

Phase relations in the system CHO and the generation of petroleum in hydrocarbon source rocks

HAROLD C. HELGESON¹, ALEXANDRA SCHMITT¹,
LAURENT RICHARD² AND JEFFREY M. DICK¹

¹Department of Earth & Planetary Science, 307 McCone Hall,
University of California, Berkeley, CA 94720, USA
(brogie@socrates.berkeley.edu)

²Université Henri Poincaré (Nancy 1), Faculté des Sciences et
Techniques, UMR 7566 G2RBP 239; Boulevard des
Aiguillettes, 54506 Vandoeuvre les Nancy, France
(Laurent.Richard@g2r.uhp-nancy.fr)

Thermodynamic analysis of metastable equilibrium phase relations among petroleum, CO_{2(g)}, water, and kerogens with various (H/C)s along the U.S. Gulf Coast fluid-pressure (p_f) geotherm indicates that oil generation by melting of immature kerogen in hydrocarbon source rocks occurs at $p_{CO_2(g)} = p_f$ over a narrow interval of $\log f_{H_2(g)}$, which decreases and becomes negligible with increasing depth, temperature, and $\log f_{H_2(g)}$. It follows that the corresponding phase assemblages constitute $f_{H_2(g)}$ buffers in hydrocarbon source rocks. For example, at $\sim 25^\circ < T < 100^\circ \text{C}$, incongruent melting of either a type-I kerogen corresponding to C₁₇₁H₂₈₈O_{9(c)} or a hydrogen-rich type II-kerogen represented by C₂₀₀H₂₆₀O_{10(c)} produces petroleum + water + a kerogen with a lower H/C (C₂₉₂H₂₈₈O_{12(c)}). With increasing temperature from ~ 100 to $\sim 150^\circ \text{C}$ the metastable equilibrium phase assemblage generated by incongruent melting of both C₁₇₁H₂₈₈O_{9(c)} and C₂₀₀H₂₆₀O_{10(c)} generates petroleum + C₂₉₂H₂₈₈O_{12(c)} + CO_{2(g)}. As temperature continues to increase above $\sim 150^\circ \text{C}$, a metastable mature kerogen (C₁₂₈H₆₈O_{7(c)}) is produced by incongruent melting of the C₁₇₁H₂₈₈O_{9(c)}, C₂₀₀H₂₆₀O_{10(c)}, and C₂₉₂H₂₈₈O_{12(c)} kerogens, which results in metastable equilibrium at depth among C₁₂₈H₆₈O_{7(c)}, petroleum, and CO_{2(g)}. With further burial of the source rock at temperatures $> \sim 225^\circ \text{C}$, both C₁₇₁H₂₈₈O_{9(c)} and C₂₀₀H₂₆₀O_{10(c)} melt congruently to produce petroleum + CO_{2(g)}, but C₂₉₂H₂₈₈O_{12(c)} continues to melt incongruently to form petroleum, C₁₂₈H₆₈O_{7(c)}, and CO_{2(g)}. However, in the latter case, the volume of C₁₂₈H₆₈O_{7(c)} produced in the process progressively decreases with increasing temperature as the volume of petroleum generated increases. It can be shown that the distribution of the hydrocarbons in the petroleum produced compares favorably with its natural counterpart. It can also be demonstrated that the volume of crude oil derived from the incongruent melting process can account for all of the oil produced and in proven reserves in the world's oil fields.

The case for catalytic gas

FRANK MANGO

Petroleum Habitats, 806 Soboda Ct., Houston, TX 77079,
USA (fmango@houston.rr.com)

The currently accepted paradigm for the origin of natural gas may be in trouble. Its central theme is this: hydrocarbons thermally crack to lighter hydrocarbons and ultimately to methane (CH₄) over geologic time and this explains the progressive conversion of oil to gas (C₁ – C₄) and gas to methane with increasing basin temperatures.

It has three serious flaws. First, hydrocarbons are too stable to decompose at the observed temperatures. Second, when oil does thermally crack, it gives a gas unlike natural gas. Finally, ethane and propane are extraordinarily stable and should not crack to methane over geologic time.

The case supporting the alternative hypothesis, that natural gas is formed catalytically by low-valent transition metals (Mango, 1992), is now compelling:

1) Source rocks in their natural state convert oil to gas catalytically.

2) They accelerate cracking rates by factors reaching well over one million.

3) The catalytic gas generated is identical to natural gas.

While the thermal paradigm cannot explain the composition of natural gas (Mango, 2001) and the conversion of wet gas to dry gas without invoking untested hypotheses, catalysis by transition metals can. Source rocks in their natural state generate natural gas catalytically (Mango et al., 1994) and convert wet gas to dry gas under the same conditions (Mango & Hightower, 1997). Thus, the evolution of petroleum (oil to wet gas and wet gas to dry gas) is uniquely replicated in catalytically active source rocks under natural conditions.

Of the two hypotheses competing for paradigm status, the catalytic hypothesis is the more economic; it explains more, needs less in the way of auxiliary help, and has broader experimental support.

References

- Mango F. D. (1992), *Geochim. Cosmochim. Acta* **56**, 553-555.
Mango F. D., Hightower J. W., and James A. T. (1994),
Nature **368**, 536-538.
Mango F. D., and Hightower J. W. (1997), *Geochim.
Cosmochim. Acta* **61**, 5347-5350.
Mango F. D. (2001), *Org. Geochem.* **32**, 1283-1287.