Gas Hydrate Instability in the Southeastern Bering Sea

Contract No. DE-FC26-05NT42665

Quarterly Progress Report

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Progress

Task # **7.0**
Task **AMS 14C Dating**

We have prepared 5 samples of *N. pachyderma* (s.) for AMS 14C dating from core 57JPC. The preparation of samples from 51JPC is in progress. The abundance of *N. pachyderma* (s.) in 51JPC is low, necessitating a detailed survey of the absolute abundance of this species in the core. We are constrained to making 14C measurements in samples that do not contain authigenic carbonate minerals, which would overprint the 14C/12C of the foraminifer shell with the 14C/12C of the diagenetic minerals, and thereby render the measurement unrepresentative of the calendar age of the sample. We are visually inspecting and measuring the d13C of an aliquot of each *N. pachyderma* (s.) sample to ensure that there is no trace of authigenic material on the samples we will submit for analysis.

Task # **8.0**
Task **Organic Geochemistry**

Mea Cook spent 4 January through 3 April at University of Bremen working with Prof. Kai-Uwe Hinrichs to study the organic biomarkers in 51JPC and 57JPC.

The first task was to freeze dry and homogenize the sediment samples to prepare them for microwave-assisted solvent extraction.

The next step was to select several background samples and test several methods to optimize a procedure to achieve maximum recovery and separation of compounds of interest. Significant quantities of biomarkers can be locked in the carbonate matrix of authigenic mineral layers associated with anaerobic methane oxidation, so we tested whether decalcification of the sample could increase the yield of these biomarkers. We also tested whether saponification of the total lipid extract would increase the yield of fatty acids. During the method testing, the gas chromatograph/mass spectrometer (GC-MS) required extensive repairs and was unusable from 24 January to 16 February.

Consequently, the method testing was not completed until mid-February, and we could not begin to process the rest of the samples until then.

We formed a strategy to first process samples at coarse resolution across the 3 stratigraphically-youngest authigenic carbonate layers in 51JPC. We then processed samples at high resolution across the youngest carbonate layer in this core. We wanted to see first whether there was a consistent difference in the distribution and d13C of biomarkers between "hot" samples (within the authigenic mineral layers) and "cold" samples (outside the authigenic mineral layers). We found that there was a higher concentration of archaeol, a biomarker of anaerobic methane oxidation, during the youngest authigenic carbonate layer. Archaeol was present, but in very small quantities in "cold" samples. Diploptene, a degradation product of diplopterol, a biomarker of aerobic methane oxidation, was present in low concentrations throughout the record.

We could tell from quantifying archaeol and diploptene that these compounds were not present in high enough quantities to be able to measure the d13C of archaeol in the "cold" samples, or measure the d13C of diploptene in any of the samples. This was problematic because we would ideally like to have continuous isotopic measurements on these compounds downcore in order to test our hypothesis that these biomarkers would have very low d13C only in the "hot" samples. So we revisited the portion of the total lipid extract we reserved from one hot sample and one cold sample and performed an ether cleavage to see whether there were significant quantities of intact membrane lipids in both samples. Membrane lipids from archaea such as anaerobic methane oxidizers include unique hydrocarbons, monocyclic biphytanes, linked by ether bonds. After the ether cleavage, we detected measurable quantities of mono-cyclic biphytanes in both samples. Therefore it is likely we can use ether cleavage to produce a continuous record of d13C of membrane lipids of methane oxidizing archaea in these cores.

We began to measure the d13C of biomarkers in the samples described above in mid-March, however, it was evident that the isotope-ratio mass spectrometer (GC-IRMS) was not functioning properly since the d13C of the internal standard fluctuated from sample to sample by up to 6 permil. The GC-IRMS was taken down for repairs, and the newly refurbished instrument was available on 2 April. We measured the d13C of archaeol in a hot sample, and we measured the d13C of the ether cleaved monocyclic biphytane in the hot and cold samples. To our delight, we found that the archaeol d13C is -70 permil, which clearly shows that there were anaerobic methanotrophs present when the authigenic carbonate formed.

We also found that the monocyclic biphytane in the hot sample was -48 permil, and -22 permil in the cold sample. Since the monocyclic biphytane in the hot sample is not as depleted in d13C as the archaeol in the same sample, it shows that the intact membrane lipid is not as specific a biomarker for anaerobic methanotrophy. That is, there are organisms making monocyclic biphytanes in their membrane lipids other than anaerobic methanotrophs. However, -48 permil is low enough that it requires the presence of anaerobic methanotrophs in the sample. So this biomarker will serve very nicely as a supporting dataset to the archaeol data.

We prepared samples from 57JPC with the same strategy as in 51JPC: coarse resolution across three authigenic carbonate layers, and at high resolution across one layer. These samples have been analyzed with the GC-MS for identification and quantification of compounds and are awaiting ether cleavage and analysis on the GC-IRMS.

The trip to Bremen was a great success. The biomarkers we found, and their d13C confirmed our hypothesis that the authigenic mineral layers formed in association with vigorous methane oxidation. The instrument breakdowns and the nature of the samples prevented all the lab work from being completed during this 3-month visit, so Mea Cook will return to Bremen in July, 2007 to finish the work.

Schedule

Mea Cook will return to Bremen in July, 2007 for ~3 weeks to analyze samples from 51JPC and 57JPC for stable isotopes on the GC-IRMS. She will also perform ether cleavage on the samples and measure the cleaved samples with the GC-IRMS. This will complete Task 8.

After the d13C of the *N. pachyderma* (s.) samples is measured, we will submit them for radiocarbon analysis. This will complete Task 7.

While in Bremen this spring, Mea Cook make the acquaintance of Dr. Sabine Kasten (Alfred Wegner Instutite, Bremerhaven), who studies authigenic barite, a mineral that forms at sulfate-methane interfaces. She took interest in this project and offered to measure samples from 51JPC and 57JPC for major and minor elements at no cost. These data will provide an additional perspective on the movement of geochemical fronts in the sediment column through time.

Other Activities

Mea Cook will submit an abstract to the 9th International Conference on Paleoceanography on this project. The meeting is in September, 2007, in Shanghai, China.