleointensity as well as by identification of magnetic field excursions (brief near reversals) such as the Laschamp Event that occurred at about 40 ka.

Dr. Cook will visit the laboratory of Dr. Kai Hinrichs (Bremen, Germany) to investigate the organic geochemical situation of Umnak plateau sediments. This analytical technique was first applied to the core samples from the Santa Barbara Channel. If there has been anaerobic methanotrophy associated with sediments low in δ^{13} C, then evidence of Archaeol should be present; if oxidation was aerobic, then evidence of Diplopterol should be present.

<u>Future</u>

Analytical methods that will be used in this project are well known and tested. The greatest risks are outcomes that will lead to rejection of our hypothesis: (1) that we only find evidence for anaerobic methane oxidation, and (2) that we find evidence for aerobic methane oxidation but it is unrelated in a systematic way with climate. As an example of the latter case, the Kennett et al. (2003) hypothesis assumes atmospheric methane concentration during the last glacial epoch was driven by changes in bottom water temperatures at upper slope depths. Indeed, this is consistent with the benthic foraminiferal and biomarker records in Santa Barbara Basin (Hinrichs et al. 2003), but very low planktonic δ^{13} C may be generated by free gas released to the water column by earthquakes and slope failure. This would still be an important result in the Bering Sea, considering the number of likely events, but it would undermine our test of the Kennett et al. hypothesis. Regardless, this project will further our understanding of abrupt climate change in the late Quaternary.

Recently there have been two advances in the search for methane seeps. First, it has been reported that side scan sonar, when deep-towed, is able to image gas plumes in the deep ocean (Klaucke et al., 2005). Second, a method has been developed to directly detect methane dissolved in the water column by towing a "sniffer" from a surface ship (Camilli and Hemond, 2004). Although neither of these methods is directly relevant to this project, if we find that indeed the Umnak Plateau has been a source of methane released to the deep ocean or the atmosphere then it would be important to further assess this process with these and similar towed devices.

References

- Borowski, W.S., C.K. Paull, and W.U. III, Global and local variations of interstitial sulfate gradients in deep-water, continental margin sediments: Sensitivity to underlying methane and gas hydrates, *Marine Geol.*, *159*, 131-154, 1999.
- Camilli, R. and H. F. Hemond, Nereus/Kemonaut, a mobile autonomous underwater mass spectrometer, Trends analytical Chem, 23, 307-313, 2004.
- Creager, J.S., D.W. Scholl, and e. al., *Initial Reports of the Deep Sea Drilling Project*, U. S. Govt. Printing Office, Washington, D.C., 1973.

- Elvert, M., E. Suess, J. Greinert, M. J. Whiticar, Archaea mediating anaerobic methane oxidation in deep-sea sediments at coled seeps of the eastern Aleutian subduction zone, *Organic Geochemistry*, *31*, 1175-1187, 2000.
- Hinrichs, K.-U., L. Hmelo, and S.P. Sylva, Molecular Fossil Record of Elevated Methane Levels in Late Pleistocene Coastal Waters, *Science*, 299, 1214-1217, 2003.
- Kennett, J.P., K.G. Cannariato, I.L. Hendy, and R.J. Behl, Carbon isotopic evidence for methane hydrate instability during Quaternary interstadials, *Science*, 288, 128-133, 2000.
- Kennett, J.P., K.G. Cannariato, I.L. Hendy, and R.J. Behl, *Methane hydrates in Quaternary climate change*, American Geophys. Union, Washington, D.C., 2003.
- Klaucke, I., H. Sahling, D. Burk, W. Weinrebe, and G. Bohrmann, Mapping Deep-water gas emissions with sidescan sonar, *EOS Transactions, American Geophysical Union*, 86, 341-346, 2005.
- Paull, C.K., W.J. Buelow, W.U. III, and W.S. Borowski, Increased continental margin slumping frequency during sea-level lowstands above gas hydrate-bearing sediments, *Geology*, 24, 143-146, 1996a.
- Paull, C.K., R. Matsumoto, and P. Wallace, *Proceedings ODP Initial Reports 164*, Ocean Drilling Program, College Station, Texas, 1996b.
- Paull, C.K., W. Ussler, III, W.S. Borowski, and F.N. Spiess, Methane-rich plumes on the Carolina continental rise: Associations with gas hydrates, *Geology*, 23, 89-92, 1995.
- Scholl, D.W., and P.E. Hart, Velocity and amplitude structures on seismic-reflection profiles--Possible massive gas-hydrate deposits and underlying gas accumulations in the Bering Sea Basin, in *The future of energy gases*, edited by D.G. Howell, pp. 331-351, U.S. Govt. Printing Office, Washington, D.C., 1993.
- Suess, E., M.E. Torres, G. Bohrmann, R.W. collier, J. Greinert, P. Linke, G. Rehder, A. Trehu, K. Wallmann, G. Winckler, and E. Zuleger, Gas hydrate destabilization: enhanced dewatering, benthic material turnover and large methane plumes at the Cascadia convergent margin, *Earth Planet. Sci. Lett.*, 170, 1-15, 1999.