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Surface Geochemical Exploration and Heat Flow Surveys in Fifteen (15) Frontier Indonesian Basins

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ABSTRACT

TDI-Brooks International, Inc., under contract to TGS-NOPEC, conducted an extensive Surface Geochemical Exploration (SGE) survey in 15 frontier basins in Indonesia between April 2007 and March 2008. The Indonesian Frontier Basins (IFB) Project is a multidisciplinary program designed to generate meaningful petroleum exploration data throughout Indonesia's under-explored frontier basins. The SGE program was the final step in this study designed to evaluate hydrocarbon charge in these offshore frontier basins. Core sites were selected based on multibeam bathymetry/backscatter anomalies at sites potentially indicative of seepage combined with 2-D seismic data where available to assist in delineating seep conduits from depth to the seafloor. A 1-km long Chirp subbottom profiler line was acquired over each target site to further refine the core position. Sub-bottom profiles were used to adjust some targets toward sites of potential seepage, or used to avoid hardgrounds that would yield little to no recovery as well as damage the core. Approximately 1,400 piston cores were acquired during the study using the TDI-Brooks research vessel *R/V GeoExplorer*. The 1,000 kg piston core rigs used 3, 6 and 9 m long x 7.5 cm OD barrels, and were positioned with an Ultra-Short Baseline (USBL) navigation system to within 25 m of the pre-selected seabed targets. Core recovery was typically 3 to 8 meters of sediment column, although recovery was affected by bottom type. Many sites with carbonate hard-bottom were selected during this program, and core recovery at such sites was sometimes limited to less than 1 m. Three sediment sections per piston core were typically sampled at about 1 m intervals from the bottom of each core to determine the presence of any thermally sourced hydrocarbons.

Analytical screening measurements included: (1) the fluorescence spectra from bagged sediment sections using dried-sediment solvent extraction, (2) the C_{15+} hydrocarbon concentrations by gas chromatography in the same sediment extracts, and (3) the interstitial light hydrocarbon gas concentrations from separately canned sediment sections using wet-sediment gas partitioning and gas chromatography. From these analyses, screening indicators of migrated liquid and gaseous thermogenic hydrocarbons were developed and used to qualify cores and distinguish them from defined background thresholds for this study area.

Sediment extracts of this study, each representing one section of a core acquired at a site of interest, were qualified for the unambiguous presence of migrated liquid petroleum (thermogenic) hydrocarbons by the following criteria using background thresholds of: TSF Maximum Intensity $\geq 10{,}000$ and UCM ≥ 10 μg/g, or T/D ≥ 1.5. Using these screening criteria, 118 of the 927 cores (13 percent) exhibited unambiguous evidence of liquid petroleum hydrocarbons. This is an unusually high percentage of oil seep shows for our SGE surveys (compared to about 8% on average globally, and <5% on average in frontier basins), and attests to the potential of the region as well as to the quality of the targets selected.

The concentrations of alkane gases in the canned samples typically increased with depth in a core. The strength of the interstitial gas screening indicators as prospecting tools improved significantly with depth over the 3-8m range typically retrieved by our method of piston coring. Coring carbonate hard-bottom sites reduced such depth-recovery at many of the sites, but high concentrations of gas were measured at some of these hard-bottom sites. Sediment samples canned for interstitial gas measurements, each representing one section of a core acquired at a site of interest, were qualified for the unambiguous presence of migrated thermogenic gases in the following manner: (1) an ethane/ethene ratio of at least unity, and (2) the product of the ethane/ethene ratio and the total alkane gas concentration (in ppmV) being at least 100, in at least one of the three core sections. Using these screening criteria, 426 of the 927 cores (46 percent) exhibited unambiguous evidence of thermogenic gas. This is an unusually high percentage of gas seep shows for our SGE surveys (compared to about 25% on average), and attests to the potential of the region as well as to the quality of the targets selected. In our experience, thermogenic gas shows always outnumber the oil shows in a prospective regional study, apparently due to the higher mobility of the gases during migration.

INTRODUCTION

The Indonesian Frontier Basins (IFB) Project is a multidisciplinary program designed to generate meaningful petroleum exploration data throughout Indonesia's under-explored frontier basins. The program covers 15 basins and about one million square kilometers; the basins are entirely offshore and mostly within deepwater. The IFB data package includes regional 2-D seismic to define basin architecture and help identify kitchen areas and traps, high resolution multibeam bathymetry for contiguous sea bottom topographic control, quantitative multibeam backscatter for lithologic characteristics of the sea bottom, accurately navigated piston cores for collection of geochemical samples and ground truth calibration, sub-bottom profiles for shallow stratigraphic control, and high-resolution gravity and magnetic data for basin architecture.

The basins surveyed extend for over 5,000 km and exhibit a wide variety of geologic terrains – tectonic settings include Mesozoic continental margins, Paleogene rifts, Neogene transtensional systems, Tertiary accretionary complexes, forearc basins, and basins of unknown affinity. In virtually all these basins, a case can be made for source, reservoir, and trap; the key missing ingredient is *charge*. The key component of the Indonesian Frontier Basins Project is the SeaSeep™ program which attempts to define charge by ground-truthing hydrocarbon seeps on the seabed. SeaSeep combines large volumes of high resolution multibeam sonar, sea-bottom coring, gravity, magnetics, 2-D seismic and hydrocarbon geochemistry information in one data suite to explore a basin via surface geochemical prospecting (SGE) juxtaposed with robust structures.

SGE is a petroleum exploration technique based on the premise that upward migrated petroleum from deep source rocks and reservoirs can be detected in near-surface sediments by acquiring and chemically analyzing sediment cores at qualified seabed sites. The high cost of deepwater exploration has made the identification of seafloor micro- and macro-seeps a well-accepted risk reduction methodology. Such surveys can provide evidence of active oil generation and migration, aid assessment of most prospective areas, and can provide an integrated seep signal over time. In addition, analyses of samples can be used to characterize oil properties, maturity, and source rock type. The spatial coincidence of seepage and geologic structure allows for the identification of migration pathways from the reservoir to the sea floor. Geophysical and/or multibeam surveys are used to select coring targets based on surface expression of faults and other features related to migration conduits. In order to pinpoint and further validate a feature to be cored, corresponding survey lines are executed with a sub-bottom profiler just prior to core acquisition. The purpose of this effort is to locate the best core target location as well as to collect information of sub-bottom structure and bottom hardness.

TDI-Brooks International, Inc. performs surface geochemical surveys using a vessel outfitted to perform 3 to 9 m depth piston coring. Piston coring offers several advantages over gravity coring, including: (1) greater penetration depths, (2) better core recovery, and (3) higher quality samples. In particular, sediment gas concentrations can increase several orders of magnitude through the 2 to 5 meter depth range in marine sediments, greatly enhancing the types and quality of measurements that can be made on the samples. Analyzing three equally-spaced sediment sections for each retrieved sediment core allows for the determination of depth trends in measured parameters. Geochemical samples are stored in a -20°C freezer until analysis in shore-based laboratories. Chemical analysis of these samples seeks to reveal unambiguous evidence of thermogenic hydrocarbon gases and/or liquids that have migrated upward. Such evidence is used to prove up charge and to further qualify samples for more detailed biological marker analysis designed to gain information about petroleum age, maturity, and quality. Screening indicators have been developed from the comparative analysis of thousands of samples from marine basins around the world for interstitial gases, total scanning fluorescence, and C_{15+} hydrocarbons by gas chromatography (GC).

Interstitial gas analysis refers to the determination of interstitial light hydrocarbon gases including methane, ethene, ethane, propene, propane, iso-butane, n-butane, iso-pentane, and n-pentane in marine sediments. The light hydrocarbon gases are only slightly soluble in water, so they can be extracted from a wet sediment sample into an adjacent gas phase by a partitioning procedure. Once in the gas phase, they are easily measured by gas chromatography. The natural presence of high levels of C_{2+} alkane gases serves as a good indicator of migrating thermally-sourced gas, because ethane, propane, the butanes, and the pentanes are not locally produced and sustained at more than a few ppmV concentration levels in near-surface marine sediments. Background ethane/ethene concentrations are typically stable in marine shelf sediments at around 1:2 (or with ethane/ethene ratios of 0.5). Each of the “first 5” light hydrocarbons, methane, ethene, ethane, propene, and propane, is present at easily measurable (>0.01 ppmV) concentrations in shelf and slope sediments due to microbial activity. Methane, ethene, and propene are microbially produced whereas ethane and propane are apparent degradation or diagenetic by-products from the alkene gases. Microbial activities decrease with increasing water depth from the shelf to the slope in marine sediments, and the levels of the light hydrocarbons decrease accordingly. With such decreases, diffusional processes tend to balance the concentrations of the alkane:alkene pairs, such that the ethane/ethene ratio in sediments further offshore grows closer to 1:1. When alkane gas concentrations in a sample are high enough, the measurement of the ratio of the stable isotopes of carbon in each of the light alkanes can be made and used as an additional indicator of migrated thermogenic gas.

Total Scanning Fluorescence (*TSF*) analysis is a semi-quantitative analytical technique using the UV light to cause trace quantities of chemical compounds in samples to fluoresce. It is applied to sediment extracts and is selectively sensitive to aromatic compounds. As such, TSF is a valuable tool for detecting the presence of petroleum related liquid hydrocarbons in sediments. Increasing TSF intensity (expressed in arbitrary intensity units) generally corresponds to increasing aromatic hydrocarbon concentrations in sediment extracts. Naturally-occurring recent organic compounds can be distinguished from thermogenic aromatics in samples by the use of specific excitation and emission spectral frequencies.

C_{15+} hydrocarbons by GC (*$C_{15+}GC$*) analysis refers to the determination of individual normal alkanes containing 15 through 34 carbons using gas chromatography with flame ionization detection. C_{15+}GC analysis is used to quantify petroleum-related normal alkanes (n-C_{15} to n-C_{34}), isoprenoids (pristane and phytane), and the unresolved complex mixture (UCM) generally associated with extracts that contain oil. The quantification of this UCM or “hump” feature of a gas chromatogram provides a measure of extractable hydrocarbon concentration in biodegraded samples. The UCM hump typically comprises the majority of hydrocarbons detected by GC/FID in marine sediments. For severely biodegraded extracts, the n-alkane and isoprenoid concentrations are largely indeterminate. Sites associated with recent, terrigenous organic matter typically have a low UCM concentration and enrichment in long-chain (greater than n-C_{23}) n-alkanes with odd-carbon predominance. The detection of a complete suite of n-alkanes plus pristane and phytane is especially strong evidence of the existence of migrated petroleum. A core extract with an elevated UCM concentration, an elevated TSF intensity, and individual C_{15} to C_{34} hydrocarbons showing a typical oil pattern, likely contains migrated petroleum.

Samples shown to contain migrated petroleum based on the TSF, C_{15+}GC, and/or interstitial gas data are further analyzed for saturate and aromatic biological markers and stable carbon isotopic compositions of various chemical constituents. These more detailed analyses can usually confirm the presence of migrated petroleum and are often used to match hydrocarbons in the sediment extract with a specific maturity or age of oil or source rock.

METHODS

Field Procedures

The core acquisition for this study was conducted from April 2007 through February 2008 aboard the TDI-Brooks survey vessel *R/V GeoExplorer*: The vessel was mobilized with a piston coring kit ready to acquire several hundred cores without re-supply. The piston-coring rig was comprised of a trigger assembly, the coring weight assembly, core barrels, tip assembly, and piston. The coring weight assembly was made up of the 900 kg lead coring weight with a coupling for barrel attachment. The core barrels used were in lengths of 3, 6, and 9 m. The core rig tip assembly consisted of the core cutter, core catcher, and the core liner. Single-use butyrate liners of 7.5 cm OD (outer diameter) lined the core-barrel and contained the acquired sediment cores.

The sub-bottom profiler mounted on *R/V GeoExplorer* was an EdgeTech Full Spectrum "chirp" imaging system. This is a wideband Frequency Modulated (FM) subbottom profiler that generates cross-sectional images of the seabed and collects digital normal incidence reflection data over many frequency ranges. The system transmitted an FM pulse that was linearly swept over a full spectrum frequency range (also called "chirp" pulses). The reflections measured by the system were displayed as shades of color on a computer monitor. This system used specially designed hull-mounted transducers with characteristics best suited for "chirp" transmissions. These transducers had a frequency response from 500 Hz to 12 kHz and were used for both transmitting and receiving acoustic signals.

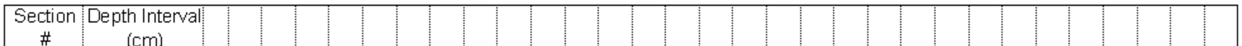
R/V GeoExplorer was outfitted with a working and previously validated C&C Technologies, Inc., C-Nav full differential GPS navigation system, a Fugro Pelagos, Inc. WinFrog (rev 3.7) navigation software package, and a gyro. In addition to these navigation components, a Kongsberg HiPAP 350P USBL system was installed and integrated into this system. The USBL system was re-calibrated at the dock during mobilization immediately prior to the survey. The USBL transducer had a built in roll/pitch sensor. The USBL transponder used on the piston core rig was a Kongsberg MST342. This was chosen for its depth rating, high source level, and narrow beam (±20°, which is will-suited to the near-vertical geometry of piston coring). The topside controller was interfaced to the WinFrog navigation system so that real-time position of the deployed transponder on the core rig could be displayed.

Sets of previously high-graded core targets were entered as waypoint files into the WinFrog navigation system. To select these core targets, the multibeam bathymetry and backscatter data had previously been integrated with all other SeaSeep data (seismic, gravity, magnetics) for interpretation of structural trends and basinal elements and to define the overall petroleum systems. Prospective targets had been identified throughout the area based upon geomorphic elements (faults, mud volcanoes, pockmarks, etc.) and within each geomorphic element, specific backscatter anomalies. Targets were selected on backscatter anomalies alone in the absence of any bathymetric feature. The proposed core targets were spread throughout the survey area and tied to specific basins, leads, or kitchens in order to test the various elements of the petroleum system(s). Targets were also proposed by different individuals to benefit from different perspectives. Prospective targets were rated and submitted to the field team based upon geomorphic *freshness, strength*, or *character* of the backscatter response, proximity to seismically defined leads and pathways, relation to source kitchens interpreted from seismic and potential fields data, and proximity to satellite synthetic aperture radar (SAR) anomalies or surface slicks observed during the survey program.

Sub-bottom profiling survey lines were run over each core target immediately prior to core acquisition. Ship speed during sub-bottom profiling was typically 5 knots. Particular features on the seabed were identified and matched against the data originally used to high-grade each prospective site. The sub-bottom profiles were used for core target adjustment during coring operations. The primary incentive for target relocation was the alignment with specific structural and sedimentological features manifested on the seabed, presumably as a result of past or active thermogenic seepage. Such features included faults, mud mounds, volcanoes, fractures, carbonate hard-bottom, upwelling features, and any other feature potentially associated with the migration of thermogenic fluids. Sub-bottom profiler data were also used to relocate cores away from sites that showed evidence of seafloor hardgrounds (high amplitude first return); cores were typically adjusted to the interpreted edge of the hardground. In some cases, distortion (wipeouts) in high-resolution data, presumably due to gas in sediments, caused the relocation to maximize the potential of coring into that zone. Other targets were adjusted to minimize risk of core rig failure or damage due to carbonate hard-bottom. Targets were also sometimes relocated to increase core recovery. Core recovery was, on occasion, greater than 8 m in extremely soft sediment, or less than a fraction of 1 m in sand or carbonate hard bottoms. After each core was extracted from the seabed, the core rig was retrieved, the core in the liner extracted from the rig, and the core sample immediately processed.

Upon retrieval, the sediment core liner was labeled in 20 cm sections. The labeled core was then cut into sections with a special core liner cutter developed by the Ocean Drilling Program (ODP). This liner cutter eliminated plastic shavings that could contaminate the sediment. Three core sections per core were sampled based on the specifications shown in *Table 1*. Geochemical samples were separated by 1m sections of undisturbed sections for later CAT scanning. Following geochemical sub-sampling all of the remaining core sections were capped and stored vertically for later studies (including sedimentology, paleontology, mineralogy, and seep biology). Samples to be dried and extracted were extruded directly into labeled plastic bags by inverting each bag inside-out and sampling about one-third of each 20 cm section length. Each bag was then carefully re-inverted and sealed, thus eliminating contact with extraneous materials and minimizing contamination. Another one-third of each section was used to sample for interstitial gases. After these sections of interstitial-gas core sample were placed into a 500 mL can, 165 mL of clean, degassed seawater with bactericide was added. The can was quickly purged with nitrogen gas to remove atmospheric gases before sealing. All samples were frozen at -20° C. Every effort was made to minimize the time between core retrieval, sample processing, and frozen sample storage.

Table 1. Sample sub-sectioning strategy for geochemical cores.



Section #	Depth Interval (cm)		
1	0	to	15
1	15	to	20
2	20	to	40
3	40	to	60
4	60	to	80
5	80	to	100
6	100	to	120
7	120	to	140
8	140	to	160
9	160	to	180
10	180	to	200
11	200	to	220
12	220	to	240
13	240	to	260
14	260	to	280
15	280	to	300
16	300	to	320
17	320	to	340
18	340	to	360
19	360	to	380
20	380	to	400
21	400	to	420
22	420	to	440
23	440	to	460
24	460	to	480
25	480	to	500
26	500	to	520
27	520	to	540
28	540	to	560
29	560	to	580
30	580	to	600

Laboratory Procedures

Core sections for interstitial gas measurements were brought back from the vessel frozen in labeled cans. The interstitial gases were first equilibrated with the nitrogen headspace inside each can by vigorous agitation with a high-speed shaker for 5 minutes at 40° C, and then sampled through the septum of the equilibrated can with the needle of an automated sampler. One mL of gas was injected onto a packed, temperature-programmed GC column. The gases were separated and then detected by flame ionization. The gas concentrations in nitrogen were converted arithmetically to concentrations originally in the sediment by measuring the volumes of sediment and headspace in the can and by knowing the partition coefficient of each gas under the equilibration conditions. When a can contained sufficient thermogenic gas for stable carbon isotope measurements, gas from the can was injected directly into a gas chromatograph coupled to a Finnigan MAT 252 mass spectrometer via a Ni-Pt-Cu organic carbon combustion reactor at 940° C. A 60 m megabore column packed with a porous divinylbenzene polymer with He carrier gas was used to separate the analytes. All carbon isotope ratios were expressed in the δ vs. PDB convention of Craig, 1953.

Core sections destined for extraction and analysis for TSF and C_{15+} hydrocarbons were brought back from the vessel frozen in labeled plastic bags. The samples were thawed at room temperature, squeezed from each bag into pre-cleaned, labeled glass jars, and placed in a convection oven to dry at 40°C. Once dry, each sediment sample was transferred to a clean mortar and pestle, ground to a powder and placed back into its glass jar for extraction. Before daily processing, all mortars and pestles were combusted at 400°C for at least 4 hours. Between samples, each mortar and pestle set was scoured with a detergent solution, rinsed thoroughly with water, then acetone, and finally hexane.

An automated extraction apparatus (Dionex ASE200) was used to extract hydrocarbons from 15 g of pre-dried sediment from each core section. The extractions were performed using hexane inside stainless-steel extraction cells held at elevated temperature and solvent pressure. Once sediment had been added to a cell, 100 µl of surrogate standard solution was added to monitor extraction efficiency directly onto the sediment in the cell using a calibrated micropipettor. The resulting extracts were transferred from the heated extraction cells to glass collection vials. Pre-cleaned, activated copper was added to each collection vial in order to minimize matrix interference. Extracts were each concentrated to a final volume of 8-mL using an evaporative solvent reduction apparatus (Zymark TurboVap II). Prior to sediment extraction, glassware was thoroughly cleaned with a detergent solution and rinsed with reagent water. After air-drying, glassware openings were covered with clean aluminum foil and the glassware was combusted at 400°C for a minimum of 4 hours. Volumetric glassware was rinsed three times with methanol to remove water, then rinsed three times with methylene chloride and sealed with solvent-rinsed aluminum foil.

A three-dimensional fluorescence spectrum was acquired for each extract using a Perkin-Elmer Model LS 50B fluorometer. Each extract was poured into a clean glass cuvette, placed in the pre-calibrated fluorometer, and scanned over a specified range of excitation wavelengths while measuring the resulting fluorescence emission intensities over a specified range of emission wavelengths. The maximum intensity, the excitation and emission wavelengths that produced the maximum intensity, the three-dimensional fluorescence spectra, and a two-dimensional map view of the spectra were used to evaluate the sample extract for the presence of petroleum related aromatic hydrocarbons. If, during the fluorescence scan, the maximum intensity exceeded 10,000 intensity units, the sediment extract was diluted by volume and re-analyzed. A method blank was extracted and fluoresced with each sediment extraction batch. An oil spike was also extracted and fluoresced with each sediment extraction batch. If specified quality indicators were not in the acceptable range, the samples from that sample batch were re-extracted.

The extracted sediment sample was then concentrated by solvent reduction, an internal standard was added for quantitation, and a portion of the extract was injected onto a capillary GC column. The analytes were separated and detected by flame ionization. Each extraction batch was analyzed as an analytical set including samples, a method blank, and an oil spike. The gas chromatograph was temperature-programmed and operated in split mode. The capillary column was a 30 m long by 0.25 mm ID and 0.25 µm film thickness. Concentrations of analytes in samples were calculated based on the concentration and response of internal standard compounds. For UCM concentration, the total area under the chromatogram was measured between the retention time of n-C_{15} to the retention time of n-C_{34}, minus the total area of all resolved analytes.

When an extract contained sufficient thermogenic component for biological marker analysis, another portion of the dried sediment sample was extracted with methylene chloride. After evaporation of the solvent, the extract was weighed and expressed as ppm relative to the dry weight of the sediment. Asphaltenes were precipitated using n-hexane, and the C_{15+} deasphalted fractions were separated into saturate hydrocarbon, aromatic hydrocarbon, and nitrogen-sulfur-oxygen (NSO) fractions using gravity-flow column chromatography, employing a 100-200 mesh silica gel support activated at 400° C prior to use. Pentane was used to elute the saturate hydrocarbons, benzene was used to elute the aromatic hydrocarbons, and methylene chloride/methanol (50:50) was used to elute the NSO fraction. Following solvent evaporation, the recovered fractions were quantified gravimetrically. The C_{15+} saturate hydrocarbon fraction was subjected to molecular sieve filtration after the technique described by West *et al*. (1990) in order to concentrate the branched/cyclic biomarker fraction. Stable carbon isotopic compositions of the C_{15+} saturate and aromatic hydrocarbon fractions were determined using the combustion technique of Sofer (1980) with a Finnigan Delta E isotope ratio mass spectrometer.

In order to determine sterane and terpane biomarker distributions and quantities in these high-graded samples, GC/MS analyses of C15+ branched/cyclic hydrocarbon fractions were performed using a Hewlett Packard 5890 GC interfaced to a HP 5971 mass spectrometer. The column (50 m x 0.2 mm; 0.11 µm film thickness) was temperature programmed from 150° C to 325° C at 2°/min and then held for 10 min for saturates, and 100° C to 325° C at 3°/min for aromatics. The mass spectrometer was run in the selected ion mode, monitoring ions m/z 125, 177, 191, 205, 217, 218, 221, 231 and 259 amu for saturates and m/z 133, 178, 184, 192, 198, 231, 253 for aromatics. In order to determine absolute concentrations of individual saturate biomarkers, a deuterated internal standard (d_4-C_{29} 20R sterane; Chiron Laboratories, Norway) was added to the C_{15+} branched/cyclic hydrocarbon fraction. Response factors were determined by comparing the mass spectral response at m/z 221 for the deuterated standard to hopane (m/z 191) and sterane (m/z 217) authentic standards. These response factors were approximately 1.4 for terpanes and 1.0 for steranes. Concentrations of individual biomarkers were determined from the response factors.

Multivariate statistical analysis was used to distinguish both source rock depositional environments and genetically related oil families using pertinent geochemical variables. Samples were classified by comparison to the oil families previously analyzed. Analytical groupings usually represent separate oil families or systems that share a common source. Most of the geochemical variables chosen for statistical treatment were dependent more upon source than on thermal maturity. Maturity trends within oil families determined by cluster and principal component analyses were then plotted based upon thermally sensitive biomarker ratios.

RESULTS

Compositions of Sediment Extracts

At the time of writing (late February 2008), core extracts have been analyzed from 11 of 15 basins for the IFB program offshore Indonesia. To date for this study, 1,884 of the 2,468 extracts analyzed for fluorescence had TSF Maximum Intensities below 10,000 intensity units. Five hundred twenty-five (525) extracts were between 10,000 and 100,000 intensity units, 44 extracts were between 100,000 and 1,000,000 intensity units, and 15 extracts had Maximum Intensities greater than 1,000,000 intensity units. A TSF Maximum Intensity value of 10,000 units is used as a starting threshold for this screening indicator for basins around the world. This means that samples with values above 10,000 are candidates for further qualification as exhibiting thermogenic seepage. Samples that exhibit intensities of 100,000 or more were also candidates for biological marker analysis, where detailed information about the quality, age, and maturity of the oil seep may be gleaned. Biological markers defined multiple sources with varying maturities for seeps discovered in this program. This information not only proves up charge in the various basins, but also adds to the understanding of the petroleum systems and migration pathways associated with the seeps.

Two thousand three hundred fifty-eight (2,358) of the 2,468 extracts analyzed for hydrocarbons had UCM concentrations less than 10 μg/g, 87 extracts had UCM concentrations between 10 and 100 μg/g, 18 extracts had UCM concentrations between 100 and 1,000 μg/g, and five extracts had UCM concentrations greater than 1,000 μg/g. A UCM concentration of 10 μg/g is used as a confirming threshold (after TSF qualification) for this screening indicator for basins around the world. This means that samples with UCM concentrations above 10 μg/g are candidates for further qualification as exhibiting thermogenic seepage. It should be noted that extracts with as little as 10 μg/g UCM may contain detectable biological markers.

The relationship between UCM concentration and TSF Maximum Intensity for all extracts of this study is shown in *Figure 1*. Data from previous programs in Angola and Nigeria are included for comparison. Most of the extracts in any SGE program plot below the defined background thresholds for one or both screening indicators, illustrating how challenging it is to find and sample seepage in the deep marine environment, even in prolific known hydrocarbon provinces. Many of the extracts analyzed as part of the IFB program, however, plot above the threshold value for both TSF Maximum Intensity and UCM concentration. Extracts that plot in this *upper-right quadrant* likely contain migrated petroleum, and extracts that plot very high in this quadrant certainly contain migrated petroleum. Such samples often yielded sufficient quantities of hydrocarbons, upon methylene chloride extraction, for the measurement of specific biological markers. There is also a trend of increasing UCM concentration as TSF Maximum Intensity increases, indicating a general increase in the presence of petroleum-related saturate hydrocarbons (evaluated using gas chromatography) with an increase in aromatic hydrocarbons (evaluated using fluorometry). Not only is this trend important for establishing the relationship between these two thermogenic indicators for a particular area, but also, the extrapolation of the trend down to the background levels of UCM concentration and TSF Maximum Intensity confirms and validates the background threshold values for this pair of indicators.

The *thermogenicity correlation* of these two screening indicators has two attributes that have been observed in sample sets analyzed from deepwater regimes all around the world: (1) the trend is linear over several orders of magnitude, and (2) the trend disappears downward into the values of the background samples at about the same point worldwide. In a few basins studied, contributions of recent organic matter raise the TSF Maximum Intensity level, and cloud the resolution of this threshold, and shift it to the right on the plot. This may be the case in the IFB study. In such a case, the individual chromatograms are examined in detail to determine if liquid hydrocarbon seepage in samples that plot near the prospective

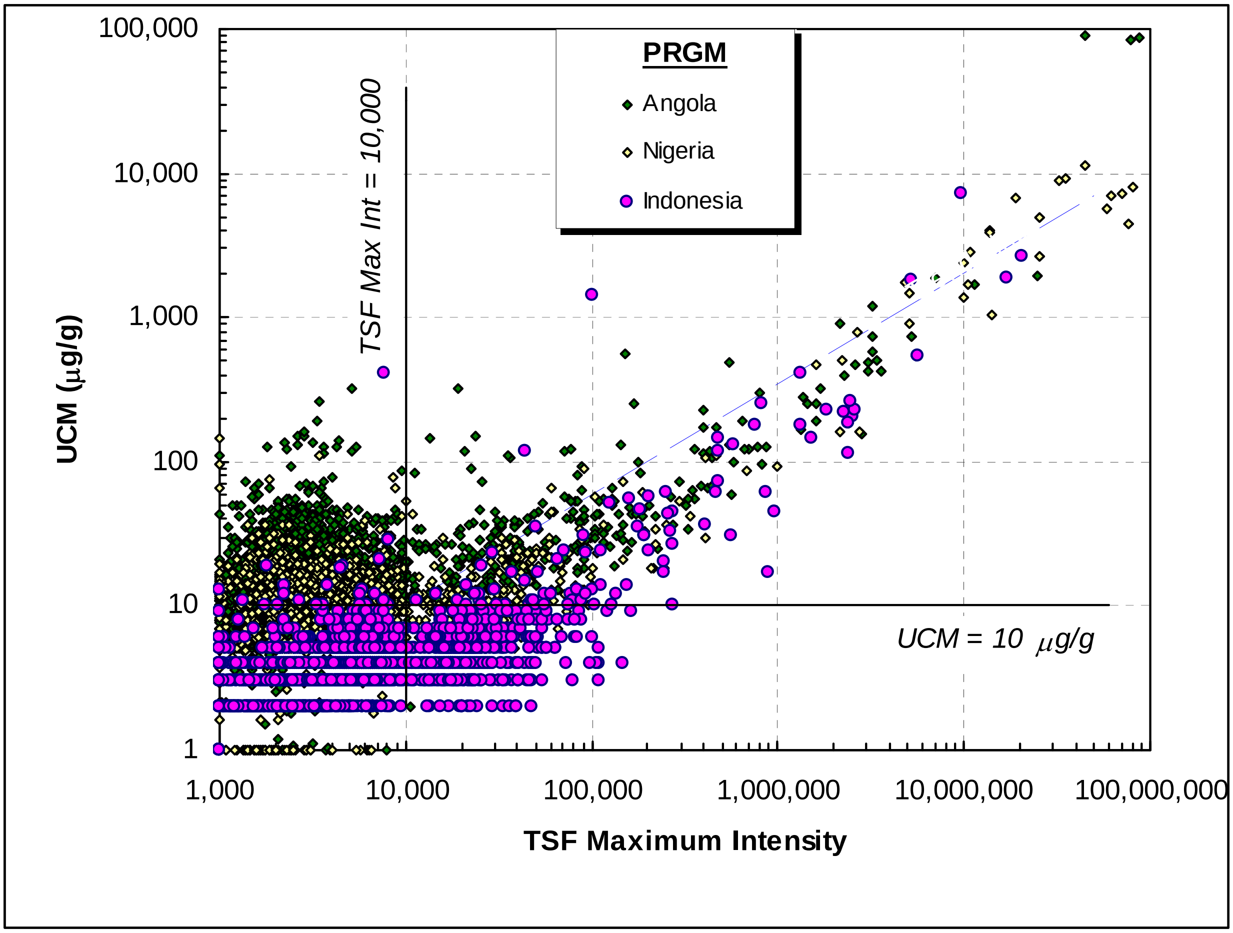


Figure 1. TSF Maximum Intensity vs. UCM concentrations for all sediment extracts.

threshold can be discerned. Alternatively, this right-shift on the plot of the thermogenicity correlation may be explained by fresh oil seepage to the seabed. So-called *fresh oil seeps* have been found in the Gulf of Mexico and the Caribbean basins, but until this IFB study, virtually no where else in the world. In contrast to the highly biodegraded seeps that have been found offshore Nigeria, Angola, and Brazil, this fresh-oil seep exhibits a full suite of individual, nonbiodegraded alkanes in its extract chromatogram, and a commensurate relative decrease in the UCM concentration. In such a case, the thermogenicity correlation of the TSF Maximum Intensity and the UCM concentration is shifted to the right on plots represented by *Figure 1.* Fresh oil seeps indicate a high flux of liquid hydrocarbons migrating from the reservoir to the seabed, the natural system not having had sufficient time to effectively biodegrade the migrating alkane hydrocarbons before we sampled them from the seabed.

To screen for the presence of fresh-seep oils in the samples, an additional thermogenic liquid hydrocarbon indicator was used to further evaluate sediment extracts. Such candidates could be passed over if TSF Maximum Intensity and UCM concentration were the only screening indicators examined. An examination of the chromatograms from a world-wide suite of study areas shows that the odd-carbon-numbered normal alkanes n-C_{27}, n-C_{29}, n-C_{31}, and n-C_{33} are predominant in sediments that have a significant contribution from plant waxes. This occurrence is considered an indicator of a *diagenetic origin* of the alkanes. A useful hydrocarbon indicator ratio is calculated by subtracting these from the sum-n-alkane value and defining the following:

$$\mathbf{T/D} = \mathbf{Thermogenic/Diagenetic} = \left[\frac{\sum \text{n-Alkanes} - \left(C_{27} + C_{29} + C_{31} + C_{33}\right)}{\left(C_{27} + C_{29} + C_{31} + C_{33}\right)} \right]$$

A low T/D Ratio in an extract would indicate a diagenetic origin when accompanied by a low UCM concentration. An extract with a high T/D Ratio may contain petroleum hydrocarbons even when accompanied by a low UCM concentration. A high TSF Maximum Intensity would be supporting evidence that the extract contains traces of fresh oil. The relationship between the T/D Ratio and TSF Maximum Intensity for all extracts of this study is shown in *Figure 2*, which is a plot of all samples except those that exhibited UCM concentrations above the 10 µg/g threshold. Those samples omitted from this plot had already been qualified as containing oil seepage based on their TSF and UCM values. *Figure 2* illustrates that dozens more sample extracts having low UCM concentrations also exhibited traces of oil seepage. From examination of the individual chromatograms, a T/D Ratio of 1.5 was used as a background threshold for this screening indicator. This means that samples with T/D Ratios above 1.5 were qualified as exhibiting thermogenic seepage. In addition, the extracts that plot in the upper-right quadrant of this plot have confirming high TSF Maximum Intensities, and were candidates for biological marker measurements.

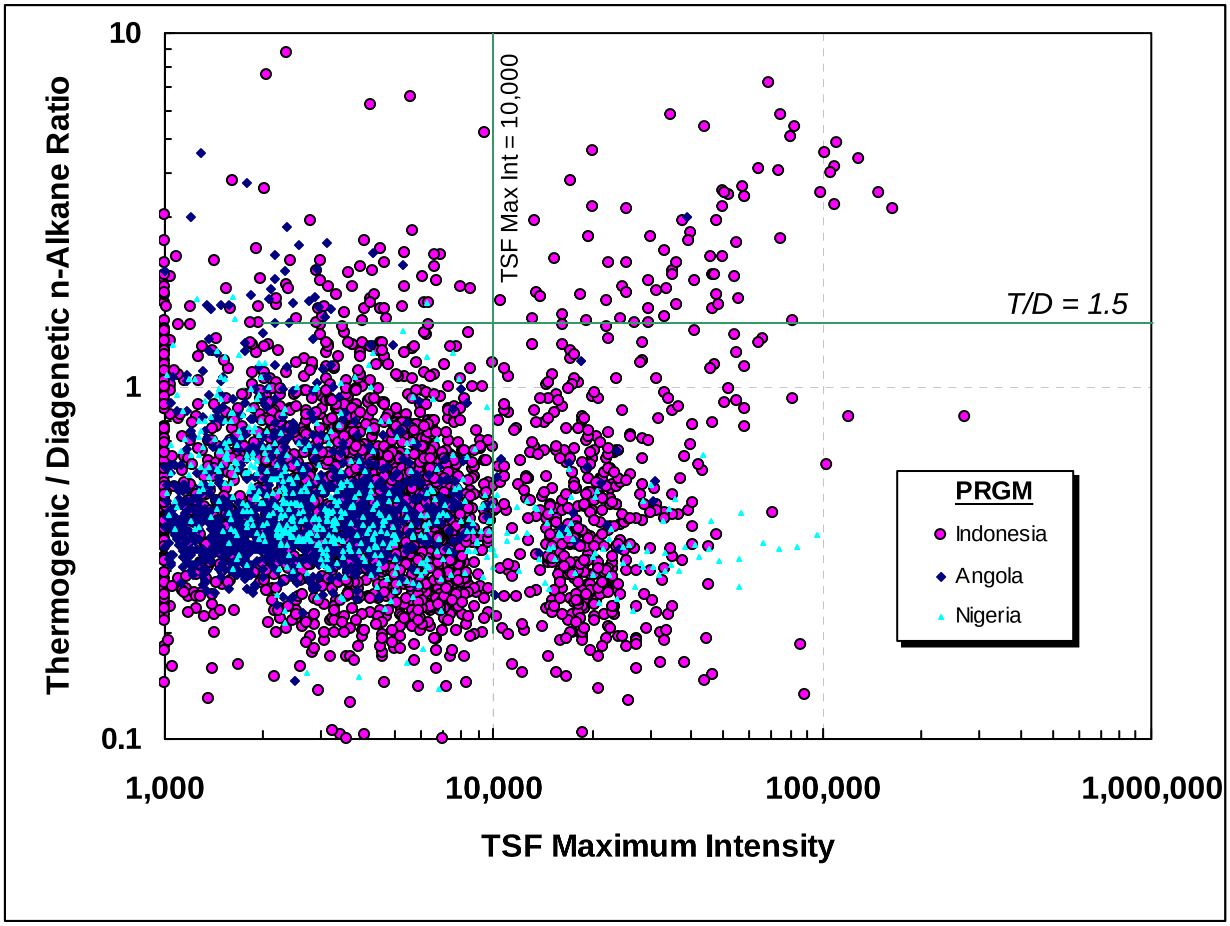


Figure 2. TSF Maximum Intensity vs. T/D Ratio for extracts containing less than 10 µg/g UCM.

Data from previous programs in Angola and Nigeria are included for comparison in *Figure 2,* vividly illustrating that the T/D Ratio is not useful in these deepwater regimes. This is because their have been no fresh oil seeps sampled there. The T/D Ratio is a valuable oil indicator for the Gulf of Mexico and offshore Trinidad where sediment extracts typically contain only-partially-biodegraded oil and have low UCM concentrations accompanied by a complete suite of n-alkanes. This ratio is not indicative for most deepwater areas of the world, because extracts containing migrated thermogenic liquid hydrocarbons almost always have very degraded petroleum. Surprisingly, extracts analyzed as part of the IFB show a similar character to the Gulf of Mexico and offshore Trinidad, with low UCM concentrations accompanied by a complete suite of n-alkanes. As such, a lower T/D Ratio limit was found to apply to the IFB samples as a valuable indicator of oil. By inclusion of the T/D ratio, three tools are available to use for screening and evaluating sediment extracts for liquid petroleum hydrocarbons

Most of the extracts in any SGE program plot below the defined background thresholds for all of these three extract screening indicators, illustrating how challenging it is to find and sample seepage in the deep marine environment, even in prolific known hydrocarbon provinces. Many of the extracts analyzed as part of the IFB program, however, plot above the threshold value for TSF Maximum Intensity, UCM concentration, and/or T/D Ratio. Extracts that plot in these *upper-right quadrants* likely contain migrated petroleum, and extracts that plot very high in these quadrants certainly contain migrated petroleum. Such samples often yielded sufficient quantities of hydrocarbons, upon methylene chloride extraction, for the measurement of specific biological markers. Sediment extracts of this study have been qualified for the presence of migrated liquid petroleum hydrocarbons in the following way:

(1) If the TSF Maximum Intensity was greater than the threshold, the extract was considered a candidate, and
(2) the extract was confirmed as qualified by a UCM concentration of more than the threshold value, or
(3) if the TSF Maximum Intensity and the UCM were both less than their threshold values, a sample extract was qualified if its T/D Ratio is greater than the threshold value.

Examination of each of the chromatograms associated with near-threshold samples confirmed that virtually all of the samples that plot above these thresholds contain low level thermogenic liquid seepage.

Although a detailed discussion of biomarkers is beyond the scope of this paper, extract samples contained enough evidence of migrated oil to be put forward for biomarker analysis. Note that biomarker analysis is rare in frontier basin SGE studies due to the need for higher concentrations of oil-related compounds. Detailed analysis of the biomarkers has shown several distinct sources for liquid hydrocarbons in the IFB program; isotopic ratios and/or detailed compound analysis has been used in some samples to constrain the age of the source(s). In some basins there appears to be one dominant source, whereas in other basins there appear to be multiple sources, implying multiple petroleum systems.

Molecular Compositions of Interstitial Gases

Gas samples were also analyzed from cores collected during the IFB program. The measurement of the alkane gases in the samples showed 1,804 of the 2,468 samples to contain sediment (interstitial) light hydrocarbon alkane gases totaling less than 100 ppmV (parts per million by volume). Two hundred seventy-seven (277) samples contained alkane gases between 100 and 1,000 ppmV, 78 samples contained alkane gases between 1,000 and 10,000 ppmV, 299 samples contained alkane gases between 10,000 and 100,000 ppmV and 10 samples contained alkane gases greater than 100,000 ppmV.

Whereas light hydrocarbon concentrations greater than 100 ppmV may be indicators of above-background natural gas, the samples were further qualified by comparison to a second prospecting parameter before any valid conclusions about the presence of thermogenically-sourced gas seeps were drawn. The measurement of the non-methane (C_{2+}) alkane gases in the sediment samples showed 1,569 of the 2,468 samples to contain C_{2+} alkane gases totaling less than 2 ppmV, 612 samples contained C_{2+} alkane gases totaling 2 to 20 ppmV, 239 samples contained C_{2+} alkane gases totaling 20 to 200 ppmV, 45 samples contained C_{2+} alkane gases totaling 200 to 2,000 ppmV and three (3) samples contained C_{2+} alkane gases totaling greater than 2,000 ppmV.

The comparison of ethane and ethene concentrations showed 1,501 of the 2,468 samples from the current program to have an ethane/ethene ratio *greater* than unity. Of the 1,501, 825 exhibited ethane/ethene ratios between 1:1 and 10:1, 358 exhibited ethane/ethene ratios between 10:1 and 100:1, 234 exhibited ethane/ethene ratios between 100:1 and 1,000:1 and 84 exhibited ethane/ethene ratios greater than 1,000:1

The ethane/ethene ratio is plotted against the concentration of the total alkane gases for each core section of this study in *Figure 3*. Data from previous consortium programs in Angola and Nigeria are included for comparison. Also drawn is the horizontal 1:1 line for ethane/ethene. Samples that plot above this line are deemed to exhibit solid evidence of thermogenic gas seepage, if total gas concentrations are sufficiently higher than background. This line meets a diagonal line that represents the arithmetic product of the ethane/ethene ratio and the concentration of total alkane gases in ppmV (marked x*y=100). Conceptually, this diagonal line marks the above-background threshold for a combination of the two parameters in a low-level sample. Points plotted to the right of the line represent samples that exhibit high amounts of alkane gas and more ethane than ethene. The further to the right of the line the sample plots, the more convincing is the indication of a thermogenic gas component. The two lines as a set can be

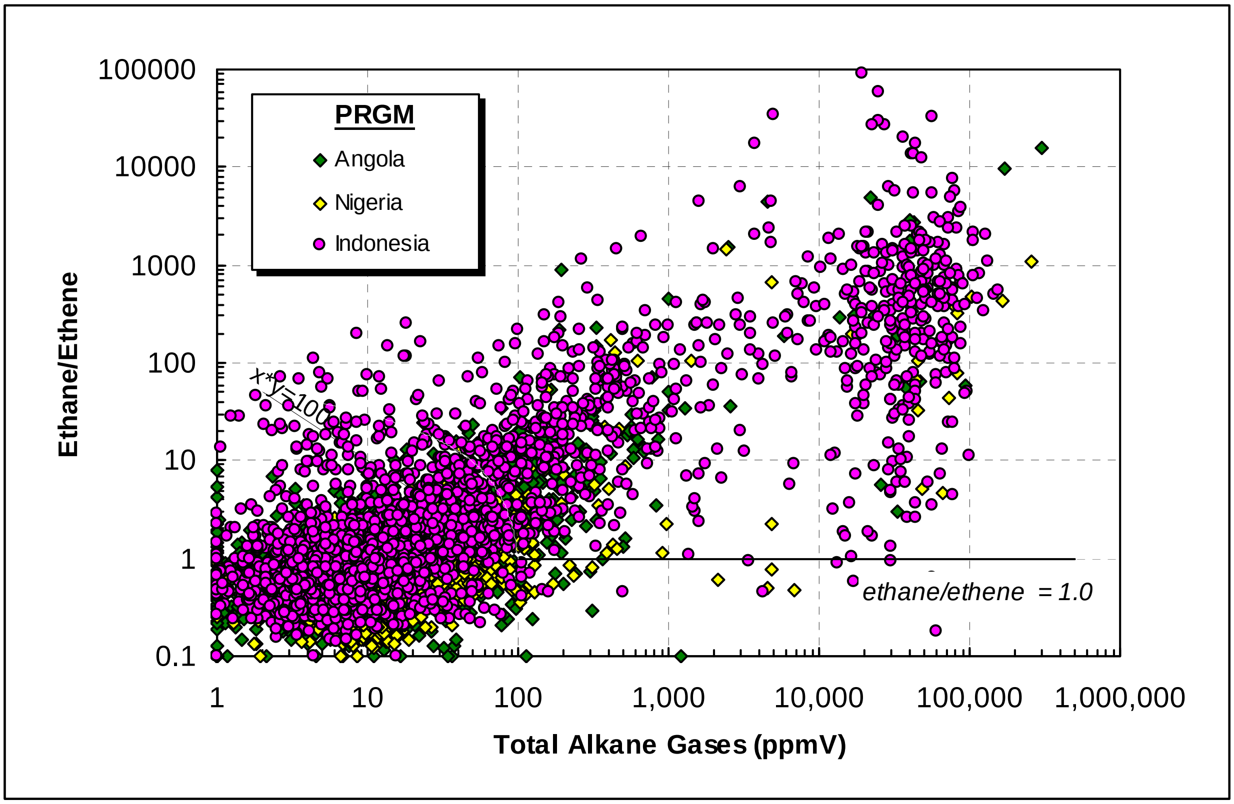


Figure 3. Ethane/ethene ratio vs. total alkane interstitial gases in sediments.

considered a qualifying threshold line for unambiguous thermogenicity of hydrocarbon gas in these samples. Points that plot near or below the 1:1 ethane/ethene line are not interesting from a prospecting viewpoint because even though they may exhibit relatively high totals of alkane gases, they do not have sufficient ethane to be classified as thermogenically-sourced to an unambiguous extent. Gases in this plot region are typically bacteriogenic methane.

Using these screening criteria, 426 of the 927 cores (46 percent) exhibited unambiguous evidence of thermogenic gas. This is an unusually high percentage of gas seep shows for our SGE surveys (compared to about 25% on average), and attests to the potential of the region as well as to the quality of the targets selected. In our experience, thermogenic gas shows always outnumber the oil shows in a prospective regional study, apparently due to the higher mobility of the gases during migration.

Stable Carbon Isotopic Compositions of Interstitial Gases

The large number of samples containing high concentrations of alkane gas, including ethane and above, allowed us to analyze stable carbon isotopic ratios in 340 (14%) of the 2,468 samples analyzed. This is a very large percentage for a frontier basin survey in our experience, and provided valuable information regarding the thermogenicity of the gas as well as on source and maturity. A plot from concepts developed by Faber (1987) is shown in *Figure 4*. This figure illustrates empirical trends in the stable carbon isotopic compositions of ethane and propane in reservoired natural gases from around the world. The figure legend shows several classifications of points plotted. The black dots represent some produced gases from around the world. The other symbols represent produced gases from the Gulf of Mexico region, and their labels represent the type of source, as determined from biological marker analysis of associated oil. The isotopic ratios of carbon in these two components of reservoired gases trend together, both components getting isotopically heavier with increasing maturity of their responsible source material. In fact, virtually all such reservoired gas compositions in our world-wide database group into this trend, and are plotted here for reference. The world-wide trend is also illustrated by the red line that overlies the bulk of the data on the plot. The plot is commonly called a *Faber Plot*. This Faber Plot can be used to distinguish natural gas samples that are derived from a specific single source from gases that are mixtures or from a separate source. Plots of the stable carbon isotopic ratios of two or more sets of propane versus ethane that group together on this empirical line supports a singly-sourced natural gas, whereas samples that do not plot together on the line represent gases from different sources, and samples that plot away from the line suggest that the gas has been isotopically altered, diluted, or fractionated since leaving the reservoir.

Because neither ethane nor propane are microbially (locally) produced and sustained in more than a few ppmV concentrations in near-surface sediments, this propane versus ethane plot is more straightforward than methane versus ethane in its interpretive potential for seabed seep samples with sufficient concentrations of light alkane gases. In gas from the seabed sediment seeps of the current study, there was sometimes sufficient ethane and propane for determination of their individual carbon isotopic compositions. These ethane:propane pairs are plotted on *Figure 4* and labeled as *Basin A, Basin B*, *etc*. Several gases from *Basin E* plot together on the mature end of the trend line. This is dramatic evidence for a mature source in this basin, and these gases are clearly distinguished from other seep gases on the plot. Other basins of this study yielded seep gas samples with compositions that do not follow the world-wide trend. In some cases, two or more such samples from a basin plot as a group but not on the trend line (*i.e*., *Basin A* and *Basin H*), and in other cases, samples from a basin do not plot as a group. The gas samples that plot to the left of the trend line have a composition of isotopically light ethane not commonly seen in our programs.

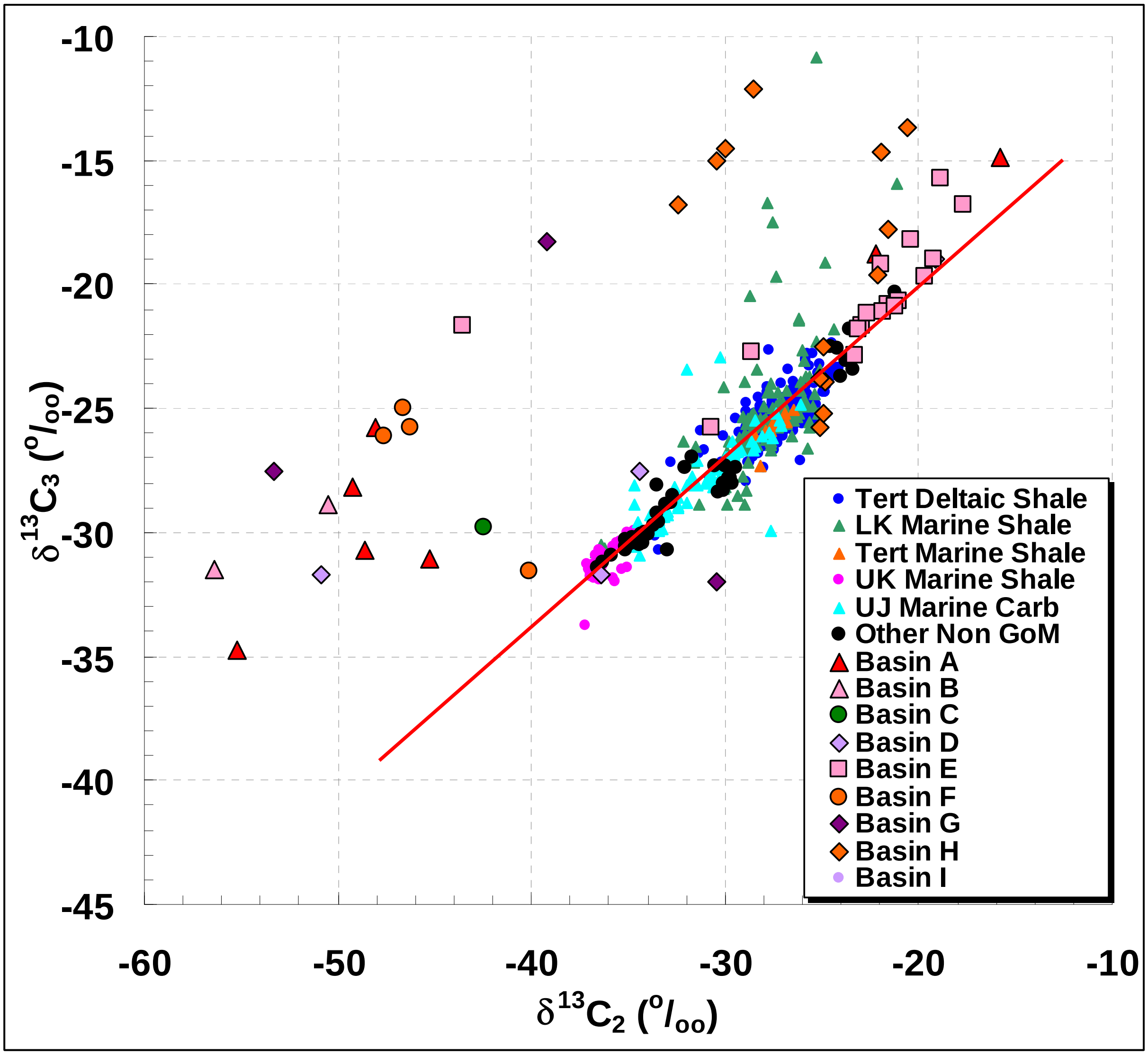


Figure 4. Faber Plot of propane vs. ethane stable carbon isotopic composition in selected samples.

This could mean that isotopic fractionation has occurred in sediment gas ethane, or that two sources of gas have mixed in a way that is very unusual. If isotopic fractionation of ethane during migration is invoked to explain this trend, one would expect the co-existing propane to be fractionated in the same direction. However, the propane trend seems to be opposite the ethane trend. In other words, the points have moved off of the world-wide trend line due to isotopically lightened ethane, or propane made heavy, or both simultaneously. This could not happen if the cause were fractionation during migration. Either could occur with the formation of gas hydrates, however. Alternatively, these cores may represent samples of migrating thermogenic gas that have reservoir compositions outside the bounds of our current understanding. Taken as a group, however, the plot presents compelling evidence of a common source of gas from one basin to another in the samples analyzed as part of the IFB program to date.

CONCLUSIONS

Sediment *extracts* were qualified for the presence of migrated liquid petroleum hydrocarbons in the following way:

(1) If the TSF Max Int was greater than the background threshold, the extract was considered a candidate,

(2) it was confirmed as qualified by a UCM value of more than its background threshold value, or

(3) if the TSF Max Int and the UCM were both less than their threshold values, it was qualified if its thermogenic/diagenetic ratio was greater than the background threshold value.

Cores with interstitial gas indicators were qualified by:

> exhibiting an ethane/ethene ratio of at least unity, *and* the product of it and the total alkane gases being at least 100, in at least one core section.

From the extract indicators, *118* of the *927* cores are qualified as containing migrated liquid petroleum. From the interstitial gas indicators *426* of the *927* cores are qualified as containing migrated thermogenic gas.

This SGE study, conducted as the final phase of the IFB program, has identified thermogenic hydrocarbons in every basin analyzed to date. Not every basin has the same number or percentage of hits, and basins differ in the composition and intensity of their gas and oil hits. One of the main goals of the IFB was to demonstrate charge in Indonesia's under-explored frontier basins, and the SGE data discussed above certainly do that. Within any given basin the geochemical data can be tied back into the multibeam, 2D seismic, gravity and magnetics data to provide an overview of the petroleum system (source, charge, migration and maturity), and the data can further be evaluated along with the available seismic data to identify the range of prospectivity within each basin. Taken together, the data show some basins to be more oily, and some to be more mature in terms of gas. When viewed as a whole, the IFB geochemical data can be used to constrain the presence, distribution and extent of the known hydrocarbon systems in Indonesia.

The large number of geochemical hits, both oil and gas, in a project on the scale of the IFB is unprecedented. We attribute the high success rate of the IFB to a combination of factors: (1) the presence of thermogenic oil and gas charge, (2) the quality of the high resolution survey program used to identify potential seep targets, and (3) the quality of the navigation that allowed precise sampling of the targets by the piston core.

The IFB sediment extract data are striking in several ways. First, a very high percentage (13 percent) of the cores shows evidence of migrated liquid petroleum. In our global experience spanning over 25 years of SGE programs, frontier basins typically yield less than 5 percent of the cores showing evidence of migrated liquid petroleum. Secondly, the IFB samples are the first frontier basin samples we have seen that shows a seep character similar to the Gulf of Mexico and Trinidad, with low UCM concentrations accompanied by a complete suite of n-alkanes that serve as a valuable indicator of oil, and indicate a high flux of oil from the reservoirs. Lastly, an unexpectedly high number of samples yielded sufficient oil-related material (including 15 samples with over 1,000,000 TSF Maximum Intensity units) for detailed biomarker analysis, providing valuable information on source type and interpreted age.

The IFB gas data are unprecedented in our experience in two ways: (1) the seep gases from several of the samples seem to carry pristine, unfractionated compositions from the reservoir, and (2) these reservoir compositions are distinct from the known compositional trends in our world-wide gas database as well as all those found in the literature. These seep samples portend the future discovery of reservoired gas of unique composition, source, and maturity. The samples show solid evidence of mature and also very immature sources.

We have no samples from reservoired natural gases from offshore Indonesia with which to compare the IFB gas data. The samples of this study may form the beginnings of our understanding of the compositions of natural gases from the source rocks producing the oils reported here. Any natural gas compositions for reservoired gases in this region that are made available to us would be extremely helpful in building our ability to interpret Indonesian seep gases.

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