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EVALUATING TRANSITION-METAL CATALYSIS IN GAS GENERATION FROM POLISH AND GERMAN KUPFERSCHIEFER BY HYDROUS PYROLYSIS

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Transition metals in source rocks have been advocated as catalysts in extent, composition, and timing of natural gas generation (Mango, 1996). This controversial hypothesis may have important implications concerning gas generation in unconventional shale-gas accumulations. Although experiments have been conducted to test the metal-catalysis hypothesis, their approach and results remain equivocal in evaluating natural assemblages of transition metals and organic matter in shale. The Permian Kupferschiefer of Poland and Germany offers an excellent opportunity to test the hypothesis with immature to marginally mature shale rich in both transition metals and organic matter. Twelve subsurface mine samples containing similar Type-II kerogen but different amounts and types of transition metals were collected and subjected to hydrous pyrolysis at 330 and 355ºC for 72 h. The generated gases were quantitatively collected and analyzed for their molecular and stable-isotopic compositions. Immiscible oils, reacted waters, and spent rock were also quantitatively collected and analyzed for transition metals. This study examines the effects of 21 detected transition metals on yield, composition, and timing of gas generated in the experiments.

A summary of the results is shown in Figure 1, with relationships expressed relative to the summation of the major transitions metals considered in the literature to be the most catalytic (e.g., Masel, 2001). This metal summation is expressed relative to the total organic carbon (TOC) in each sample. Figures 1a and 1b show that transition metals have no effect on methane yields or the gas dryness relative to ethane, respectively. Similarly, $\delta^{13}C$ values of generated methane, ethane, and propane show no systematic changes with increasing transition metal content. The potential for transition metals to enhance gas generation and oil cracking was also examined by comparing the ratio of the generated hydrocarbon gases to generated immiscible oil (i.e., GOR). Figure 1c shows that there is no systematic change in GOR with increasing transition metal content. Assuming maximum yields at 355ºC for 72 h and first-order reaction rates, pseudo-rate constants for methane generation at 330ºC were calculated. As shown in Figure 1d, no increase in the rate constant for methane generation is observed with increasing transition metal content.

The apparent lack of a significant catalytic effect of transition metals on the extent, composition, and timing of natural-gas generation in these experiments is attributed to the form in which the metals occur. As an example, nickel has been shown to have a high catalytic activity as pure Ni^o and NiO. Eh-pH diagrams for seawater concentrations of nickel, sulfur, and carbon dioxide indicate these solid phases are thermodynamically unstable under the anoxic conditions typically prescribed for source rock deposition and thermal maturation. Although highly reducing conditions exist (–227 to –345 mV), the redox potential is not reducing enough for the formation of Ni^o. Aqueous Ni^{+2} activities are not sufficient to form NiO but are sufficient to form Ni-sulfides, which have been shown not to be catalytic in methane generation (Mango, 1996). Ni^{+2} coordinated with oxygen may occur in detrital clay minerals of a source rock, but its limited charge-imbalance substitution for Al^{+3} in insular octahedral layers curtails its effectiveness as a catalyst.

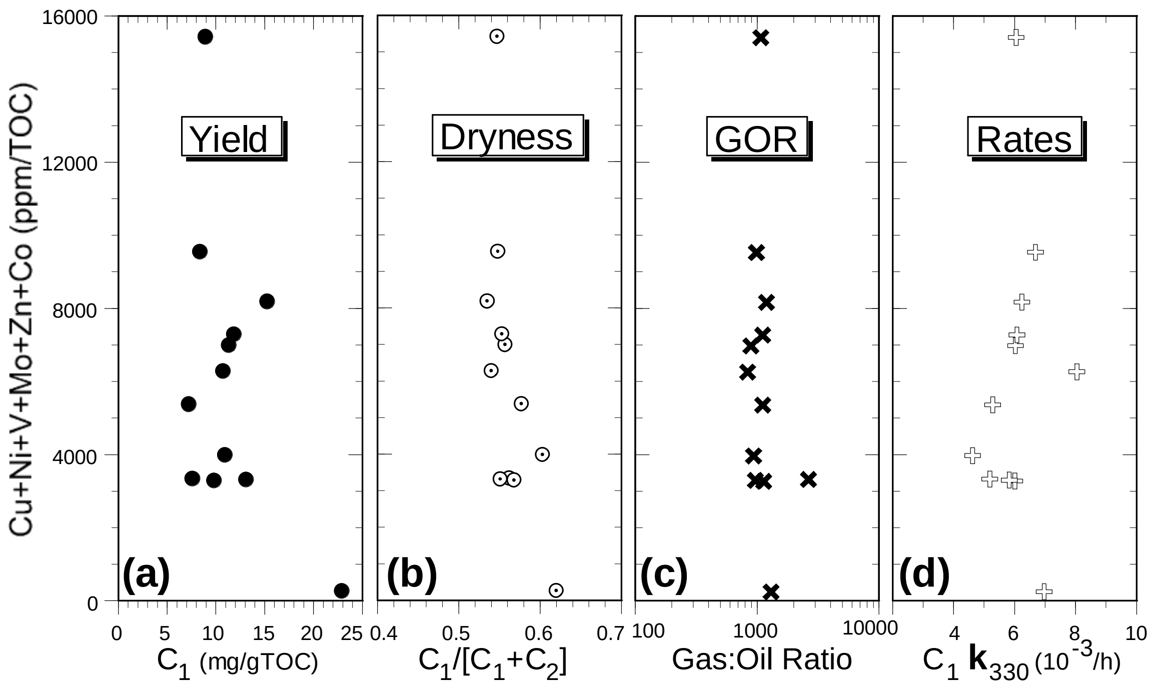

Figure 1. Hydrous pyrolysis results at 355ºC for 72 h: (a) methane yields; (b) methane-ethane dryness on a mass basis; (c) ratio of standard cubic feet of C_1-C_4 gas to barrels of immiscible oil; and (d) pseudo-rate constants at 330ºC for methane generation.

REFERENCES

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