Seal Control of Hydrocarbon Migration and its Physical and Chemical Consequences

VOLUME I: EXECUTIVE SUMMARY

FINAL TECHNICAL REPORT
(6/19/1997-12/31/2001)

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This report includes an executive summary and 5 volumes documenting a project to: (1) assemble a geochemical database in an active basin large enough in its areal coverage to capture all important processes, (2) construct models of those processes, and (3) use the models to interpret the data. The Executive Summary (Volume I) summarizes each subsequent volume with ~3 pages of text and key figures. The remaining volumes concern a 125 x 200 km area of the offshore Louisiana Gulf of Mexico and are titled: Volume II Geology, Geophysics, Geochemistry and GoCAD Database, Volume III Organic Geochemistry, Volume IV Gas Washing of Oil and Its Implications, Volume V A Modeling Analysis of the Hydrocarbon Chemistry and Gas Washing, Hydrocarbon Fluxes, and Reservoir Filling, and Volume VI A Theoretical Analysis of the Inorganic Alteration by the Flow of Brines Through Seals.

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Research Summary

TITLE: Quantifying gas, oil, and brine migration in a 125 × 200 km area of the offshore Louisiana Gulf of Mexico: Executive Summary

CONTRACTOR: Cornell University

PRINCIPAL INVESTIGATOR: Lawrence M. Cathles III

REPORT PERIOD: January 1, 1997 to December 31, 2001

OBJECTIVES: This report is an executive summary of a 5-year project to:
  (1) assemble a geochemical database in an active basin large enough in its areal coverage to capture all important processes,
  (2) construct models of those processes, and
  (3) use the models to interpret the data.

The full report, which is summarized here, is comprised of six (6) volumes.

TECHNICAL PERSPECTIVE: The northern Gulf of Mexico Basin is an area of active hydrocarbon generation and one of the world's most active areas of hydrocarbon exploration. The interior of this basin is divided into a complex system of variously over-pressured compartments. Despite much work it is not clear how hydrocarbons migrate through these pressure compartments, the nature of the impermeable seals that separate the compartments is uncertain, and it is unclear how the flow of gas and brine affects hydrocarbon chemistry and inorganically alters sediments. Processes operate on a mini-basin (~30 km) scale or greater, and regional trends have scales of 100 km or more. There are no databases relating geology and chemistry on these scales that are consistent and detailed enough to constrain models of basin processes.

RESULTS: We have assembled an electronic GoCAD project in a 125 × 200 km area of the most active portion of offshore Louisiana Gulf of Mexico Basin. GoCAD, a cad-based GIS software package widely used in the oil industry, allows geographically-referenced visualization of large point (geochemical) data sets, and efficient assembly and visualization of geologic surfaces (time-stratigraphic horizons and faults) and culture data such as block boundaries, shorelines, reservoir temperatures, etc. The GoCAD project we have assembled

incorporates:

(1) the regional geology (10 time-stratigraphic horizons) of the GRI Corridor plus detailed geology at 4 sites (Tiger Shoals, SEI 330 area, SMI 9, and Jolliet) within the Corridor,
(2) gas chromatographic and GCMS/MS data for 217 oils
(3) geochemical biomarker indices for the oils
(4) gas chemistry and isotopic measurements
(5) the 12 pound mud surface (a proxy for the top of overpressure) determined from mudweight data in 2131 wells and a surface derived by krigging this point set, and
(6) extensive physical, chemical and cultural data extracted from the MMS Atlas of Gulf of Mexico Gas and Oil Sands (Bascle et al., 2001).

Interpretation of this data by conventional geochemical (biomarker) analysis and by numerical modeling resulted in a number of major conclusions:

(1) The top of overpressure (proxied by the 12 pound equivalent mud surface) is a highly irregular (spiky) surface that crosscuts lithology dramatically on a local scale, and possibly trends across lithology on the regional scale.
(2) Heat flow is half normal across the corridor, but temperature gradients are normal and vary coherently on a ~50 km scale from 19° to 25°C/km. These gradients extend to depths of at least ~5 km, and thus affect the timing of hydrocarbon maturation.
(3) Organic chemistry combined with restrictions imposed by the lack of biodegradation of reservoired oils requires active hydrocarbon migration and reservoir filling in the Corridor.
(4) There are regular trends in oleanane and sulfur content from north to south across the Corridor that indicate a shift from Eocene- to Jurassic-sourced oil.
(5) Oil maturity decreases from 1 to 1.2%R_e in the north to ~0.8%R_e in the south of the Corridor. "Hot spots" punctuate this trend. Gas maturity is much higher than oil maturity throughout the Corridor.
(6) The removal of 90 wt% of the n-alkanes from oils in the north of the Corridor, and a regular trend in removal to the south (discovered in this project) requires the washing of earlier-generated oils with large amounts (~3.5 kg gas/kg oil) of late-generated dry gas.
(7) A careful literature determination of parameter values and a from-the-ground-up modeling analysis show that the low heat flows are due to rapid sedimentation, the normal

temperature gradients are due to low thermal conductivity of abundant shale, and the maturation trends are a consequence of the southward progradation of the shelf edge.

(8) Maturation and migration modeling shows that all the chemical characteristics of the hydrocarbon system can be explained naturally if (and only if) the retention of hydrocarbons in migration pathways is very small. The hydrocarbon system in the Corridor is a dynamic, flow-through system in which hydrocarbons (oil and gas) are vented into the ocean almost as soon as they are expelled from their source.

(9) Provided hydrocarbons are drawn from areas similar to the scale of the salt-withdrawal minibasins that structurally divide the Corridor, the current rate of hydrocarbon generation is sufficient to fill reservoirs on the north end of the Corridor in ~1 Ma and reservoirs on the south end (Jolliet) in ~20 ka, as required by geological data and the lack of biodegradation.

(10) Inorganic alteration caused by the flow of brines should be intense if brine venting is focused in the same fashion as hydrocarbon venting.

(11) Mineral alteration in the steep pressure gradients of capillary seals may be unique and therefore could provide a way to demonstrate the existence of this type of seal.

(12) Maps of inorganic alteration can be converted to maps of the mass of brine that has flowed through a basin.

TECHNICAL APPROACH: We compile geological and geochemical data from an area of one of the most active parts of the Gulf of Mexico Basin that is large enough to incorporate all major basin processes. We construct models of these processes, and compare the model predictions to observations. This method has been remarkably productive, and the results produced appear to be unusually simple and robust.

PROJECT IMPLICATIONS: There are many implications, but perhaps the most important derive from our conclusion that hydrocarbon retention in migration conduits is low. This conclusion requires, for example that, in the last ~13 Ma, as much hydrocarbon (~1000 Bbboe) has been vented into the ocean from one small 125 × 200 km area of the Gulf of Mexico Basin as has been produced and consumed by humans over the entire petroleum era. The flow-through chemistry required by low migration retention allows gas washing and produces the chemical trends observed. It also means that the hydrocarbons in reservoirs reflect very recent and actively ongoing subsurface processes, and that these current processes are those most relevant to reservoir filling. Current hydrocarbon chemistry is thus highly relevant to the exploration process. The success of our analysis suggests that integrating advanced chemical models with large-scale databases is an effective way to define the nature of the hydrocarbon system in such areas.

PROJECT MANAGERS: Richard Parker and Robert Siegfried

Quantifying Gas, Oil, and Brine Migration in a 125 × 200 km Area of the Offshore Louisiana Gulf of Mexico: Executive Summary

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A. Introduction

The project summarized here grew out of previous GRI-funded work that identified capillary sealing as a potentially important control on hydrocarbon migration and inorganic and organic alteration in basins. That and other relevant work is now published in many publications (Powley, 1987; Hunt, 1990; Powley, 1990; Whelan, Eglinton et al., 1994; Whelan, Kennicut et al., 1994; Whelan, Eglinton et al., 1994; Cathles, 1996; Meulbroek, 1997; Whelan, 1997; Meulbroek, 1998; Cathles, 2001; Erendi and Cathles, 2001; Revil and Cathles, 2001; Shosa and Cathles, 2001; Whelan, Eglinton et al., 2001; Losh, Walter et al., 2002; Losh, Cathles et al., 2002; Cathles, Colling et al., accepted).

The initial proposal was to investigate 10 specific corollaries of the capillary seal hypothesis. As work progressed some hypotheses were resolved. Lack of sample access made addressing others impossible. The oil industry was distracted by a wave of mergers, which made expensive efforts to collect critical samples more difficult. New ideas emerged that had not been anticipated. For all of these reasons, the research ultimately took quite different directions than originally planned. Because many of the original hypotheses remain of interest I will first indicate how these original objectives were addressed, and then summarize the work that has actually been completed.

B. Ten Corollaries of the Gas Capillary Seal Hypotheses

The title of the proposal under which the work reported here was carried out was: "Seal Control of Hydrocarbon Migration and its Physical and Chemical Consequences." Laboratory experiments funded by GRI had shown that capillary seals form where there are numerous fine-coarse (sand-shale) interfaces and both aqueous and non-aqueous fluids are present. In these areas, the flow of all fluid phases is stopped until the sum of the gas entry capillary pressures at all the interfaces that comprise the seal is exceeded. If there are enough interfaces, the seal thickness should expand until hydrofracture becomes the primary rupture mechanism. The gas capillary seal hypotheses had many corollaries that are fully discussed in Cathles (2001). The ten corollaries we proposed to test were:

1. The position of a capillary seal can be predicted from sediment lithology and the depth at which supercritical gas-oil phase separates into distinct gas and oil phases (gas provides the greatest capillary contrast with water and thus the tightest seals).
2. The expulsion of both aqueous and hydrocarbon fluids will be focused to the topographic highs of the top of overpressure because these localities will hydrofracture first.

3. The seal topographic highs will be the sites of unusually intense inorganic alteration produced by the leakage of brines, and the cumulative mass of brine leaked will be measured by the inorganic alteration of the seal.
4. The porosity of sands within and below the top of overpressure depends on how the seal has migrated and is predictable from lithology.
5. The chemistry of hydrocarbons near the seal will reflect the depth of seal formation because the seal will tend to form where gas and oil segregate from supercritical gas-oil.
6. Gas and oil chemistry may indicate leakage from deeper reservoirs.
7. Polar compounds such as phenols can be used to compute rates of oil migration.
8. The amount of asphalt precipitation in a particular stratigraphic interval is directly related to mass of hydrocarbons that have passed through the phase transition from supercritical gas-oil to distinct gas and oil in the strata. Asphalt abundance may thus identify past top seals and quantitatively measure the cumulative hydrocarbon throughput.
9. Better kinetic data on gas generation will allow better gas generation models to be constructed.
10. A broad and complete organic geochemical database will provide constraints for models of hydrocarbon migration and aid assessment of other processes such as biodegradation.

Testing the first corollary failed because it proved impossible to obtain hydrocarbon samples from seals other than at leak locations, and the corollary was disproved at these locations. We found that the leaks are indeed located at topographic highs in the top of overpressure (TOOP), but the leak zones are comparatively methane-rich. Phase separation should occur at relatively greater depths for methane-rich hydrocarbons, and the leak points should therefore be depressions in the TOOP not topographic highs. Furthermore we found the TOOP surface to be too spiky to be plausibly explained as a phase boundary. Although the TOOP might start out as a phase boundary, established leak zones seem to take on a life of their own, grow into dramatic topographic highs, and persist as leak sites for protracted periods. Leaking chimneys may be stabilized by gas-capillary sheaths, but this is a separate subject. For more discussion see Volume II and III of this report series.

The second corollary holds. Volume II shows that discovered hydrocarbon reservoirs do cluster near topographic highs in the TOOP. But the reasons that the persistent vents are topographic highs is not simply related to the chemistry of the venting hydrocarbons.

We have laid an extensive theoretical foundation for investigation of the third corollary. In Volume VI of this series we show how to calculate the inorganic alteration caused when brines are forced through seals. The alteration should be intense enough at leak points that it could be mapped seismically. If feasible, seismic mapping could provide quantitative maps of brine movement in a basin (e.g., maps that show not only the brine migration pathways, but also, using the methods we have developed, the mass of brine that has moved along these pathways). The work presented in Volume VI is entirely

theoretical. We have not analyzed alteration data in actual basins, and have not shown how seismic data could be analyzed to map flow paths in basins.

The 4th corollary is partially validated in an extensive published discussion of porosity profiles in the South Eugene Island Block 330 area (Revil and Cathles, 2001). This analysis shows that the top of overpressure has migrated vertically, and that the porosity profiles are modified where the seal has migrated. Porosity profiles contain information relevant to hydrocarbon and brine migration, and methods for extracting this information are developed and illustrated. However we have not demonstrated methods for predicting where and when seal migration will occur.

The 5th and 8th corollaries failed for lack of proper sample availability. What data we have been able to assemble are presented in Whelan, Eglinton et al. (1999). To evaluate these hypotheses further we need detailed sampling through deep parts of the TOOP (away from spikes) and detailed sampling of the overpressured interior. We were not able to obtain suitable samples.

Construction of the GoCAD database allowed us to address corollaries 6, 7 and 10 in an effective way (see Volume III and IV). If gas washing occurs in the deepest sand in an area as suggested in Volume IV, the nature of gas washing does have implications for the potential for filling reservoirs in that sand. Phenol adsorption may measure hydrocarbon-rock contact. The low phenol concentration in Corridor oils compared to North Sea oils suggests migration through many minor fractures rather than through a few major faults or channelways (Volume III).

Gas washing and our modeling emphasizes the importance of gas generation in driving hydrocarbon migration and altering oil chemistry. Proper gas generation kinetics are critical (corollary 10), but we contribute no new gas kinetic data in this series of reports.

C. Executive Summary

The work reported here covers all aspects of a large portion of a sedimentary basin and is thus broad in scope. A great deal of diverse data is assembled and interpreted. New phenomena of regional scale and process relevance (e.g., gas washing) are documented for the first time. Modeling conclusions are reached that, if borne out by subsequent work, are of major significance. Although there are many details that are not resolved, the overall story that emerges from the data and models is coherent and compelling, and aspects of the analysis appear to be unusually robust. The results are summarized below by volume.

1. Volume II

Volume II, "Geology, Geophysics and Geochemistry and GoCAD Database," by L. M. Cathles, M. Wizevich, and S. Losh provides the geological context for the project, describes the GoCAD database we have assembled, and illustrates its use.

A brief summary of the geologic history of Triassic rifting, Jurassic evaporite and source bed deposition, carbonate deposition, and the onset of siliciclastic deposition from the

Mississippi drainage in the Cenozoic, and two regional cross sections through or near the Corridor, provide the context for our Corridor studies. Within the Corridor, the regional geology is summarized by 10 time-stratigraphic and top of salt horizons assembled from the literature and contributed by industry. Local geology is summarized by stratigraphic horizons and faults at four sites in the Corridor. We defined the local geology by digitizing horizon maps (South Marsh Island 9 and extensions at South Eugene Island 330) or by interpreting 3D seismic surveys contributed by industry (Tiger Shoals, SEI 330, Jolliet). All our interpreted horizons and faults, including top and bottom of salt, are part of the GoCAD project distributed with this report.

Geophysical data compiled in Volume II include offshore Louisiana water temperature as a function of depth (needed for model boundary conditions), subsurface temperature and pressure in the Corridor, and surface heat flow. Subsurface temperatures are defined by 2762 reservoir temperatures in the MMS Atlas of Gulf of Mexico Gas and Oil Sands (Bascle et al., 2001) and other data from the SEI 330 area. Temperature gradients are shown to vary between 19° and 25°C/km and they extend linearly to over 4 km depth. Deviations from the mean gradient of 22.5°C/km are shown to occur coherently over distances of ~50 km. Such changes will affect the timing and extent of hydrocarbon maturation. Surface heat flow, compiled from the literature, is unusually low in the Corridor, dropping to ~25 mW/m^2 (half normal) on the shelf.

Subsurface pressures are extracted from the MMS Atlas (Bascle et al., 2001) and included in the GoCAD project. The top of overpressure (proxied by the fraction of lithostatic pressure that would be equivalent to the 12 pound mud surface where water depth is zero) was determined by us from header log mud weight data in 2131 Corridor wells. The top of overpressure (TOOP) surface is shown to be a highly irregular, spiky surface where spikes are kilometers high (Figure 1). Superimposing hydrocarbon reservoir outlines on a krigged version of the TOOP shows that hydrocarbon accumulations cluster near topographic highs in the top of overpressure surface. Overlying the top of salt on the TOOP shows that topographic highs in the TOOP are generally associated with salt domes. The TOOP crosscuts lithology locally and possibly regionally. The latter is suggested by plots of the location of the paleo-shelf edge strata (13.4 Ma to present) along 4 sections that show the present TOOP cutting across the paleo-shelf positions. Since lithology is tied to the shelf edge, the TOOP could also crosscut lithology.

All the geochemical data analyzed and collected under this project, all data in the MMS Atlas, and all data otherwise contributed or obtained are incorporated in the GoCAD project and Excel spreadsheets. Three aspects of the hydrocarbon system are discussed. First we report the results of a literature review of source rock distribution in the northern Gulf from which we abstract two source strata: A 100 m thick, 5 wt% TOC Jurassic source that underlies the entire Corridor, and a 30 m thick 4 wt% Eocene source which underlies the northern half of the Corridor. These two sources have the potential to generate more than ~200 billion tonnes of hydrocarbons. The discovered reserves of the Corridor are 1.4 Bt, or less than 0.7% of this amount. Second the gas-oil ratios (GORs) of 1287 samples from initial production and production header logs clearly show the

effects of phase fractionation when plotted against sample depth, and initial solution gas-oil ratios from the MMS Atlas reflect reservoir pressure, suggesting the reservoired oils are gas-saturated.
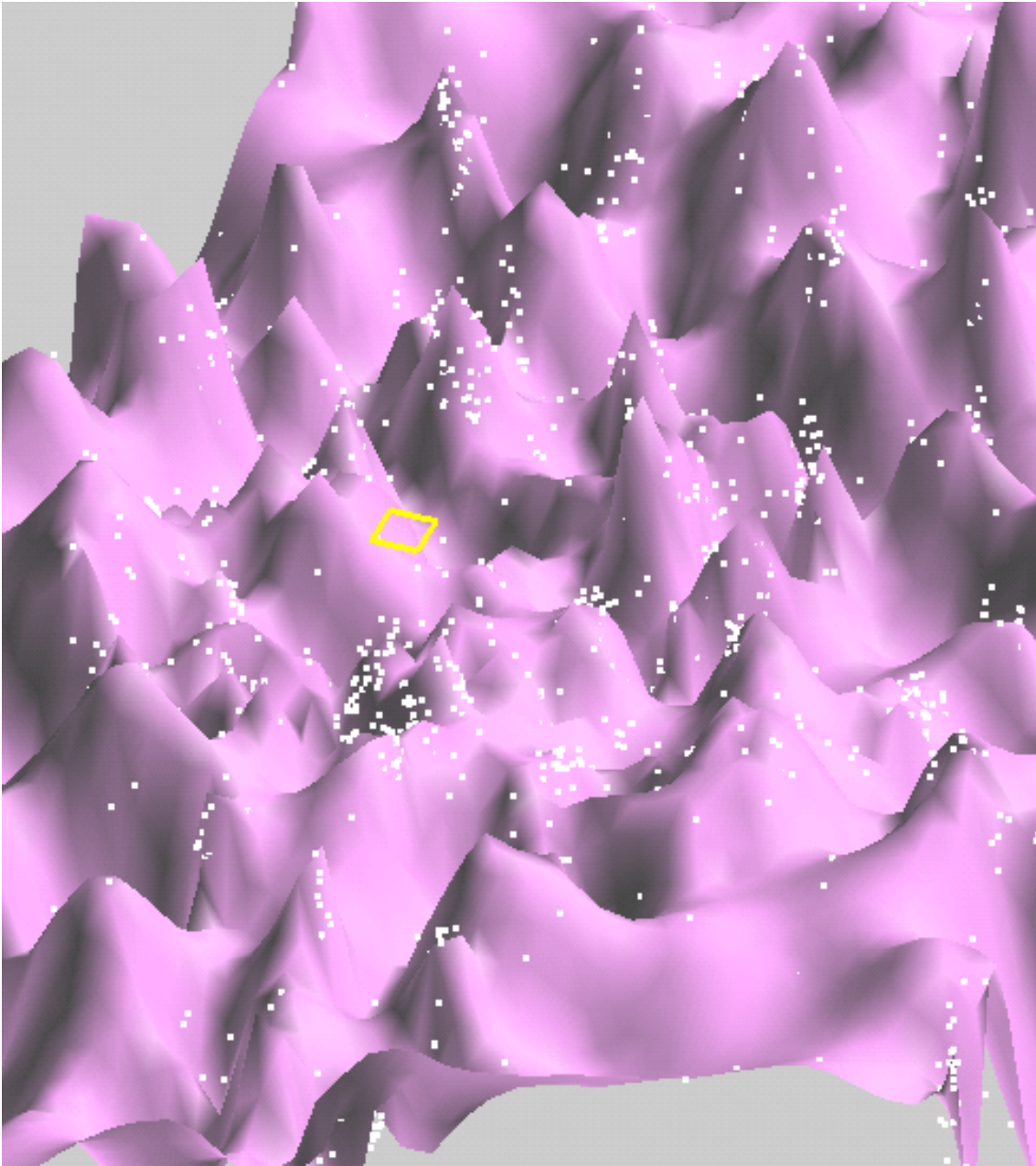

Figure 1. A subset of the data defining the 12 ppg equivalent pressure surface (white points) displayed against the krigged representation of the same 12 pound mud surface. The yellow square is South Eugene Island block 330. The krigged surface represents the pressure data reasonably well but fails to capture the full height of the peaks.

Finally, Volume II fully describes the contents of the GoCAD project and illustrates the basic procedures required to load and use this project.

2. Volume III

Volume III, "Organic Chemistry," by Woods Hole scientists J. Whelan and L. Eglinton describes the analysis and interpretation of oils and gases we collected in the Corridor.

The Woods Hole Laboratory analyzed 124 new samples. The gas chromatograph analysis with mass-specific detection was combined with simultaneous flame ionization detection (GC-MSD with FID). A method was developed to analyze for methylated phenols and the absolute concentrations of hopanes was measured in selected samples. Interpretations are based on this data set plus previous analysis of 93 oils from Eugene Island Block 330 area.

A multivariate analysis was performed on the full data set. Principal component and principal coordinate analyses were made using the SIRIUS Windows software package. Two components dominate. PC1 contains 87.4% and PC2 8.2% of the total data set variance. PC2 distinguishes 3 clusters of data that relate to the northern, middle, and southern parts of the Corridor. The southern and middle ("a" and "b") clusters are dominated by high sulfur abundance, while the northern ("c") cluster has low sulfur. Naphthalenes and oleanane also contribute to the cluster identity of a sample. The cluster identity (e.g., "a", "b", etc.) is included in the Excel spreadsheets that report the oil chemistry.
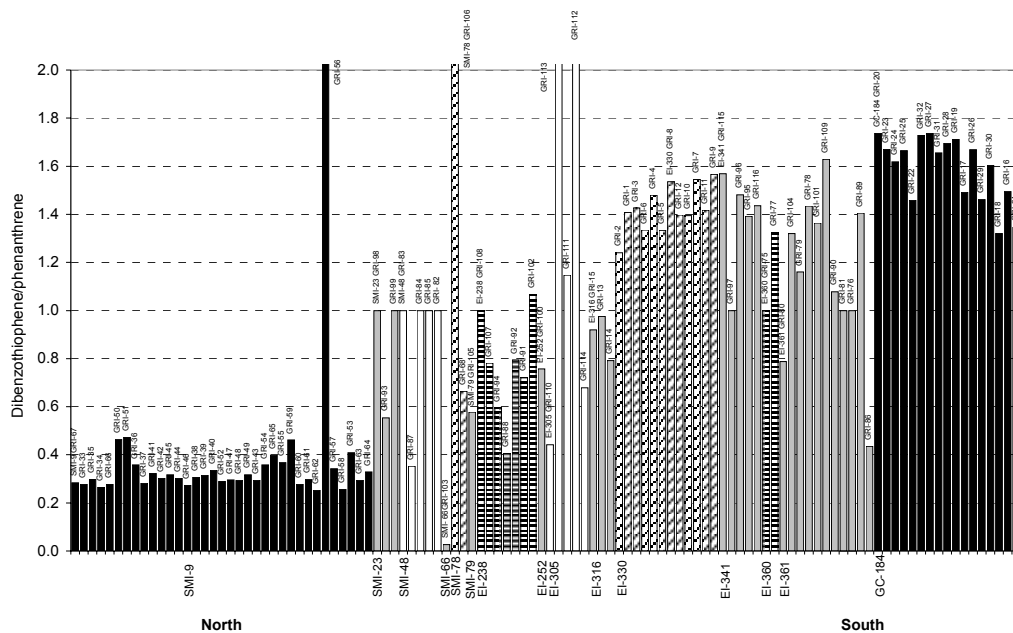

Figure 2: Ratio of dibenzothiophene to phenanthrene in oils going from north (left) to south (right). Individual fields and samples numbers are indicated.

All conventional biomarkers were examined geographically using GoCAD plotting tools and also by plotting Excel bar charts in which the bars were ordered from north to south across the Corridor (e.g., Figure 2). The best source biomarker trends are oleanane abundance which drops abruptly from ~30 ppm to ~3 ppm south of South Marsh Island

Block 9 (Excel spreadsheet), the ratio of oleanane to C_{30} $\alpha\beta$ hopane which shows the same behavior (Figure III-13), and the ratio of dibenzothiophene to phenanthrene which increases abruptly exactly where the oleanane drops (Figure III-32a and Figure 2 above). Since oleanane is a hopanoid derived from angiosperms (flowering plants) that evolved since the mid-Cretaceous, its presence in the northern part of the section suggests the influence of Eocene-sourced oils. Benzothiophenes contain sulfur and thus are of low abundance in oils sourced from shale and abundant in oils sourced from carbonate rocks. High benzothiophene in the south suggests Jurassic-sourced oils dominate the southern half of the Corridor.

The best maturity indicators are two methylphenanthrene indices and a C_{30} hopane index. The MPI-1 oil maturities (Figure III-35) decrease from ~1.1 in the north to ~0.9%R_e in the south, but there are several ~30 km intervals along the section where the maturity is significantly higher (~1.2%R_e). These anomalies could be produced by the temperature gradient anomalies noted in Volume II. The MPI-2 maturity shows a very similar trend as does C_{30} hopane, but the C_{30} hopane trends and local anomalies are magnified. Interestingly the triaromatic steroid index and the C29 sterane 20S/(20S+20R) index (Figure III-40, 41) indicate oil maturity increases to the south (the opposite of the other maturity indicators). Source effects, selective oil destruction, or the sterane dominance of lower maturity Tertiary oils could explain the contradictory sterane maturity results.

Corridor oils show varying degrees of alteration. Most show little or no biodegradation in their n-alkane makeup. Those that do are typically from relatively shallow reservoirs where temperatures are less than the "sterilization temperature" of 65-70°C. The lack of biodegradation of so many of the corridor oils indicates the majority of sampled reservoirs were filled after they were buried below the "sterilization isotherm." Sampled fields must have been charged much more recently than the time of main oil generation for this to be the case (see also discussion in Volumes IV and V).

In some places the lack of biodegradation suggests present-day filling. In the Jolliet Field, unbiodegraded oils are present in reservoirs where temperatures are low enough to allow bacterial activity. Many of the Jolliet oils show an unbiodegraded n-alkane envelope superimposed on a biodegraded "hump" (Figure III-58), suggesting that biodegradation occurred in the past and new oil has recently been injected. Whelan et al. (1994) suggest oil injection into low temperature South Eugene Island Block 330 reservoirs is rapid enough to counteract the biodegradation which must also be occurring presently. If biodegradation is ongoing at SEI 330 and Jolliet, reservoir charging must be ongoing and occurring at the same or greater rates as biodegradation.

Whelan and Eglinton caution that there are conspicuous discrepancies in the biomarker interpretation. This is due in part to the fact that biomarkers are affected by many independent processes (e.g., source, maturity, migration, biodegradation). Biomarkers can also be misleading when their absolute abundance in the oil is very small. Where the absolute amounts of oleanane are very low, for example, the oleanane to C_{30} $\alpha\beta$ hopane biomarker could be misleading. This is the case south of SMI 9. The Woods Hole group states that "the most striking characteristic of all the transect oils is the overall similarity

of their biomarkers, including the shallower shelf oils to the north (SMI-9) and the deeper water oils to the south (CG-184)", and feels that the original parent for all the oils was an early Cretactous or Jurassic marine source rock. They note however, that "many of the oils in [the north of] our transect [Corridor] appear to be mixed with some Tertiary sourced oil as shown by higher amounts of hopane and oleanane." They regard the Tertiary contamination as minor.

The chemical variability around South Marsh Island 9 is particularly interesting. The oils on the west and east flanks of the salt dome have different principal component cluster identities and thus probably different sources. Higher oleanane concentration occur nearer the diapir, and the west flank oils have higher maturity.

Finally carbazoles are very low in SEI 330 oils compared to most North Sea and Canadian oils. The nitrogen-bearing carbazoles are preferentially adsorbed on mineral surfaces encountered in migration. Their low abundance suggests migration in the Louisiana Gulf Coast may be through many fractures rather than a few major fault conduits.

3. Volume IV

Volume IV, "Gas Washing of Oil and its Implications," by S. Losh and L. Cathles describes the newly-discovered gas washing phenomena, distinguishes it carefully from biodegradation, and discusses its implications.

The most profound alteration process to affect many of the transect oils is gas washing: the removal of compounds from oil by a more mobile gas stream (Figure 3). Other processes that alter oil composition, such as migration contamination and water washing, have had variable, but generally limited effect on oils from the GRI Corridor. Biodegradation is limited or non-existent for most of the oils analyzed, including some at low reservoir temperatures where we would expect severe biodegradation. Condensation of liquid oil from a supercritical phase, proposed by Price et al. (1983) and expanded upon by Gatenby (2001), does not account for the simultaneous depletion of light ends and preservation of heavy compounds that is observed in Corridor oils. The ubiquitous gas condensates, not the oils themselves, are the products of subsurface phase separation. The residual oils were already liquids at the time of gas washing, and their composition records the pressure-temperature-composition conditions of fractionation.
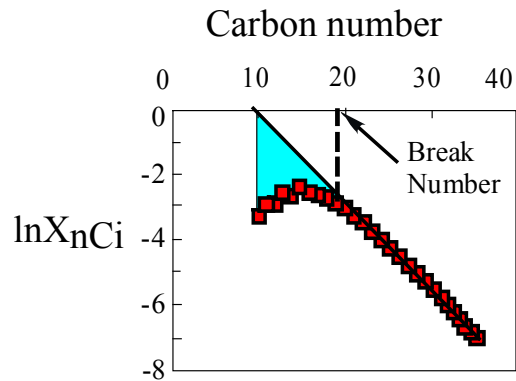
Carbon number

Figure 3. 'Molar fraction plot' showing $\log_e$ of the mole fraction of a particular n-alkane in an oil versus the carbon number of that n-alkane. Unfractionated, mature oils are typified by exponential abundance of n-alkanes with respect to carbon number, and so show a linear distribution on this type of plot. Depletion by gas washing (blue area) is indicated at relatively low carbon numbers by a deficiency relative to a straight line fit extrapolated from unfractionated compounds. Depletion is computed for the nC_{10+} fraction to minimize effects of light-end loss due to separator fractionation or evaporation during storage.

Reservoir gases are typically of significantly higher maturity than the oils with which they are found, and were thus generated distinctly later than the oils. Carbon isotopic compositions of gases relative to oils in the same field also indicate they have different sources. Thus it is not likely that the sampled oils and gases migrated together, but rather that they mixed at some point along their migration pathways or in the reservoirs themselves.

Oils in the GRI transect show a remarkable north-south gradient in depletion of n-alkanes and other compound types. The n-alkane depletion is the blue-shaded area in Figure 3. The depletion is profound in the northern end of the GRI Corridor where up to 91% of the oil's nC_{10+} fraction, corresponding to 85% of the oil's overall C_{10+} fraction, has been removed. Normal alkanes are removed systematically with respect to carbon number, and oil compound types are removed preferentially in the order n-alkanes, isoalkanes, naphthenes, aromatics. The intensity of washing decreases systematically from north to south across the Corridor (Figure 4).

Gas washing is the best explanation for the compositional patterns of depletion. Equation of state modeling indicates that the most-washed oils interacted with gas at a mass ratio on the order of 3.5 kg gas per kg oil. This is far greater than the mass of gas that can be dissolved in oil at any one time, and points to the interaction of the oil with a separate gas stream that mixed with, fractionated, and then separated from the oil.
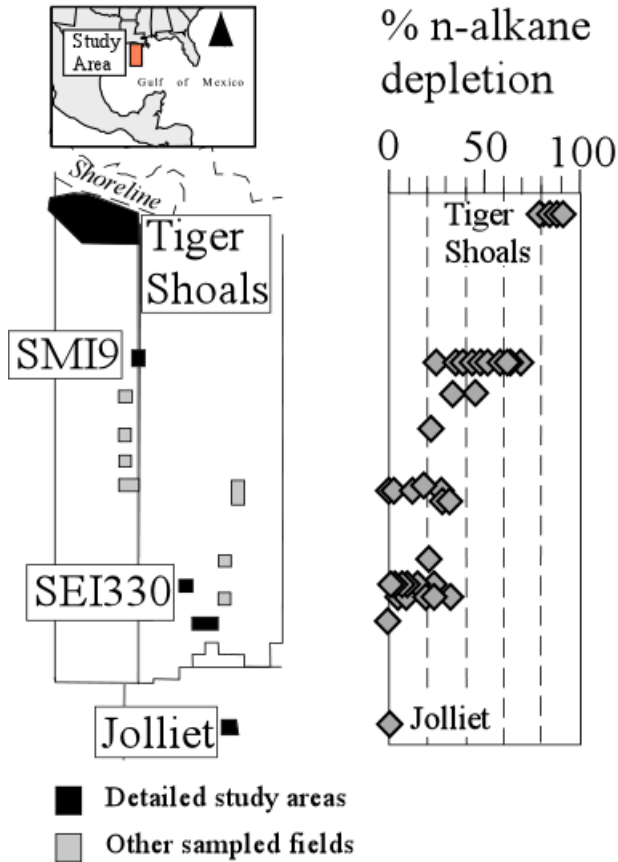
Figure 4. Map showing detailed study areas and other sample locations in the GRI transect. Plot at right shows calculated percent n-alkane depletion in transect oils at the same scale as the map. The maximum n-alkane depletion shows a systematic decrease in the offshore direction.

Equation of state modeling of gas washing shows that the carbon number of the heaviest n-alkane that is fractionated into the vapor phase (termed here as the "break number") is primarily a function of pressure. The higher the pressure, the greater the "break number." The amount of gas that washes the oil exerts a secondary effect on this parameter. The maximum "break number" decreases with distance south from the shoreline. Oils were gas-washed at lower pressures, hence at shallower depths, in the southern portions of the Corridor.

Reconstruction of the history of fluid pressure, oil migration, and burial since gas washing leads to the conclusion that gas-washing primarily takes place in deep, continuous sands, perhaps the first such sand that the migrating oil and gas encounter during their ascent (Figure 5). In the two locations where equation of state modeling and geologic reconstruction were done, the sand in which gas washing took place is the deepest known sand in the area. Oils that were gas-washed at that depth then ascended to their current reservoirs. This model explains the decrease in break number with distance from the shoreline. The generally offlapping nature of the deltaic sedimentary sequence means the deepest continuous sand lies at progressively shallower depths in the offshore direction.
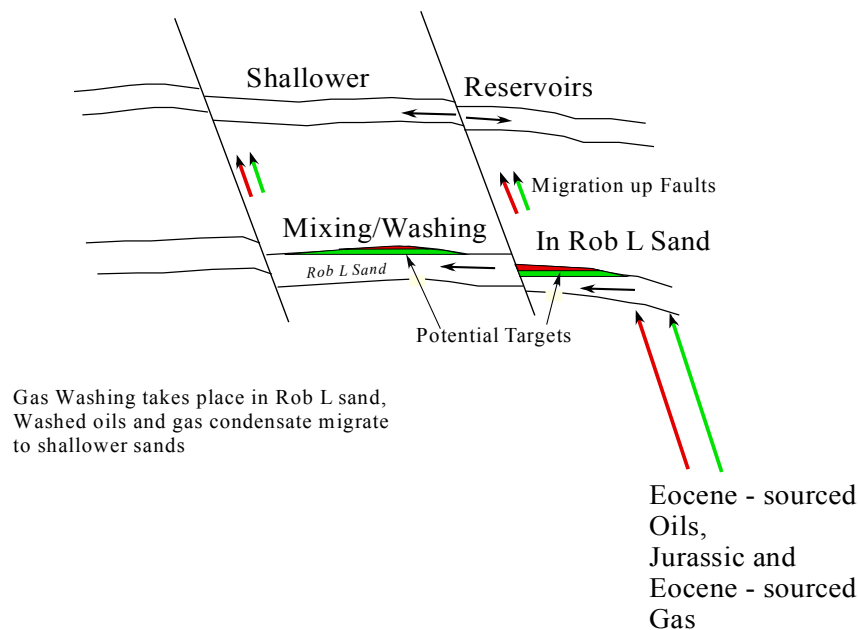
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Figure 5. Schematic model for gas washing, here shown for the Tiger Shoals field at the north end of the Corridor. Oil and gas mix and separate in the Rob L sand, the deepest productive sand in the field, and ascend to shallower reservoirs.

Analysis of gas washing predicts the depth of the sand where the oil was washed. This sand could contain residual oil and could thus be an exploration target. Gas washing also provides a unique window into, and constraint upon, oil and gas migration processes in the deep subsurface. The insights and constraints allow better modeling of subsurface fluid flow processes.

4. Volume V

Volume V, "A Modeling Analysis of Hydrocarbon Chemistry and Gas Washing, Hydrocarbon Fluxes, and Reservoir Filling," by L. Cathles and S. Losh models the physical evolution, hydrocarbon maturation in Eocene and Jurassic sources, and the migration, mixing along a typical N-S section through the Corridor, and shows that all chemical observations are naturally explained if the fraction of hydrocarbon retained in migration pathways is very small.

The modeling starts with the premise that Eocene oils dominate the northern half of the Corridor, and Jurassic oils dominate the southern half. This is not a conclusion reached by Whelan and Eglinton in Volume III, but it is one used in our modeling. It is true that only a slight contamination by Eocene oil in the northern part of the Corridor could produce the oleanane/C_{30} hopane ratios observed there (see Figure 6a) and perhaps the drop in oleanane abundance from ~30 to ~3 ppm at ~80 km south of the shoreline. However, the very low sulfur content of oils in the northern half of the section (Figure 6b) cannot be explained in this fashion. The sulfur content of Eugene Island oils is

~1 wt% of the oil, and is comparable in Jolliet oils. Oils sourced from the Jurassic carbonate should be relatively uniform in sulfur content across the section, as it is difficult to remove sulfur in the subsurface. The simplest explanation for the coincident drop in oleanane and rise of sulfur is that the Jurassic oils have been displaced by Eocene oils in the northern half of the Corridor where there is an Eocene source.
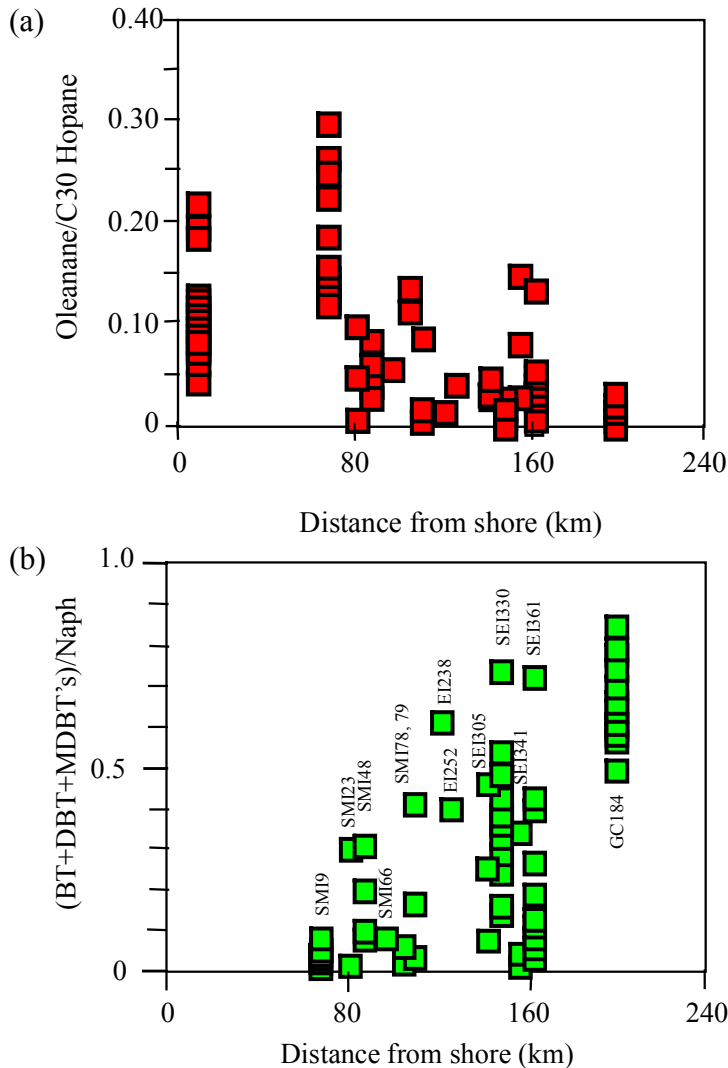

Figure 6. The decrease in oleanane to C30 hopane ratio to the south suggests a decreased contribution of oleanane-bearing Eocene-sourced hydrocarbons. An increase in sulfur-bearing benzothiophenes (BT+DBT+MDBT) to the south suggests an increase in marine Jurassic-sourced hydrocarbons. Note Tiger Shoals oils are included in this plot but not in Figure 2.

Physical models are constructed from basic first principles. Crustal extension is inferred from sediment thickness and water depth along a 1050 km N-S section that extends from the Arkansas-Louisiana Border to the Sigsbee Knolls. A 150-km thick one-dimensional (1D) plate-rifting model is used to determine the heat flow to the base of the sediment section. The plate model computes the thermal effects of extension and sediment deposition at the geologically observed rates, and takes into account radiogenic heat

production in the crust and basin sediments. Heat flow to the base of the sediment section from this model is then used in a 2D basin model in which thermal conductivity, radiogenic heating and other critical parameters are functions of compaction, temperature and lithology. These models reproduce both the unusually low surface heat flow (~half normal) and ~22°C/km temperature gradients in the Corridor using accepted literature values for all parameters (e.g., thermal conductivity, heat generation, etc.).

The computed temperature history is then used to mature both Jurassic and Eocene source rocks in the 125 by 200 km GRI Corridor. The history of sediment deposition and salt diapirism is reconstructed over the last 144 Myrs for a section published by McBride (1998) that lies ~50 km east of our study area. The model simulates the deposition of the Louann salt and overlying carbonates and siliciclastics including the two hydrocarbon source intervals. It also simulates the inversion of the Louann salt to form a sill, and the loading of that sill and the formation of two salt withdrawal minibasins. The Jurassic Type II source is 100 m thick and extends across the full 200 km N-S section at the top of the Louann Salt. This source bed contains 5 wt% TOC and has an HI of 628 mg/g. The model Eocene Type III source is 30 m thick, extends only under the northern half of the section, has a 4 wt% TOC, and an HI of 205 mg/g. The kinetic maturation models are standard Burnham and Sweeney for the Jurassic Type II source, and an industry standard Wilcox coal model for the Eocene Type III source. A 20 vol% hydrocarbon saturation of the pore space is required before hydrocarbons are expelled from the model source strata. The hydrocarbon saturation required for migration is treated as a parametric variable. Hydrocarbons mix in each element they enter. Migration of the mixed hydrocarbons is allowed only once migration saturation is reached in an element. Application of this model to the GRI Corridor, where we have carefully assembled diverse chemical data on the oils and gases, yields a large number of important conclusions:

1. The source beds in the GRI Corridor have almost completely matured. Vastly more hydrocarbons have been generated and expelled from the source strata (186 Bt) than have been discovered in producible reservoirs (1.35 Bt).
2. Gas and oil are venting from innumerable seeps in the Corridor. Our modeling indicates this could not occur unless the retention of hydrocarbons in pore space along the migration pathways connecting the source strata to the surface is less than 0.5% of that pore space (Figure IV-20).
3. Hydrocarbon chemistry requires that retention of hydrocarbons in migration pathways is 10 times less than this, or <0.05%. Only if this is the case can Eocene-sourced oils displace earlier-generated Jurassic-sourced oils in the northern half of the section as we believe is required by field data (Figure 6 above). Near the venting limit (0.5%) the oils in all the reservoirs would be Jurassic. The Jurassic oils must be displaced in the northern half of the section by Eocene oils. This can be done nearly completely for a migration fraction (e.g., the fraction of the out-of-source pore space that is filled with hydrocarbons) of 0.025%. In this case the shallow oils at the north end of the Corridor are ~90% Eocene and half way across the section are ~50% Eocene. This north-south variation is similar to that suggested by the sulfur and oleanane data (Figure 6

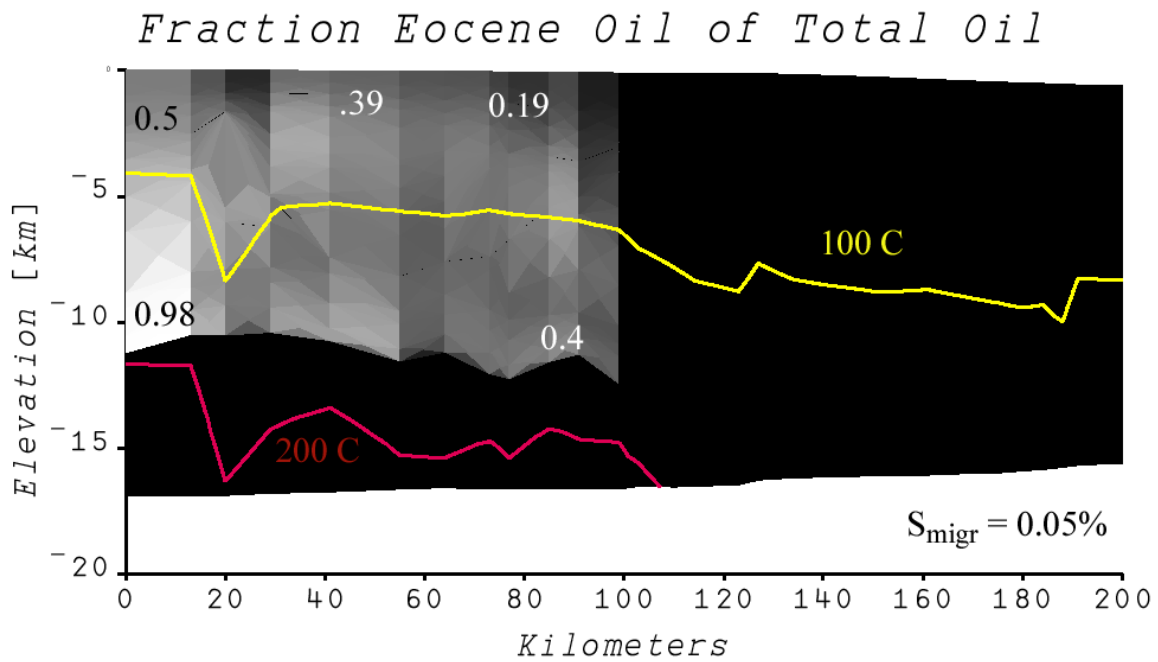above). For a migration fraction of 0.05%, the Eocene oil is less dominant (Figure 7).

Figure 7. Fraction Eocene oil as a mass fraction of total oil.

4. Washing of Eocene oils in shallow migration pathways can be accomplished if they interact at shallow depths with Jurassic dry gas. Jurassic gas floods the section (Figure 8) and the gas-oil ratio is high enough to accomplish the washing (Figures V-12, 16, 24, and also Figures V-21 to V-30).
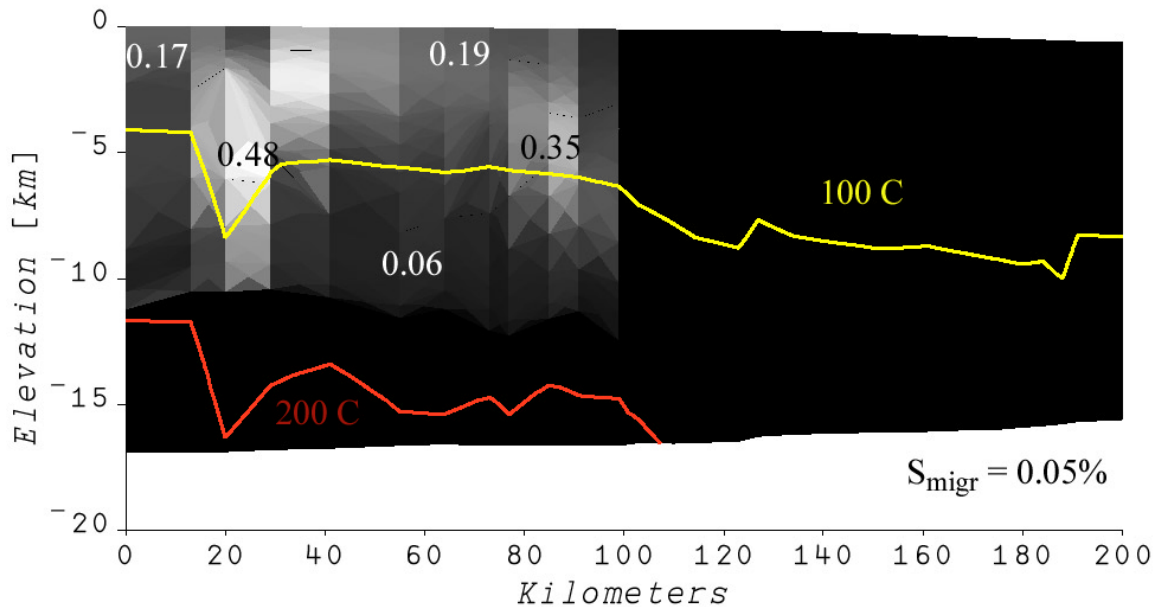
Figure 8. Eocene gas and condensate as mass fraction of the total gas and condensate. Shading indicates fraction. Numbers are values at particular elevations. Contour lines are for 100ºC and 200ºC temperatures.

5. The decrease in gas washing to the south parallels and is logically explained by the decrease in GOR (Figures V-12 and V-16).

6. All the reservoirs have filled recently. This is indicated by the lack of biodegradation of the oils in the northern half of the corridor (Tiger Shoals, SMI 9, ~SEI 330), and by the lack of biodegradation and other geologic constraints in the southern half of the Corridor (SEI 330, Jolliet).

7. If hydrocarbons are drawn from distances of 2 to 20 km, the reservoirs in the 4 GRI study sites could be filled with hydrocarbons in < 1 Ma at Tiger Shoals and at the progressively much shorter time intervals required for the sites to the south (Figures V-21-30). The hydrocarbon draw radii are of the same scale as salt withdrawal minibasins in the area (Figure 9).

8. The 2 to 20 km draw radii are reasonable in terms of the distribution of discovered hydrocarbon reservoirs (Figure 9).

9. The rate of gas venting inferred at Jolliet is supported by a recent independent estimate based on the mass of gas hydrate that has accumulated at a Jolliet surface vent.

10. With low retention along migration pathways, the amount of hydrocarbons vented into the ocean from the GRI Corridor is massive (131 Bt; Table V-9). This is equivalent to over 1000 billion barrels of oil, or more hydrocarbon than has been produced and consumed by humans since the start of the petroleum era. At least in this area of the Gulf of Mexico Basin humans are, in effect, intercepting hydrocarbons from a massively leaky flow-through petroleum system that would otherwise vent naturally. If this is a general situation, human hydrocarbon usage may have intercepted some of the natural hydrocarbon venting and human

consumption of hydrocarbons might therefore have had less impact on CO_2 in the atmosphere than otherwise would be predicted.

11. All the above suggests that the hydrocarbon reservoirs in the GRI Corridor are ponds along migration conduits that may persist for protracted periods of geologic time, but whose contained hydrocarbons are constantly replenished and replaced by the introduction of new hydrocarbons. As so appropriately stated by Gatenby (2001), "in the Gulf of Mexico the present is the key to the present".

12. The above suggests that almost all the hydrocarbons in a minibasin may vent through a single vent. Reservoirs on migration pathways to this vent should be particularly promising exploration targets.

13. Hydrocarbon chemistry reflects current, large scale, and significant basin processes that can be unlocked by basin models that compute the generation and migration of hydrocarbons from two or more sources. Chemical variations interpreted by more refined models could have exploration utility. Low migration retention allows new parameters such as draw radius to be calculated from basin models that could also have exploration utility.
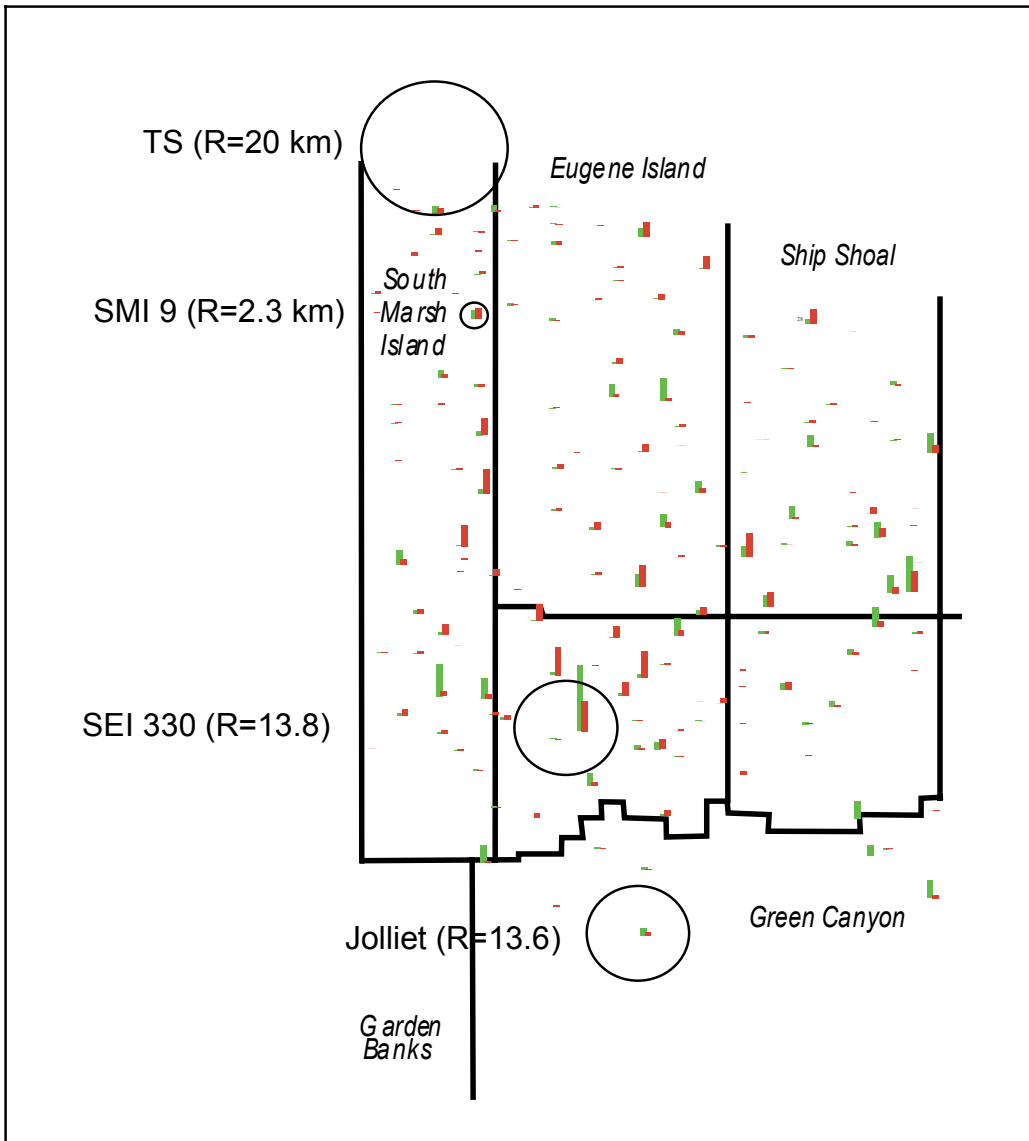
Figure 9. Draw areas from Figures V-21 ,25, 27, and 30 are plotted against hydrocarbon resource histograms (oil in green, gas in red) from Bascle et al. (1999).

The model is compelling because it is very simple and yet ties many phenomena together in a geologically natural way. To displace Jurassic with Eocene oil enough to remove almost all sulfur, we need a migration fraction of ~0.025%. With this low a fraction, there is plenty of gas to wash the oils, but there would not be with a migration fraction of even 0.1%. We must have a Jurassic source in the northern part of the section because the Eocene source does not produce enough gas at the right time to wash its own oils. A decrease in the degree of gas washing across the section similar to that observed is predicted by the model. For a geologically reasonable draw, the model system can supply hydrocarbons at the rates required by the lack of biodegradation. The filling is dynamic and presently ongoing as suggested by many kinds of data. In fact, if the retention of hydrocarbons during migration is very low all the geochemical observations can be accounted for in a very natural way. The displacement of Jurassic with Eocene

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oils may explain many of the conspicuous discrepancies in the biomarker data noted in Volume III. Conversely, if the migration retention is large, most observations would be contradicted by the model.

Some of the most important conclusions are unusually robust. For example, the source richness could be greater than estimated, but this would only increase the amount of hydrocarbon vented into the ocean. Displacing Jurassic with Eocene oils would require the same *ratio* of hydrocarbon retained in migration to that expelled from the source. Increasing the source richness would thus increase the mass of hydrocarbons expelled to the ocean. Similarly, even a small introduction of Eocene oil would require a migration fraction almost as low as 0.05%.

5. Volume VI

Volume VI, "A theoretical Analysis of Inorganic Alteration by the Flow of Brines Through Seals," by L. M. Cathles and J. D. Shosa develops a theoretical framework for predicting the inorganic alteration produced when brines are forced through basin seals and calculates the alteration for flow through two kinds of hypothetical seal subject to two different mineral buffers, different brine salinities, and various fractions of gas in the fluid.

Brines and hydrocarbon fluids are driven across basin seals when sediment loading and hydrocarbon generation increases fluid pressure to the hydrofracture limit. The brines and hydrocarbons cross steep pressure gradients, elevated temperature gradients, and possibly salinity gradients when they transit a seal. Since basin fluids are in equilibrium with sediment minerals, and since the solubility of these minerals is a function of pressure, temperature, and chlorinity, the movement of brines through pressure, temperature, and salinity gradients causes mineral alteration of the sediments.

A theoretical foundation is developed for calculating alteration due to the flow of brine and gas through seals. A new, simplified method for estimating the log dissolution equilibrium constants of aqueous complexes that are required to predict brine chemistry from a mineral buffer is also developed. The theory and parameter estimation methods are then used to calculate the mineral alteration that occurs when brine is driven across a variety of hypothetical seals (Figure 10).

The alteration expected from a minimum estimate of fluid flow through seals is significant. For a minimum total fluid flux of 200 kg/cm^2 (normal compaction, hydrocarbon maturation expulsion, and focusing by a factor of two), about 1 wt% of sediment minerals will be precipitated as the result of fluid flow. By comparison a minimum estimate of the diagenetic alteration produced when pore waters of seawater composition equilibrate with the mineral buffer during burial is ~0.1 wt%. At the steep pressure gradients expected in capillary seals, a throughput of 200 kg/cm^2 would produce an alteration of ~9 wt %. Increasing fluid salinity increases the alteration intensity more than proportionately. If brine flow is focused to discharge points on a minibasin scale, as the hydrocarbon flux analysis suggests, inorganic alteration intensity will be the maximum allowed by the exhaustion of buffer minerals.
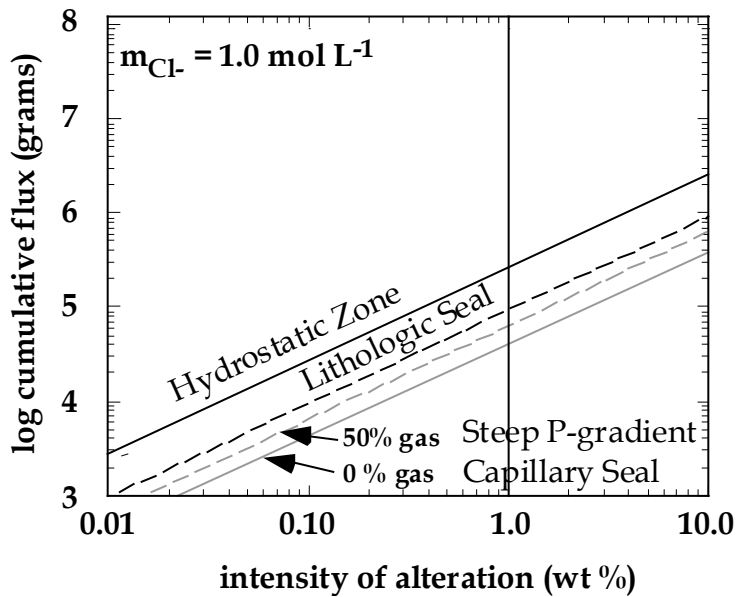
Buffer 1

$m_{Cl^-} = 0.5 \text{ mol L}^{-1}$

Hydrostatic Zone

Lithologic Seal

50% gas   Steep P-gradient

0% gas   Capillary Seal

log cumulative flux (grams)

intensity of alteration (wt %)

$m_{Cl^-} = 1.0 \text{ mol L}^{-1}$

Hydrostatic Zone

Lithologic Seal

50% gas   Steep P-gradient

0 % gas   Capillary Seal

log cumulative flux (grams)
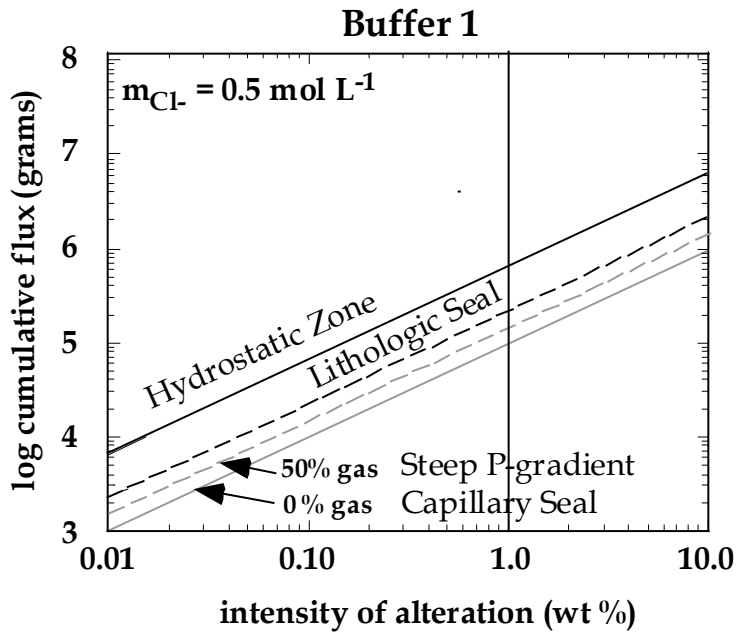
intensity of alteration (wt %)

Figure 10: The log of the cumulative flux through sediments as a function of the intensity of total Buffer 1 alteration. Vertical line at 1% alteration shows approximate intensity of minimum expected flow-related alteration. Together the two figures show the effect of brine salinity on alteration intensity. The higher the salinity the less fluid is required to produce a given intensity of alteration.

The mineralogy of the alteration contains information on the fluids and conditions of alteration. The alteration mineralogy in the steep pressure gradient portions of a capillary seal is unique for one of the two mineral buffers we use in our calculations. This suggests it may be possible to identify a capillary seal from its mineralogy. The passage

of gas (as well as water) through a seal also changes the alteration mineralogy in characteristic ways. Because mineral alteration is complex it contains valuable information regarding basin processes and the nature of sealing.

The simplest and perhaps most useful aspect of seal alteration is that it measures the amount of fluid that has been forced through a seal. Figure 10 shows how fluid throughput is related to the wt% of new minerals deposited. This figure allows conversion of maps of mineral alteration to quantitative maps of cumulative fluid fluxes in a basin. The expected alteration is intense enough that it should impact seismic wave velocities. Our methods could convert seismic alteration maps to maps of cumulative fluid flow in basins.

6. Future Work

The work presented suggests many areas that could be fruitfully investigated in the future:

1. *The spikes in the top of overpressure:* How do these spikes form, and what determines whether they become persistent hydrocarbon leak points? Is capillary sheathing a factor in their stability?
2. *The ~50 km checkerboard changes in temperature gradient that appear to affect biomarker maturity:* What is its cause? What is its impact on the timing of local hydrocarbon maturation?
3. *Gas washing:* Can other homologous series be found that show the same gas washing pattern as the n-alkanes? Can more rigorous equation of state modeling provide better predictions of deep processes and reduce exploration risk? Does the gas washing process apply in other basins or is the northern Corridor unique because of the relation of its two source beds?
4. *Biodegradation:* Can it be quantified sufficiently to measure the filling rate of hydrocarbon reservoirs?
5. *Source:* Can compound specific isotope determinations remove uncertainties in biomarker source identifications?
6. *Site-specific 3D modeling:* Can site-specific models on a minibasin scale use gas washing, brine salinity variations, sediment alteration, and biomarker data to constrain the hydrocarbon and brine flow systems, predict deep exploration potential, decipher how faults and spikes in the top of overpressure direct hydrocarbon and brine migration, etc.?
7. *Seal alteration:* Can alteration be mapped using seismic data, and can those maps be inverted to provide quantitative maps of brine flow in basins?

D. Acknowledgements

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