

Accomplishments during last reporting period: 1 September 2002 to 31 August 31 2005:

- 1) Completed collaborative work between Cornell and Woods Hole using a comprehensive organic geochemical data base of oil compositions from Woods Hole together with basin and fluid flow modeling and data visualization from Cornell. The goal of this work was to complete preliminary interpretations of fluid flow in the transect of the offshore Gulf of Mexico, both as a whole and at individual oil fields along the transect (SMI-9, EI-330, and GC-184 in Fig. 1)
- 2) Completed $\delta^{13}\text{C}$ compound specific isotopic work (IRGCMS) analyses to better classify the Gulf Coast transect oils with respect to source.
- 3) Determined the relative degree of biodegradation of all the transect oils using ratios of biodegradable to non-biodegradable compounds. Used resulting data to constrain depths of reservoir filling.
- 4) Completed work with Dr Chris Reddy to look for relatively non-biodegradable homologous series of compounds that can be used to determine the degree of gas washing of oil in shallow biodegraded oils via the new technique of GCxGC. GCxGC was applied as means of investigating various migration fractionation processes in oils
- 5) Examined Gulf Coast transect oils for molecular markers of terrestrial oil sources using higher plant biomarkers (methylated naphthalenes, retene, methyl retene, bicadinanes, isopimarane and phylcladane).

Papers credited to this project during previous research period :

Published:

Eglinton, L.B., Lim, D., Slater, G., Osinski, G.R., Whelan, J. K., Douglas. (2006) Organic Geochemical Characterization of a Miocene Core Sample from Houghton Impact Structure, Devon Island, Nunavut, Canadian High Arctic: *Organic Geochemistry* v. 37, pp 688-710.

Whelan, J., L. Eglinton, L. Cathles III, S. Losh, and H. Roberts (2005) Surface and subsurface manifestations of gas movement through a N-S transect of the Gulf of Mexico, *Marine and Petroleum Geology*, v. 22, pp 479-497.

Losh, S., L. Walter, P.Meulbroek, A Martini, L. Cathles, and J. Whelan (2002): Reservoir fluids and their migration into the South Eugene Island block 330 reservoirs, offshore, Louisiana, *Amer. Assoc. of Petro. Geol. Bull.*, v. 86, pp 1463-1488.

Abrams, M. and J. Whelan, eds (2005) "*NEAR-SURFACE HYDROCARBON MIGRATION: MECHANISMS and SEEPAGE RATES*" Special Issue of *Marine and Petroleum Geology*, collected papers drawn from a 2002 Hedberg Research Conference in Vancouver, BC and a special session at the American Association of Petroleum Geologists meeting in Salt Lake City, Utah in the spring of 2003.

Whelan, J.K. (2004) When the seafloor meets ocean, the chemistry is amazing. In more and more places, scientists are finding large amounts of natural gas on the ocean bottom, *Oceanus*, v.42, pp 66-71. (online version available from: <http://www.oceanusmag.whoi.edu/v42n2/whelan.html>).

J. Whelan (2005), Profile in special issue on "Women in Oceanography", *Oceanography*, v.18, No.1, p235.

ORGANIC GEOCHEMISTRY OF CONTINENTAL MARGIN
AND DEEP OCEAN SEDIMENTS

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3. Research Period: 1 September 2002 to 31 August 2005

4. Overview of the project

Our overall research has focused on understanding the complex processes of fossil fuel formation and migration, particularly with respect to gas. Over the past several years in collaboration with other scientists in the Global Basin Research Network (GBRN) at Cornell, Louisiana State University and Texas A&M, we have found oil, and to an even greater extent gas migration in a north-south transect of the offshore Louisiana Gulf Coast (Fig. 1) to be very important. This work together with that

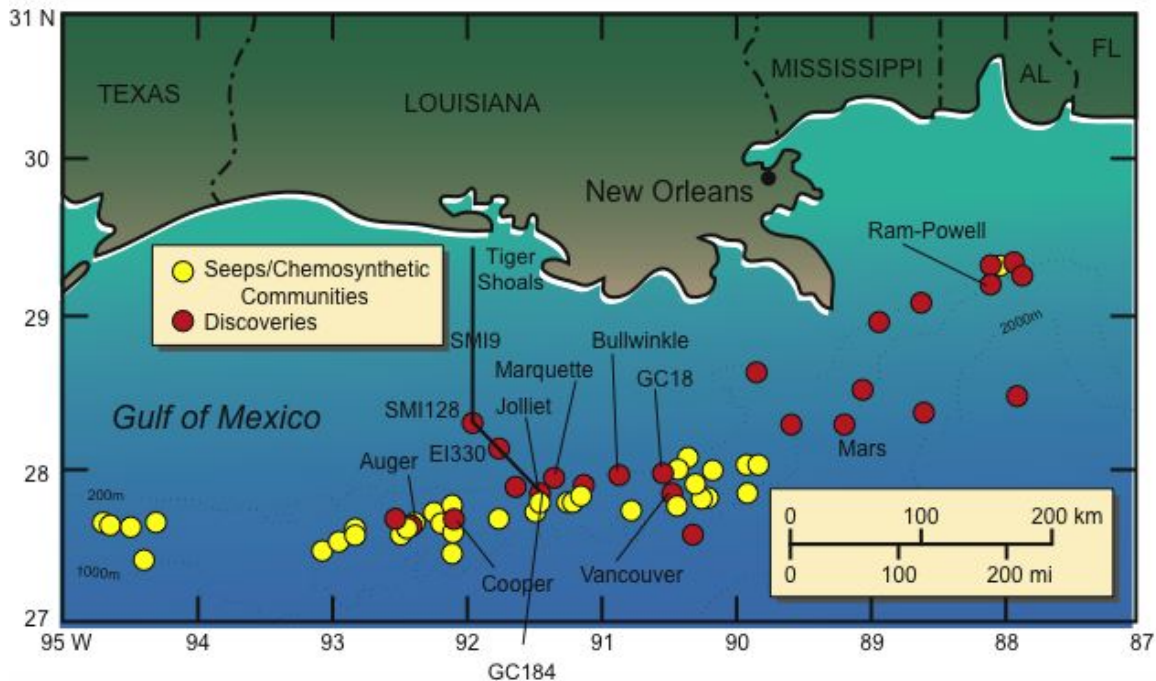


Figure 1: Map of oil and gas seeps/chemosynthetic communities and recent petroleum discoveries (adapted from Sassen et al., 1993a,b). The location of N–S well transect on upper slope of northern Gulf of Mexico is indicated by the heavy black line.

previously carried out for Eugene Island block 330 (Whelan et al., 1993 & 2001) has focused on analysis of organic geochemical parameters related both to long term fluid flow in this area and also dynamic subsurface flow occurring on modern (less than 10 year) time scales. In the course of documenting effects of these flow processes both in the surface and subsurface of the Gulf of Mexico, we have assembled an excellent geochemical, geological, and geophysical database. This area provides an important case study for examining the often surprising effects of rapid upward movement of large volumes of gas throughout the transect (Roberts and Carney, 1997; Whelan et al., 1994&2001; Meulbroek et al 1998; Sassen et al., 2001 as summarized in Whelan 1997 and 2001)

Similar processes appear to be important throughout the Gulf of Mexico, even in the deep water and generally on the continental slopes and river deltas of the worldwide (*e.g.* Whelan et al 2005, Hovland and Judd, 1988 & 1992; Hovland & Thomsen, 1997; Hovland et al, 2001), particularly in areas of rapid sediment deposition where gas generation is ongoing. These areas include several of the major oil and gas provinces of the world such as the North Sea, the Niger Delta, and the Amazon Delta. Some manifestations of this rapid upward movement of gas include:

- i) 3D seismic profiles showing large subsurface gas plumes;
- ii) large craters or pockmarks on the ocean floor that occur worldwide and are probably the relic of past gas venting to the ocean floor
- iii) mud volcanoes caused by huge gas plumes ejected rapidly through the seafloor from great depth;
- iv) large off-shore surface oil slicks in ocean waters too deep to be caused present day oil production;
- v) globally large subsurface reservoirs of gas hydrates that are at least partly derived from thermogenic gas coming from depth;

vi) abundant and vigorously growing ocean bottom biological communities similar to those found in hydrothermal vent areas that depend on the venting oil and gas as their food source.

vii) a potential source for the large pools of dissolved organic carbon, DOC, that are too old (5000 years) considering their probable recent, marine sources (less than 200 years; Druffel et al., 1992; Wang et al., 2001, Whelan 1997).

viii) a potential source of the green house gas, methane, venting from the ocean floor to the atmosphere (Kvenvolden and Lorenson, 2001 & 2004)

This work began with research on the highly productive EI-330 oil and gas province, considered to be one of the giant oil and gas fields of the world (Carmalt and St. Johns 1986) and has now been extended to a N-S transect across the Northern Gulf Coast shelf and slope (Fig 1) .

(Summary source and maturity variations thru transect)

Fluid compositions throughout the transect are highly variable with different sands producing a variety of admixtures of gas, condensate, and oil despite fairly homogeneous biomarker compositions (Figures 2 and 4), indicative of a relatively homogeneous Early Cretaceous or Jurassic source (Whelan et al., 1993, 1995, and 2001 and Whelan et al., 2005). Recent modeling combined with organic geochemistry showed that oil generation probably took place in the Miocene from rocks currently buried directly beneath their present day Pleistocene reservoirs (Erendi, 2001). Therefore, oil generation probably occurred considerably before the time of formation of the present day Pleistocene reservoirs and was initially trapped beneath salt sheets as shown *via* basin modeling of the area. More recently, further rapid sediment deposition caused the salt to flow so that the trapped oil was able to flow rapidly upward through holes in the salt into present day reservoirs, a process that is probably still in progress at the present time in southern portions of the transect including EI-330 and Green Canyon 184 (Fig 1; Erendi, 2001). Salt movement is very dynamic in this area during sediment loading, so that recent development of holes through the salt as it flows and moves would have allowed oil and gas to flow upward into Pleistocene reservoirs. This scenario is consistent with all of the organic geochemical data assembled by our group and with the basin and fluid flow modeling carried out by the Cornell group. Thus the oil maturities and sources previously deduced from organic geochemical biomarkers (Whelan et al., 1994) that were previously very puzzling have now become compatible with the most recent Cornell basin and fluid flow modeling showing oil and gas generation to be much deeper than previously thought. Furthermore, the Woods Hole organic geochemical data is also very compatible with the idea that oil and gas became temporarily trapped beneath salt prior to its migration upward into modern reservoirs.

The combined work of the Woods Hole and Cornell groups has now also demonstrated a number of surprising effects caused by the rapid upward movement large volumes of gas. Oils in several intervals show evidence for extensive alteration *via* flushing and equilibration with multiple volumes of gas (Meulbroek et al., 1998; Whelan et al., 2001; Losh et al, 2002a). The gas involved in this process probably comes from deeper and more mature intervals than the oil (Whelan et al., 1993). However, the mechanics of the process are currently a mystery because oil and gas that are separated in the subsurface are difficult to remix at subcritical temperatures and pressures. For oil and gas to mix efficiently, they may have to be generated together. However, our previous measurements show gas maturities to be significantly higher than those of the associated oil (Whelan et al., 1993). Alternatively, if gas and oil are generated separately, then some as yet uncharacterized mechanism must exist for remixing the gas and oil in the subsurface. Our previous work with the Cornell along with the current data suggests the existence of mixing chambers in isolated subsurface pressure cells that persist below subsurface depths of about 10,000 ft. (Hunt et al, 1998; Hunt 1996 ; Whelan et al, 1997). At these pressures and temperatures, methane can act as a supercritical fluid that can dissolve large volumes of oil (Whelan et al., 1997).

There is considerable evidence that oil and gas movement are occurring in the southern part of the transect at the present time. Surface sediment gas hydrates found within a fault overlying the Green Canyon oil and gas reservoirs are derived from the underlying thermogenic gas deposits (Sassen et al 2001). Visually, this gas is observed to flow continuously through the seafloor gas hydrate deposits that overlie the GC-184 (Conoco Jolliet field) reservoirs, suggesting that these seafloor hydrates may be a steady state rather than a semi-permanent component of the seafloor. That is, gas is continuously being lost as gas venting into the overlying ocean as the hydrates come into contact with overlying warmer seawater and are continuously being reformed at the bottom by the arrival of new up-flowing gas.

Just to the north of GC-184 at EI-330, Anderson et al., (1995) has presented geophysical evidence consistent with plumes of oil and gas in the subsurface beneath EI-330 at the present time and has shown changes in the 3D seismic profiles within EI-330 reservoirs over time periods of several years (4-D seismic). These changes have been interpreted in terms of production effects (Anderson 1995), but are also consistent with upward movement of fluids from deeper intervals (Anderson, et al., 1991 & 1995; Anderson 1993). In addition, oil compositions in some EI-330 reservoirs change on time scales of 3 to 8 years or less due to recharging with upward flowing gas (Schumacher 1993; Whelan et al., 1993 and 2001). Similar processes are probably occurring in subsurface reservoirs in Green Canyon 184 at the southern end of our transect (Fig. 1) where highly biodegradable and diffusible light *n*-alkanes also occur together biodegraded oil. This pattern is also observed in the shallowest EI-330 GA and HB reservoirs (Whelan 1993) and in some of the South Marsh Island 9 (SMI-9) oils at the north of the transect (Fig. 1). In any petroleum reservoir having a temperature of less than 60°C, bacterial biodegradation is probably on-going (Palmer 1991) so that the presence of unbiodegraded oil together with a biodegraded background is interpreted to be indicative of on-going hydrocarbon injection occurring on time scales less than the rates of the biodegradation. These rates are typically weeks to years in the laboratory for aerobic oil biodegradation (Gough et al., 1992) and up to a few years under *in-situ* reservoir conditions at higher pressures (Jannasch & Taylor, 1984; Reuter, et al 1994; Stetter et al., 1993; Gibson 1984; Singer, M.E. and W. R. Finnerty 1984). Alternatively, anaerobic sulfate reducing microbes of a moderately thermophilic nature (60°C) have been isolated that can utilize *n*-alkanes from C₆ to C₁₆ as substrates (Rueter et al., 1994) with the best growth occurring in the C₈-C₁₂ range. This is the carbon range that is commonly depleted in these Gulf Coast oils.

Stacked faulted reservoirs have been described in other areas that also show the presence of light hydrocarbons superimposed over a biodegraded oil background (e.g. Dzou and Hughes, 1993; Holba et al., 1996). These reservoirs typically show the aromatic compounds as the most prominent light hydrocarbon component, a pattern observed here for the biodegraded SMI-9 oils. However, EI-330 is unusual in having the lightest and most volatile and the most highly biodegradable *n*-alkanes as the most predominant C₃ to C₁₀ hydrocarbon fraction (Whelan et al., 2001 and unpublished). The only way that these light *n*-alkanes can survive in reservoirs undergoing active biodegradation, is by active on-going oil recharge of the intervals in question.

The GC-184 oils are remarkably homogeneous both with respect to source (marine) and maturity (Fig.2) and very similar to the EI-330 oils. However, all of the Jolliet oils show varying degrees of biodegradation (Fig 3 and 4). In one case, oils from the same reservoir show varying degrees of biodegradation. There is no evidence based on *n*-alkane envelopes for gas washing of the Jolliet oils (Losh, et al., 2002a). However, gas washing might not be observed if biodegradation was removing *n*-alkanes faster than they could be replaced by reservoir recharging.

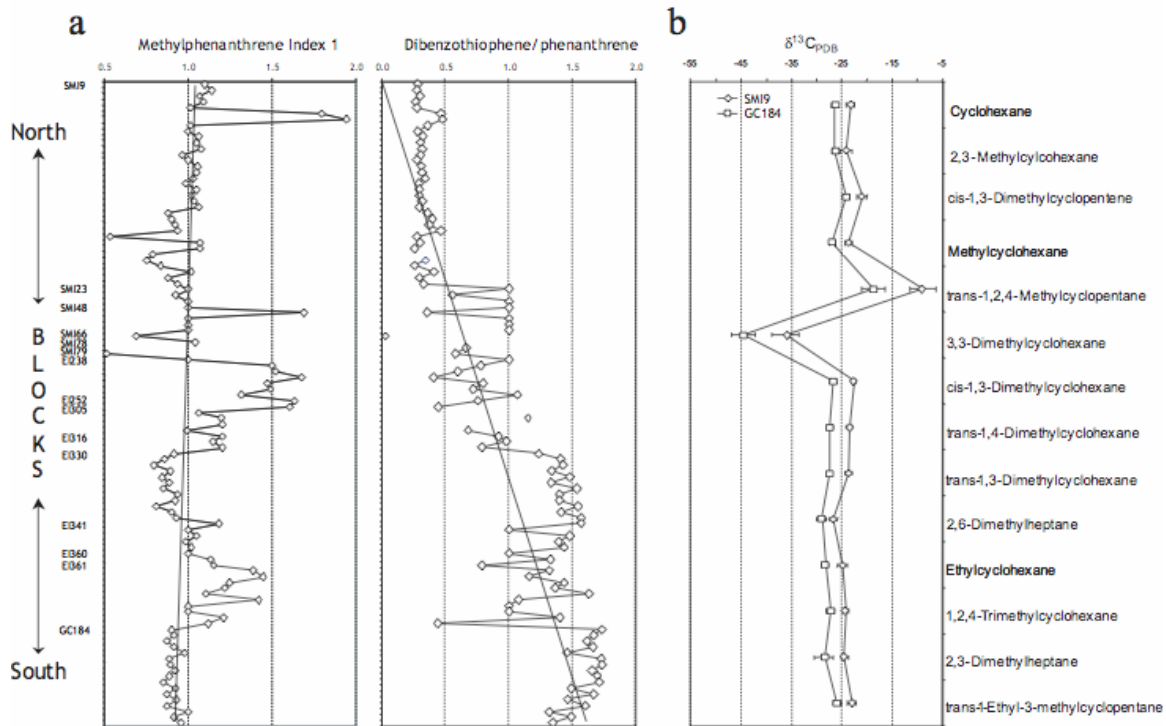


Fig 2: Gulf Coast transect oil source and maturity indicators for wells toward the north, SMI9, and proceeding to GC184 furthest to the south. Each point indicates data for one well in the transect. a) Methyl Phenanthrene Index I, a maturity indicator as defined by Radke 1988; Radke et al 1982, 1983, and 1990). Note the general slight increase in maturity of oils to the north with anomalous zones of higher maturity, 'hot spots' occurring for a number of EI wells in the center of the transect. These hot spots are postulated to represent upward injection of more mature oils from deeper sections through holes in overlying salt layers. Also shown is a source indicator, dibenzothiophene to phenanthrene which tends to increase

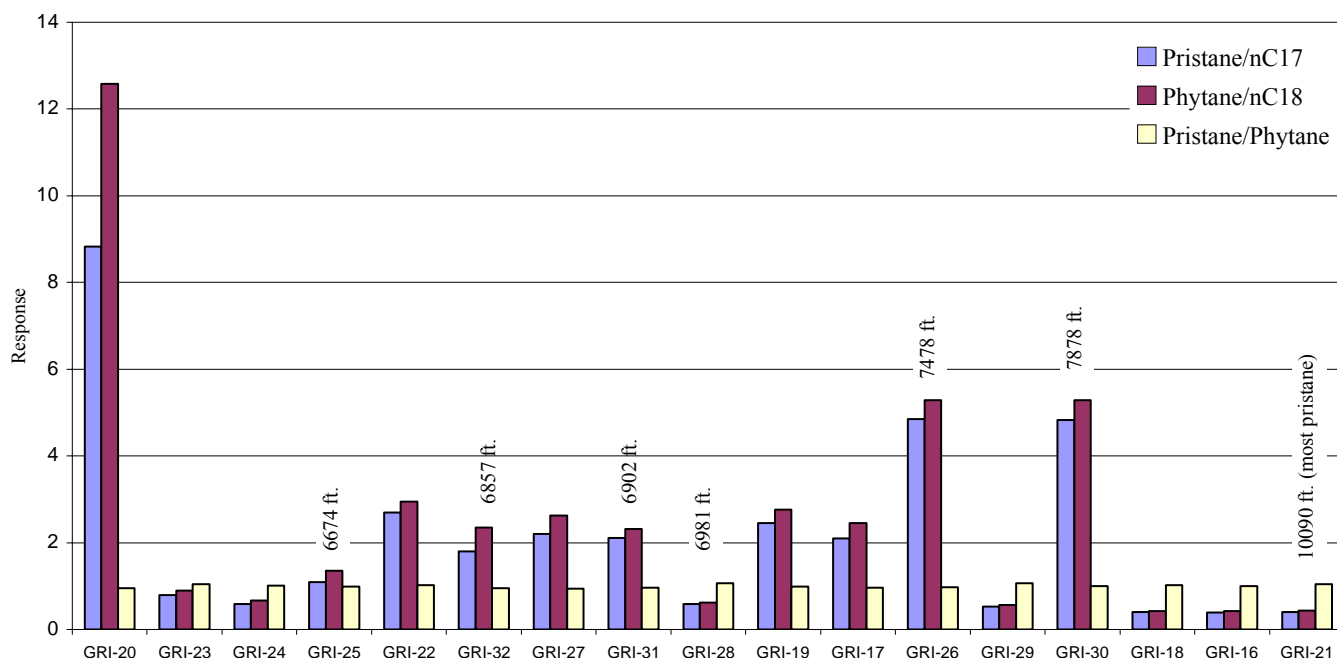


Figure 3: The relative intensity of branched to *n*-alkanes is shown for all of the Joliet oils in Fig. 2 where the ratios of pristane to phytane, pristane to nC_{17} , and phytane to nC_{18} are plotted together.

The relative intensity of branched to *n*-alkanes is shown for all of the Joliet oils in Fig. 3 where the ratios of pristane to phytane, pristane to nC_{17} , and phytane to nC_{18} are plotted together. Because all of these oils have a common source and uniform maturities, the pristane to phytane ratios also remain constant. As the degree of biodegradation increases, the ratios of Pr/ nC_{17} and Ph/ nC_{18} increase due to the preferential biodegradation of the straight chain (nC_{17} and nC_{18}) versus the isopenoids (Pr and Ph). In addition, the longer *n*-alkanes become more prominent than the shorter *n*-alkanes in the more biodegraded oils. Throughout the transect, even when biodegradation has occurred, it appears to have been relatively mild - the cyclic steranes and hopanes that are among the compounds most resistant to biodegradation, appear relatively unaffected.

We have been very surprised at how active gas migration processes appear to be in the subsurface of the northern Gulf of Mexico - both on geological and modern time scales. This natural Gulf Coast laboratory, in which we have accumulated an excellent sample and database both in the water column and in the subsurface in collaboration with a number of other universities and oil companies, turned out to be an excellent analog for a number of other offshore actively subsiding basins, including the Niger Delta and the Amazon Delta, and even the North Sea where upward seepage of gas through huge gas chimneys in the subsurface is observed. As in the case of the Gulf of Mexico, large volumes

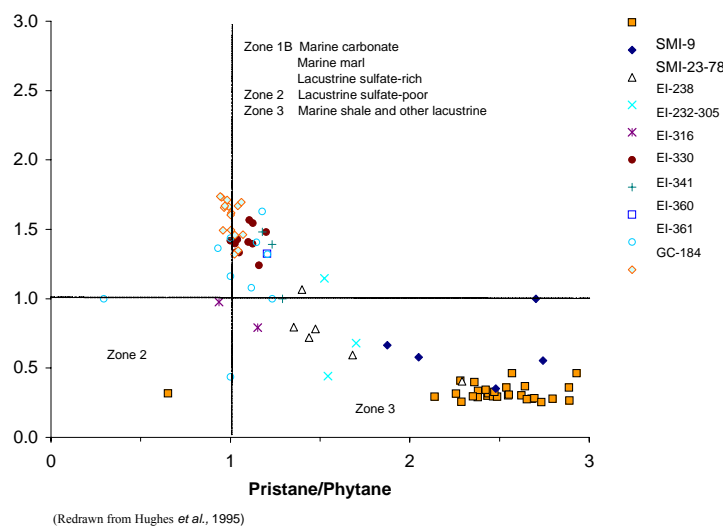


Fig. 4: p. 7 Ratio of pristane/phytane versus Dibenzenothiophene for Gulf Coast transect oils.

of gas are also estimated to have vented through North Sea petroleum reservoirs (Larter, unpublished data). In one example, thermogenic hydrocarbons were shown to have vented upward through the center of the chimney, but not outside as shown by the elevated concentrations of C₂-C₅ hydrocarbons in the chimney mud gas. It was proposed that gas pressure builds up inside the chimney and caused fracturing in the top so that hydrocarbons can vent upward. These features are very extensive in North Sea reservoirs and are now thought to be indicative of good drilling targets rather than the failed reservoir seals of leaky and empty reservoirs as previously thought.

If the rates of upward gas flow are as fast and as extensive as our combined Woods Hole-Cornell data seems to show, then many geological processes dependent on subsurface fluid flow could be affected. The implications of such rapid and widespread upward gas flow could be profound both with respect to gas and oil exploration and with respect to global climate change issues that could be highly dependent on rates of delivery of a number of key elements (e.g., C, N, S, P, Fe, trace metals) to the ocean from the underlying sediments. Our current research in the Gulf of Mexico demonstrated the potential magnitudes and extents of these subsurface gas and fluid flow processes in one Gulf Coast transect. By extrapolation, these effects are probably just as important throughout the Gulf Coast and in many other subsiding ocean basins and continental margins worldwide (Whelan *et al* 2005).

5. Summary of other work completed during the past proposal

A) Compound Specific Carbon Isotope Characterization of C₅-C₉ hydrocarbons from a Gulf of Mexico transect

Introduction

Our goal in this phase of this work was to use $\delta^{13}\text{C}$ compound specific-isotope data for light C5-C9 hydrocarbons to distinguish families of oils within the Gulf of Mexico transect. We had previously determined that many oils showed very similar biomarker patterns, but also showed some subtle differences. We decided to test isotope ratio monitoring gas chromatography-mass spectrometry (irmGCMS) of some individual compounds to gain a better distinction of sources and families of oils with common sources. This study would also allow us to examine isotopic shifts associated with other reservoir processes such as biodegradation and gas-washing (Meulbroek et al 1998). Conventional biomarker data provided good indications of oil families throughout this transect, however, clear-cut relationships were difficult at best to determine for a series of oils in the central portion of the transect. Additional processes such as gas washing, biodegradation, water washing and multiple reservoir filling episodes have all played a varying role in the composition of the petroleum fluids throughout the transect.

Results

Individual C5 to C9 hydrocarbons from thirty-five whole oil samples from a GOMT were characterized using stable carbon isotope ratios. Identification of key isotope relationships between compound classes and isomers in the gasoline-range has helped to unravel some of the inconsistencies borne in the biomarker data (Figs. 5-11). For example 1-trans-3-dimethylcyclohexane when plotted against the 1-trans-4-dimethylcyclohexane provides an excellent correlation of oil families in different well and reservoir intervals (Fig. 5). This plot also indicates the extent of mixing of fluid sources and/or discrete migration conduits within reservoirs. Additionally, this relationship is providing evidence of shifts in stable isotope compositions as a result of in-reservoir alteration. An example of this can be seen in oils from a suite of samples from Eugene Island Block-330 (EI-330), fault block-A (green triangles on figure 5) have lighter carbon isotopic values compared to a known biodegraded oil from the GA-2 reservoirs that shows a 2.5 ‰ shift to heavier values. Light hydrocarbon relationships like this provide excellent diagnostic tools for oil-oil correlations and oil-source rock correlation.

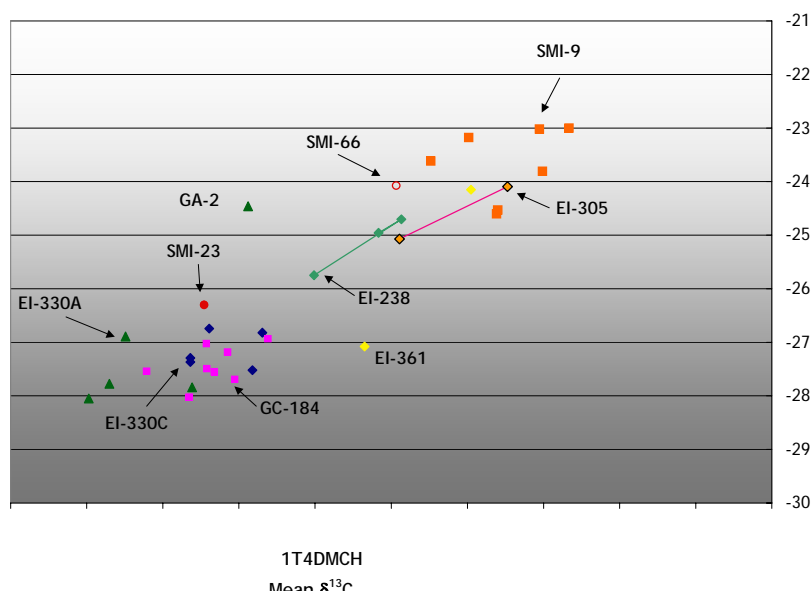


Figure 5: $\delta^{13}\text{C}$ of 1-*trans*-3-dimethylcyclohexane plotted against the $\delta^{13}\text{C}$ of 1-*trans*-4-dimethylcyclohexane shows discrete oil families.

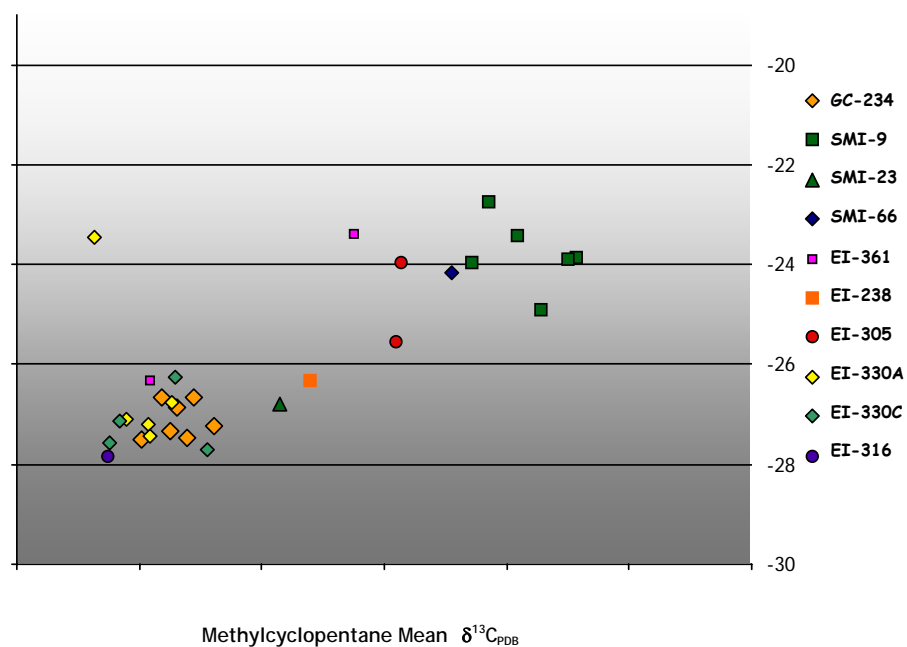


Figure 6: Delta 13C of methylcyclopentane plotted against Delta 13C for methylcyclohexane for Gulf Coast transect oils

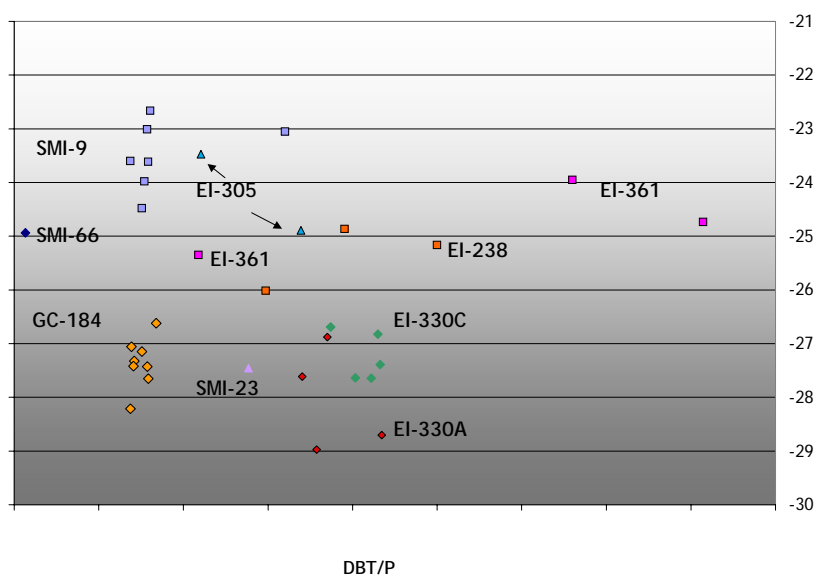


Figure 7: Delta 13C of 1T4DMCH plotted against DBT/P

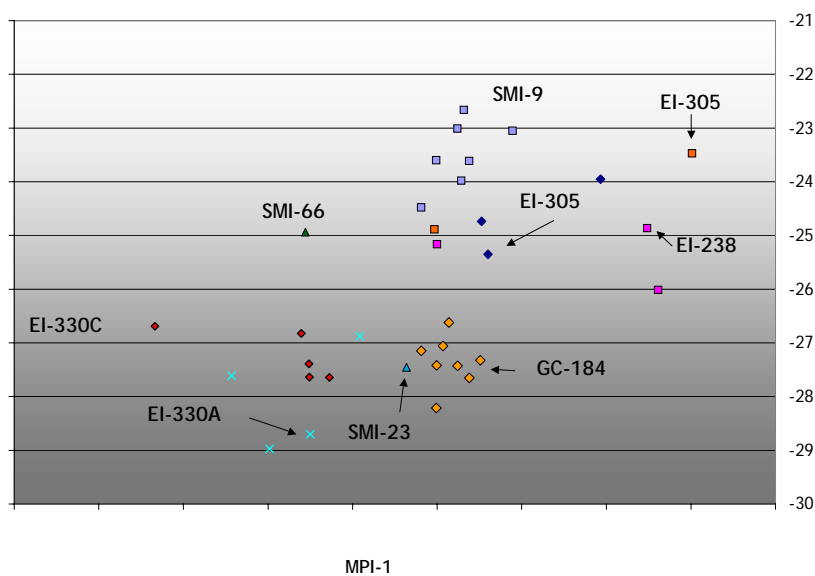


Figure 8 Delta 13C of 1T4DMCH plotted against Delta 13C of MPI for Gulf Coast transect oils

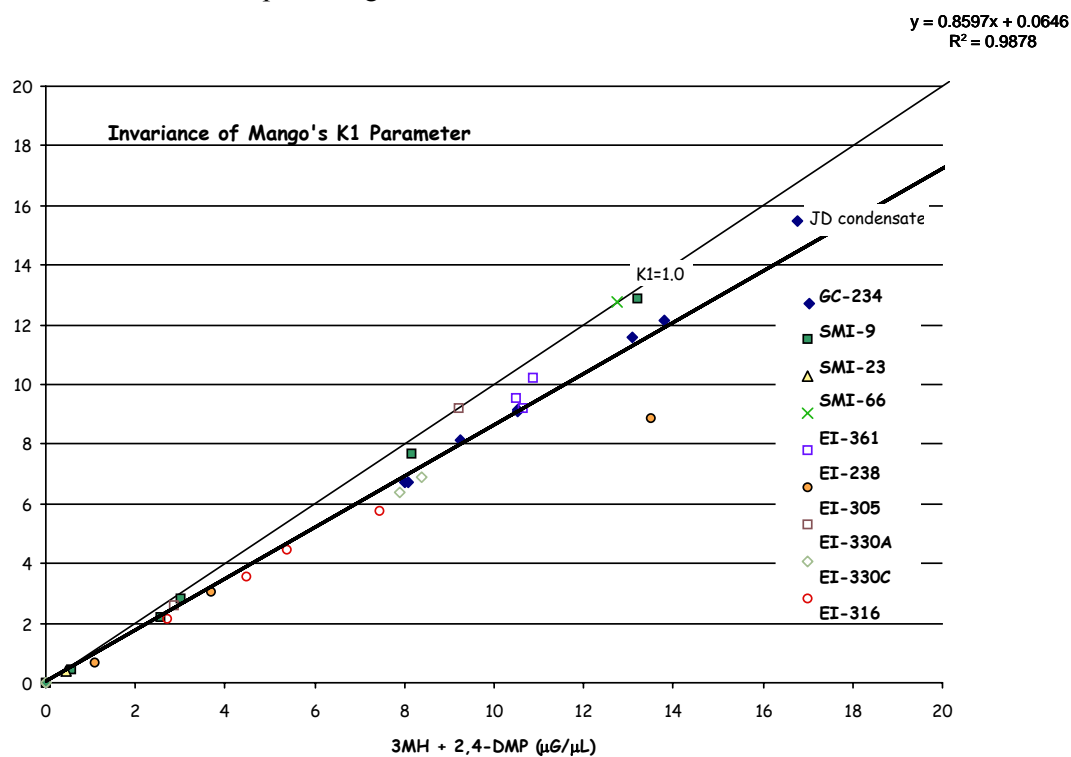


Figure 9: Mango's invariance parameters plotted for Gulf Coast transect oils. Heavy line in that found in this work. The lighter line in that previously found by Mango (1998)

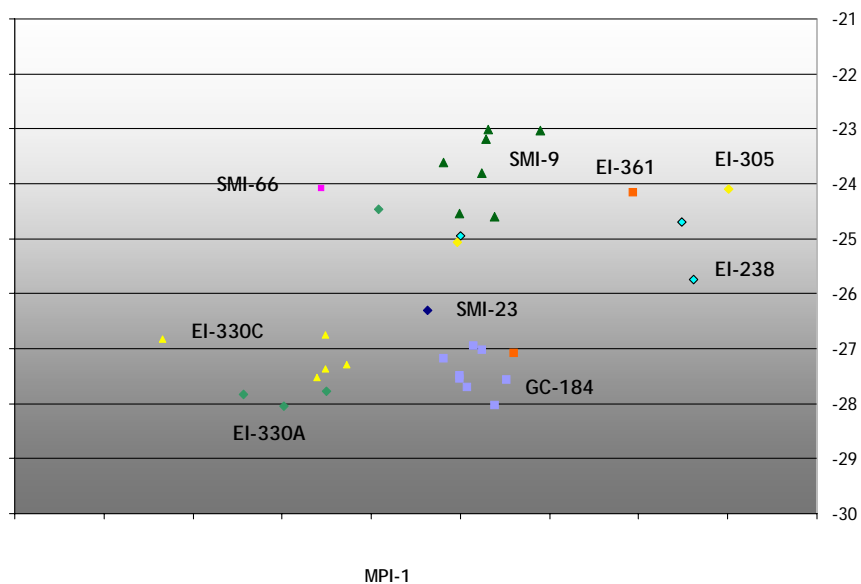


Figure 10: Delta 13C values of 1T3DMCH versus maturity indicator MPI-1 for in gulf coast transect oils.

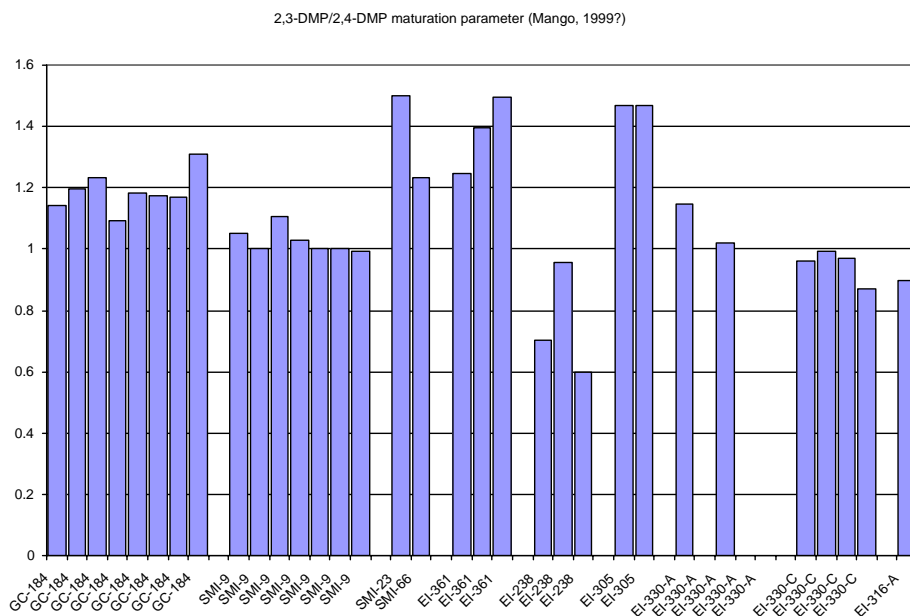


Figure 11: Mango maturation parameter, 2,3DMP/2,4DMP plotted for Gulf Coast transect oils. Well locations shown in Fig 1.

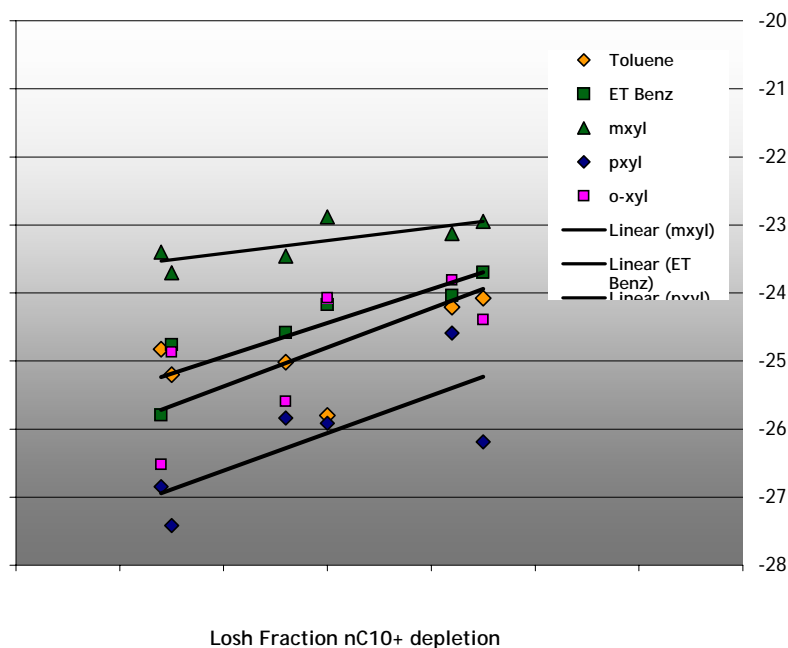


Figure 12: Mean delta 13C for specific aromatic compounds versus Losh et al 2002a & b calculated fraction of nC10 depletion, of degree of gas washing for Gulf Coast transect oils.

Previous work

Previous data have shown that SMI-9 oils are similar, but possess real differences which are outside of analytical error. For comparison, all of the GC-184 oils examined so far are fairly homogeneous and appear to be comprised of one major oil family. The different isotopic profiles from the two oil fields provide a clear indication that they are derived from different sources. Between these two groups of oils at opposite ends of the GOMT the SMI-66, EI305, EI 238, and EI-361 oils fall between those of SMI-9 GC184 and EI330 (Figs 5-6).

Moving to the south, the two EI-305 oils in appear to be very different from each other and also quite different from the SMI oils (Fig 5 and 6). EI-330 oils appear to form several distinct families. A graph of delta 13C of 1T4DMCH versus DBT/P, a parameter changing primarily according to degree of contribution from marine oil sources (Hughes et al, 1995) shows that the difference are probably related primarily to slight changes in oil source in moving between proximal reservoirs and depths (Fig 7). Isotopic changes in the gasoline range hydrocarbons appear to be a much more sensitive marker of oil source than the heavier *n*-alkanes or the biomarkers.

In our last proposal, it was suggested that compositional differences in dimethylcyclopentanes (DMCPs) in EI-330 oils might be a useful in tracking the migration paths of the C₇ hydrocarbons. For example, different relative concentrations of these isomeric compounds in EI-330 condensates from the JD well in comparison to those in oils in the OI reservoirs do not support the hypothesis of Losh, *et al.*, (2002 a & b) that OI oils migrate upward through faults into JD reservoirs. The slight differences in

concentrations of DMCP isomers are more consistent with each of these reservoirs having been filling separately as suggested by fluid flow modeling by Erendi, 2001.

A plot of delta ^{13}C of 1T4DMCH and 1T3DMCH versus MPI-1, a maturation parameter, shows no correlation showing that the ^{13}C isotopic changes are not caused by maturation changes (Figs 8 and 10). Instead, a number of oils falling at a specific MPI-1 fall in bunches of points reflecting specific well intervals. Again, the results are most consistent with the ^{13}C values for specific compounds being dominated by source and not by maturity.

Interpretation of results

Recent research has shown that co-varying compound specific delta ^{13}C isotopes in a series of oils are only minimally altered by oil migration, or even storage effects and are, therefore, useful in to showing groups of oils having a common source (Bjoroy et al., 1994; Whiticar & Snowdon, 1999; Neto et al., 1998 & 1999). However, George *et al.*, (2002) reports definite isotopic shifts associated with biodegradation processes. The position of methylation in light hydrocarbons has a significant effect on biodegradability, according to George *et al.*, (2002). For example, adjacent methyl groups are less likely to be attacked by bacteria. Hence, 1,2,3-Trimethylbenzene is the most resistant of the C_2 alkylbenzenes isomers under moderate biodegradation, whereas, 2-Methylalkanes are the most susceptible to biological attack. In general, ongoing biodegradation leads to d^{13}C enrichments of the remaining hydrocarbons (George *et al.*, (2002).

We proposed that the DMCP isomers, having almost identical sizes, polarities, and solubilities, are less likely to be altered *via* migrational fractionation, however, recent results show a significant shift in the isotopic values for cis-1,2-Dimethylcyclopentane to heavier values across the area. This suggests a distinct source for this isomer compared to the other DMCPs. The standard error of analysis of replicate samples for 1C3DMCP, 1T3DMCP, and 1C2DMCP are much improved with analytical errors reduced for most localities. Even so, the various families of oils appear to show different isotopic signatures for these three compounds.

Alternatively, non-equilibrium adsorption-desorption between liquid or gas and solid phases can cause significant isotopic shifts, particularly if migration is very rapid so that non-steady state conditions are present as would be the case here when compositional changes are observed on time scales of less than 8 years. The absorption-desorption process would be expected to cause at least a small degree of isotopic migration fractionation if a high degree of fluid-rock interaction were involved during migration through a fracture system. Thus, these data are consistent either with a) separate pipes from the source to individual reservoirs or parts of reservoirs; or b) rapid migration through rock intervals that allow extensive non-equilibrium interaction of gasoline range hydrocarbons with the walls of the carrier and reservoir beds, possibly through a system of fractures having a high surface area. Nonequilibrium adsorption-desorption between a gas and liquid or solid phases can cause significant isotopic shifts, particularly if migration is rapid enough so that non-steady state conditions prevail as the petroleum travels through the migration conduit or the reservoir

Our data confirm that specific ratios of branched alkanes are invariant in oils having a common source or a common family of sources as shown in Figs 9 and discussed previously for other fields in Mango, 1990; 1994 and Ten Haven *et al.*, 1996. However, notice that our gulf coast transect oils consistently fall slightly off of the trend line defined by Mango (lighter line in Fig 9).

Mango (1998) has proposed that the ratio 2,3DMP/2,4DMP can be used as a maturation parameter. Our Gulf Coast transect data, plotted in Fig 8 and 10, do not uphold this view. It has previously been shown that the oils in the north of the transect (SMI 9) are more mature than those from the southern-most GC184 intervals (Fig 2 and Whelan et al 2005). The 2,3DMP/2,4DMP ratios of Mango

are not consistent with this trend (Figure 11) so that processes other than maturation must be responsible for changes in these ratios.

This IRGCMS data examined in this work are most consistent with that the formation of petroleum as a is kinetically, not thermodynamically, controlled process and supports ideas proposed in Whiticar & Snowdon, (1999) and Neto *et al.*, (1998 & 1999).

B) Unsolved riddles from Gulf of Mexico Transect work.

1) "Holes" in overall transect data trends

There are some fairly general trends in the overall transect data set: 1) A change from more terrigenous less mature to more marine and less mature oils moving from north to south if just SMI-9, EI-330 and GC-184 are considered (Figures 2 and 4). However, there are some obvious discrepancies in these trends that show up in a number of the different parameters which we measured. These generally occur in the area from SMI-23 south to EI-316 and to the south and east of EI-330 at EI-341 to EI-360 (see Figs 1 and 2 for relative locations). Minor source differences are a possible cause based on the results so far with the IRGCMS data and the pristane to phytane ratios (Figures 2, 4, and 5-8). The Cornell group has proposed that faulting in some sections of the transect, particularly to the north, has caused mixing of shallower Tertiary with the deeper more marine oils. If the resulting generated oil migrates vertically initially, as suggested by the fluid flow modeling then slightly different oil sources even in a single reservoir might be observable, particularly if oil had entered the reservoir very recently and not had time to homogenize with fluids already present.

(Note: A magnitude 6 earthquake occurred just to the east of our transect suggesting that earthquakes periodically may cause fault opening and closing triggering upward episodic oil and gas movement. The possibility of seismic activity being responsible for changes in Gulf Coast oils has been suggested in Losh et al, 2002a & b and is supported by our work.) Alternatively, if some oils were trapped longer under the salt longer than others causing maturity anomalies around salt diapirs, then the changes in maturity of these oils might reflect localized changes in maturity and movement of the oils upward through salt. Variations in degree of biodegradation or extent of gas washing could also be causing these differences. There is currently no 3-D seismic data for midsections of our transect to provide constraints on various oil and gas generation-migration-alteration scenarios suggested by our work.

2) Scenario for fluid flow in Green Canyon; proposal for further work on oil biodegradation and reservoir recharging

Green Canyon 184 lies at the southern end of the Gulf Coast transect under study (Fig. 1). Based on work to date, this appears to be the ideal place to examine changes in a variety of organic markers during the early stages of reservoir oil and gas charging. The Cornell basin and fluid flow modeling show that oil generation and migration into present day reservoirs probably progressed from SMI-9 in the north to GC-184 reservoirs in the south that are currently being charged. Oil source and maturation differences between GC-184 reservoirs and wells appear to be minimal - the GC-184 sterane and hopane biomarkers and IRGCMS patterns are almost identical to each other.

In previous work at EI-330, we found that movement of oil was easiest to detect experimentally in reservoirs undergoing on-going biodegradation, causing preferential loss of the *n*-alkane envelop in the GC. Subsequent recharging of those same intervals with new oil produces the typical *n*-alkane envelope superimposed over a biodegradation hump (Dzou and Hughes, 1993; Whelan et al., 1994 & 2001). At

GC-184, these processes are expected to be even more pronounced because almost all the reservoirs that are currently at temperatures of $<60^{\circ}\text{C}$ where active bacterial growth and oil biodegradation are expected. Simultaneously, the reservoir may also be experiencing active charging. Many of the GC-184 oils examined to date show a relatively unbiodegraded *n*-alkane envelope superimposed over a biodegraded "hump" of unbiodegraded material. If biodegradation at GC-184 is on going, then the rates of oil recharge should be higher than rates of *in-situ* biodegradation that probably occurs *in-situ* in reservoirs within a few years at the most (Whelan et al., 1994, 2001). This new unbiodegraded oil could be derived either from localized oil redistribution within the reservoir or from a continuous new oil supply flowing up from deeper intervals.

A more quantitative measure of the degree of biodegradation of the Jolliet oils is reflected in the relative intensity of branched to *n*-alkanes (Fig. 3) where the ratios of pristane to phytane, pristane to $n\text{C}_{17}$, and phytane to $n\text{C}_{18}$ are plotted together. The pristane to phytane ratios in these oils remain constant because all have very similar sources. As the degree of biodegradation increases, the ratios of $\text{Pr}/n\text{C}_{17}$ and $\text{Ph}/n\text{C}_{18}$ also increase due to the preferential biodegradation of the straight chain ($n\text{C}_{17}$ and $n\text{C}_{18}$) over the isoprenoid hydrocarbons (Pr & Phy). A second measure of the degree of biodegradation is the total heavy *n*-alkane content ($n\text{C}_{25}$ to $n\text{C}_{41}$ /mg oil) of the same oils. The longer $n\text{C}_{25}$ - $n\text{C}_{41}$ alkanes tend to be biodegraded more slowly than the lighter $n\text{C}_{17}$ and $n\text{C}_{18}$ alkanes so that we would expect the $\text{Pr}/n\text{C}_{17}$ and $\text{ph}/n\text{C}_{18}$ ratios to be affected by biodegradation sooner than the $n\text{C}_{25}$ - $n\text{C}_{41}$ values.

Unlike the EI-330 oils, the Green Canyon oils show no evidence of gas washing based on the shapes of the *n*-alkane envelopes (Losh, et al, 2002a &b). However, gas washing would not be observable if biodegradation were removing *n*-alkanes faster than they were being replaced by recharging with new unbiodegraded oil.

A puzzle arises from our results so far - why is there no evidence for gas washing of the GC-184 oils? There is overwhelming evidence for extensive ongoing upward movement of thermogenic gas through fault and fractures in surface sediments over the entire GC-184 Jolliet field (Roberts and Carney, 1997; Sassen et al., 2001). Sassen et al., 2001 argues convincingly for a close relationship between surface to and sub-surface gas movement in this area. For example, surface sediment gas hydrates are found within a fault overlying the Green Canyon oil and gas reservoirs and are probably derived from on-going upward seepage of underlying thermogenic gas. Thermogenic gas is observed to flow continuously through these seafloor gas hydrate deposits that are also intimately associated with a very active biological community. An enormous amount of gas could be involved if these surface gas hydrates are actually a steady state feature as argued by Buffet (2000) where gas is continually lost at the top as hydrates come into contact with warmer seawater and added at the bottom of the solid hydrate formation from the continuously upward flowing gas. This gas, which originates from deeper thermogenic sources, also would be expected to have a strong effect on compositions of the underlying oils- either by outgassing of gas from oil or by flow through and equilibration of gas with oil.

Because of capillary effects, oil and gas do not remix easily in the subsurface once they have separated. However, we know that most gases are more mature than their associated oils in many Gulf Coast oils, including those at GC-184 (Whelan et al, 1994) so that the two phases must have been unmixed at some point in the subsurface. Yet at GC-184, we observe both gas and oil together seeping in surface sediments and into gas hydrate deposits implying that oil and gas must have moved upward together. Where and how is this mixing of gas and oil occurring? It is possible that upward gas seepage began only recently and therefore has not yet had time to cause observable gas washing in the subsurface oils. The mixing could be occurring under supercritical conditions below the top of overpressure that typically occurs at about 10,000 ft depths worldwide (Hunt, 1996 and Hunt et al 1998; Cathles in Whelan et al., 1994b) Alternatively, if on-going subsurface biodegradation is occurring at approximately the same rate as oil charging, then there would be no evidence for gas washing of oils in the reservoir since all of the *n*-alkanes except for those injected very recently would have been biodegraded.

3) Specific areas - South Marsh Island 9 (SMI-9) - fluid flow around salt dome

SMI-9 reservoirs all lie in close proximity to a large salt diapir that is also surrounded by a complex series of faults. Thus, these oils provide an opportunity to examine the relationship between salt diapirs and oil and gas flow that has occurred in the past. Most of the SMI-9 oils have been affected by some degree of biodegradation often followed by some degree of reservoir recharge as shown by the *n*-alkane envelope superimposed over a biodegradation hump. Many of these oils have also been strongly affected by gas washing - in one case by as many as 1000 volume of gas per volume of oil (Meulbroek, unpublished results).

Differences in oil source appear to be related to proximity of reservoirs to the salt dome. For example, higher oleanane concentrations appear to be present in oils nearer to the salt diapir than in oils further away. In the Gulf of Mexico, the edges of the salt domes have been found to provide good migration conduits for subsurface upward flow both in on-shore (Louisiana, Hanor et al., 1999) and offshore wells (e.g. Holba, et al., 1996). In addition, oleanane is higher in samples in the fault than for those away from it. One interpretation of these data consistent with the geological data is that oil has flowed from slightly different source areas that have been strongly directed by the subsurface position of the salt. Because salt moves and flows, this effect and its direction have probably changed over the geologic times involved in SMI-9 reservoir charging.

The gas chromatograms of *n*-alkanes show alterations to the oils that have probably occurred in the reservoirs. For example, the gas chromatograms of the three samples that lie in the fault plane in SMI9 do not have the flat baseline characteristic of a unbiodegraded oil. These chromatograms also show an abundance of C₇ to C₂₀ normal paraffins. If a moderately biodegraded oil that has been stripped of normal and iso-paraffins has been subsequently mixed with a fresh oil with abundant normal and iso-paraffins, the fresh oil would appear as the unbiodegraded *n*-alkane envelope superimposed over the baseline hump typical of the more resistant unresolved mixture of cycloparaffins and aromatic compounds. Furthermore, there is a gradual depletion in light aromatic hydrocarbons in the range C₂-C₁₀ with depth in these three samples. The oils on the eastern flank of the salt dome show that oils with a low abundance of oleanane also have flatter baselines indicating less biodegradation and an *n*-paraffin maximum at *n*-C₁₅ and *n*-C₁₆. These latter oils all have the same maturity (except for the deepest samples, based on their MPI indices and the same source based on their biomarker ratios. They also show depletion of front-end, light hydrocarbons including the aromatics (circled) that is probably indicative of water- or gas- washing.

i) Maturity determinations

Relative maturity of these oils based on the methyl phenanthrene index 1 (MPI-1) indicates peak oil generation maturity for all the SMI-9 oils (Fig. 2). However, the oils enriched in oleanane in the fault plane to the west are slightly less mature and range 0.76 %– 0.84 %R_{o equivalent} while the oils to the west with oleanane depletion have marginally higher maturities 0.88 % - 0.92 % R_{o equivalent}. This trend is mirrored by the Triaromatic maturation ratio. In addition, a moderate odd over even carbon predominance. This indicates a lower maturity and an enhanced terrestrial higher plant input. We suggest preferential flow from deeper more mature and more marine oils have migrated into reservoirs on the east side of the salt dome while a greater contribution from younger, less mature, and more terrigenous oils is observed to the west.

A range of values for the dimethylnaphthalene ratios occurs at depths of 12,000 – 13,000 ft. and at 15,500 ft and show that oil reservoirs have been most affected by whatever specific processes control these distributions. Most notable is that within a narrow depth range (100ft) there is a rapid increase in the dimethylnaphthalene ratio in the three oils lying in the fault plane. This may represent migration fractionation that has proceeded up the fault planes and stripped oil from deeper samples leaving them

front-end depleted and in shallower reservoirs, where lower pressure and temperatures cause further exsolution of a lighter liquid phase. Whatever the exact process involved, it appears to occur over a very short depth interval of 100ft. on the western flank of the salt diapir. Krooss et al (1991) has argued that only fractionations involving a moving gas phase can cause fractionation effects of this magnitude over so short an interval.

ii) Gas washing

Front end depletion of *n*-alkanes in many of these oils using the procedures of Meulbroek et al., (1998) indicate that there has been considerably more gas washing of SMI-9 oils than of any of those further south (Fig_16 in Losh, et al., 2002a & b)

C Paper preparation and publication in progress:

Work is in progress on several additional papers on this work including:

- a) Biomarker and organic geochemical changes with respect to source and maturation along a N-S transect of the offshore Gulf of Mexico, by Jean Whelan and Lorraine Eglinton
- b) IRGCMS analysis of gasoline and oil range compounds along a N-S transect of the offshore Gulf of Mexico, initial results. Jean Whelan and Lorraine Eglinton.
- c) Organic geochemistry and geology related to changes in gas and oil at South Marsh Island 9, offshore Louisiana in specific areas, by Jean Whelan, Lorraine Eglinton and Cornell scientists, Larry Cathles, Steven Losh and Michael Wizewich
- d) Organic geochemistry and geology related to changes in gas and oil at Green Canyon 184, offshore Louisiana in specific areas, by Jean Whelan, Lorraine Eglinton and Cornell scientists

D) Organic Geochemical Characterization of a Miocene Core Sample from Houghton Impact Structure, Devon Island, Nunavut, Canadian High Arctic

This work resulted in a publication:

Eglinton, L.B., Lim, D., Slater, G., Osinski, G.R., Whelan, J. K., Douglas. (2006) Organic Geochemical Characterization of a Miocene Core Sample from Houghton Impact Structure, Devon Island, Nunavut, Canadian High Arctic: *Organic Geochemistry* v. 37, pp 688-710.

Introduction

We examined the Houghton Impact sediments to look for evidence that oil or gas from very deep sources might be present. These intra-crater sedimentary rocks can potentially act as hydrocarbon source rocks and/or cap rocks, depending on the conditions of deposition, and subsequent geological evolution.

Impact craters have been a focus of significant study in recent years due to their potential as sources of petroleum and ore deposits. At least 25 % of the currently known impact craters worldwide are associated with various economic deposits (Grieve and Masaytis, 1994). Impact craters have been considered to be both potentially good sources and good reservoirs for petroleum fluids, in particular. For example, the Steen River impact crater, Alberta, is ~25 km in diameter, ~97.5 million years old and

produces approximately 1,000 barrels of oil per day with a gas production approaching 35 million cubic feet per day from rim structures resulting from impact (Mazur *et al.*, 2000). While impact events generally do not produce hydrocarbons, the resultant structures provide favorable conditions for hydrocarbon migration (*i.e.*, fractured, faulted, and brecciated target rocks), and form basins in which post-impact sediments can accumulate if conditions are favorable.

Devon Island in the Canadian High Arctic is the site of a ~39 million year old terrestrial impact crater. This ~23 km diameter crater is currently under much investigation as an analogy for geological features on Mars (e.g., Lee *et al.*, 1998). Of the approximately 170 impact craters known to exist at the present time (Earth Impact Database, 2004), the Devon Island crater is one of the best exposed and best preserved. The crater itself is known as the Haughton impact structure (HIS). Palaeontological and paleolimnological studies have proposed the existence of a post-impact lake, near the center of the crater that was subsequently in-filled with series of sediments now characterized as the Haughton Formation (Hickey *et al.*, 1988). The development of an impact-associated hydrothermal system has been documented at the HIS (Osinski *et al.*, 2001). Fluid flow would likely have been enhanced in the crater due to the formation of impact derived fractures and fissures and listric faulting. The age of the impact was determined by Jessberger (1988) to have occurred at 23 Ma; however, recent findings by Osinski & Lee (in press) suggest that a significant period of post impact erosional activity occurred before the Haughton Formation was deposited and this supports new data from Sherlock *et al.*, (in press) dating the impact some 16 Ma older.

Sectioning of a core from the HIS revealed an unusual 1 cm thick organic-rich band that had a strong hydrocarbon odor. A manuscript stemming from this work reports on the geochemical characterization of this band and its possible origins has been published (Eglinton *et al.* 2006). Studying the provenance of hydrocarbons associated with the HIS can give insights, not only into the post-impact geology, but also into processes that may contribute to generation of petroleum fluids at other sites.

Three key compound groups in Haughton work

C₃₁–C₃₅ 17a, 21b(H)-hopanes

Isomerization reactions at the C-22 position for C₃₁ and C₃₂ 17a(H)-hopanes are frequently used molecular proxies of thermal maturity. Siefert and Moldowan (1980) calculated the ratio reaches thermodynamic equilibrium at 0.57 – 0.62. The C-22 biological precursors favor the 22R configuration. The C-22 Epimer ratios often increase for the higher homologs. These values indicate mature hydrocarbons (0.57 - 0.62) *i.e.* main phase of oil generation has been reached or surpassed (Peters and Moldowan, 1993). C-22 epimer ratios at Haughton indicate a mature oil with values for C₃₁, C₃₂ and C₃₃ rising linearly from 0.58, 0.60, 0.62 respectively. However, the C₃₄ and C₃₅ sharply deviate from this trend. C₃₄ homohopane epimerization ratio indicates a level of maturity barely entering the oil window (0.53). Whereas, C₃₅ indicates a level exceeding equilibrium at 0.77 and may be influenced by co-eluting compounds. C₃₄ yields an immature pattern for what is generally accepted to be a mature homohopane pattern. Biodegradation usually results in selective demethylation of 22R epimers at the C₃₄ for C₃₅ hopanes (Peters *et al.*, 1996 from Köster). This would preclude any influence from biodegradation. Selective preservation during early diagenesis of sulfur-bound homohopane precursors have been associated with elevated C₃₅ homohopane under anoxic conditions (Sinninghe Damsté *et al.*, 1995). Kösta *et al.*, (1997) demonstrated how natural sulfurisation can influence both carbon number distribution and epimer ratios for homohopanes. These workers show free 17 α , 21 β (H)-hopanes indices from an organic rich marlstone and a dolomite sequence from the Upper Triassic Hauptdolomit Formation (HD) that are remarkably similar to the homohopanes at Haughton in terms of total C₃₁ through C₃₅. The epimer distribution for the Triassic Marlstone differs in that it is less mature compared to Haughton. Both these samples show a significant increase in C₃₅ epimer ratios results from a reduction in C₃₅ 22R

epimers. The Hauptdolomite also shows similarity to the Haughton sample as both exhibit dominant C₃₄ homologs compared to C₃₁ – C₃₃ and C₃₅ homologs. Kösta *et al.*, (1997) report that a phosphoritic member of the Jurf-ed-Darawish shales also has dominant C₃₄ homohopanes (Sinninghe Damste *et al.*, 1995). They attribute these findings to a more intense degradation of the side chain prior to sulfur incorporation. However, one unique feature of Haughton is that the biologically configured C₃₄ 22R isomer is much more prevalent. Thus, while evidence for natural sulfurisation is compelling, it does not fully explain the C₃₄ homohopane distributions in the Haughton sample. It may be possible that a bacterially mediated shortening of the side chain has occurred. Peters and Moldowan (1993) proposed this can occur under sub-oxic environmental constraints. They give an example of a Yugoslavian oil with elevated C₃₄ that with supporting evidence also infers anoxic/suboxic depositional conditions. However, this sample also shows C₃₄ epimer is dominated by the 22S. It may be the case that distributions of the Haughton homohopanes derive from a combination of S-bound hopanoids from a sediment that were deposited under anoxic/sub-oxic marine conditions with an additional input from immature hopanoids from present in contemporaneous bacterial biomass that have been entrained in the migrating fluid that is now resting in the HIS.

C₃₂ to C₃₆ 2 α -methylhopanes, 3 β -methylhopanes

Extended C₃₂ to C₃₆ 2 α -methylhopanes are diagnostic for cyanobacteria and prochlorophytes (Bisseret *et al.*, 1985; Farrimond *et al.*, 2004) while extended C₃₂ to C₃₆ 3 β -methylhopanes may be diagnostic for some microaerophilic proteobacteria (certain methylotrophs, methanotrophs and acetic acid bacteria) (Zundel and Rohmer, 1985a, Zundel and Rohmer, 1985b, Zundel and Rohmer, 1985c, Summons and Jahnke, 1992; Farrimond *et al.*, 2004). Trace abundances of homologous series of 2 α and 3 β methylhopanes (m/z 205) in the Haughton extract are highlighted in Figure 4 of Eglinton *et al.* 2006). These assignments were based on mass spectra, retention indices and published data (Pancost *et al.*, 1998; Farrimond *et al.*, 2004). Although, 2 α and 3 β methylhopanes can derive from a variety of prokaryotes, Summons and co-workers (1996) and Collister and co-workers (1992) suggest these biomarkers indicate the presence of cyanobacteria and methylotrophic bacteria respectively. Isotopic data for the *n*-alkanes range between -29 ‰ and -31 ‰ and are not significantly depleted (e.g. -40 ‰ to -85 ‰ for methanotrophic bacteria). Unfortunately, resolution was insufficient to determine values for individual hopanes.

Diterpenoid hydrocarbons

Several diterpenoids were found in the solvent extract of the Miocene AH98-3 core. In recent plants diterpenoid hydrocarbons are primarily found in gymnosperms with only a few documented occurrences in angiosperms (van Aarssen *et al.*, 1990; Otto *et al.*, 1997). The distribution of non-derivatized diterpenoids in the saturated hydrocarbon fraction of the Haughton extract is dominated by pimarane, isopimarane, abietane and phyllocladane classes. Structural assignments were made based on key fragmentation ions, relative retention times and comparison with published data (Otto *et al.*, 1997; Otto and Simoneit, 2001; Kalkreuth *et al.*, 1998; Mackenzie, 1980, 1984; Philp, 1985). Fichtelite (norabietane) and isonorpimarane represent a degraded series of diterpenoids with isonorpimarane as the major compound and fichtelite as the minor component of the series. These diterpenoids are interpreted as the diagenetic derivatives of natural product precursors such as abietic and pimaric acids commonly found in extant species of *pinaceae* (Thomas, 1970; Otto and Wilde, 2001; Otto and Simoneit, 2002). Since, pimarane, isopimarane and abietane classes of diterpenoids are the major components of extant species of *Pinaceae* it is, therefore, reasonable to conclude that *Pinaceae* derived flora are major contributors to the organic matter in Haughton infill sediments. These data are in accordance with botanical assignments made in Hickey *et al.*, (1988), who show palynoflora is dominated by *Pinus* and *Picea*, sp. Phyllocladane represents a broader origin from other coniferales families (Podocarpaceae, Taxodiaceae, Araucariaceae and Cupressaceae) but is generally not found in the *Pinaceae* family (Sukh Dev, 1989; Otto *et al.*, 1997). Since the Podocarpaceae, Araucariaceae and Cupressaceae families did not

evolve until Late Triassic times and are thought to be restricted to the Southern hemisphere it seems more likely that Phyllocladane is related to the Taxodiaceae or Voltziales (Late Carboniferous genesis) families. This, therefore, represents contribution from more than one family of Coniferales into the Haughton sediment and is consistent with mixed gymnosperm forestation.

An oxidative diagenetic pathway would lead to the formation of retene, whereas, decarboxylation of the natural product abietic acid followed by reduction would result in saturated minor abundances of the saturated fichtelite (Otto and Simoneit, 2002). Since retene is absent and minor amounts of fichtelite are present in the Haughton extract, it is reasonable to assume that a reductive depositional environment was present at Haughton.

$\delta^{13}\text{C}$ Isotopes

Further evidence to constrain the origin of organic carbon in the Haughton extract was provided by carbon isotopic ratios for individual hydrocarbons. The $\delta^{13}\text{C}$ values for $\text{C}_{16} - \text{C}_{22}$ *n*-alkanes range from -26 ‰ to -31 ‰. $\text{C}_{21} - \text{C}_{35}$ *n*-alkanes, within the error of the analysis, do not show significant variation from an average $\delta^{13}\text{C}$ of -31 per mil. *n*-Alkanes in oils derived from a common kerogen rarely show $\delta^{13}\text{C}$ values this consistent for individual *n*-alkanes. This data proves that the *n*-alkanes in the AH98-3 core extract are derived from a common source.

Conclusions from this work

Extremely well preserved sedimentary deposits in the Haughton impact structure (HIS) provide a unique record of the post-impact Miocene lacustrine depositional environment. Detailed organic geochemical characterization of a hydrocarbon-impregnated band found in a core from the crater-lake sedimentary infill reveals a complex source history for the hydrocarbons. These include contributions from eroded pre and post-impact formations together with inputs from contemporaneous flora and fauna, a deep, possibly lower Paleozoic petroleum as well as a contribution from hydrothermally altered organic biopolymers.

Elucidation of basin architecture *via* hydrocarbon characterization of the HIS reveals a complex history of provenance. The extractable organic solute represents a mixture of hydrocarbons derived from a variety of sources that reflect a unique history for the basin. Moreover, there appears to be distinct groups of compounds that each provides insight to potential sources, depositional environment and thermal evolution. These are; a) *n*-alkanes; pyrolysis of a biopolymer either in-situ or through incorporation of reworked particles, b) hopanes, 2 α -, 3 β -methylhopanes: bacterial biomass, c) dibenzothiophenes, benzothiophenes; sulfur rich environment d) C_{29} steranes and diterpenoids, in-situ or low-level reworked terrestrial organic matter e) aromatic steroids, *n*-24-propylcholestanes and naphthalenes a more mature deeper seated source or affected by hydrothermal fluids and f) Polycyclic aromatic hydrocarbons and phenanthrenes indicate the probability of hydrothermal activity and associated elevated temperatures have played an important role during the genesis of the hydrocarbons.

The depositional environment seems to be dominantly reducing and high in sulfur. Particulate matter from eroded older formations and extant plant debris may have been incorporated in the in-fill sediments. Invertebrate skeletal material may have been washed into the basin in periods of localized floods or could represent shallower lacustrine/marshes that existed at the margins of the lake.

This sample from a Miocene impact crater supports the notion that (a) Post-impact erosion and re-sedimentation in a crater lake creates a localized source of hydrocarbons and (b) Impact-induced brecciation and fracturing coupled with hydrothermal activity has likely caused the re-mobilization of older petroleum fluids that have migrated into the lake in-fill sediments.

E) Toward analysis of "humpane" compounds in Gulf of Mexico oils via GCxGC

Description of problem: In past work, the shape of the *n*-alkane GC envelop in oils was found to be a valuable quantitative indicator of the number of volumes of gas that have passed through and equilibrated with a subsurface oil accumulation (Meulbroek, et al., 1998). As multiple volumes of gas pass through and equilibrate with a petroleum accumulation during this "gas washing" process, the lower molecular weight alkanes are preferentially depleted with the effect falling off exponentially with increasing carbon number. This depletion provides a powerful new quantitative tool for determining the amount of gas that has flowed through and equilibrated with an oil in a reservoir. Unfortunately, the technique is not applicable to oils where biodegradation has preferentially depleted the *n*-alkanes as is the case with many of the Gulf Coast transect oils studied here.

The GCxGC or 2-dimensional GC technique, described below, was tested as a possible means to find and quantitate other homologous series of both aromatic and aliphatic hydrocarbons and heterocyclic compounds in oils that might also show the gas washing effect but would be more resistant to biodegradation than the *n*-alkanes. Most of the compounds of interest are not easily analyzed by conventional GC techniques because they are unresolved and form part of the complex mixture of hydrocarbons that typically make up the "hump " in biodegraded oils. In contrast, GCxGC is rapid and allows quantitative analysis of a number of homologous series in a single analysis. In GCxGC, single eluant peaks from a first GC column are further separated on a second column (Figure 16). This technique has proven to be very powerful in fingerprinting and quantifying most hydrocarbon constituents in petroleum and gasoline samples from oil spills and in Santa Barbara seep oils (see next section).

The GCxGC technique may also be useful in quantitatively delineating hydrocarbon changes caused by gas washing versus water washing versus biodegradation. If a non-polar column were used in the first dimension and a polar compound in the second dimension, then the homologous series from first separation would separate according to their degree of (Fig. 16), while further separation on the second more polar column would more closely follow the pattern expected from water washing that has a much stronger affect on the more polar aromatic fraction of oil than on the non-polar *n*-alkanes. In contrast to both of these washing processes, biodegradation is effective in either wiping out whole classes of compounds simultaneously or in depleting very specific compounds. Therefore, it may be possible to gain a great deal of information about the specific alteration processes that have affected specific oils just from the shapes of the GC-GC profiles in the two directions. Significant progress in testing and applying these ideas is described in the next section in our initial results on Santa Barbara basin oils.

F.) Results to date -Using Comprehensive Two-dimensional Gas Chromatography to Explore the Geochemistry of the Santa Barbara Oil Seeps - test of GCxGC in characterization of highly altered seep oils

1. Introduction

The study of petroleum in the subsurface and surface environment has made great strides in the last four decades with the advent of gas chromatography (GC) (Peters *et al.* 2005a&b). Initially, GC employed short packed columns (several meters long) that were capable of resolving a select amount of petroleum hydrocarbons. More recently, capillary columns (30 to 100 meters long) have been used to separate, identify, and quantify (with the aid of mass spectrometric detectors) hundreds of compounds.

Despite these advances, many more compounds present in petroleum have not been studied because of the inability of traditional GC to separate these compounds. These unresolved and hence unidentified compounds remain unused by geoscientists interested in the behavior of petroleum in subsurface and surface environments.

Recent advances in chromatography have led to the development of comprehensive two-dimensional gas chromatography ($\text{GC} \times \text{GC}$), which has expanded the analytical window of petroleum hydrocarbons. $\text{GC} \times \text{GC}$ is a nascent analytical tool ideally suited for studying complex mixtures like oil. Compared to traditional GC, this novel technology is capable of separating and resolving at least an order of magnitude more compounds, has a much larger signal to noise ratio, and sorts compounds based on their chemical class; hence, providing highly refined inventories of previously unattainable petroleum hydrocarbons in geochemical samples. In addition to the increased resolution afforded by $\text{GC} \times \text{GC}$, the resulting chromatograms can also be used to estimate the liquid vapor pressures, aqueous solubilities, octanol-water partition coefficients, and vaporization enthalpies of petroleum hydrocarbons. With these relationships, powerful and incisive analysis of phase transfer processes affecting petroleum hydrocarbon mixtures in the environment can be studied. For example, $\text{GC} \times \text{GC}$ retention data can be used to quantitatively deconvolve the effects of phase transfer processes such as water-washing and evaporation. In short, the positive attributes of $\text{GC} \times \text{GC}$ sample analysis has led to a methodology that will revolutionize the analysis of petroleum hydrocarbons.

Here, we carried out preliminary $\text{GC} \times \text{GC}$ to investigate sources and relationship of the highly altered Santa Barbara seep oils (Figure 14). The Santa Barbara seeps are a natural laboratory, and the location is ideal for studying petroleum in the environment. It is a site for collaborative testing of new in situ instrumentation via future collaborations between WHOI engineers and scientists and UCSB geoscientists. Some of the key attributes of the site and the associated research include the large volumes of oil seeping and its proximity to critical residential and recreational areas, and existing collaborative ties with Professors David Valentine, Libe Washburn, Jordan Clark, Bruce Lyandyk, and Ira Leifer at the University of California at Santa Barbara (UCSB).

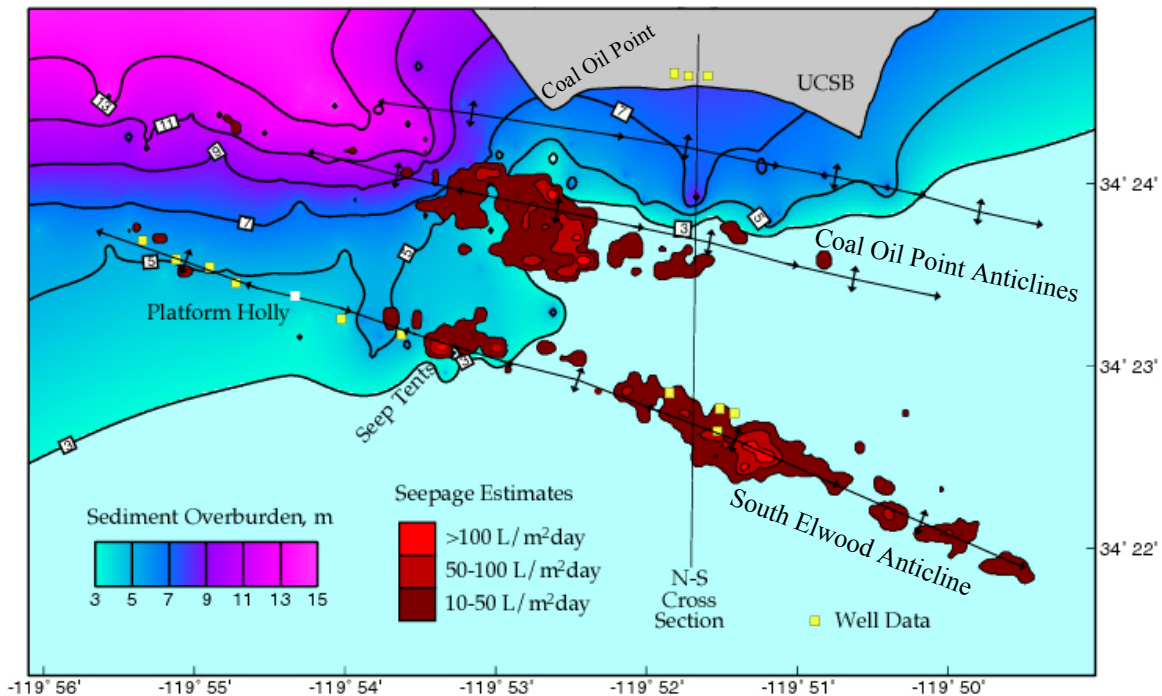


Figure 14. Map of the Santa Barbara basin, showing the location of known oil seeps (red) and Platform Holly (toward the western end of the South Elwood Anticline). Figure from UCSB Hydrocarbon Seeps Project webpage (<http://seeps.geol.ucsb.edu/>).

2. Introduction

a. Background on gas chromatography. Most chemical research on petroleum has been performed with traditional gas chromatography (GC). Briefly, GC works by measuring the time it takes for a compound to travel through a column and be detected. Ideally, when a mixture of compounds is injected into a gas chromatograph, each compound will have a distinct retention time and, thereby, be “resolved.” The identity of each peak in the resulting chromatogram is determined by injecting each compound separately and matching the retention times. Identifying compounds in mixtures by comparing them to pure, individual standards can be tedious, and mass spectrometric detectors have evolved to help identify a compound by its characteristic mass spectrum. Unfortunately, traditional gas chromatographs are not able to resolve the complex mixtures of compounds in petroleum even with the assistance of mass spectrometers. For example, a traditional gas chromatogram of oil residues that were extracted from salt marsh sediments impacted by the 1969 spill of the *Florida* oil barge in Buzzards Bay, Massachusetts, is shown in Figure 15A. Chris Reddy's laboratory group has been studying this diesel-fuel spill for the past five years with an overall goal of understanding the fate of spilled oil on decadal time scales (Reddy *et al.*, 2002; Frysinger *et al.*, 2003). The sample shown in Figure 15A was collected in 2000 and revealed that oil continued to persist at this site three decades after the spill. However,

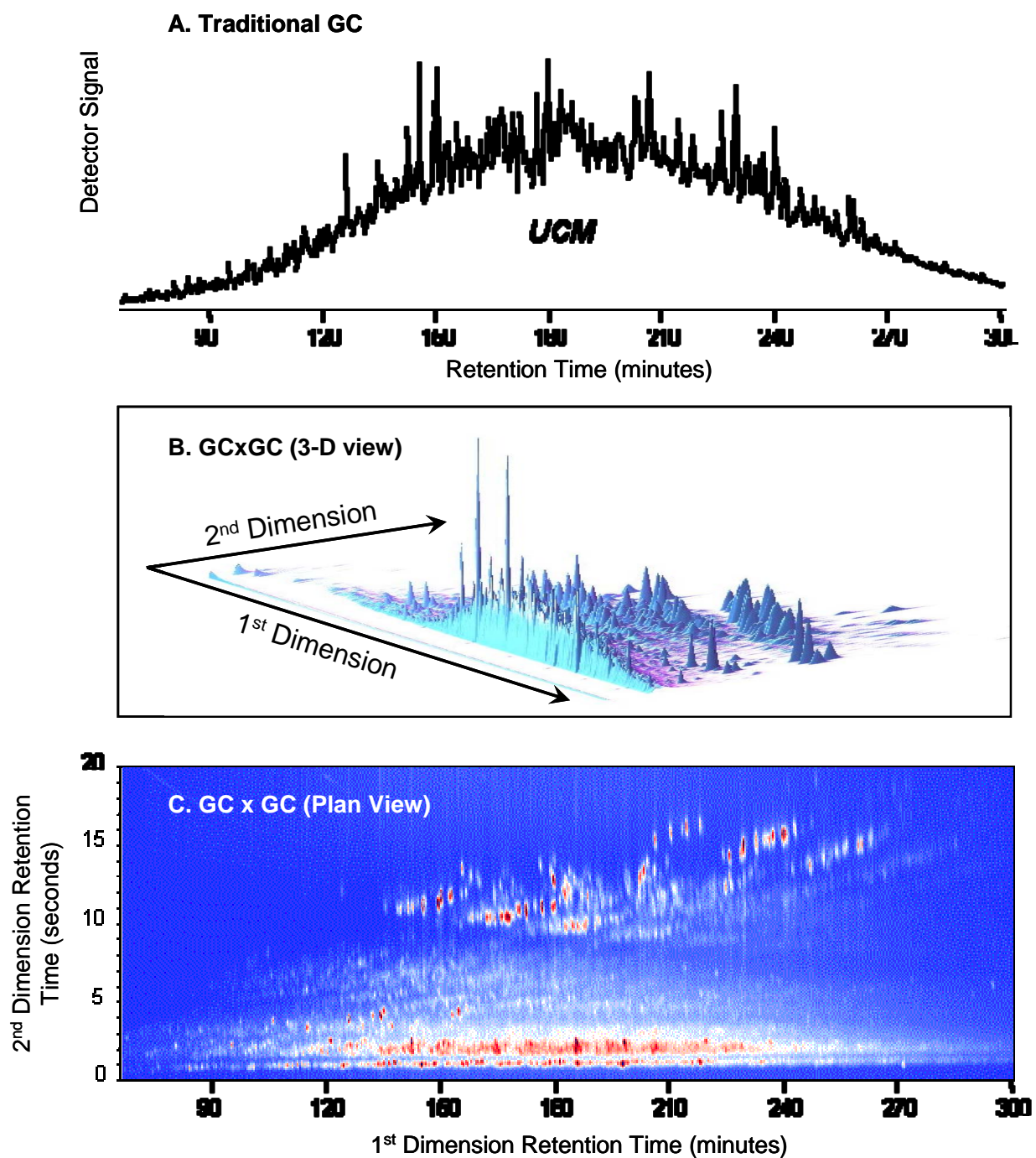


Figure 15. Gas chromatograms of oil residues from salt marsh sediments that were impacted by a diesel fuel spill in 1969. (A) Traditional GC analysis. Few compounds are resolved and, instead, a single broad hump called the unresolved complex mixture (UCM) is present. (B) GC \times GC analysis (3-dimensional view). Each resolved compound appears as a peak in two-dimensional space. (C) Plan-view projection of the GC \times GC data. Blue corresponds to base-plane; white corresponds to small peaks; red corresponds to large peaks. Figures B and C are from the same analysis of the same sample shown in A but viewed differently.

there are no perfectly separated peaks in this chromatogram but rather a large hump called the “unresolved complex mixture” (UCM). The UCM is present because many of the compounds in the sample have the same retention time, creating this characteristic hump. Some compounds could be identified in the UCM, but the overall lack of separation power afforded by traditional GC provided very little chemical information about the oil still residing in the marsh. The UCM has hindered nearly all geoscientists interested in the composition of petroleum whether it has been in the subsurface, such as reservoirs, or surface environments as in Wild Harbor.

b. Introduction to comprehensive two-dimensional gas chromatography (GC × GC). Recent advances in chromatography have led to the development of comprehensive two-dimensional gas chromatography (GC × GC), which has expanded the analytical window of petroleum hydrocarbons. This acronym, GC × GC, is used because orthogonal gas chromatographic separations are used in both analytical dimensions by using stationary phases with different selectivities (Figure 16). GC × GC relies on thermal modulation to transfer analytes from the first-dimension column to the second-dimension column (Phillips *et al.*, 1999). The loop jet modulator serves as an analyte trap and is positioned at the interface between the first and second dimension capillary columns. The loop jet modulator has two main components: a cold jet that creates a cold spot on a piece of fused silica in the loop jet modulator where compounds eluting from the first dimension column are trapped and concentrated for a fixed modulation period (4 to 20 seconds), and a hot jet that is capable of ballistically heating and launching compounds that have been trapped in the modulator loop onto the second dimension column. In the routine analysis of a crude oil, injection into the second column is very fast and produces a peak width on the order of 50 to 100 milliseconds for the least retained compounds (such as isoprenoid alkanes) and up to ~400 milliseconds for 4-ring polycyclic aromatic hydrocarbons (PAHs) that are more retained on the second dimension column. Narrow peaks allow fast chromatography in the second dimension where as many as 12 to 15 separate peaks have been observed in a 10-second modulation. Spatial band compression during modulation has the additional advantage of more than an order of magnitude increase in signal-to-noise ratio, thus improving the

Comprehensive Two-Dimensional Gas Chromatograph

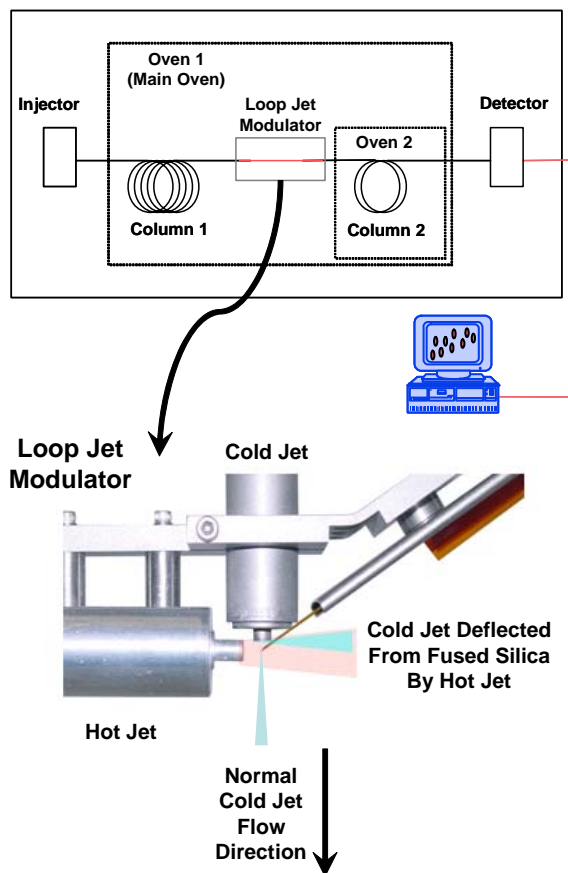


Figure 16. GC × GC instrument configuration. Compounds eluting from the first column are cryogenically trapped for a precise time interval (the modulation period) and then rapidly heated and injected onto the second column at the loop jet modulator. Since the columns used to perform the first and second dimension separations are chosen to separate components by different physical properties (like boiling point on the first dimension column and polarity in the second), the resolution of components in a complex mixture like crude oil is far superior on a GC × GC instrument than that achieved by traditional GC analysis.

detection and quantification of minor components (Phillips *et al.*, 1999).

GC \times GC has been used successfully to identify and quantify individual compounds and classes of compounds in crude oil and refined petroleum products. Gasoline was analyzed with GC \times GC to quantify benzene and oxygenates individually, and total aromatics as a group (Frysiner *et al.*, 1999, Frysiner and Gaines, 2000). GC \times GC chromatograms of crude oil showed distinct groupings of alkylated PAHs, sulfur-containing aromatic hydrocarbons (PASHs), and sterane and hopane biomarkers (Frysiner and Gaines, 2001).

GC \times GC chromatograms are usually viewed three dimensionally where the first-dimension retention time is on the x-axis and the second-dimension retention time is on the y-axis. The data can be displayed with 3-D views or as color-contour plots (plan view), with blue representing the base-plane, white representing low to moderate signal, and red representing a high signal. In order to visualize the minor peaks, the dynamic range that is plotted is often less than the total dynamic range of the sample, with the tops of the tallest peaks “chopped off.” This produces a larger red area near the center of large peaks. In 2002, my research group was the first to apply this technique to a real-world oil spill. Shown in Figures 15B (3-D view) and 15C (plan view) are GC \times GC chromatograms of the same sample analyzed by a traditional GC in Figure 15A. Clearly, many more compounds are resolved. This analysis provided a refined inventory of existing petroleum hydrocarbons in the salt marsh and revealed to us that only one class of compounds (*n*-alkanes) was completely degraded and that all other compound classes typical of diesel fuel remained. This new data also suggested that the degradation of the oil-derived compounds ceased in the mid 1970s, when the oil-contaminated sediment became anoxic.

Several methods can be used to identify the peaks in a GC \times GC chromatogram. They can be identified by comparing the first and second dimension retention times to chemical standards. Peaks can also be tentatively identified based on their well-defined elution pattern on the second dimension. This “chemical order” of GC \times GC chromatograms provides valuable insights into the properties of unknown species and allows for easy identification of homologous series of compounds within complex mixtures (Giddings, 1995). Finally, peaks can be identified by their mass spectra when GC \times GC is coupled to a mass spectrometer. For example, in Figure 17 several mass spectra are displayed along with the peak identities in a partial GC \times GC chromatogram of diesel fuel. As shown, the mass spectra of each compound are not affected by other components that would otherwise co-elute in traditional GC. Figure 17 also depicts how polarity separations in the second dimension provide the necessary resolution for separating individual compounds in complex mixtures. For example, the saturated alkanes, which are the least polar components in diesel fuel, have the least retention in the second column. The one and two-ring cycloalkanes have more retention than the alkanes, and the one and two-ring aromatics have the most retention. At many positions in the chromatogram, several components that co-elute on the first column were resolved with the second column.

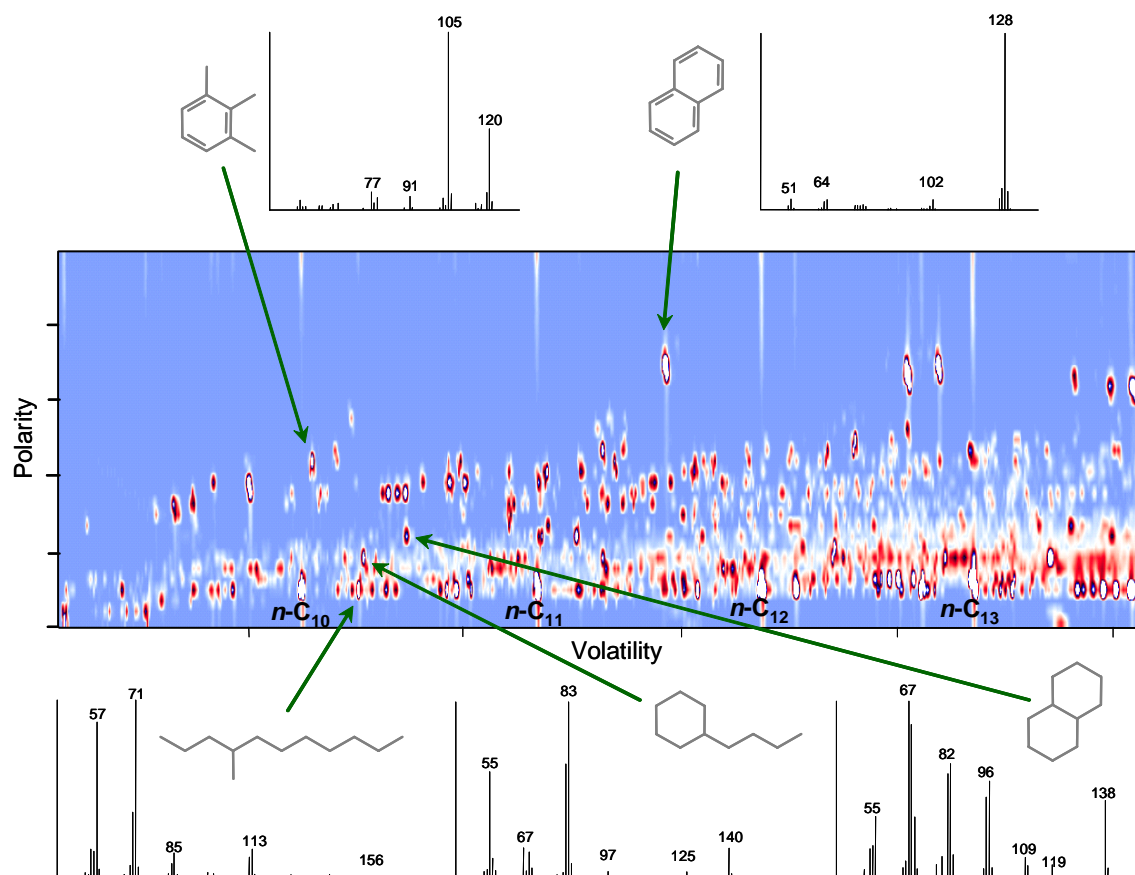


Figure 17. Partial GC \times GC/MS chromatogram of diesel fuel. The x-axis is volatility-based chromatographic separation. The n-alkanes, decane (C10) to tridecane (C13), are identified. The y-axis is polarity-based chromatographic separation.

c. Santa Barbara Oil Seeps. The Santa Barbara oil seeps are considered some of the most active in the world (Figure 14). Carbon-rich marine sediments from the Tertiary period (Sisquoc, Monterey, Rincon, and Vaqueros formations) provide the source material for the generation of oil in this area. Archeological evidence of the use of tar from these seeps by the indigenous people of the Santa Barbara area date back approximately 5,000 years (pre-Chumash coastal inhabitants) (Norris, 2003). Uranium-Thorium (U-Th) measurements of calcite cements around areas where hydrocarbons are believed to have seeped to the surface in the past suggest that hydrocarbons have been moving along faults around the rim of the basin for the past 120,000 and perhaps up to 500,000 years before the present (Boles et al. 2004). Currently, widespread seepage of hydrocarbons occurs at offshore faults in the waters of the Santa Barbara basin. Estimates of the amount of hydrocarbons migrating into the environment by way of the seeps around Coal Oil Point put the combined gas-liquid hydrocarbon seepage flux at approximately 37 tons per day, with the gaseous emissions making up 65% of this total (24 tons per day) (Quigley et al., 1996 and Washburn et al., 1996). Recent measurements using sonar to estimate seepage rates of escaping gas bubble plumes, report 40 metric tons of methane per day entering the environment from the seep field (Clark et al. 2000). Analysis of the seep gas indicates that the gas is 85% methane, 5% ethane, and the remainder is composed of other short chain length alkanes, carbon dioxide (CO₂), molecular nitrogen (N₂), and a trace of molecular oxygen (O₂) (Clester et al. 1996, Hornafius et al. 1999). It has been noted that the volume of gas emanating from the seeps has been fluctuating over time (Quigley, 1999; Boles, 2001; Leifer & Boles; Leifer et al, 2004) and that the causes for these fluctuations are most likely linked

to daily tidal cycles, oil production at the nearby Holly Platform, and seismic activity along the faults in Santa Barbara county.

Modern scientific investigations of the Santa Barbara seeps began in earnest during the middle of the 20th century. The earliest GC separations of hydrocarbons upwelling in the Santa Barbara channel date back to 1973 (Mikolaj, 1973). The resolving power of GC coupled to mass spectrometers advanced the study of oil from these seep areas (Kaplan and Reed, 1977; Stuermer et al. 1982). Some of the many chemical structures of compounds extracted from these seep oils were assigned using this approach.

More recent efforts have focused on analyzing seep fluids for the presence and ratios of biomarkers to determine the possible reservoir sources and transport directions of the fluids. Targeted compounds or their ratios typically include trisnorhopane, sterane/hopane ratios, refractory index, C₂₈/C₂₉ hopane ratios (Kvenvolden, 2004). Other researchers studying the toxicological effects of seep fluids on marine organisms have measured PAHs (Davis, 1981, Spies; 1981; Stuermer, 1981; Seruto et al., 2005). Geochemical tracing of tarballs from these seeps have been investigated, too (Hostettler et al., 2004). All of this work has been limited to traditional GC, which is a technology that is at least two decades old and has provided a limited number of analytes.

d. Initial Research on Santa Barbara Seeps. For the past year, our group at WHOI (Dr Chris Reddy, his research associate Robert K. Nelson with some initial funding from this grant) have been collaborating with Professor David Valentine (UCSB) and his graduate student George Wardlaw on the Santa Barbara oil seeps (Figure 14). A GC × GC plan view projection of a Monterey Shale crude oil sample from Platform Holly (Well 2342-15) is shown in Figure 18A. The star in this chromatogram indicates the position of the internal standard dodecahydrotriphenylene (DDTP). The first dimension axis is labeled with both retention time on the bottom and retention index on the top; the retention index is used in order to aid in comparisons with samples run on different columns or different temperature programs (Kovats, 1965, Kovats & Weisz, 1965). An expanded view of the box in Figure 18A is depicted with component identities annotated in Figure 18B. Inspection of Figure 18B reveals how well compounds belonging to specific chemical classes are resolved in two-dimensional chromatographic space.

To gain some perspective on the increased resolving power of GC × GC, consider the number of resolved peaks in a vertical slice through any plan view projection of a GC × GC chromatogram. For example, focus on the resolved peaks that elute between 125 and 130 minutes on the x axis and between 1 and 4 seconds on the y axis highlighted in Figure 18B (highlighted in the green rectangle). Again, all of these peaks were eluted from the first dimension column, trapped at the loop jet modulator, ballistically heated and injected onto the second dimension column, where they were resolved and detected with a flame ionization detector. This time period (125 to 130 minutes on the x axis) represents 30 modulations from the original chromatogram and each modulation represents a group of compounds that co-elute from

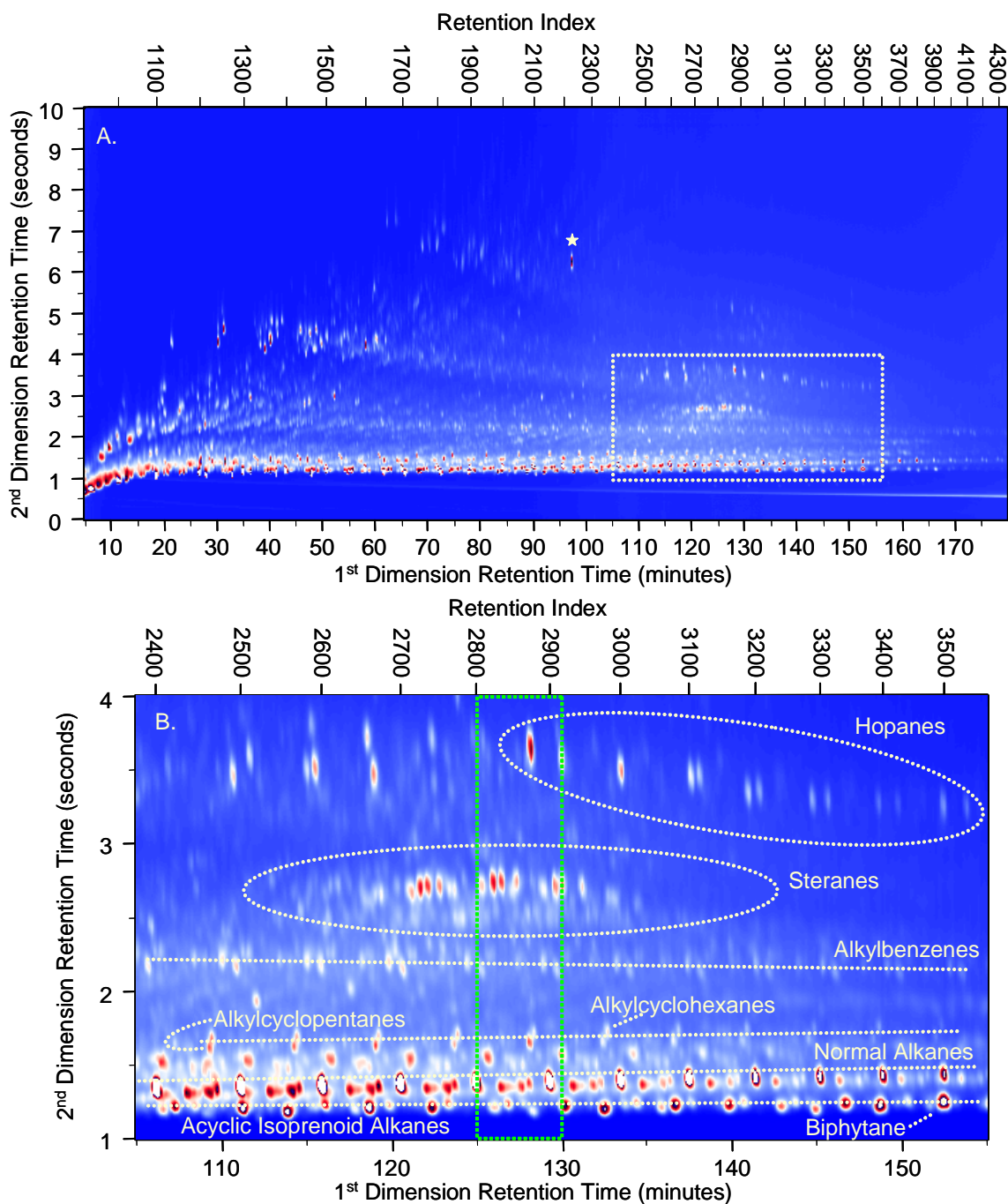


Figure 18. Monterey shale crude oil (Well 2342-15) collected from Platform Holly. (A) Plan view projection of whole GC \times GC chromatogram. The star indicates the position of an internal standard dodecahydrotriphenylene (DDTP). (B) Expanded view of area highlighted by box in Fig. 18A with peak classes and identities annotated. Blue corresponds to base-plane; white corresponds to small peaks; red corresponds to large peaks.

the first dimension column. In essence, any vertical slice through any GC \times GC chromatogram shows the compounds that are eluting on top of each other in a traditional GC chromatogram. GC \times GC is called “comprehensive” because all of the compounds that elute from the first dimension column are cryogenically trapped and then injected onto the second dimension column. There are no valves in place between the columns to divert components, every component that elutes from the first column is trapped and injected onto the second column.

Since we are using a second dimension column that resolves peaks on the basis of polarity (or polarizability), the vertical order of compounds eluting from the second dimension column (y axis) arranges molecules by compound class starting with the most non-polar and ending with the most polar molecules. For instance, if we consider the same portion of Figure 18B (125 to 130 minutes on the x axis and 1 to 4 seconds on the y axis), the molecules eluting at the bottom of the chromatogram are the most non-polar while the molecules at the top of the chromatogram are the most polar. The second dimension elution order (vertical order) of this portion of the chromatogram is as follows, the most non-polar compounds are the acyclic isoprenoid alkanes, followed by the branched and normal alkanes (the branched alkanes elute between the normal alkanes along the x axis). Just above the branched and normal alkanes, the cyclic alkanes elute. Above the cyclic alkanes, the alkylcyclopentanes and alkylcyclohexanes elute. Next, the alkylbenzenes elute followed by the steranes and finally the last and most polar molecules in this portion of the chromatogram, the hopanes. Up until this point in time, this level of peak resolution has been unattainable. Close inspection of this small portion of the chromatogram shown in Figure 18B (125 to 130 minutes on the x axis and 1 to 4 seconds on the y axis), yields nearly 70 well resolved peaks.

To compare the differences in the composition of petroleum from Well 2342-15 to what is naturally seeping out along coastal Santa Barbara, a series of samples were collected and analyzed by GC \times GC. They included an oil stringer emerging through the seafloor at Jackpot Seep, an oil droplet collected as it spread on the sea surface above the Jackpot Seep, and a tarball collected on the beach in Isla Vista, CA. Please note that the oil droplet and surface sample from Jackpot Seep were collected nearly simultaneously. GC \times GC chromatograms of Platform Holly (Well 2342-15), the oil stringer, the sea surface sample, and tar balls are shown in Figures 19A-D, respectively. The star in each chromatogram indicates the position of an internal standard, DDTP, which was added to each sample. These images reveal substantial changes that occur as petroleum hydrocarbons are transported from the reservoirs to the beach. Although these types of contour plots are extremely useful in cataloging all of the components present in an oil sample, other types of data visualization techniques provide even more insight into the environmental processes acting upon these hydrocarbons. For example, Figure 19 was produced by subtracting the GC \times GC data matrix of the oil Seep Stringer from Platform Holly (Well 2342-15). The resulting chromatogram highlights the differences between the two oil samples. Peaks that are large in the Platform Holly (Well 2342-15) sample and small in the Seafloor Seep Stringer sample appear red. Peaks that are large in the Seep Stringer sample and small in Well 2342-15 sample appear blue, and peaks that have the same volume in both chromatograms vanish. In this case, the major differences between the reservoir and seafloor appear to occur in the relative abundances of the naphthalene peaks, the branched and isoprenoid alkane peaks, and most noticeably in the normal alkane peaks. It is likely that the alkane components of this oil

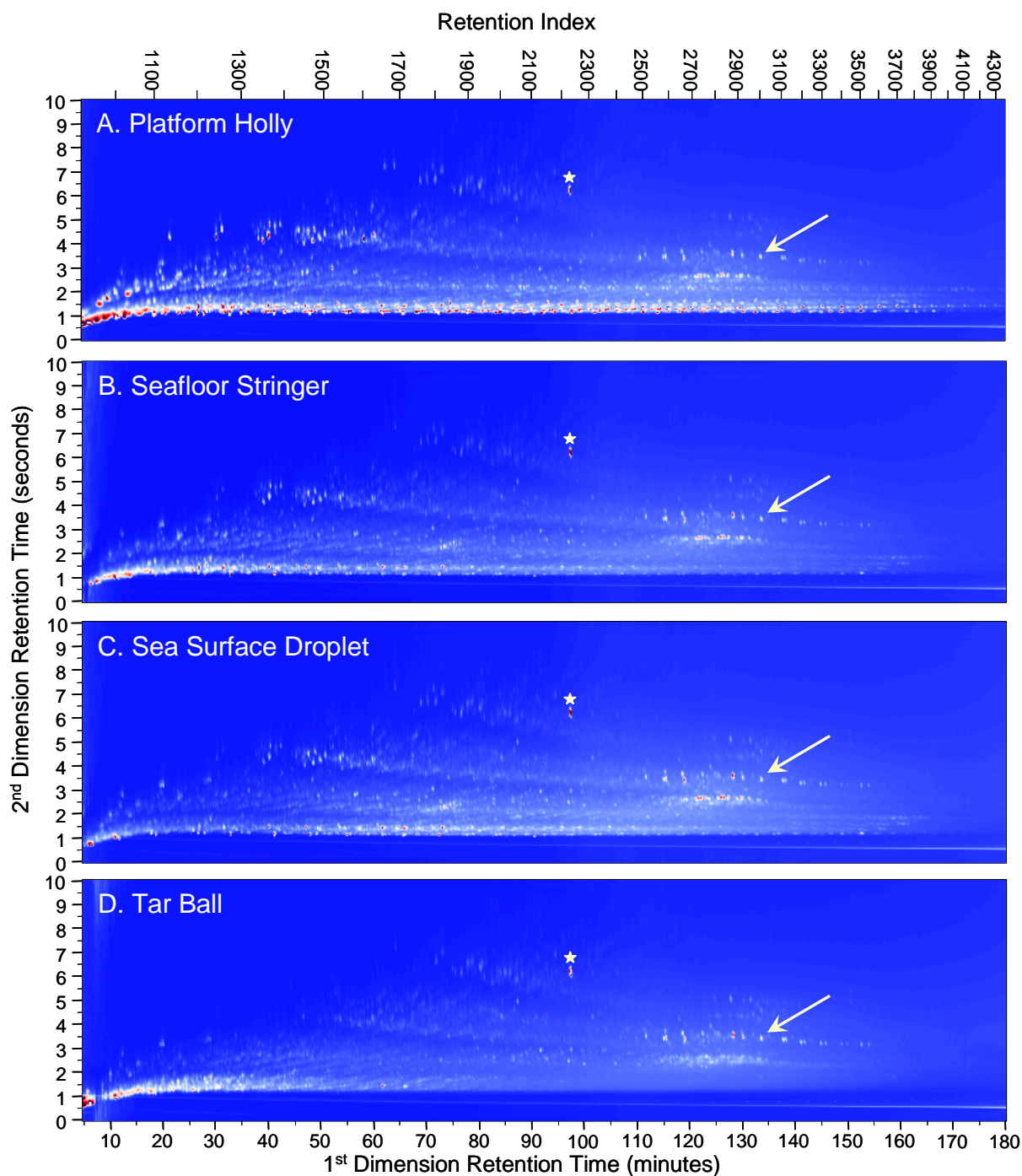


Figure 19. GC \times GC chromatogram comparison of (A) crude oil from Platform Holly (Well #2342-15) (B) an oil “stringer” emerging through the seafloor collected at the Jackpot Seep field. (C) an oil droplet collected as it was spreading at the sea surface above the Jackpot Seep field. (D) a tar ball collected on the beach in Isla Vista, CA. A star on each chromatogram indicates the position of an internal standard (dodecahydrotriphenylene) added to each sample and an arrow indicates the position of a bacterially- derived biomarker ($17\alpha(H)$, $21\beta(H)$ -hopane) that was used to normalize each image.

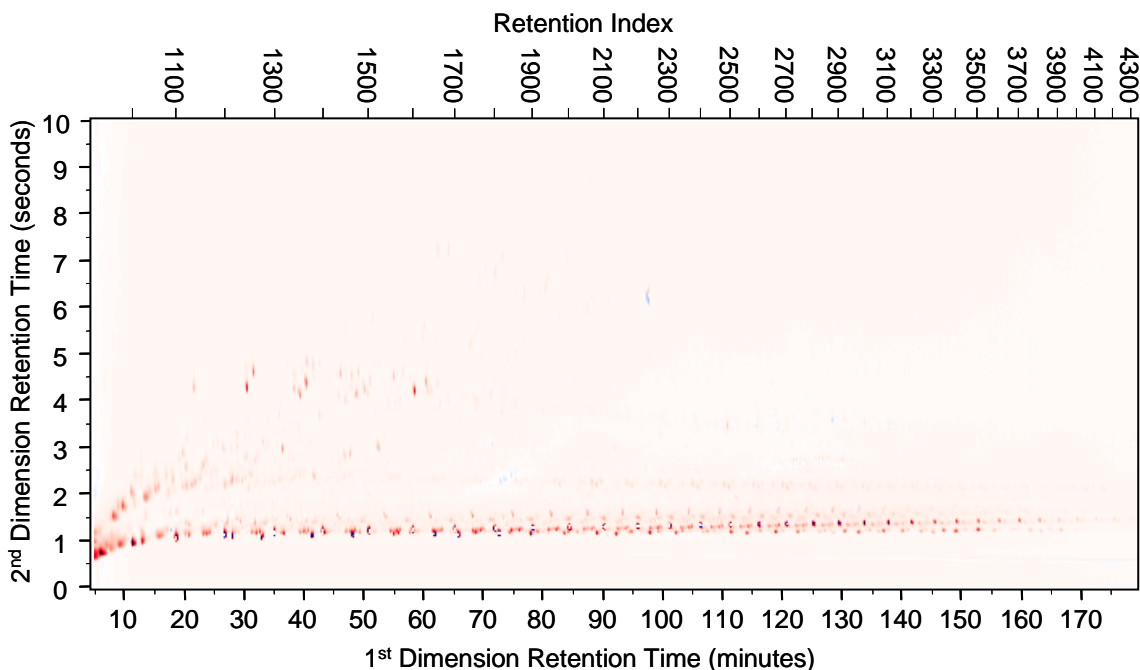


Figure 20. Difference chromatogram produced by subtracting the Seep Stringer chromatogram (Figure 19B) from the Oil Reservoir chromatogram (Platform Holly Well #2342-15 Figure 19A). This difference chromatogram highlights the loss of crude oil hydrocarbons that occurred as the oil migrated up from depth along faults in the Santa Barbara basin. In this figure, the base-plane appears white, peaks that are larger in the Oil Reservoir sample appear red, and peaks that are larger in the Seep Stringer chromatogram appear blue, and peaks that are the same volume in both samples vanish. The Seep Stringer chromatogram and the Platform Holly Oil Reservoir chromatogram were normalized to the peak volume of 17 α (H), 21 β (H)-hopane prior to subtraction.

were removed as the oil migrated up to the seafloor from depth by biodegradation. Another very powerful, visual data display technique is the three-dimensional surface rendering. Figure 21A and 21B shows the same data that was plotted as contour plots in Figure 19A and 19B now displayed as 3-D plots where evidence for biodegradation is readily apparent. All of the chromatograms shown were normalized to the peak volume of 17 α (H), 21 β (H)-hopane (indicated by the arrow in the contour plots). This hopane has been demonstrated to be environmentally recalcitrant and as such, is useful in monitoring oil weathering processes when crude oil is accidentally released into the environment (Prince et al. 1994). Inspection of the difference chromatogram shown in Figure 20 reveals that all the peaks in the area where the steranes and hopanes elute vanish, meaning that all of these peaks were of very nearly the same volume in both the Platform Holly reservoir sample and the oil emerging from the seafloor. This finding provides strong evidence that these two oil samples are related since the likelihood of all of the sterane and hopane peak volumes matching in two unrelated crude oil samples is remote.

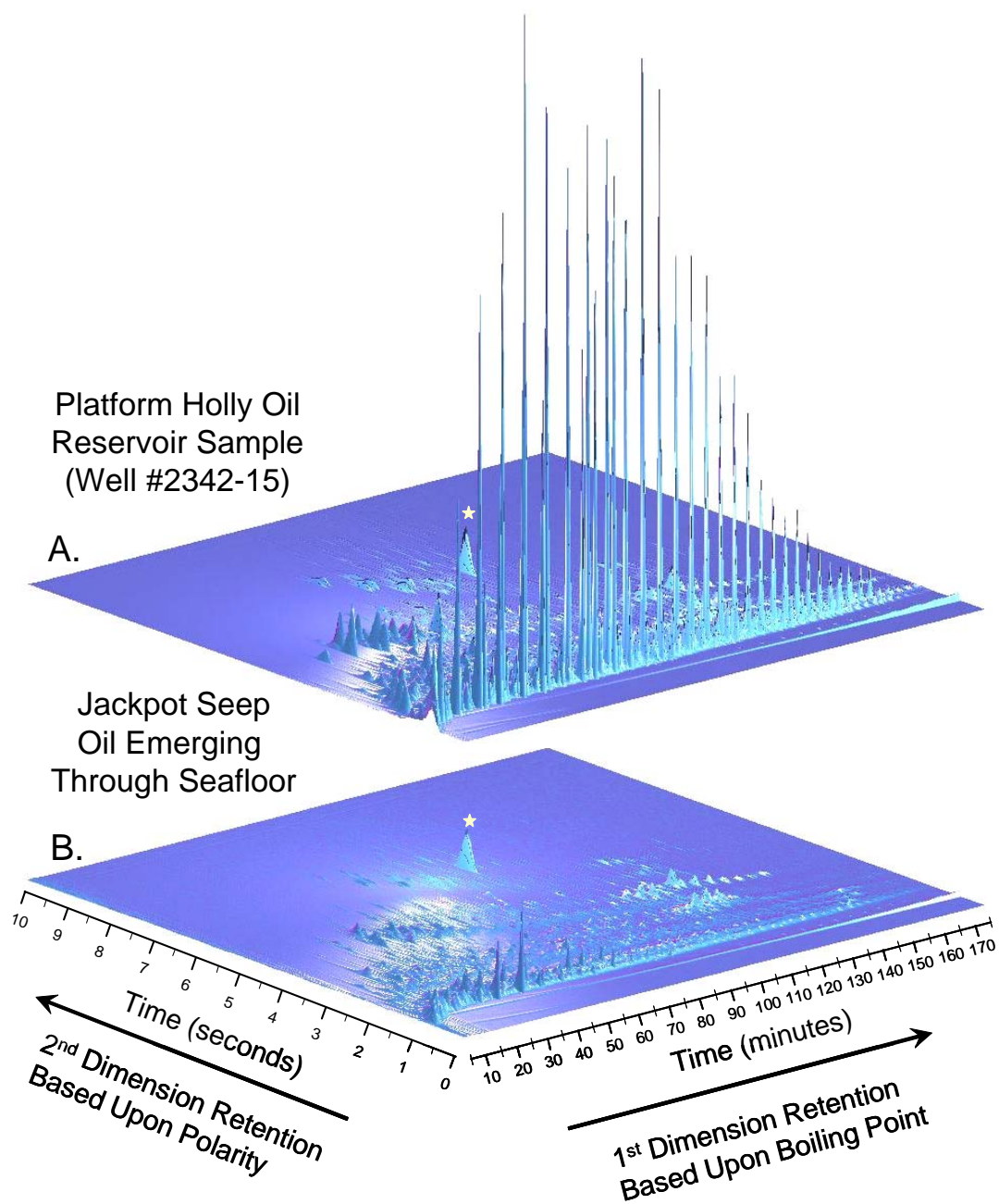
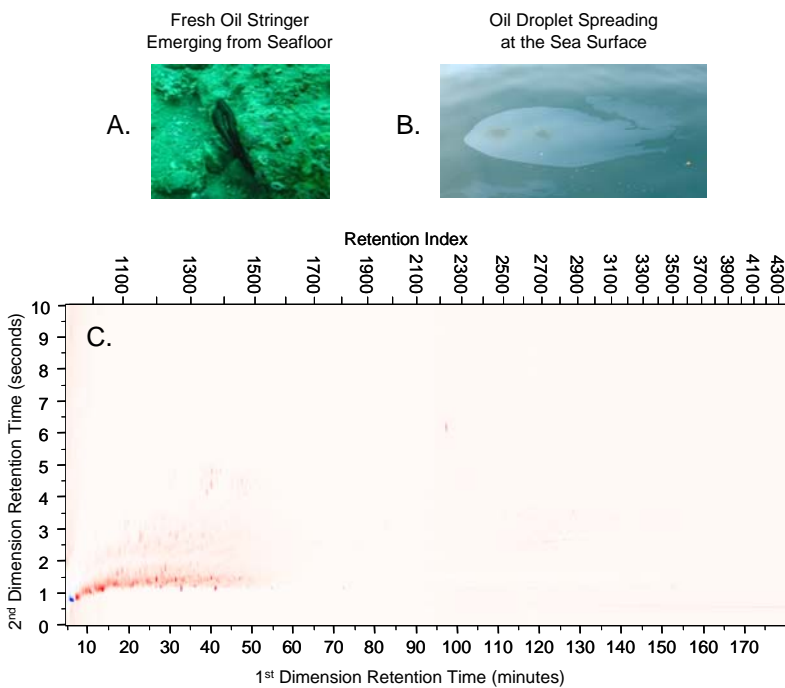


Figure 21. The same data presented in figures 19A and 19B now displayed as three-dimensional surface renderings. The star denotes the position of the internal standard dodecahydrotriphenylene (DDTP) in each chromatogram. The complete loss of the normal alkanes in the Seep Stringer chromatogram (21B) is clearly evident in this figure. Selective loss of normal alkanes while other components like the steranes and hopanes remain in a sample is a good indication of subsurface microbial activity.

Figure 22C is another difference chromatogram produced by subtracting the GC \times GC data matrix of an oil droplet spreading on the ocean surface (shown in Figure 19C) from the GC \times GC data matrix of oil emerging through the seafloor (shown in Figure 19B). Photographic images of the actual seep stringer emerging from the seafloor and the oil droplet spreading at the surface are shown in figures 22A and 22B. This figure shows how rapidly the lighter components of this oil are lost from the ocean surface likely by evaporation. As oil emerges through the seafloor and then as oil droplets rise through the water column, the only molecules that are in contact with the surrounding water are the molecules at the surface of the oil droplet. Some of these molecules may have a slight tendency to dissolve into the water column but most of the components of the oil remain sequestered within the droplet primarily because the temperature of the water is low enough and the viscosity of the oil is high enough that surface renewal of the oil droplet occurs very slowly. However, when the oil droplet reaches the ocean surface and begins to spread, the situation changes dramatically. The surface area of the oil droplet expands as the oil spreads at the air/water interface and all of the components of the crude oil that were previously sequestered within the oil droplet are now exposed to the atmosphere. The lighter components are now free to leave the droplet by evaporation. This process is clearly represented in Figure 22C where the difference chromatogram indicates that the components eluting from 5 to approximately 45 minutes were present in the oil emerging from the seafloor, but absent in the oil droplet collected directly above the seep. What is remarkable about this finding is the short time scale over which this process takes place. Since the Jackpot Seep is located at a depth of about thirty feet of water, the time that it takes for oil droplets to emerge through the seafloor, rise through the water column, and then spread at the surface is on the order of a few minutes.

Figure 22. Difference chromatogram (22C) produced by subtracting the Sea Surface Oil Droplet chromatogram (Figure 19C) from the Seep Stringer chromatogram (Figure 19B). This difference chromatogram highlights the loss of hydrocarbons due to evaporation at the sea surface. In this figure, the base-plane appears white, peaks that are larger in the Seep Stringer sample appear red, and peaks that are larger in the Surface Droplet chromatogram appear blue, and peaks that are the same volume in both samples vanish. The Seep Stringer chromatogram and the Surface Droplet chromatogram were normalized to the peak volume of 17 α (H), 21 β (H)-hopane prior to subtraction. The blue dot at 5 minutes in the 1st dimension is from the solvent used in the sample preparation.



Please note that with the exception of Figure 17, all of the GC \times GC images presented so far in this proposal were produced from data acquired with a flame ionization detector (FID), which is a nearly universal detector for petroleum hydrocarbons. The FID remains a useful and productive GC detector for all sorts of GC analyses, but detailed structural information about the molecules eluting from a GC \times GC or standard GC instrument can only be inferred using retention times of known standards with this detector. Mass spectrometry provides the most useful structural information about molecules eluting from a GC column. Because of the speed that compounds elute from the second dimension on a

GC × GC, fast scanning instruments are needed. Currently, the only mass analyzers capable of producing high enough quality mass spectral data and sufficient data density to effectively characterize components eluting from a GC × GC instrument are time of flight (ToF) mass spectrometers. ToF mass analyzers are capable of scanning from 50 to 1,000 atomic mass units (amu) at scan rates of 50 to 500Hz. Figure 10 shows a suite of resolved and characterized isoprenoid alkane biomarkers specifically linked to early life forms of the domain Archaea. The combination of these two potent technologies (GC × GC chromatography and ToF mass spectrometry) GC × GC and TOF-MS has the potential to revolutionize the study of petroleum hydrocarbons, such as in the highly resolved biomarkers shown in Figure 10.

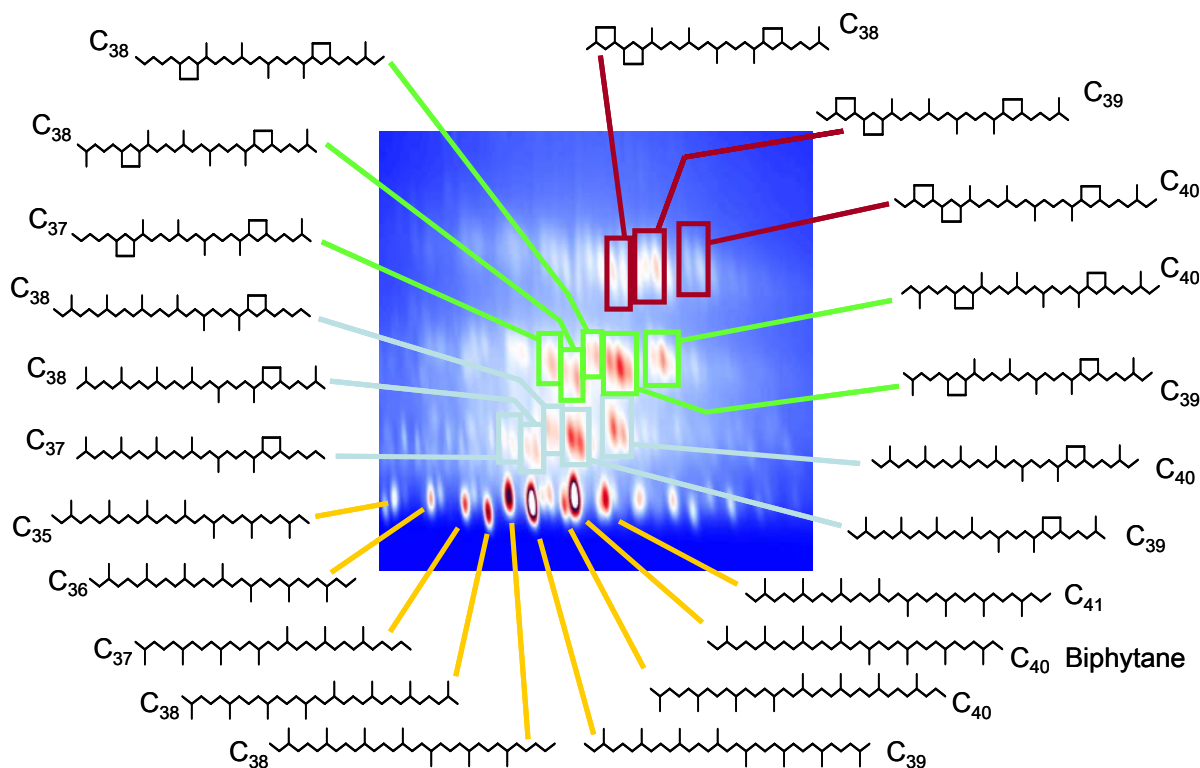


Figure 23. A small portion of a GC × GC chromatogram (C35 thru C40) of an argillitic sediment collected 80 meters below ground level from a gold mine in Timmins, Ontario, Canada. Using a GC × GC instrument equipped with a time of flight mass analyzer, a suite of acyclic (yellow), monocyclic (light blue), bicyclic (green), and tricyclic (maroon) isoprenoid alkane biomarkers derived from early life forms from the domain Archaea were resolved and enough high quality mass spectral information was acquired to make molecular structural assignments for over 20 individual peaks from this one chromatogram.

e. Expanding past the increasing resolution afforded by GC \times GC. As demonstrated in this proposal, GC \times GC can provide nearly complete composition data for petroleum hydrocarbons. However, the potential wealth of physical property information contained in the corresponding two-dimensional chromatograms has remained largely untapped. Recently, our laboratory group has developed a simple but robust method to estimate GC \times GC retention indices for petroleum hydrocarbons. By exploiting *n*-alkanes as reference solutes in both dimensions, we were able to calculate retention indices that were insensitive to the uncertainty in the enthalpy of gas-stationary phase transfer for a suite of representative components (Arey et al. 2005). The resulting two-dimensional retention indices can then be used to estimate the liquid vapor pressures, aqueous solubilities, octanol-water partition coefficients, and vaporization enthalpies of a wide range of petroleum hydrocarbons, which, in turn, can be used to investigate phase transfer processes affecting petroleum hydrocarbon mixtures in the environment. One key result of the powerful relationships developed from these retention indices is that the exact compound structure of each hydrocarbon in each complex mixture does not have to be fully identified in order to model the effects of phase transfer processes on the complete mixture—only the retention times for both dimensions need to be known. This dramatically expands the number of compounds that can be used to model processes like water-washing or gas washing, which are typically limited to less than 20 compounds that are within one or two compound classes in traditional GC (Peters et al., 2005a&b). To highlight this approach, a GC \times GC chromatogram of a typical diesel fuel is shown in Figure 24A. In Figure 24B, the latter image was transformed into what we call a “physical property” plot that arranged each peak based on its estimated water solubility and vapor pressure. By assuming that the rates of volatilization and dissolution of hydrocarbons from this diesel fuel were directly controlled by solute vapor pressure and water solubility values, we calculated the anticipated GC \times GC chromatograms with 75% of its mass lost to either water-washing (Figure 24C) or evaporation (Figure 24D). (Please note that for this modeling exercise, we removed the *n*-alkanes from the images since in actual field samples they are often biodegraded). Clearly, the effects of water washing and evaporation result in significantly different chromatograms. In general, evaporation tends to remove components in a nearly vertical orientation along the first dimension retention axis whereas water washing removes components in a more diagonal direction tilting from the low mass/low

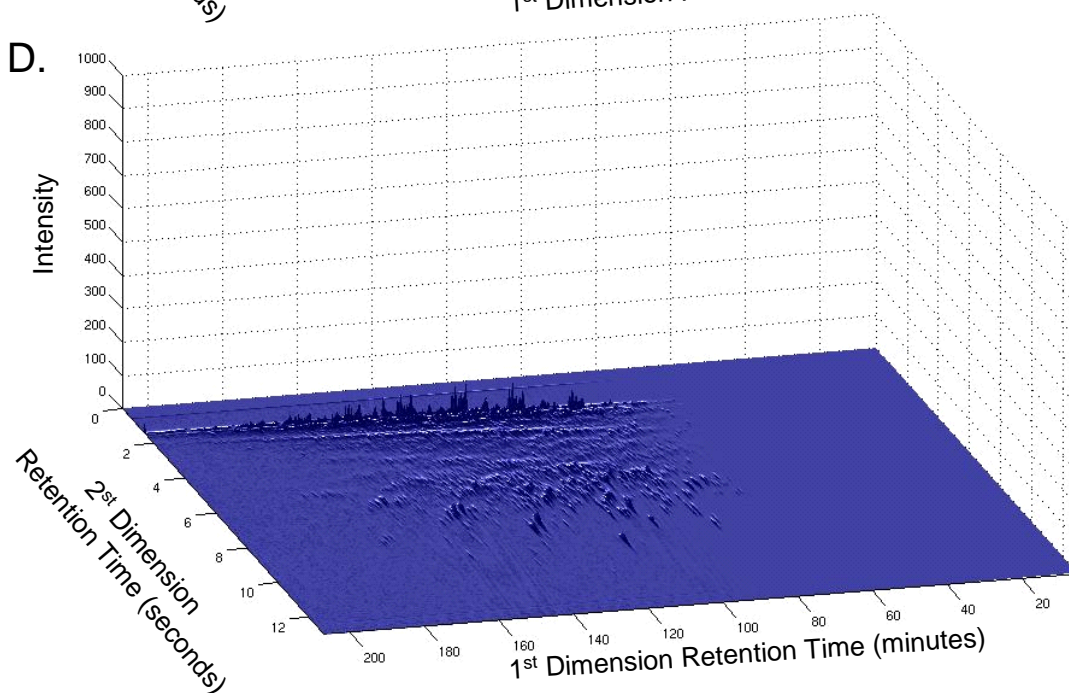
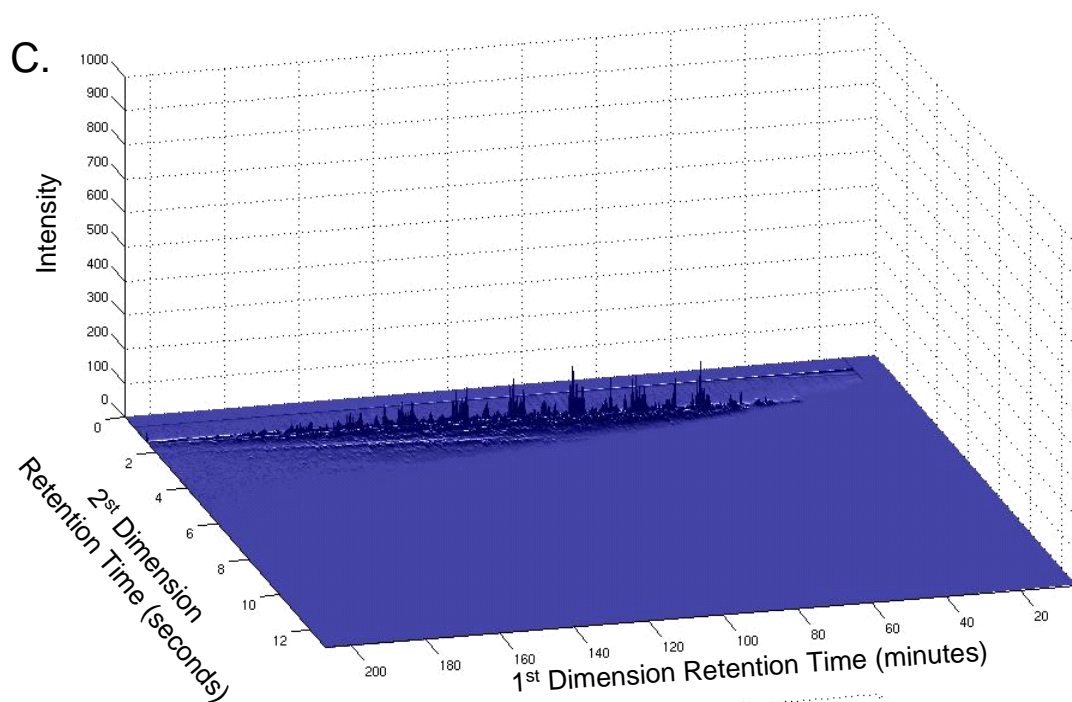


Figure 24C and D. The modeled effects of water washing and evaporation are presented in figures 24C and 24D respectively. The normal alkanes have been removed from both of these images since we commonly observe the loss of these diesel fuel constituents in samples collected in the field. Figure 24C illustrates the effects of water washing on a typical diesel fuel. In this figure, 75% of the diesel fuel mass (after the normal alkanes were removed) is removed using the modeled effects of individual diesel fuel component solubilities. Figure 24D highlights the effects of evaporation. In this figure, 75% of the diesel fuel mass (after the normal alkanes were removed) is removed using the modeled effects of individual diesel fuel component vapor pressures.

boiling components towards the higher mass multi-aromatic ring components of the second dimension. More detailed approaches to match modeled data to field samples are underway with the overall goal to predicatively apportion physical processes acting on petroleum hydrocarbons. For example, one goal would be to quantitatively determine the losses of hydrocarbons due to evaporation versus water washing during the transition in petroleum hydrocarbons from the seep stringer to surface samples discussed previously.

In summary, the increased resolution and physical property estimates afforded by GC×GC will significantly advance our understanding of processes that act on petroleum hydrocarbons in the environment.

G-. Oklahoma Potato Hills Field gases.

During the course of this work, Dr Jeff Seewald of Woods Hole and I had an opportunity to make time series measurements of gases in a more conventional on-shore dry gas field, the Potato Hills field in southeastern Oklahoma. Dr. Robert Hefner, the president of GHK Company and a geologist, has been interested in deep gas sources for some time and became interested in our Gulf of Mexico work. He proposed that we examine the Potato Hills field for episodic pulses of gas coming into the field that might be indicative of on-going filling through faults from deep underlying formations. Dr. Hefner is interested in the possibility that the faults are causing episodic gas pulses to the field from the deep underlying formations.

The Potato Hills Field is southeast of Oklahoma City in the Ouachita Mountains. The Arkoma Basin is just to the north and the gas in the field probably originates from the Arkoma that is strictly a gas province. In Eastern Oklahoma, the Arkoma is sandwiched between the Ozark uplift to the North and the Ouachita Mountains to the south. The boundary between Arkoma tectonic province and the Ouachita Mountain area is assumed to be Choctaw fault. Gentle dipping mountains in Arkoma change to thrust faulting in Ouachita. Until very recently, conventional exploration wisdom was that there are no gases were present in formations in Oklahoma south of the Choctaw fault. Therefore, the GHK development of the Potato Hills Field was a real pioneering effort and highly speculative effort. The Potato Hills fields has been very productive considering its small and low tech nature and has led to other wildcat exploration efforts in this area.

This project was attractive to our group for a number of reasons. First of all, the Potato Hills Field has been productive in an area where production was not predicted using conventional geological wisdom. Secondly, the operators of the field have been very helpful and accommodating in providing samples and well data as well as easy access to the wells. Thirdly, from a sampling logistics point of view, this field is ideal for a long-term time-series study. Even if no changes are detected, it would give our group a better feel for how a "normal" gas field behaves. In addition, there are no complicating effects from oil-gas phase separation because this is a dry gas field. Sample collection quality is assured because gas samples are collected directly from the wellhead into the gas collection cylinders and sampling can be done before the gases enter the water separator. There is also the potential for examining the waters from these wells for polar organic compounds including the carboxylic acids and phenols.

Under this proposal, gases were collected directly from the wellhead for each of the 22 producing gas wells in the field. This work is being continued by Dr. Jeffrey Seewald of Woods Hole under a separate DoE grant. This work involves simultaneous measurement of $\delta^{13}\text{C}$ in methane, CO_2 , and any higher hydrocarbons present along with studies of any deep microbiological communities affecting the gases.

H) Influence of upward seeping gases on the water column

More and more evidence has accumulated both in our own laboratory and others showing that very large volumes of gas are escaping episodically into the ocean from very localized bottom fractures. The episodic and localized nature of these seeps means that they are not being detected by our very limited current methods (primarily visual observations from manned and unmanned submersibles.) Our work on this topic under this grant are described in three publications describing the interaction of gas hydrates, oil, microorganisms, and gas seeps on the floor of the Gulf of Mexico: Wang et al., 2001 entitled: "Contribution of 'Old' carbon from natural marine hydrocarbon seeps to sedimentary and dissolved organic carbon pools in the Gulf of Mexico"; Whelan et al 2005 entitled: "Surface and Subsurface Manifestations of Gas Movement Through a N-S Transect of the Gulf of Mexico, Marine and Petroleum Geology, pp 479-497. and Sassen et al., 2001 "Massive vein-filled gas hydrate: relation to ongoing gas migration from the deep subsurface in the Gulf of Mexico".

In the Green Canyon seep area and in the sediments and reservoirs underlying as well as elsewhere in our transect, the rate of upward movement oil and gas seepage is the big unknown in understanding how these seeps affect resource estimates and might affect global climate change. Our collaborative work with Cornell showed the rate and extent of gas movement to be a key variable driving many aspects of these dynamic gas driven systems in the subsurface, the water column, and ultimately gas venting to the atmosphere. However, it is extremely difficult to measure rates of flow in the subsurface. Measurement of thermogenic gas flux at selected seeps above known oil accumulations would place some important observational limits on upward gas flow.

We are currently working with ocean engineers at WHOI and elsewhere to develop and test in situ instrument packages which can be deployed from a variety of ocean platforms (i.e. manned and unmanned submersibles, gliders, towed packages, and stationary packages deployed over time on the ocean floor) to track the movement of seep oil and gas associated with these dynamic subsurface oil and gas reservoirs. Funding for future work has been obtained from Woods Hole Oceanographic Institution, NSF, NOP/NSF, and NOAA. Initial work is summarized in Whelan 2005:

(<http://oceanusmag.whoi.edu/v42n2/whelan.html>).

A very successful cruise in Sept 2006 in the Gulf of Mexico, Mississippi Canyon 118 allowed initial testing of some in-situ gas and oil flow monitoring equipment to be deployed for time-series measurements on the floor of the Gulf of Mexico.

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