Offshore surface geochemical exploration

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The migration of fluids, both brines and hydrocarbons, in the subsurface is a well established geologic phenomenon.

Surface geochemical exploration is based on the premise that the detection of upward migrated hydrocarbons in near-surface sediments from deep sourced rocks, natural gas, or crude oil accumulations is useful information for the petroleum explorationist. Surface geochemical data historically have been used both to map fields (Horvitz, 1985) and as regional indicators of whether an area is oil or gas prone (Faber and Stahl, 1985; Gervirtz et al., 1983).

The Geochemical & Environmental Research Group (GERG) at Texas A&M University has been developing surface geochemical exploration methodologies through cooperative programs with the oil industry for the last 5 years. GERG has analyzed more than 35,000 samples from the Gulf of Mexico, California, Alaska, North Sea, West Africa, eastern South America and the Caribbean Islands during this period.

Although most of this work has been performed for five or six major U.S. companies, GERG has performed surveys for more than 20 major oil companies. This extensive data base has provided GERG with unique experience in interpreting offshore surface geochemical data.

Direct detection. Historically, most geochemical exploration methods have dealt with the detection of gas (Methane through butanes) in sediment or overlying water (Horvitz, 1985; Sackett, 1977).

These compounds are useful because they are the most mobile phase of petroleum and are easily detected with simple and inexpensive analytical instrumentation. Thee differentiation of dry, gas, and oil prone areas using these data is derived from the concentration and molecular ratios of hydrocarbon gases, as well as methane stable carbon isotopic ratios (delta<13>C). With the development of modern analytical instrumentation, cpapable of measuring parts per billion or lower levels of hydrocarbons, GERG has taken a different approach to surface geochemical exploration for oil. Certain high molecular weight hydrocarbons (HMWHs) and their molecular distributions are unique to mature petroleum hydrocarbons.

GERG has developed and utilized sensitive analytical techniques to detect these HMWHs. Thus, the thermogenic nature of hydrocarbons in near-surface sediments does not have to be inferred solely from gaseous hydrocarbon molecular and/or isotopic compositions.

Total scanninng fluorescence (TSF). Fluorescence is a very sensitive analytical technique that is selectively sensitive to aromatic hydrocarbons.

Fixed wavelength fluorescence was introduced in the 1970s as a supplemental geochemical indicator in gas surveys

(Horvitz, 1985). However, this technique suffers from the fact that oils contain a broad range of aromatic compounds that exhibit fluorescence maxima at various emission/excitation wavelengths. It was for this reason that GERG developed a TSF procedure to characterize the aromatic hydrocarbons in sea-bottom sediments (Brooks et al., 1983). The amount of data obtained by TSF is far superior to fixed wavelength or synchronous scanning techniques.

GERG freeze dries sediments at -40 degrees C. in an effort to minimize the loss of volatile compounds prior to the extraction of HMWHs. The sediments are then ground and Soxhlet extracted for 12 hr with hexane. This technique provides a more efficient extraction of the HMWHs than shaking or ultrasonic extraction. Hexane is used for extraction instead of methylene chloride or a more polar solvent in order to minimize the extraction of more polar compounds. Polar compounds are also found in sea-bottom sediments but are not of interest in the search for petrogenic hydrocarbons. The extracts are rotoevaporated to near dryness and then scanned by TSF between 200 and 500 mm wavelengths.

The advantage of TSF is that the spectra provide a semiquantitative estimate of total HMWH aromatic compounds (fluorescence intensity) and an estimate of the ring-number distribution of fluorescent aromatic compounds. In general, the fluorescent maximum increases in wavelength with increasing number of aromatic rings. Thus, sediment extracts contaminated with migrated oil contain predominantly three-ring and larger aromatic compounds (higher wavelength fluorescence). Sediments recovered over dry, gas, or condensate reservoirs have extracts that exhibit lower wavelength fluorescence.

Figs. 1 and 2 show oil and sediment extract fluorescence patterns over offshore condensate and oil reservoirs.

Another advantage of fluorescence spectra are that they are not susceptible to extensive spectral alteration during biodegradation or water washing, though certainly during severe degradation aromatic distributions are altered. In the near surface, migrated oil can be substantially altered by biodegradation. Kennicutt and Brooks (1983) have shown that fluorescence patterns are relatively insensitive to biodegradation.

Bacteria initially cleave only side chains from aromatic compounds and possibly functionalize the ring structures which result in little spectral alteration. Fluorescence pattern alteration is dependent on ring cleavage which only occurs during severe biodegradation.

Aromatics in general are moderately resistant to degradative removal and this resistance increases with ring number. Oil fluorescence spectra have been shown to have only minor spectral shifts (<10 nm) toward lower wavelengths during macroseepage, separate phase migration. Migration of oil can alter the composition of an oil by various processes including selective dissolution and adsorption.

Capillary gas chromatography (GC). The same sample used for TSF is also analyzed for aliphatic HMWHs by capillary gas chromatography (flame ionization detection).

Internal standards are added before Soxhlet extraction to facilitate the quantitative determination of hydrocarbon levels. Typical gas chromatograms of sediment extracts containing large amounts of upward migrated hydrocarbons and those containing little thermogenic HMWH are shown in Fig. 3.Offshore sediments containing moderate levels of upward migrated HMWHs are characterized by an unresolved complex mixture (UCM), discernible C[15]-C[32] n-alkanes and isoprenoids, and an overpring of odd carbon number n-alkanes >C[23] from terrigenous plant biowaxes. Samples containing high levels of bitumens are often extensively biodegraded containing only an UCM (Fig. 4).

The advantage of GC is that precise quantitative data for the n-alkanes (C[15]-C[32]), isoprenoids, and the UCM are obtained. It is important to obtain quantitative GC data for several reasons.

First, it is possible that the aromatic hydrocarbons could be derived from recycled organic matter, i.e., weathered and river transported older rock material. Significant concentrations of n-alkanes in the C[15]-C[20], range suggest an upward migration of hydrocarbons since hydrocarbons in this molecular weight range do not generally survive

depositional transport from riverine sources. Second, the even number n-alkanes and several isoprenoids are principally sourced in mature, thermogenic hydrocarbons and as such indicate upward migrated petroleum-related hydrocarbons.

Sampling approach. GERG pursues several possible approaches to surface geochemical prospecting depending upon (1) the amount of geophysical and well-control data available in an area and (2) the ultimate purpose of the survey.

One approach is to core specific prospects based on geophysical data and analyze multiple samples per core by TSF and GC. The purpose of this approach is to (1) determine if the area is an oil or gas prospect and (2) rank that prospect as to its oil potential. This approach is often taken in offshore continental U.S. areas since considerable well control and geophysical data already exist, such that companies are often interested in only a relatively few prospects. The coring of specific sites is more economical than broadly based grid-type programs.

In most surveys that employ the specific coring approach, the sole objective of the program is to differentiate between oil and gas prospects.Consequently, many of GERG's surveys have concentrated on continental slope and outer shelf areas where the economics often dictate that oil discoveries are necessary for production.

Our coring and analytical protocol in these areas has been to take deep cores, sample several sections throughout the core to establish trends and intracore varability, and analyze for migrated HMWHs using TSF and GC.

Most companies that use our specific coring approach base their site selection on geophysical evidence of faulting. When using this approach to geochemical prospecting for oil, GERG recommends coring locations over the surface expressions of the fault. Although GERG has shown that coring on faults is not essential to an effective geochemical exploration effort, it appears to be the most successful methodology. All else being equal, cores that show migrated petroleum hydrocarbons in all four core sections analyzed in one or more cores over a prospect enhances that prospect. The presence of petroleum hydrocarbons in sediments over a fault or prospect does not guarantee that a recoverable oil discovery underlies that location. However, it does indicate that oil has been generated in the area and that if a proper reservoir is present it should contain oil.

Conversely, if no oil signature is found over a prospect, this would detract from the prospect. If cores are positioned on top of structures or in the middle of a block of interest more uncertainty is introduced in characterizing the prospect. In this case, GERG uses the presence of an oil signature as a positive indicator, although its absence is not necessarily a negative indicator. However, our experience has shown that nonfault core positioning still provides a reliable indicator of the oil versus gas potential of that prospect.

The approach of coring specific prospects based upon geophysical data for HMWHs is only valid if the purpose of the survey is to evaluate the oil versus gas potential of a prospect. If one's primary interest is gas or gas/condensate, the above mentioned approach is insufficient. Although the intensity of lower wavelength fluorescence, in the naphthalene range, is useful in differentiating between dry and gas/condensate zones, it should be used in conjunction with either headspace or absorbed gaseous hydrocarbon (C_1-C_7) analyses.

Although a few cores per prospect can provide some information on the dry gas versus wet gas/condensate potential of an area, it is generally insufficient for prospect evaluation. The reason being that background C_1-C_7 gaseous hydrocarbons in marine sediments are considerably more variable than the HMWH signature. This is due to the fact that HMWHs are predominantly produced by thermogenic processes deep in the sedimentary column whereas gaseous hydrocarbons can be produced and affected by many biological and physical processes in near-surface sediments. Therefore, if one is primarily interested in gas or condensate more than two to three cores per prospect should be taken.However, GERG again recommends placement of these cores along and across faults over the prospect. We feel this is more productive than a grid approach designed to delineate halos around a prospect where spacing becomes a crucial consideration.

In a frontier area where well control and sufficient geophysical data do not exist, GERG has used a grid approach to delineate the potential oil producing areas from gas/dry areas with success. These grids have had spacing of 1-5 miles

between cores. GERG's experience has been that upward migrated HMWHs are found in a fairly broad area (a few square miles) over significant prospects. The only difference between a core located directly over a leaking fault and one near the structure is often the intensity of the signature.

Therefore, one can approach a frontier area by performing coring on a 1-5 mile grid spacing to differentiate oil-prone areas with possible followup coring on a more tightly spaced grid in anomalous areas.

Sample collection. GERG typically performs surface geochemical surveys using a 150-200 ft workboat as a platform (Fig. 5). The boat is outfitted with the necessary winch, A-frame, shop vans, laboratory vans, PDR van, PDR transducers, etc. necessary to perform heavy piston coring. GERG uses a 2,000 lb piston core with 20 ft of pipe lined with a polybutyrate liner (Fig. 6). The piston core uses a collapsible piston and a bottom trigger released at 30 ft off the bottom.

GERG provides a laboratory clean van in the field for processing samples in a hydrocarbon-free environment. As soon as the piston core is retrieved on deck, sample processing begins. Every effort is made to minimize the time between piston core retrieval, sample processing, and storage at -15 degrees C. GERG's typical sample processing protocol is to take eight 20 cm sections evenly spaced over the length of the core.

The bottom four sections are analyzed and the top four archived. Each section is placed into cans or plastic bags depending upon the analysis requirement. All core samples are stored frozen. GERG maintains a permanent archive of all core samples at TAMU.

Many past geochemical exploration surveys have been of limited value due not only to inadequate analytical methodologies but also to poor sampling design. GERG's experience with geochemical surveys has produced several recommended guidelines to be adhered to in order to produce significant and reliable results.

First, deep penetration of the sediment column is highly desirable. All of GERG's sampling is below 2 m and most often between 3 and 6 m.

Bioturbation can mix surface hydrocarbons derived from pollution or natural seepage to a sediment depth of at least 1 m. There is often significant intracore variability in HMWH levels in the top few meters, which is minimized by sampling below 2 m.

Second, it is important to analyze more than one section per core to obtain reliable, integrated information. This is especially important when only a few cores are obtained per prospect. GERG typically analyzes four sections per core to establish the variability of the parameters measured. This analysis scheme allows one to determine intracore variability and depth trends. Consistent downcore trends provide more conclusive evidence for the stated interpretation as compared to variable down-core signatures.

Data interpretation. From our experience, TSF and GC have been most effective in evaluating seepage areas, although supporting evidence obtained from gas (molecular and isotopic) analyses is also useful. GERG had developed a 0-15 ranking of the oil potential of a prospect based on TSF and GC analyses of four sections per core.

In GERG's data interpretation, the oil potential of a prospect in considered first. Oil shows are initially evaluated on the basis of the fluorescence intensity and the ratio (R) of fluorescence at 360/270 and 320/270 (Em [lambda]/Ex [lambda]). General guidelines are that R values > 1.5 show a significant presence of oil and that R values between 1.0 and 1.5 are lesser oil shows. Increases in the R values above 1.5 often indicate an increasing presence of oil.

However, higher R values also can result from: (1) fluorescence quenching of the lower wavelength fluorescence in high intensity (Int > 1000) samples, (2) extensive biodegradation in high HMWH content sediments, and (3) input of oil of a different composition (R values for oils vary with composition). The R value interpretation is based on the ratio of these two fluorescence intensities giving a qualitative estimate of the ratio of three and four ring aromatics to two ring

aromatics. Three and four ring aromatics dominate the fluorescence of lower API gravity oils and 2 ring aromatics dominate in high API gravity oils (Figs. 1 and 2). The R ratio of an oil is a function of its aromatic composition. R values are interpreted on the basis of a 0-5 scale (Table 1).

Table 1

Guidelines used for ranking the oil potential of a core based on fluorescence	
Evaluation Factor	Rank
Fluorescence intensity *	
>1200	5
800-1200	4
400-800	3
200-400	2
100-200	1
<100	0
R value	
>2.2	5
1.7-2.2	4
1.2-1.7	3
1.0-1.2	2
0.8-1.0	1
<0.8	0

* These are arbitrary units for GERG's given sample size (15 g), dilution (14 ml) and standardized instrumentation conditions.

The next parameter evaluated is fluorescence intensity (Int). It is our experience that on our arbitrary scale Int < 100 is low level and near to background level (for 15 g samples). Intensities between 100 and 1,000 are significant shows and intensities > 1,000 are very good shows. A 0-5 ranking is given to fluorescence intensity for oil potential evaluation (Table 1).

The fluorence signal considered is the nonperylene fluorescence. Perylene is an indigenous aromatic compound not related to migrated hydrocarbons. Perylene is ignored in determining the presence or absence of migrated petroleum hydrocarbons.

To evaluate the quality of the observed fluorescence spectrum, the wavelengths of nonperylene maximum intensity are considered (perylene has an emission lambda of [SYMBOL OMITTED]440 and excitation lambda of [SYMBOL OMITTED]410 and is easily recognized by its spikey spectrum). The nonperylene fluorescence intensity can be obtained from either the 3-D or 2-D presentation (Fig. 7).

The final parameter evaluated is the gas chromatographic data. The basis for this evaluation is that oils contain a complete suite of n-alkanes, pristane, and phytane, whereas in situ organic matter of sediments contains only a relatively few specialized aliphatic compounds (mainly odd carbon number C[25]-C[31] normal alkanes). The gas chromatograms are analyzed at the same dilution and instrument conditions and are thus directly comparable. Internal standards are also added so that the interpreter can adjust for variations in sample extraction and recovery. The patterns are assigned a number from 0 to 5 based on the criteria mentioned.

Individual cores are ranked based on a combination of fluorescence intensity, the R ratio, and gas chromatography (see Fig. 7 for a total ranking of 15 for a sediment extract). A total core ranking on a scale of 0-15 is provided by a simple summing of the three parameters (each based on a 0-5 scale). The rankings are interpreted as:

Oil show ranking

12-15   excellent

 8-12   good

 4-8   fair

 0-4   poor

Gaseous hydrocarbon analytical results can be used to confirm conclusions based on TSF and GC analyses. Generally, the same concepts apply to the gas interpretation as with the previously mentioned parameters. Methane (C[1]), propylene (C[3]<=>), and ethylene (C[2]<=>) are produced by organisms. Though still controversial, there is evidence that small amounts of ethane may be microbially produced. Oil, condensates, and natural gases contain a complete suite of alkanes.

Various parameters reflect a thermogenic gas presence including C[1]/C[2] + C[3], C[2]/C[2]<=>, C[3]/C[3]<=> and percent wetness (SIGMA C[2-4]/SIGMA C[91-4] x 100). The background level of gases is highly variable and must be established for a given area. Therefore, these data are primarily used to support the TSF and GC data.

On a more subtle level, the difference between oil, condensate, and gas can be inferred by the location of the fluorescence wavelengths, the molecular level distribution of the HMWH gas chromatograms, and the gas composition.

Shallow seismic. The shallow seismic (3.5 kHz) can often be utilized to great advantage in surface geochemical exploration.

GERG has shown on the Gulf of Mexico continental slope that shallow seismic "wipe-out" zones (Figs. 8 and 9) are very often associated with high concentrations of upward migrated hydrocarbons (Brooks et al., 1984, 1986). Therefore, the acquisition of shallow seismic data along with deep seismic surveys can provide useful information for subsequent geochemical coring. Specific coring of seismic "wipe-out" zones can confirm the seepage of fresh oil as well as provide samples containing large enough concentrations of oil for correlations with produced oils and/or source rocks. However, "wipe-out" zones may infer various geological conditions not always associated with seepage.

Correlations with produced oils and/or source rocks. In most of the areas worldwide that GERG has samples and/or analyzed, a portion of the survey samples contain extractable bitumens in excess of 100 ppm.

In these samples containing high extractable concentrations, it is often possible to perform gas chromatography/mass spectrometry (GC/MS) analysis for (1) aliphatic and aromatic biomarkers and (2) extract stable carbon isotopic compositions.

These more sophisticated analyses can often be used to match the sediment extract in the core with a specific produced oil and/or source rock. For example, Figs. 10 and 11 show the analysis of a sediment extract from the Barents Sea (off Norway) and a Kimmeridgian oil. There is a close association of the molecular level biomarkers in these samples. Stable isotopes and biomarkers on high hydrocarbon level sediments can be a powerful "fingerprinting" tool in

determining the source of the migrated fluids.

For a discussion of ancillary techniques, onshore surveys, and the authors' summary and references, please contact James M. Brooks, Dept. of Oceanography, Texas A&M University, College Station, Tex. 77843-3146.

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GRAPHIC: Cover Photo, A specially outfitted work boat is used for surface geochemical survey work in the Gulf of Mexico. Surface geochemical exploration uses the information provided by the detection of upward-migrated hydrocarbons. Surface geochemical data have been used in the past to both map fields and as a regional indicator of whether an area is oil or gas prone. In the past 5 years, Texas A&M's Geochemical & Environmental Research Group has developed an extensive data base to help interpret offshore surface geochemical data. GERG, Texas A&M University.; Figure 1, Total scanning, OGJ; Figure 2, Total scanning, OGJ; Figure 3, Gas chromatogram, OGJ; Figure 4, Gas chromatograms, OGJ; Figure 5, The HOS Citation rigged for piston coring by GERG. The winch and A-Frame are located on the starboard side of the vessel; Figure 6, Piston coring operations aboard Texas A&M University's research vessel, the R/V Gyre; Figure 7, TSF and GC, OGJ; Figure 8, A typical hazard survey, OGJ; Figure 9, Two 3.5 KHz seismic, OGJ; Figure 10, Biomarker (triterpanes and steranes), OGJ; Figure 11, Aromatics, molecular level, OGJ