[PS]Evidence of Several Charges of Migrated Gas in Austin Chalk, Eagle Ford, and Buda Reservoirs on the San Marcos Arch*

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Abstract

Geochemical data measured on mud-gas samples indicate: (1) high-maturity wet gas generated by Eagle Ford (EF) source-rock (SR) beds migrated laterally and updip to different stratigraphic levels at two wells located on the San Marcos Arch in Gonzalez County; and (2) a distinct dry gas charge (principally isotopically-heavy methane) generated by a different SR is present in Upper Cretaceous and Lower Cretaceous intervals. These gas charges probably influence the GOR of oil in Upper Cretaceous reservoirs and their drive mechanism. Oil and wet gas migrated updip toward the San Marcos Arch via the Buda Formation, and then vertically into the Austin Chalk via faults penetrating the EF Formation: i.e. oil fingerprinting results indicate the Austin Chalk contains a migration mixture of oil generated by local and distant EF SRs.

Geochemical data measured on mud-gas samples collected from the Anacacho Formation through the Georgetown Formation at two vertical monitor wells were used to identify the top of one of these gas charges, where an abrupt change occurs in the C isotopic composition of methane, ethane, and propane (which are heavier below that boundary). This feature is present ≈30 ft below the top of the Buda Formation at Well #1. But it occurs at a much higher stratigraphic level (≈180 ft above the base of the Austin Chalk) at Well #2 located ≈7.5 miles northeast of the other well (where EF SR beds are ≈700 ft deeper than at Well #1). The boundary in the middle Buda Formation corresponds to two good gas shows at Well #1, where the methane/ethane ratio increases from 5.6-8.0 (in the upper Buda Formation and the overlying Eagle Ford Formation) to 9.8-11.4 at those gas shows. Haworth ratios indicate the presence of wet gas, and fractures are present in the Buda reservoir.

The middle Buda apparently is the regional carrier bed through which light oil and wet gas generated by deeper EF SR beds sequentially migrated updip: e.g. a ≈35°API oil sample produced from the Buda reservoir at Well #1 apparently is gas-washed because it is depleted in compounds more volatile than nC_{11}. Another good wet gas show occurs in Well #1 ≈25 ft below the top of the Georgetown Formation, where the mud logger observed dull yellow fluorescence and "asphalt" - probably EF oil that migrated into that zone. A good show of wet gas (identified using Haworth ratios) occurs in the Austin Chalk at Well #2 just below the top of the isotopically-heavy gas charge. Furthermore, in all mud-gas samples collected at Well #1 from the Austin Chalk (and deeper intervals) the C isotopic composition of methane is ≈7.5 per mil

heavier than predicted using the C isotopic composition of ethane and propane. This also is true for mud-gas samples collected above and below the boundary marking the appearance of high-maturity gas in the middle Buda Formation. Methane in mud-gas samples obtained at Well #2 is ≈6.0 per mil heavier than expected. An additional very dry gas charge explains these results.

Development, Calibration, and Applications of C_7 Source, Maturity, and Transformation Parameters

1. A KINETIC MODEL OF THE ORIGIN OF LIGHT HYDROCARBON COMPOUNDS

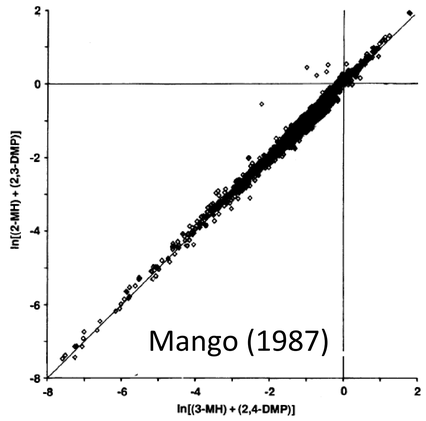

Fig. 1. Invariance in the abundance of four isoheptanes in ≈1,880 oil samples.

The structure of light HCs suggests they might form during the catagenesis of more complex macromolecules in kerogen and bitumen. During the late 1970s, Frank Mango (a Shell Oil research chemist) explained the origin of a remarkable invariance in the sum of the four isoheptanes 2-MH, 3-MH, 2,4-DMP, and 2,3-DMP using a novel concept (Fig. 1).

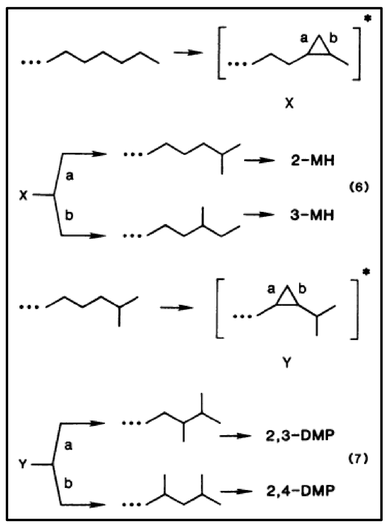

Fig. 2. Origin of four isoheptanes by ring-opening of unstable 3-member ring structures (Mango, 1987).

These compounds form pairwise during the ring-opening of unstable, intermediate three-member ring structures during a catalytic process that operates at steady-state conditions (Fig. 2). Mango furthermore developed a kinetic scheme for all 14 C_7 isomers (Fig. 3).

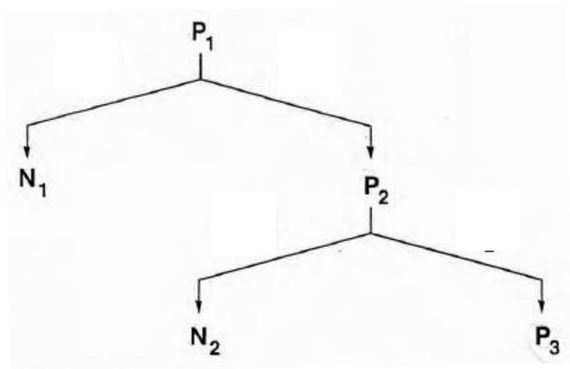

Fig. 3. Schematic model for the origin of C_7 isoalkanes and cyclopentanes (Mango, 1990). MCH and toluene (not shown) are associated with the N_1 branch.

P_1 = n-heptane
P_2 = 2-methylhexane + 3-methylhexane
P_3 = 3-ethylpentane + 3,3-dimethylpentane + 2,3-dimethylpentane + 2,4-dimethylpentane + 2,2-dimethylpentane
N_1 = ethylcyclopentane + 1,2-dimethylcyclopentane (cis + trans)
N_2 = 1,1-dimethylcyclopentane + 1,3-dimethylcyclopentane (cis + trans)

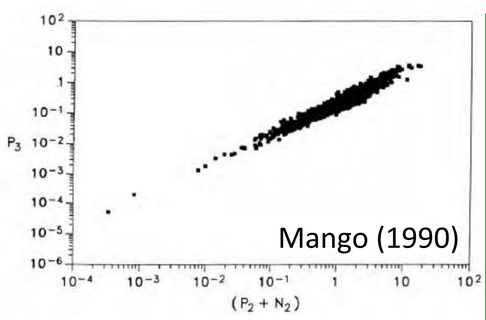

Fig. 4. Invariance in the abundance of P_2, N_2, and P_3 compounds in ≈2,200 oil samples.

This kinetic model also explains a second invariance between P_3 compounds (ΣDMPs+EP), and the sum of the P_2 compounds (2-MH and 3-MH) and the N_2 compounds (1,1-DMCP and 1,3-DMCP(*c*+*t*) (Fig.4). Several C_7 source and maturity parameters are derived from this model. The parent-daughter selectivity ratio figure P_2 vs. ln X_2 (where $X_2 = P_3/N_2$) describes if the parent isomers 2-MH and 3-MH isomerize to DMPs or to five-member ring compounds. The C_7 oil expulsion temperature (= 15 x ln 2,4-DMP/2,3-DMP + 140°C) describes how an unstable intermediate 3-ring structure opens (shown in Fig. 2) (Bement et al., 1994).

Mango's idea is that simple structures (e.g., nC7; 2-MH; 3-MH) isomerize to more complex DMPs, cycloalkanes, and toluene.

2. ORIGIN OF OILS GENERATED BY MONTEREY SOURCE ROCKS (SANTA MARIA BASIN)

I used C_7 source and maturity parameters to study the origin of sour Monterey oils in the Santa Maria Basin, California (Kornacki, 1993).

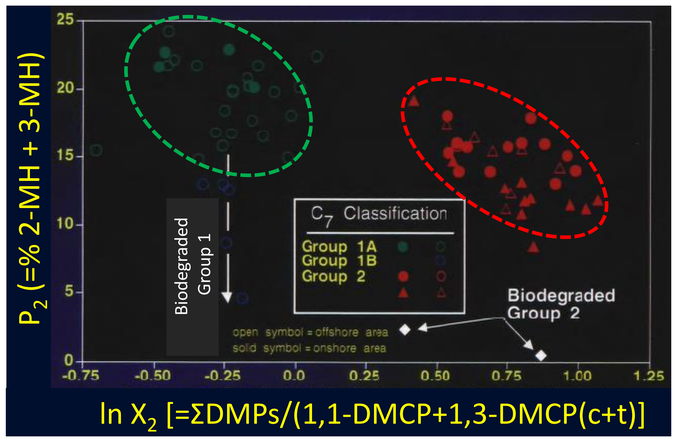

Fig. 5. C_7 correlation of Santa Maria Basin oils.

Two oil groups are apparent on the P_2 vs. ln X_2 correlation diagram. Group 1 oils (green and blue) have higher P_2 values (2-MH+3-MH) and lower X_2 values (i.e., isomerization favored DMCPs -- not DMPs) than do Group 2 oils (red) (Fig. 5).

The Monterey Formation consists of a lower phosphatic-calcareous marl and an upper siliceous shale (Isaacs, 1983). C_7 source parameters in core extracts demonstrate: (1) phosphatic SRs generated the Group 1 oils; (2) siliceous SRs generated the Group 2 oils; and (3) SR thermal maturity does not significantly influence the value of the X_2 selectivity ratio (Fig. 6)

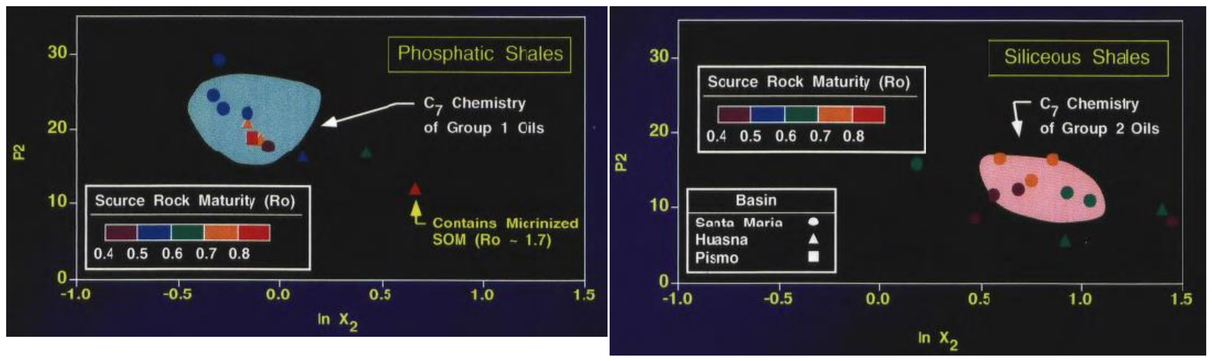

Fig. 6. C_7 correlation of Monterey source rocks and oils produced in the Santa Maria Basin.

Siliceous Monterey shale generated oil at a higher temperature than phosphatic Monterey shale (Fig. 7). An unexpected result of this study was the conclusion that although siliceous Monterey SRs generate heavy and medium-gravity oils, phosphatic Monterey SRs apparently only generate commercial volumes of <15°API oil in the Santa Maria Basin (Fig. 8).

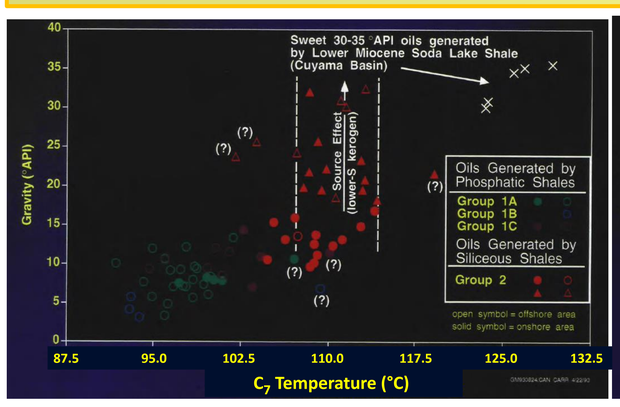

Fig. 7. C_7 oil-generation temperatures of Group 1 and Group 2 oils in the SMB.

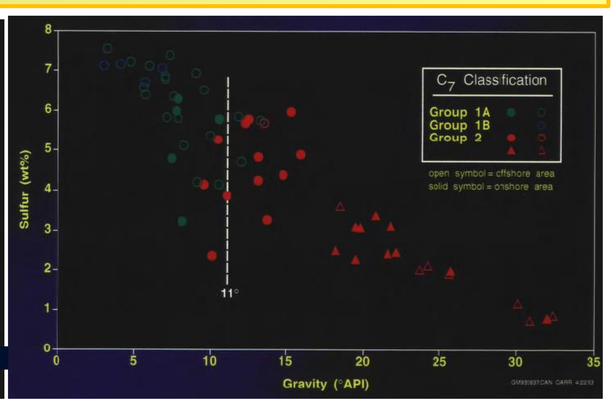

Fig. 8. API gravity and sulfur content of Group 1 and Group 2 oils in the SMB.

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Peters et al. (2019) recently used biomarker data to show that distinct SR organofacies associated with different Monterey lithofacies generated different types of oil in the onshore and offshore Santa Maria Basin.

3. HOW BIODEGRADATION INFLUENCES C_7 SOURCE AND MATURITY PARAMETERS

My principal contribution was to demonstrate how transformation processes (e.g., biodegradation; water washing; evaporation) influence C_7 source and maturity parameters, and to help develop new gasoline-range parameters that can be used to characterize altered oil samples.

Mango developed a parameter (C_7 primary test sum) that can be used to screen oil samples: i.e., unaltered oils have "primesum" values ≈1.0, but that parameter decreases with increasing amounts of biodegradation and water-washing. C_7 primary test sum values of oils in fields located on the SW margin of the Los Angles Basin increase systematically with depth because the shallow reservoirs contain biodegraded oil (Fig. 9 and Fig 10).

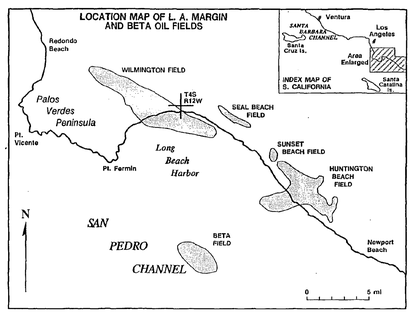

Fig. 9. Location of oil fields on the SW margin of the Los Angeles Basin.

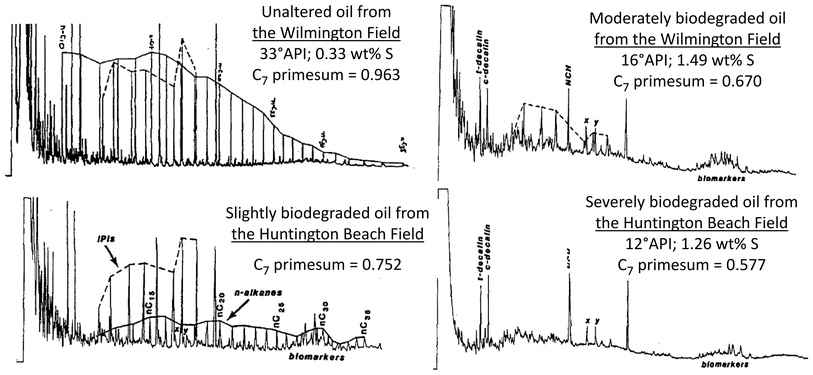

Fig. 10. SATGCs measured on unaltered and biodegraded oils from the SW margin of the LA Basin. C_7 primesum values decrease with increasing biodegradation.

The position of a related suite of biodegraded oils on C_7 parent-daughter selectivity ratio diagrams changes systematically based on the resistance of different C_7 compounds to being metabolized by microbes (Fig. 11).

Halpern (1995) used a few of these criteria in C_7 oil transformation "star" diagrams: e.g., the microbially-resistant "gem" compound 1,1-DMCP appears in the denominator of the Tr1 - Tr7 parameters.

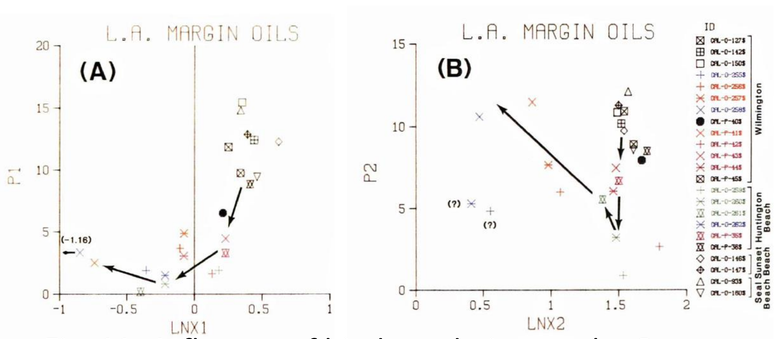

Fig. 11. Influence of biodegradation on the C_7 parent-daughter selectivity ratio diagrams P_1 vs. ln X_1 (A) and P_2 vs. ln X_2 (B).

4. USING C_7 SOURCE AND MATURITY PARAMETERS TO STUDY OIL IN SR RESERVOIRS

SR reservoirs (e.g., mudrocks; marls) typically are so impermeable that valid C_7 source and maturity parameters can be measured on core extracts. The crucial step is to perform extractions in sealed vials using frozen center-cut plugs obtained from conventional core butt sections.

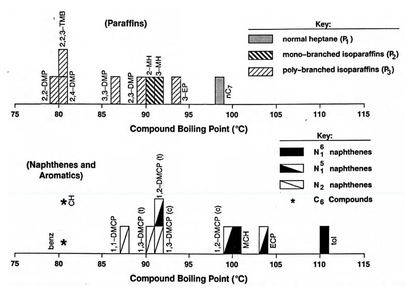

Fig. 12. Volatility of C_7 compounds.

The boiling point temperatures of C_7 compounds range from ≈80°C to ≈110°C (Fig. 12). The preferential evaporation of more volatile C_7 compounds influences C_7 source and maturity parameters: e.g., because 2,4-DMP is more volatile than 2,3-DMP, C_7 temperatures are artificially low in oil samples and core extracts from which volatile HC compounds have evaporated.

I used this method to study oils produced from the Austin Chalk, the Eagle Ford (EF), and the Buda Formation, and extracts obtained from center-cut EF core plugs at two vertical wells located 7.5 mi from each other (Fig. 13) (Kornacki, 2018).

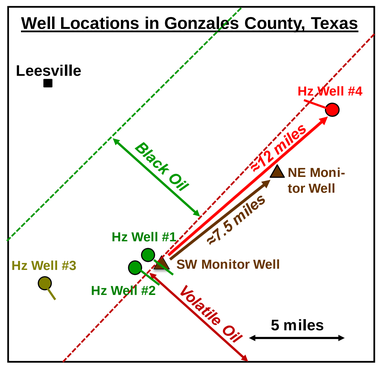

Fig. 13. Map showing the location of vertical and horizontal wells on the San Marcos Arch.

I used nC_6/nC_7 ratios to identify samples with disturbed C_7 temperatures (Fig. 14). EF core-plug extracts obtained at Vertical Well A correlate to most produced oil samples (Fig. 15). EF core-plug extracts obtained from Vertical Well B correlate to each other (but not the oils or Well A extracts)

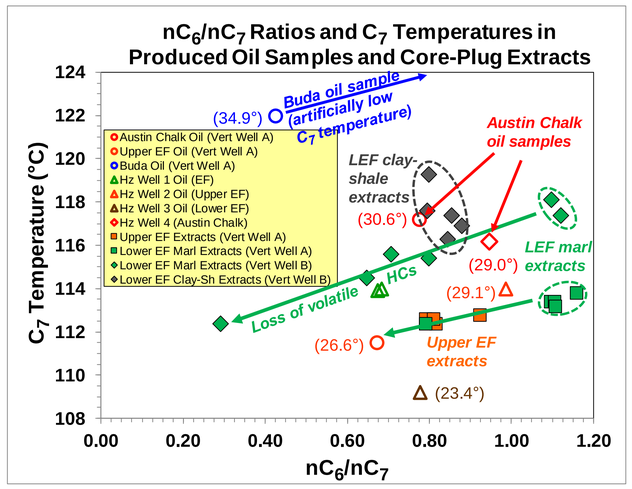

Fig. 14. C_7 temperatures in core extracts and oil samples produced on the San Marcos Arch.

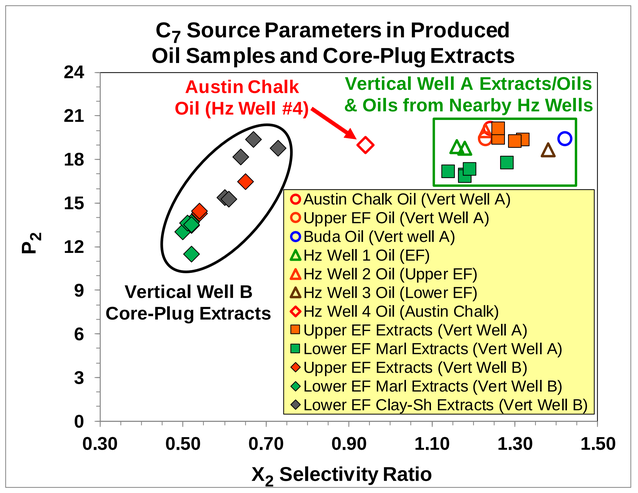

Fig. 15. C_7 correlation of core extracts and oil samples produced on the San Marcos Arch.

Acknowledgements: Other Shell Oil geochemists in addition to Frank Mango who made significant contributions to the development of the C_7 kinetic model include Henry Halpern, Everly Keenan, Ray Levey, Patricia O'Neal, and Michelle Stafford. I thank Royal Dutch Shell for permission to republish results from the SMB and the LA Basin.

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