

# THE ROLE OF WATER DURING DECOMPOSITION OF OIL AT ELEVATED TEMPERATURES: CONSTRAINTS FROM REDOX BUFFERED LABORATORY EXPERIMENTS

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## INTRODUCTION

Oil and natural gas coexist with water and minerals in sedimentary basins. There is increasing evidence that inorganic chemical processes play a critical role in regulating organic reactions responsible for the generation of oil and its decomposition to form natural gas. In particular, water has been implicated as both a solvent and reactant during organic reactions at elevated temperatures and pressures (1,2,3). Moreover, the redox state of subsurface environments and the presence or absence of catalytically active transition metals may influence the absolute amounts and relative distribution of organic alteration products (2,4,5). Understanding the extent to which such processes affect the stability of petroleum at elevated temperatures is essential to predict the timing and location of natural gas formation.

The present study was undertaken to examine the stability of oil in the presence of water at elevated temperatures and pressures. Hydrous pyrolysis experiments have proven to be an effective tool for examining organic-inorganic interactions during oil and natural gas generation. Experimental apparatus utilized during conventional hydrous pyrolysis, however, results in the coexistence of source rocks, liquid water, floating oil, and volatile species occupying the pressure vessel head space at experimental conditions (6). As a result it is not always possible to distinguish whether secondary reactions involve gaseous, aqueous, or oil phase species. The experiments presented here were designed to minimize such uncertainties and allow a comparison of reactions involving oil dissolved in water with reactions taking place within a separate oil phase. Because organic reactions are influenced by their chemical environment, we used naturally occurring mineral assemblages to regulate key chemical variables such as redox, sulfur fugacity, and pH.

## EXPERIMENTAL

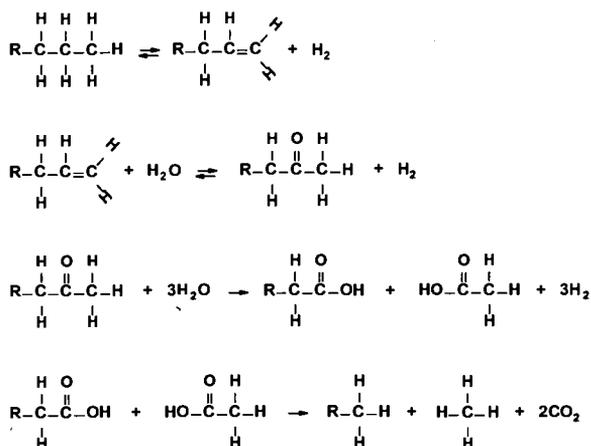
Two experiments examining the decomposition of a medium weight oil from Eugene Island block 330 in the U.S. Gulf Coast were conducted in a flexible-cell hydrothermal apparatus (7) consisting of a flexible gold and titanium reaction cell contained within a stainless steel pressure vessel. This equipment allows external control of pressure at sufficiently high values to preclude the formation of a vapor filled head space during an experiment. A titanium sampling tube connected to the reaction cell allows reaction progress to be monitored as a function of time by periodic extraction of fluid samples. Experiment PPM-AQ was conducted at 350°C and 350 bars and contained 37.2 g an aqueous Na-Mg-Cl solution and 52.9 mg of oil. The relatively small amount of oil in this experiment did not exceed the aqueous solubility of oil at 350°C and 350 bars (8) ensuring all reactions involved aqueous species. In contrast, experiment PPM-OIL was designed to maintain a separate oil phase floating on top of liquid water at experimental conditions. This experiment initially contained 13.3 g of aqueous Na-Mg-Cl solution and 10.7 g of oil. To allow sampling of both the oil and water the flexible-cell hydrothermal apparatus was modified to include two titanium sampling lines at opposite ends of the tubular reaction cell. By orienting the apparatus vertically, the aqueous phase could be sampled through the lower sampling line while the oil was sampled through the upper sampling line. Experiment PPM-OIL was initially conducted at 325°C and 350 bars but after 1130 h of heating the temperature was increased to 350°C.

To regulate redox and sulfur fugacity during the experiments a mineral assemblage containing equal amounts of pyrite, pyrrhotite, and magnetite were added to each experiment. In addition, brucite and amorphous silica were added to PPM-AQ and brucite was added to PPM-OIL to regulate *in situ* pH. Because the densities of the added minerals are greater than water and oil, the minerals resided within the aqueous phase at the bottom of the reaction cell during experiment PPM-OIL. Fluid samples were removed from the experiments at selected times and analyzed for the concentrations of CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>S, inorganic anions and cations, and numerous organic species including C<sub>1</sub>-C<sub>6</sub> hydrocarbons, alcohols, aldehydes, ketones, organic acids, and phenols.

## RESULTS AND DISCUSSION

Heating of oil in the presence of water and inorganic minerals during both experiments resulted in extensive alteration of the oil and the generation of low molecular weight carbon compounds. In general, generation of dissolved gaseous products proceeded at a faster rate during PPM-AQ relative to PPM-OIL (Fig. 1) and produced dissolved gas containing a substantially higher proportion of CO<sub>2</sub> (Fig. 2). Examination of the dissolved gaseous hydrocarbon fraction reveals a significant enrichment in CH<sub>4</sub> during PPM-AQ relative to PPM-OIL (Fig. 3). Dissolved H<sub>2</sub> concentrations during PPM-AQ were consistent with values predicted for thermodynamic equilibrium between water and the pyrite-pyrrhotite-magnetite mineral assemblage. In contrast, measured H<sub>2</sub> concentrations in the aqueous phase of experiment PPM-OIL were higher than those predicted for equilibrium with a pyrite-pyrrhotite-magnetite mineral assemblage suggesting that the rate of H<sub>2</sub> generating reactions involving carbon compounds in the oil exceeded the rate at which the redox buffer consumed H<sub>2</sub>. The higher H<sub>2</sub> concentrations during PPM-OIL in comparison to PPM-AQ indicate redox conditions were considerably more reducing during the PPM-OIL experiment.

Maturation of oil during experiment PPM-AQ also resulted in the continuous generation of substantial amounts of organic acids, ketones, and lesser, but measurable, quantities of alkenes. Production of these compounds is consistent with data from redox buffered experiments examining the stability of individual aqueous hydrocarbons under redox buffered conditions (2,9,10). These experiments have demonstrated the degradation of aqueous *n*-alkanes via a stepwise oxidative processes to produce CO<sub>2</sub> and CH<sub>4</sub>. This process can be represented in general as follows:



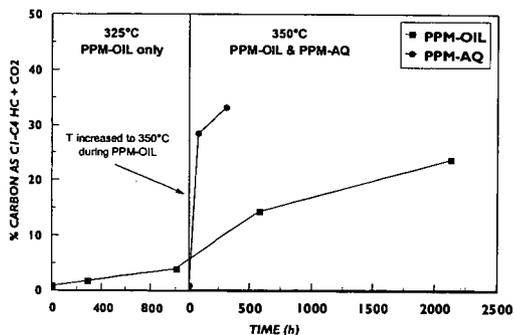
Reactions in the above scheme that do not involve breaking of C-C bonds are reversible in aqueous solution and may approach a state of redox dependent metastable thermodynamic equilibrium (2,9,10). Under sufficiently reducing conditions the abundance of reaction intermediates decreases, resulting in an overall decrease in the rate of *n*-alkane decomposition. Accordingly, during experiment PPM-OIL, high H<sub>2</sub> produced relatively reducing redox conditions and lower amounts of CO<sub>2</sub> and CH<sub>4</sub> were generated. In the absence of extensive oxidative decomposition during experiment PPM-OIL, it is likely that decomposition of hydrocarbons residing in the oil phase occurred predominantly via thermal cracking to produce a relatively CH<sub>4</sub>- and CO<sub>2</sub>- poor gas.

The formation of natural gas is conventionally viewed as a two-step process in which kerogen maturation initially produces both oil and gas. Continued heating over geologic time and increasing temperatures associated with progressive burial subsequently results in the decomposition of generated oil to form natural gas. As discussed by Mango *et al.* (5), a purely thermal model for the cracking of *n*-alkanes cannot account for the generation of dry gas at geologically reasonable heating rates. The stepwise oxidation of aqueous *n*-alkanes, however, may represent an alternative mechanism to generate a CH<sub>4</sub>-rich gas at relatively low thermal stress. For such a mechanism to be active in natural systems, however, suitable oxidizing agents are required. Likely candidates include sulfate minerals present in evaporites and commonly occurring sedimentary components containing ferric iron, such as pyrite, magnetite, hematite, and a variety of aluminosilicates. In addition to providing a mechanism for the generation of dry-gas at thermal maturities lower than those required for thermal cracking, the absence of a suitable oxidizing agent and/or water could preclude stepwise

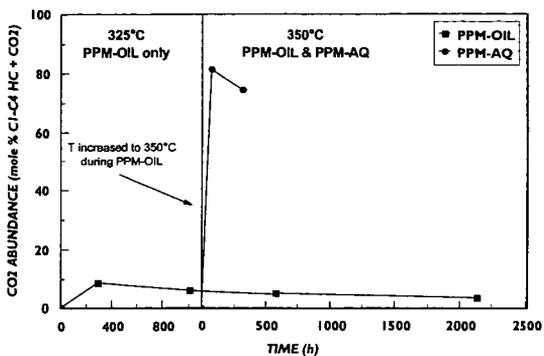
oxidation and account for the persistence of oil in a variety of environments at temperatures higher than conventional models predict (11). The results presented here emphasize the fact that time and temperature are not the only variables influencing the stability of petroleum in sedimentary basins.

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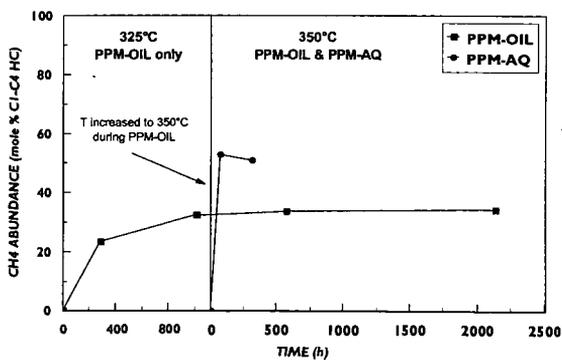
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**Figure 1.** Variations in the percentage of carbon in the total oil as C<sub>1</sub>-C<sub>4</sub> hydrocarbons and CO<sub>2</sub> with time during experiments PPM-OIL and PPM-AQ. Note that only experiment PPM-OIL was initially conducted at 325°C.



**Figure 2.** Variations in the relative abundance of CO<sub>2</sub> in the dissolved gas fraction (mole % of C<sub>1</sub>-C<sub>4</sub> hydrocarbons and CO<sub>2</sub>) as a function of time during experiments PPM-OIL and PPM-AQ. Note that only experiment PPM-OIL was initially conducted at 325°C.



**Figure 3.** Variations in the relative abundance of CH<sub>4</sub> in the dissolved hydrocarbon gas fraction (mole % of C<sub>1</sub>-C<sub>4</sub> hydrocarbons) as a function of time during experiments PPM-OIL and PPM-AQ. Note that only experiment PPM-OIL was initially conducted at 325°C.