

Catalytic Gas in Deltaic Basins

Thermodynamic equilibrium is a fundamental characteristic of a catalytic reaction sustained over time. The proposal that natural gas is largely catalytic (Mango, 2000) would suggest that natural gas should be at or very close to thermodynamic equilibrium, particularly when gas resides in active reservoirs over geologic time. In the Gulf of Mexico, deltaic reservoir rocks with interbedded marine shales (Paine, et al. 1968) show high levels of catalytic activity in our laboratory experiments. If equally catalytic in the subsurface, their gas compositions should be near thermodynamic equilibrium K (T) for reservoir temperatures T according to:

$$([C_2]^2 / [C_1][C_3]) = K(T) \quad (1)$$

This proved to be the case for the 64 gas deposits published in Paine, et al. (1968). Since the equilibrium compositions corresponded to reservoir temperatures, they suggest in situ catalytic oil-to-gas at reservoir temperatures. We estimate $\gg 10^9$ years to attain equilibrium thermally at these temperatures, and $< 10^6$ years catalytically and therefore must rule out in-reservoir thermal cracking as the source of equilibrium.

There is now substantial evidence that non-biogenic gas is largely catalytic as opposed to thermogenic. Thermal cracking is inherently a low-methane process, typically yielding gas with between 30 and 60 % wt CH₄ (C1-C4), while natural gas is rarely found with this composition and more typically contains ~ 85% CH₄, the composition of catalytic gas generated in marine shales. One hypothesis for the discrepancy is that gas is somehow fractionated between source and reservoir (Price & Schoell, 1995; Snowdon, 2002). Although methane enrichment can be obtained through physical fractionation, thermodynamic

equilibrium cannot. Because gas compositions from thermal cracking are far from equilibrium, it is impossible to explain deltaic gas compositions at equilibrium without invoking robust catalytic intervention. ■

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References

- Mango, Geochim. Cosmochim. Acta. 64, 1265-1277 (2000).
- Paine et al., Memoir 9, Vol I, AAPG (1968).
- Price & Schoell, Nature 378, 368-371 (1995).
- Snowdon, Org. Geochem. 32, 913-931 (2001).

Biographical Sketch

FRANK D. MANGO received his PhD in 1963 in organic chemistry at Stanford University. He joined Shell Oil Company that year working in metal catalysis, petroleum chemistry and geochemistry. He retired from Shell in 1991 and joined the Department of Geology and Geophysics at Rice University as an adjunct professor. He was a research scientist and the principle investigator on consecutive DOE grants (Transition Metal Catalysis in the Generation of Oil and Natural Gas) in the Department of Chemical Engineering from 1992 to 2002. He has 36 publications and 9 patents in catalysis and geochemistry, and was awarded Best Paper in Organic Geochemistry in 1990, by the Geochemical Society. He is the founder and CEO of Petroleum Habitats, a service company that predicts oil or gas in target reservoirs based on a proprietary rock assay for oil-to-gas catalytic activity (US Patent 7,153,688).

