

Gas: A Messenger from Subsurface Resources

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A detailed chemical and modeling analysis of a 77-mile by 124-mile area of the offshore Louisiana Gulf of Mexico shows how gas venting from deep sources alters shallower hydrocarbons and carries information that could guide exploration.

Clean-burning, energy-rich natural gas is an increasingly desirable hydrocarbon resource. Gas can be retained in a basin for hundreds of millions of years (as in the Anadarko) yet vents almost continuously in active basins such as the Gulf of Mexico Basin. Five years ago, the Gas Research Institute awarded a research contract to Cornell University to examine the way gas moves in the deeper portions of a very active basin. Could the capillary forces that arise when gas is present in grain-size layered sediments produce the very low permeability surfaces, called seals, that divide basin interiors into compartments of variable and often very high overpressure, and could this affect gas and hydrocarbon migration? Laboratory experiments reported from a previous GRI-funded study suggested this was possible (Shosa and Cathles, GCSSEPM, 2002). But could it be demonstrated in the field?

To be sure to catch all relevant processes, the GRI study cast its investigative net over a large (79-mile by 124-mile) area of the offshore Louisiana Gulf of Mexico (Figure 1). What was caught was not so much an improved understanding of seals, which is commented on only briefly in this article, but a clear view of unanticipated and possibly more important processes. The study discovered and documented the dramatic and systematic effects gas can have on oil through a process called gas washing. In the north of the study area, more than 90% by weight (wt%) of the n-alkanes in reservoir oil have been carried off by gas. The pattern of washing decreases in a regular fashion to zero in the southern end of the study area. Modeling shows this variation

is expected from the changing pattern of sediment deposition. Modeling also shows the gas washing and observed decrease in oleanane and increase in sulfur-bearing benzoethiophenes to the south (the next clearest chemical trends in the study area) are possible only if very little petroleum is retained in migration conduits between the source and the surface. The washing seems to take place in the deepest sand in any area, for example, the first sand encountered by upward-migrating hydrocarbons. The analysis shows the petroleum system in the northern Gulf of Mexico is a flow-through system in which only about 10% of the petroleum that escapes from the source strata is retained in basin sediments and more than 90 wt% is vented into the ocean. The venting is happening today through hundreds of seafloor sites, and known reservoirs have been filled very recently. Therefore, the chemistry of the gas and washed oils carry information on the current pattern of subsurface petroleum migration relevant to exploration for subsurface hydrocarbon resources.

The Offshore Louisiana Study Area

Figure 1 shows a GoCAD image of the top of salt (gray surface with spiky salt domes) in the study area, which henceforth will be called the GRI Corridor, and stratigraphic layers from four sites where 3-D seismic data from the industry was acquired and interpreted. The stratigraphy, all chemical analyses, and selected physical and petroleum data are assembled in a

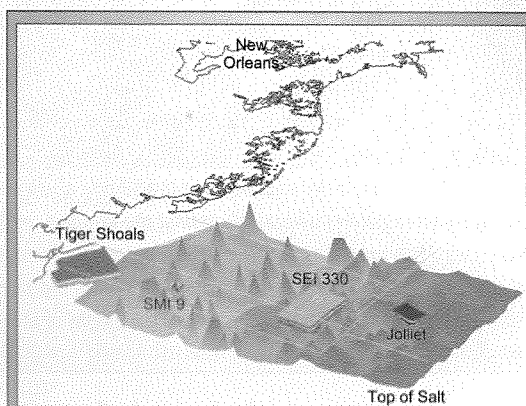


Figure 1: This figure shows the location of the GRI study corridor in the offshore Louisiana Gulf of Mexico Basin. The base is the top of salt compiled from 2-D seismic data. Strata interpreted from 3-D seismic data at four locations also are shown. SMI 9 is ChevronTexaco's South Marsh Island 9 salt piercement-related field, SEI 330 in Pennzoil's (Devon Oil) South Eugene Island Block 330 field, and the southernmost stratigraphic package contains ConocoPhillips' Joliet field.

GoCAD project that is included with the six-volume final report available from GRI (GRI-03/0065). Corridor source rocks have a generative potential of 1,400 billion bbl of oil and 8,600 Tcf of gas; 2.6 billion bbl of oil and 45 Tcf of gas have been discovered. The top of overpressure (12 lb equivalent mudweight surface), determined from mudweight data in 2,131 wells, is a highly irregular, spiky surface that cuts thousands of feet across stratigraphy in many areas (Figure 2). Many, but not all, of the spikes are related to salt domes. Temperature gradients can change from about 65° to 76°F per 0.62 miles over distances of about 31 miles in a checkerboard pattern, which would dramatically affect hydrocarbon maturation.

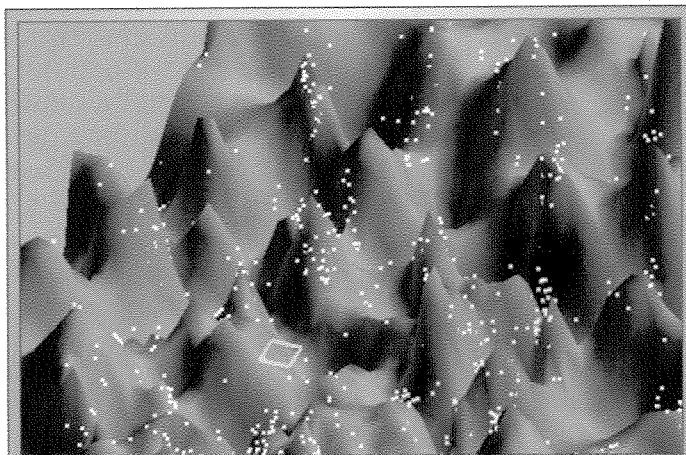


Figure 2: A subset of the data defines the 12 ppg equivalent pressure surface (white points) displayed against the krieged representation of the same 12-lb mud surface. The yellow square is South Eugene Island Block 330. The krieged surface represents the pressure data reasonably well but fails to capture the full height of the peaks.

Chemical analyses of 138 un-biodegraded oil samples show remarkably regular trends in gas washing (Figure 3) and source-related biomarker indices.

The spikes in the top of overpressure surface complicate relating this surface to hydrocarbon phase separation of a relatively constant composition petroleum. Leak zones appear to be localized

temperature distribution in the corridor is that expected. Local anomalies are partially related to salt and variations in sedimentation rate, but that is not their full explanation, and they remain enigmatic to some degree. Oil chemical variation turned out to be the most interesting, surprising and process-significant data.

in faults and shear zones bounding salt sheets and diapirs. Once established, they persist and become increasing methane-rich. Away from spikes, the top of overpressure surface could be a phase boundary, and its depth might be at least partly controlled by petroleum chemistry. Sufficient data to test this possibility was unable to be assembled. The temperature pattern is significant and interesting. The general

the n-alkanes has been removed by gas washing in the northern end of the Corridor (Tiger Shoals). All the oils there have break numbers of ~24 and show ~90 wt% oil removal. The washing intensity decreases in a reasonably regular fashion from north to south. No washing is observed at the south end of the Corridor. The chemistry of the Corridor oils is extensively discussed in the report cited above. After gas washing, the next most process-significant aspect of the oil chemistry is the clear presence of oleanane in the north but not in the south and a dramatic increase in sulfur-bearing benzothiophenes to the south. This result is interpreted to come from the maturation of two source beds: a carbonate Jurassic one that extends uniformly across the Corridor and a silicate Eocene one that extends across only the northern half of the Corridor. Eocene-sourced oils should contain oleanane, since their source is younger than mid-Cretaceous and plants containing oleanane had evolved, and should be sulfur-poor because iron from the shale will precipitate sulfur as pyrite in the source. Jurassic-sourced oils, on the other hand, should be sulfur-rich because carbonates contain insufficient iron to precipitate the sulfur as pyrite at their source and are too old to contain oleanane.

The importance of these observations becomes clear when the evolution of the Corridor is reconstructed and petroleum generation and migration modeled. The Jurassic source lies at about a 9-mile depth in the Corridor. Unless the petroleum retention in migration conduits above the source is less than ~0.5% of the pore space in the sediments, no petroleum can escape the surface. The migration fraction must be smaller than this because oil and gas are venting at hundreds of seafloor localities. For the oil to have an Eocene signature, such as containing oleanane and being sulfur-poor, the later-generated Eocene oil must displace the earlier-generated Jurassic oil.

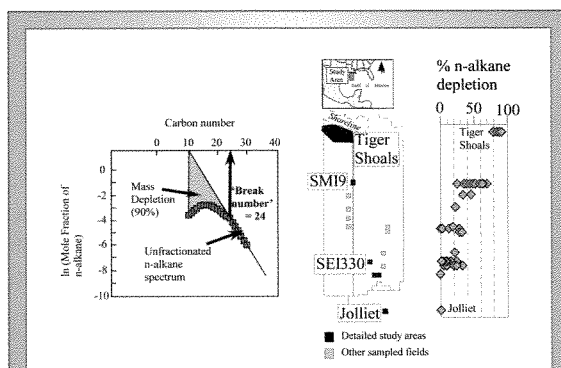


Figure 3: A total of 138 oils are analyzed for gas washing (left). The percent mass depletion of n-alkane components $\geq C_{10}$ is defined as the gap between an unaltered oil with exponentially decreasing n-alkane mole fractions and the sample oil (shaded area). The graph on the right shows the regular decrease in the percent of n-alkane mass removed by gas washing from north to south across the GRI Corridor.

Hydrocarbon Chemistry

Gas washing is measured by comparing the mole fractions of n-alkanes in an oil with the distribution expected if the oil were unaltered. In unaltered oils, the mole fraction of n-alkanes decrease exponentially with carbon number, C_n . Figure 3 shows the n-alkane mole fractions in one Tiger Shoals oil peel off from the exponential trend at $n \sim 24$. The shaded zone is the missing oil. In this case, the missing oil represents about 90 wt% of the original $C_n > 10$ oil. The north-south profile in Figure 3 plots the n-alkane removal in 138 unbiodegraded oils cross the Corridor. More than 90 wt% of

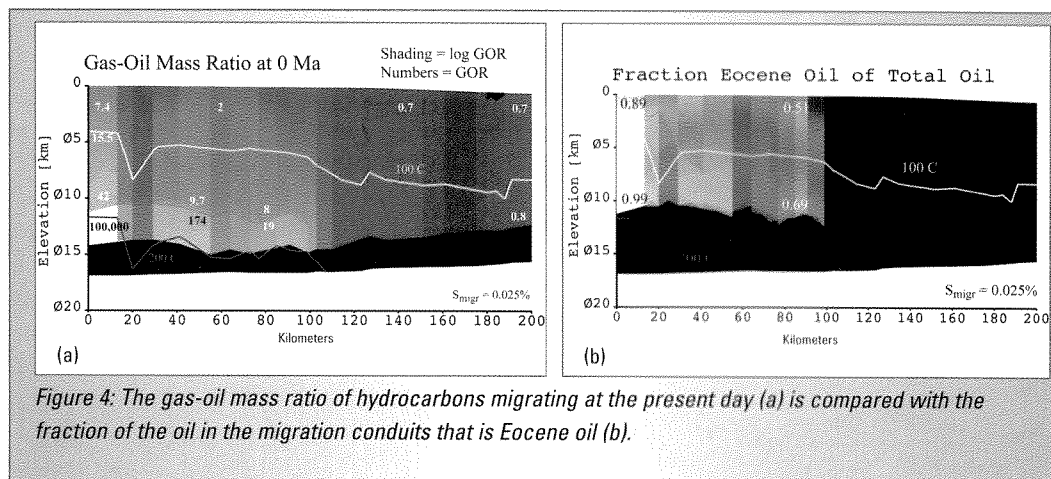


Figure 4: The gas-oil mass ratio of hydrocarbons migrating at the present day (a) is compared with the fraction of the oil in the migration conduits that is Eocene oil (b).

This is possible only if the migration pore fraction is less than $\sim 0.05\%$. If this is the case, all the chemistry fits nicely. Figure 4 shows at a migration pore fraction of 0.025% the oil at Tiger Shoals (in the north) is 89% Eocene and 51% Eocene in the middle of the Corridor. Furthermore, because the Jurassic source is now generating gas, the gas-oil ratio in the migrating hydrocarbons is high enough in the north and middle of the section (Figure 4b) to wash the Eocene oils as observed. For 90 wt% oil removal, about 4 lb of gas are required to wash each pound of oil. The migrating gas-oil ratio decreases to the south such that we expect no gas washing at the southern end of the Corridor, as observed.

A final matter of importance is that equation-of-state modeling of the washing process indicates that the break number (Figure 3) is a direct measure of the depth at which the oil is washed. Combining this with Corridor geology at the four sites where 3-D seismic data suggests the gas washing occurs in the deepest sand at any locality. Hydrocarbons can be delivered at the rate needed to fill known reservoirs as recently as geologically indicated if collected from areas ~ 10 miles to 12 miles in radius (the scale of the salt-withdrawal minibasins in the area). Gas and oil mix in the deepest sand, and the oil is washed there. The hydrocarbons then

escape at a few localities along the faulted margins of minibasins.

Conclusions and Implications

Oil chemistry requires the petroleum system in the northern Gulf of Mexico basin to be a flow-through system in which very little hydrocarbon is retained between the source and the surface, and almost all ($>90\%$) the petroleum that escapes its source vents into the ocean. About 30% more hydrocarbons than have been produced and consumed by humans throughout the entire petroleum era have vented into the ocean from the small Corridor. Admittedly, this occurred during a fairly long period of time (about 10 million years), but clearly humans and nature are promoting the same basic process (the venting of hydrocarbons).

Because so much gas is required to wash the oils as observed, the washing process reflects major aspects of the subsurface flow system. Overall, the pattern of washing in Figure 3 is regular, but significant variations in washing intensity occur in its mid-section. The variable washing in this area must reflect variations in flow and mixing in the migration conduits. For example, areas where oils are relatively intensely washed must connect to subsurface zones where gas is preferentially transmitted compared with oil, and

conversely areas where oils are comparatively unwashed must connect to migration pathways that transmit relatively little gas. Structures along major migration conduits will have a greater probability of being filled with hydrocarbons. Thus, analysis of the gas washing pattern could help guide exploration to structures more likely to be filled and more likely to be filled with oil or gas. Washing may have other economic implications. For example, washing may cause

asphaltenes to precipitate in the subsurface, and gas-washed oils may therefore be less prone to precipitate them in seafloor transmission pipes. ♦

Acknowledgements

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