

**FINAL REPORT**

**Laboratory Constraints on the Stability of Petroleum at Elevated Temperatures: Implications for the Origin of Natural Gas**

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## ABSTRACT

Results of prior DOE supported research conducted at the Woods Hole Oceanographic Institution have demonstrated the participation of sedimentary minerals and water as reactants and catalysts in chemical transformations associated with the degradation of oil and the formation of low molecular weight organic compounds. The occurrence of such processes in natural environments can be difficult to recognize because the composition of organic alteration products may not be substantially different than those produced by thermal cracking. The goals of this study were the development of diagnostic tools based on hydrogen and carbon isotopes that can be used to identify geochemical processes responsible for the formation of thermogenic natural gas. In addition, our activities were expanded to include experimental investigation of CO<sub>2</sub> reduction in aqueous systems at elevated temperature and pressures and an assessment of microbial activity in relatively low temperature (<70°C) natural gas reservoirs in southeastern Oklahoma. Specific objectives included:

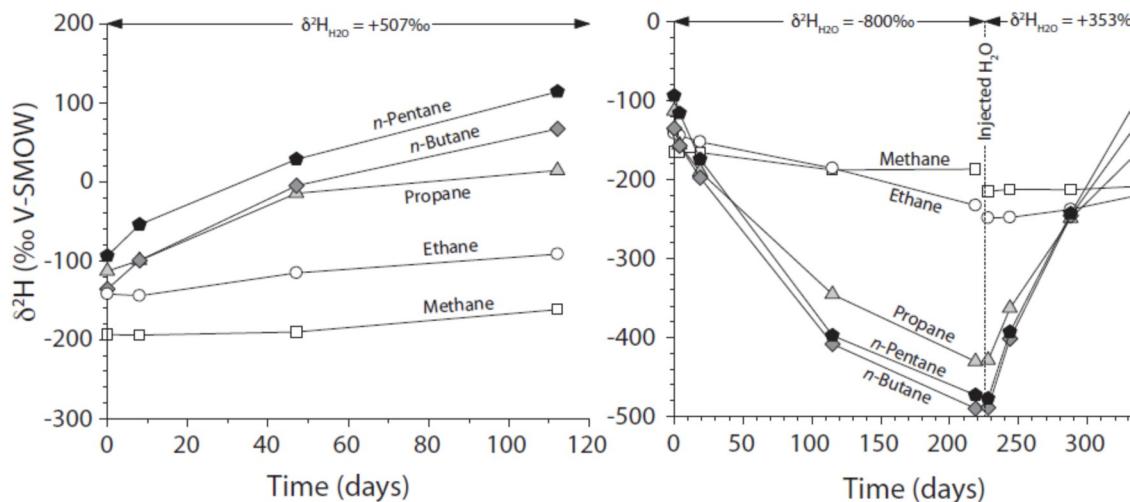
- A laboratory investigation of geochemical processes that regulate the hydrogen isotope composition of low molecular weight hydrocarbons in natural gas at elevated temperatures and pressures.
- A laboratory investigation of factors that regulate the carbon isotope composition of organic acids in basinal brines.
- A laboratory assessment of the role of methanol during reduction of CO<sub>2</sub> to CH<sub>4</sub> under hydrothermal conditions.
- Characterization of microbial ecosystems in coproduced fluids from the Potato Hills gas field to assess the role of microbes in the generation of natural gas.

## SUMMARY OF RESULTS

### Hydrogen Isotope Exchange

To investigate the extent of <sup>2</sup>H/<sup>1</sup>H exchange between hydrocarbons and water under hydrothermal conditions, we performed experiments by heating C<sub>1</sub>–C<sub>5</sub> *n*-alkanes in aqueous solutions of varying initial <sup>2</sup>H/<sup>1</sup>H ratios in the presence of a pyrite-pyrrhotite-magnetite redox buffer at 323°C and 35–36 MPa. Extensive and reversible incorporation of water-derived hydrogen into C<sub>2</sub>–C<sub>5</sub> *n*-alkanes was observed on timescales of months (Figure 1). In contrast, comparatively minor exchange was observed for CH<sub>4</sub>. Isotopic exchange is facilitated by reversible equilibration of *n*-alkanes and their corresponding *n*-alkenes with H<sub>2</sub> derived from the disproportionation of water. Rates of  $\delta^2\text{H}$  variation in C<sub>3+</sub> *n*-alkanes decreased with time, a trend is consistent with an asymptotic approach to steady-state isotopic compositions regulated by alkane-water isotopic equilibrium. Substantially slower  $\delta^2\text{H}$  variation was observed for ethane relative to C<sub>3</sub>–C<sub>5</sub> *n*-alkanes, suggesting that the greater stability of C<sub>3+</sub> alkenes and isomerization reactions may dramatically enhance rates of <sup>2</sup>H/<sup>1</sup>H incorporation in longer chain hydrocarbons.

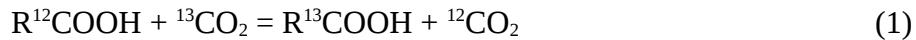
Thus, in reducing aqueous environments, metastable equilibration of alkenes and their corresponding alkanes facilitates rapid  $^2\text{H}/^1\text{H}$  exchange between alkyl- and water-bound hydrogen on relatively short geological timescales at elevated temperatures and pressures. The proximity of some thermogenic and purported abiogenic alkane  $\delta^2\text{H}$  values to those predicted for equilibrium  $^2\text{H}/^1\text{H}$  fractionation with ambient water suggests that this process may regulate the  $\delta^2\text{H}$  signatures of some naturally occurring hydrocarbons.



**Figure 1.**  $\delta^2\text{H}$  values for aqueous  $\text{C}_1$  to  $\text{C}_5$  *n*-alkanes as a function of time during two laboratory experiments heating in the presence of a pyrite-pyrrhotite-pyrite redox buffer at  $323^\circ\text{C}$  and 35 MPa. The vertical dashed line at 226 days in the second graph represents injection of  $^2\text{H}$ -spiked water to raise the  $\delta^2\text{H}_{\text{H}_2\text{O}}$  value of the solution in the reaction cell. Values of  $\delta^2\text{H}_{\text{H}_2\text{O}}$  are annotated for each experimental stage.

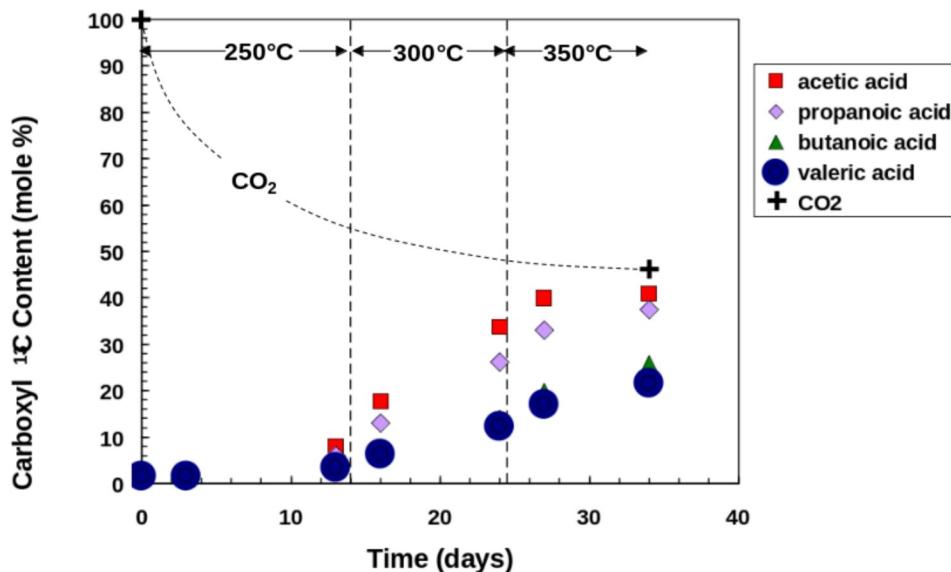
### Carbon Isotope Exchange Involving Organic Acids

Additional laboratory experiments designed to investigate mechanisms of hydrogen and carbon isotopic exchange during heating of aqueous organic compounds in subsurface environments were conducted. A particularly exciting laboratory result has been the unequivocal demonstration that carboxyl carbons in aqueous organic acids exchange carbon with aqueous carbonate. During an experiment heating aqueous  $\text{C}_2$ - $\text{C}_5$  organic acids at 250 to  $350^\circ\text{C}$  in the presence of fully labeled  $^{13}\text{CO}_2$ , the carboxyl carbon for each organic acid was observed to rapidly incorporate  $^{13}\text{C}$ -labelled carbon without the formation or degradation of individual organic acids (Figure 2). This process can be represented by the reaction:



Such a process may influence the isotopic composition of organic acids and both aqueous and solid carbonate species in natural environments.

We have also demonstrated that reduction of organic acids to their corresponding alkanes occurs readily at the relatively reducing conditions that characterize subsurface environments, thereby providing a mechanism for incorporation of inorganic carbon into organic compounds. Accordingly, the carbon isotope composition of low molecular weight thermogenic hydrocarbons may reflect the isotopic composition of coexisting carbonate species. The possibility that alkanes



**Figure 2.**  $^{13}\text{C}$  content (mole %) of the carboxyl carbon in  $\text{C}_2\text{-C}_5$  aqueous organic acids during heating at 250 to 350°C and 350 bar in the presence of fully labeled  $^{13}\text{CO}_2$ .

constituting petroleum may derive some of their carbon from dissolved carbonate species has large and diverse implications for the use of carbon isotopes as a tool for oil-source correlations and as an indicator of thermal maturity. Current models typically attribute systematic variations in the carbon isotopic composition of thermogenic hydrocarbons to kinetic isotope effects during degradation of petroleum and kerogen. Our results suggest that these models may require modification to include isotopic exchange with inorganic carbon sources.

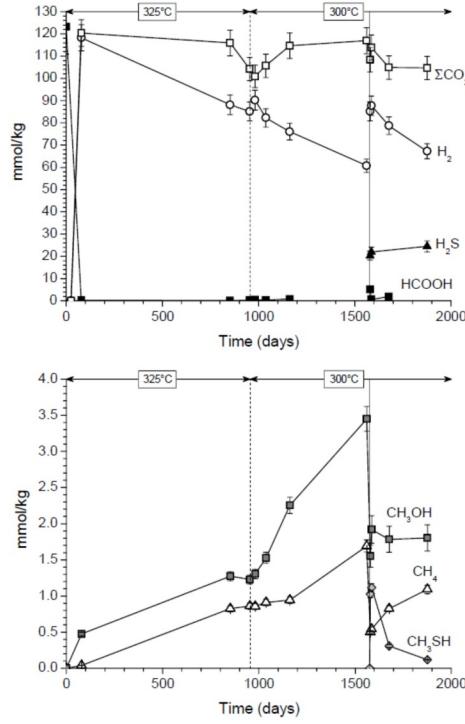
### Aqueous $\text{CO}_2$ Reduction Under Hydrothermal Conditions

Previous work investigating reactions involving formic acid and carbon dioxide was expanded to include examination of the reactivity of CO,  $\text{CH}_3\text{OOH}$ , and  $\text{CH}_4$ . Of particular interest is the reaction:



This reaction is commonly referred to as the water-gas shift reaction and is of direct relevance to the abiotic production of hydrocarbons since it may represent a source of CO, a key reactant in Fischer-Tropsch-type processes. Our experiments conducted at 150 to 300°C and 350 bars demonstrated extremely rapid reaction rates on a geologic time scale. The CO experiments in conjunction with the earlier  $\text{CH}_3\text{OOH}$  studies have now demonstrated that the rates of reaction between aqueous CO,  $\text{CO}_2$ ,  $\text{CH}_3\text{OOH}$ ,  $\text{H}_2$  and  $\text{H}_2\text{O}$  are sufficiently rapid that these species are likely to be in thermodynamic equilibrium in aqueous subsurface environments such as natural gas and oil reservoirs. This conclusion is consistent with low CO concentrations in natural gas and the absence of formate in oil-field brines. Results of these experiments were published in *Geochimica et Cosmochimica Acta* (Seewald et al., 2006).

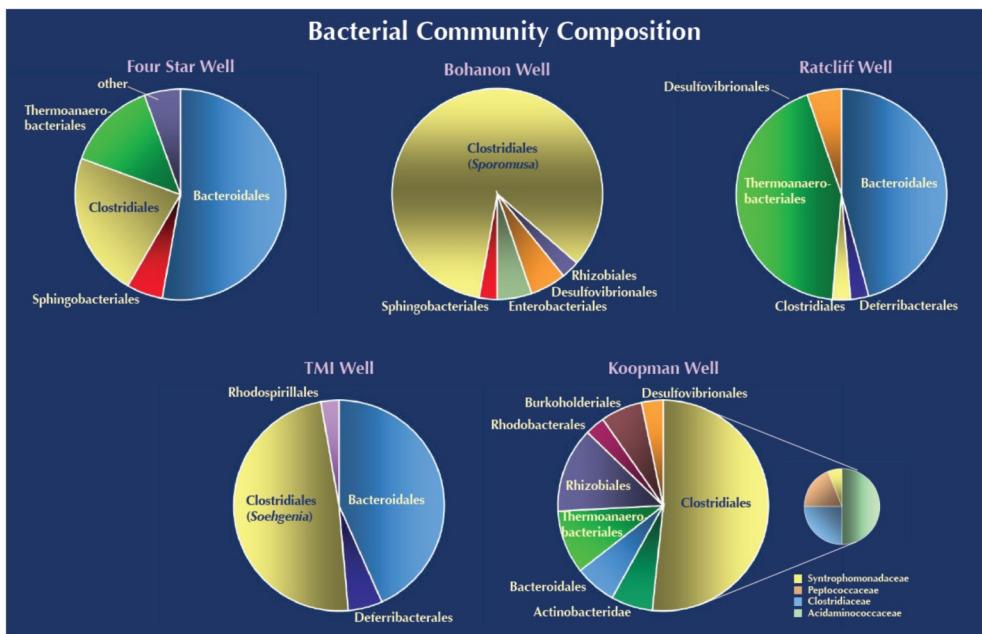
The role of methanol during complete reduction of  $\text{CO}_2$  to  $\text{CH}_4$  was explored through additional experiments that build on the initial results of Seewald et al. (2006). Abiotic synthesis of  $\text{CH}_4$  in ridge-crest hydrothermal fluids and petroleum systems is often presumed to occur on the surfaces of catalytically active minerals. However, aqueous reduction of  $\text{CO}_2$  represents an alternative pathway to form reduced carbon compounds such as  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{CH}_3\text{OH}$  and  $\text{HCOOH}$ . To investigate whether  $\text{CH}_3\text{OH}$  is a metastable intermediary crucial to hydrothermal  $\text{CH}_4$  production, aqueous fluids containing  $\text{CO}_2$  and  $\text{H}_2$  were heated at 325 and 300°C at 350 bar without added mineral catalysts (Figure 3). Results indicate that reaction of  $\text{CH}_3\text{OH}$  to  $\text{CH}_4$  represents the rate limiting step during the complete reduction of  $\text{CO}_2$ . To assess the response of  $\text{CH}_4$  production rate on temperature, the experiment was cooled from 325 to 300°C. Upon cooling, the rate of  $\text{CH}_4$  production increased due enhanced stability of the  $\text{CH}_3\text{OH}$  intermediary at the lower temperature, providing further evidence of the critical role that  $\text{CH}_3\text{OH}$  plays in aqueous  $\text{CH}_4$  formation. Injection of  $\text{H}_2\text{S}$  to the experimental solution did produce  $^{13}\text{C}$ -labelled methanethiol ( $\text{CH}_3\text{SH}$ ) from  $\text{H}^{13}\text{COOH}$  but direct reduction of  $\text{CO}_2$  to  $\text{CH}_3\text{SH}$  was not observed, suggesting that  $\text{CH}_3\text{SH}$  does not fulfill the same role in regulating aqueous  $\text{CH}_4$  formation rates. This study indicates that, even in the absence of heterogeneous catalysts, aqueous synthesis of  $\text{CH}_4$  from  $\text{CO}_2$  is observable on a laboratory timescale, and may be a significant source of  $\text{CH}_4$  to hydrothermal fluids at unsedimented mid-ocean ridge systems. A manuscript discussing the results of this work is in final stages of preparation for submission to *Geochimica et Cosmochimica Acta* (Reeves et al, in prep).



**Figure 3.** Measured concentrations of dissolved species as a function of time during a laboratory experiment to examine  $\text{CO}_2$  reduction at 325°C and 300°C. The solid vertical line at 1575 days represents injection of a solution of  $\text{H}_2\text{S}$ ,  $\text{H}^{13}\text{COOH}$  and  $\text{NaCl}$ .  $\text{CH}_4$  accumulation in solution was initially slow but increased to a constant rate by the end of the 325°C phase and increased further upon cooling to 300°C.

## Characterization of Microbial Ecosystems in Potato Hills Gas Reservoirs

Formation waters from five producing wells from the Potato Hills gas field, southeastern Oklahoma were sampled in June 2004 for microbiological and chemical analyses. All of the wells contained substantial numbers of microorganisms (ranging from  $1.1 \times 10^6$  cells/ml in the 4Star well to  $4.9 \times 10^6$  in the TMI-25 well). We were able to isolate five thermophilic sulfate-reducers from the 4Star well. Four of these isolates can grow at 70°C, and one grows at temperatures up to 75°C. Methods that require the growth of organisms in the laboratory, i.e. cultivation, are not well suited as the sole method for investigating the overall composition of microbial communities, since only a small percentage of the microorganisms can be cultured. Thus, we used an additional cultivation-independent approach based on the detection of signature molecules that are present in all organisms, i.e., the gene encoding 16S ribosomal RNA



**Figure 4.** Bacterial communities identified with 16S rDNA clone libraries at five different wells in the Potato Hills natural gas field show broad diversity across the system. Members of the order Bacteroidales dominate the clone libraries at Four Star, Ratcliff and TMI wells. These sequences all fall among the Porphyromonadaceae and are 95% similar to species of *Proteiniphilum* and *Ruminobacillus*. Members of Clostridiales at the Bohanon well are comprised almost entirely of *Sporomusa* spp., while Clostridiales at the TMI well are 94% similar to *Soehngenia saccharolytica*. Four Star and Koopman wells host diverse groups of Clostridiales. At the Four Star well the Thermoanaerobacteriales are most similar to *Thermoacetogenium phaeum*, while those at Ratcliff and Koopman wells are similar to both *Thermoacetogenium phaeum* and *Thermoanaerobacter ethanolicus*.

(16S rDNA). Phylogenetic analysis revealed putative syntrophic communities dominated by heterotrophic bacteria and methanogenic archaea (Figure 4). The bacterial communities consisted predominantly of members of the Clostridiales and Thermoanaerobacteriales. These bacteria often use fermentative metabolisms that consume and/or produce organic acids and are also known to grow syntrophically with methanogens. Archaeal sequences belonged to the Methanosaarcinales and the Methanomicrobiales. Based on sequence similarity, resident microbes are likely thermophiles, with optimum growth at 60-80°C, which is consistent with the optimum growth temperature of the obtained isolates and the in situ production temperatures of the wells. Thus, these organisms might be involved in syntrophic fermentation of organic acids in the gas well resulting in the production of C<sub>2+</sub> hydrocarbons in natural gas. The abundant presence of aqueous organic acids in formation waters produced at Potato Hills is consistent with this hypothesis.

#### *Publications Resulting from this Grant:*

Seewald J.S., Zolotov M., and McCollom T.M. (2006) Experimental investigation of carbon speciation under hydrothermal conditions, *Geochim. Cosmochim. Acta* **70**, 446-460.

Reeves E.P., Seewald J.S., and Sylva S. (2011) Hydrogen isotope exchange between *n*-alkanes and water under hydrothermal conditions. *Geochim. Cosmochim. Acta* (submitted).

Reeves E., (2010) Laboratory and field-based investigations of subsurface geochemical processes in seafloor hydrothermal systems. *Ph.D. Thesis, MIT/WHOI Joint Program in Chemical Oceanography*, p. 279.

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