LIPIDS AND STABLE ISOTOPE BIOGEOCHEMISTRY OF GAS HYDRATES IN THE GULF OF MEXICO. C. L. Zhang\textsuperscript{1}, R. Sassen\textsuperscript{2}, A. Peacock\textsuperscript{3}, D. C. White\textsuperscript{3}, Y. Huang\textsuperscript{4}, J. D. Wall\textsuperscript{5}, and L. Larsen \textsuperscript{5}, \textsuperscript{1}Dept. Geol. Sci., University of Missouri, Columbia, MO 65211 (zhangcl@missouri.edu), \textsuperscript{2}Texas A&M University, \textsuperscript{3}University of Tennessee, \textsuperscript{4}Brown University, \textsuperscript{5}Dept. Biochemistry, University of Missouri-Columbia.

\textbf{Introduction:} Gas hydrates are ice-like crystalline deposits in which hydrocarbon and non-hydrocarbon gases are held within rigid cages of water molecules. The Gulf of Mexico has numerous locations of gas hydrates. Geochemical evidence indicates that methane oxidation occurs in these gas hydrate environments \cite{1}. The goal of this study was to use an integrated lipid biomarker-stable isotope approach to delineate the mechanisms of microbial methane oxidation in the Gulf of Mexico.

\textbf{Material and Methods:} Grab samples were collected from two locations on the Gulf slope using research submersibles. Sample GC234 was collected in 1998 and sample GC286-g was collected in 2000. A control sample (GC286-c) was collected in normal marine sediments at the same time GC286-g was collected. Samples of about 80 grams were freeze-dried and processed for analysis of bacterial phospholipid fatty acids (PLFA).

\textbf{Results and Discussion:} For collections made in 2000, total PLFA was about 30-fold higher in GC286-g (22.1 \textmu mol/g) than in GC286-c (0.7 \textmu mol/g). This indicates that bacterial biomass was significantly enhanced at this gas hydrate deposit compared to normal marine sediments. Total PLFA was 8.0 \textmu mol/g for the GC234 sample, and this lower concentration may be due to degradation during storage or reflect a different biological activity at this location.

PLFA of the three samples consisted mainly of monounsaturated fatty acids (32.3-56.0 mole\%), branched saturated fatty acids (13.3-41.5 mole\%), and normal saturated fatty acids (13.9-29.6 mole\%). Fractions of branched monounsaturated fatty acids, cyclic fatty acids, and polyunsaturated fatty acids (PUFA) were < 10 mole\%. Significantly higher PUFA occurred in sample GC286-g (2.3 mole\%) than in GC286-c (0.8 mole\%). PUFA are known to be relatively high in low-temperature or high-pressure adapted species \cite{2}, thus their presence in these samples may reflect the physical conditions of bacterial activity at the gas hydrate deposits. No PUFA were detected in sample GC234, which may be due to chemical degradation during sample storage.

All three samples contained abundant lipid biomarkers (3.0 – 30 mole\% of total PLFA) that are indicative of sulfate-reducing bacteria (a15:0, i15:0) \cite{3} or methanotrophs (18:1w7c) \cite{4}. Both types of bacteria can potentially oxidize methane at gas hydrates. Methane is the most $^{13}$C-depleted hydrocarbon known: thermogenic methane has $\delta^{13}$C values ranging from $-30\%$ to $-50\%$ whereas biogenic methane has $\delta^{13}$C values commonly less than $-60\%$ \cite{5}. It is expected that bacteria oxidizing methane will also have low $\delta^{13}$C values in biomass and in their lipid biomarkers. Our next step is to analyze the carbon-isotope ratios of the PLFA indicative of sulfate-reducing bacteria or methanotrophs to decipher whether these microorganisms are involved in methane oxidation at these gas hydrate deposits.