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Interstitial Light Hydrocarbon Gases in Jumbo Piston Cores Offshore Indonesia: Thermogenic or Biogenic?

Bernie B. Bernard, James M. Brooks (TDI-Brooks International, Inc.), Dan L. Orange, John Decker (Niko Resources, Ltd.)

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Abstract

Interstitial light hydrocarbon gases were measured to 12 m below seabed in two Jumbo piston cores acquired in deepwater sediments offshore Indonesia. Determinations were made for dissolved methane, ethene, ethane, propene, propane, iso-butane, n-butane, iso-pentane, and n-pentane, as well as for carbon dioxide. Stable carbon isotopic ratios of methane and ethane were also measured. Such gas measurements are typically performed in deepwaters around the world as elements of surface geochemical exploration programs for the purpose of distinguishing biogenic from thermogenic sources in seep gases. Various gas source models have been developed in the literature to aid in accurate interpretation for systems that have been biodegraded, fractionated, and/or mixed during migration. In these models, assumptions are made about the ranges of composition of the end-member gas types and maturities. The compositional ranges of the thermogenic and biogenic end members have been empirically derived from a large database of drilled-hole gas data and various theoretical considerations. In addition to this literature base, tens of thousands of near-surface marine sediment cores have been acquired worldwide and analyzed for interstitial gases on a proprietary SGE basis over the last 35-40 years. Interpretation of these results has helped to fine-tune the accepted end-member compositions of the source models. However, essentially all of the SGE sediment cores have reached a maximum 5 m below the seabed. Our acquisition and analysis of cores down to 12 m has revealed information about gas compositions not apparent from the former SGE coring efforts. In particular, ethane concentrations are in the accepted thermogenic range, but their stable carbon isotopic compositions are not. Near-surface gases formerly interpreted to have an unambiguous thermogenic component are here shown to be purely biogenic. Our conclusions may change the boundaries of the biogenic end member used for the indication of thermogenic gas traces in near-surface sediments.

Introduction

Deepwater surface geochemical exploration (SGE) is a method of hydrocarbon prospecting that presumes upward migrated oil and gas from deep source rocks and reservoirs can be detected in near surface marine sediments and therefore be used to prove up charge and further evaluate exploration potential of selected sites (Bernard, 1982; Jones and Drozd, 1983; Faber and Stahl, 1984; Horvitz, 1985; Brooks and Carey, 1986; Price, 1986; Cameron and White; 1998, Cole *et al.*, 2001; Bjoroy and Ferriday, 2002; Abrams, 2005). Effectively identifying such sites is dependent on the ability to favorably select and sample sediments from specific seabed locations, and then analytically distinguish prospective samples from those having natural microbial/diagenetic background concentrations of hydrocarbons.

Geophysical surveys are used to select deepwater seabed sampling locations based on various surface expressions of deep faults, seabed hard grounds, and other anomalous physical features associated with upward migration of hydrocarbons (Abrams, 1992; McConnell *et al.*, 2008). Vessels deployed to sample these sites typically collect additional acoustic data with a sub-bottom profiler prior to sample acquisition (Cole *et al.*, 2001). Piston coring is used in order to collect sediment samples down to about 5 m below the seabed (Cameron and White, 1998). Sediment samples from the cores are then analyzed with robust, well-accepted methods for the presence of trace concentrations of gaseous and liquid hydrocarbons (Abrams, 2005).

The detection and analysis of methane and the other light hydrocarbons in terrestrial soils, bottom waters, and near-surface marine sediments is perhaps the earliest and long-lived geochemical method used for petroleum prospecting, dating back to the 1930s (Laubmeyer, 1933; Sokolov, 1933; Horvitz, 1939; Fenn, 1940; McDermott, 1940; Rosaire, 1940; Kartsev, 1959; Karim, 1964; Galimov, 1968; Horvitz, 1969; Debnam, 1969; Frank *et al*., 1970; Devine, 1977; Sackett, 1977; Hunt, 1979; Duscherer, 1980; Philp and Crisp, 1982; Brooks *et al*., 1986; Abrams, 1996a). Light hydrocarbons can reside in near-surface marine sediments in a variety of phases, often together in equilibrium:

(1) as free gas in the effective porosity (Emery and Hogan, 1958; Bernard *et al*., 1976, Kennicutt *et al*., 1988; Fleischer *et al*., 2001),

(2) as interstitial gas dissolved in water-filled pore spaces between grains (Claypool and Kaplan, 1974; Martens and Berner, 1974; Martens and Berner, 1977; Bernard *et al*., 1977a; Bernard *et al*., 1977b; Bernard, 1978; Bernard, 1979; Anderson *et al*., 1983; Claypool and Kvenvolden, 1983; Abrams, 1996a),

(3) adsorbed onto the sedimentary particles or trapped within carbonate cements (Horvitz, 1945; Horvitz, 1969; Horvitz, 1981; Horvitz, 1985; Pflaum, 1989; Bjoroy and Ferriday, 2002; Whiticar, 2002; Heeschen *et al*., 2007; Mani *et al*., 2011) and

(4) as gas hydrates (Brooks *et al*., 1986; Kvenvolden, 1988; Kvenvolden, 1993; Dickens *et al*., 1997).

Light hydrocarbon gas concentrations can change several orders of magnitude through the 1 to 5 meter depth range in marine sediments (Bernard, 1978, Bernard, 1979, Whiticar, *et al*., 1986, Faber *et al.*, 1990, Abrams, 1992). Core samples deeper than this are more difficult and expensive to obtain, so with a few exceptions (notably the cores from the NSF-funded ocean drilling projects and hydrate studies, and Abrams, 1992) the worldwide SGE database of available sediment gas data, currently comprised of more than 20,000 deepwater sites, is essentially limited to the first 5 m below seabed.

Scope and Methods

Interstitial light hydrocarbon gas samples were analyzed from cores collected from deepwater Indonesia in 2011 (**Figure 1**). Interstitial light hydrocarbon gas analysis in this context refers to the determination of gases dissolved in sediment pore waters by equilibrium partitioning (#2 above). Analytes included methane, ethene, ethane, propene, propane, the butenes, iso-butane, n-butane, neo-pentane, iso-pentane, and n-pentane. Equilibrated carbon dioxide was also measured. We report and interpret the results from two Jumbo piston cores that reached 12 m below the seabed. These two cores were acquired for the specific purpose of investigating whether new and revealing SGE information could be discovered on deeper samples obtainable by such deeper coring.

As soon as each core was retrieved on-deck, sediment material was carefully sub-sampled at 1-m intervals down each core. About 200 mL of sediment from each interval was quickly inserted into a 500 mL metal can, and then 165 mL of clean, degassed, bactericide-laced seawater was added. Each can's headspace was then briefly purged with nitrogen gas to remove ambient air before sealing. All canned samples were inverted and frozen on-board at -20°C.

After transport to the land-based laboratory, the cans were allowed to thaw, and then were kept at 40°C for 4 hours. The light hydrocarbons dissolved in the interstitial water were then equilibrated with the nitrogen gas phase at that temperature by vigorous agitation for five minutes with a high-speed shaker (Bernard, 1978, Abrams and Dahdah, 2011). The interstitial gas method of sediment gas concentration measurement was chosen because it has been shown to be the most robust method for assessing gases with respect to their original source (Logan *et al*., 2009). Due to the, repeatability, fecundity, and longevity of the method in the literature, there also exists an SGE database of tens of thousands of such measurements in marine sediments, which we have used for comparison of results.

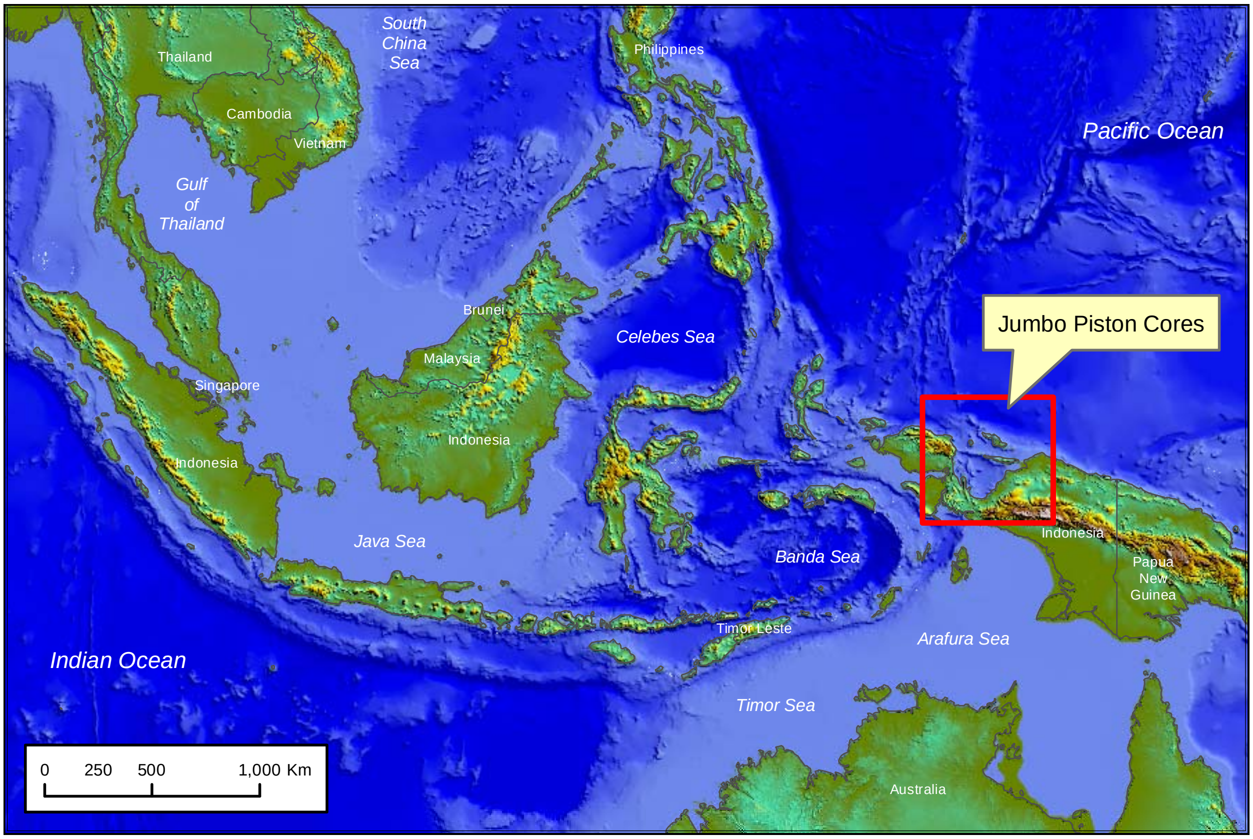

Figure 1. General location of two Jumbo piston cores acquired offshore Indonesia.

The interstitial gases now partitioned into the headspace were sampled through the septum of the equilibrated canned sample with the needle of an automated sample loop. One (1.0) mL of gas was injected onto a packed GC column. The gases were separated and detected by a flame ionization detector (GC/FID). Certified external standards were used for quantitation of each gas concentration. These headspace concentrations were converted to the interstitial concentration (in ppmV) of each gas originally in the sediment by measuring the volumes of sediment and headspace in the can and by applying the individual gas equilibrium partition coefficients (Bernard, 1978).

Analytical Results

The analytical results are presented in **Table 1**. Molecular concentrations were determined on each gas component for every sample, whereas stable carbon isotope ratios were determined only for gas components of sufficient molar concentration for the analysis. Ethane from each can was cryo-focused to obtain sufficient concentration for stable isotope measurements. Ethene concentrations on a few of the samples were high enough for cryo-concentrated stable isotope measurements, but the ratios could not be accurately measured in the presence of close-eluting ethane at significantly higher concentrations.

Figure 2 presents sediment depth profiles of selected gas concentrations and carbon isotope ratios. Methane, ethane, and propane concentrations are plotted on a log scale for comparison of the homologs.

Table 1. Interstitial gas concentrations (ppmV) and stable carbon isotope ratios ($^{o}/_{oo}$ vs. PDB) of two Jumbo piston cores acquired offshore Indonesia.

CORE #	Depth (m)	Methane	Ethene	Ethane	Propene	Propane	i-Butane	Butenes	n-Butane	neo-Pentane	i-Pentane	n-Pentane	CO_2	$\delta^{13}C_1$	$\delta^{13}C_2$
JPC1	1.0	26.6	0.19	0.48	0.05	0.09	0.00	0.05	0.00	0.00	0.00	0.00	4,343		
JPC1	2.0	212.1	0.35	3.36	0.05	0.12	0.00	0.05	0.00	0.00	0.00	0.00	4,211		
JPC1	3.0	350.4	0.52	10.46	0.04	0.17	0.00	0.11	0.00	0.00	0.00	0.00	8,544		-56.4
JPC1	4.0	3,667.1	0.25	37.17	0.07	0.86	0.00	0.05	0.07	0.00	0.06	0.00	5,396	-110.2	-62.4
JPC1	5.0	68,607.0	8.61	64.25	0.02	1.89	0.02	0.04	0.12	0.03	0.09	0.00	13,851	-86.2	-63.1
JPC1	6.0	37,576.5	0.34	55.29	0.08	2.26	0.04	0.08	0.19	0.00	0.11	0.00	6,081	-81.2	-64.1
JPC1	7.0	11,232.8	0.69	32.58	0.29	1.76	0.11	0.13	0.18	0.04	0.76	0.33	11,725	-77.0	-64.1
JPC1	8.0	21,009.4	0.24	40.63	0.07	1.65	0.03	0.07	0.13	0.04	0.17	0.00	9,129	-79.9	-64.5
JPC1	9.0	14,840.2	1.64	25.13	0.02	1.04	0.00	0.04	0.06	0.00	0.11	0.00	12,036	-79.9	-64.3
JPC1	10.0	15,451.7	6.43	24.59	0.02	1.00	0.02	0.04	0.08	0.03	0.12	0.00	15,312	-79.9	-64.7
JPC1	11.0	15,361.2	1.26	23.04	0.01	0.90	0.01	0.03	0.08	0.02	0.15	0.00	12,175	-78.4	-63.7
JPC1	12.0	15,952.2	0.67	32.49	0.23	1.93	0.06	0.12	0.27	0.03	0.81	0.22	27,017	-77.8	-64.0
JPC2	1.0	81.0	0.24	1.20	0.05	0.09	0.00	0.04	0.03	0.00	0.00	0.00	2,195		
JPC2	2.0	307.2	0.63	4.74	0.05	0.13	0.00	0.06	0.06	0.00	0.00	0.00	9,717		
JPC2	3.0	320.8	5.65	7.22	0.03	0.06	0.00	0.04	0.03	0.00	0.00	0.00	14,164		
JPC2	4.0	497.1	0.33	12.21	0.07	0.22	0.00	0.08	0.05	0.00	0.00	0.00	11,302		-54.4
JPC2	5.0	429.3	4.79	12.88	0.05	0.19	0.00	0.08	0.06	0.00	0.00	0.00	71,915		
JPC2	6.0	807.5	6.59	23.83	0.06	0.36	0.00	0.09	0.05	0.00	0.00	0.00	19,748		-54.8
JPC2	7.0	100,924.7	18.35	99.18	0.03	1.32	0.00	0.53	0.39	0.10	0.11	0.00	28,740	-86.9	-63.5
JPC2	8.0	39,824.6	0.21	59.19	0.09	1.28	0.04	0.00	0.12	0.09	0.20	0.00	9,303	-78.1	-61.9
JPC2	9.0	25,978.1	3.54	43.47	0.02	0.93	0.04	0.05	0.15	0.09	0.00	0.00	14,842	-78.2	-64.0
JPC2	10.0	26,994.3	0.13	43.75	0.03	0.86	0.06	0.05	0.12	0.15	0.28	0.00	7,537	-76.8	-64.7
JPC2	11.0	27,390.8	0.16	43.26	0.04	0.80	0.04	0.03	0.13	0.08	0.00	0.00	8,283	-76.2	-65.0
JPC2	12.0	31,224.6	0.18	47.91	0.04	0.92	0.05	0.03	0.11	0.06	0.33	0.00	5,873	-73.9	-62.9

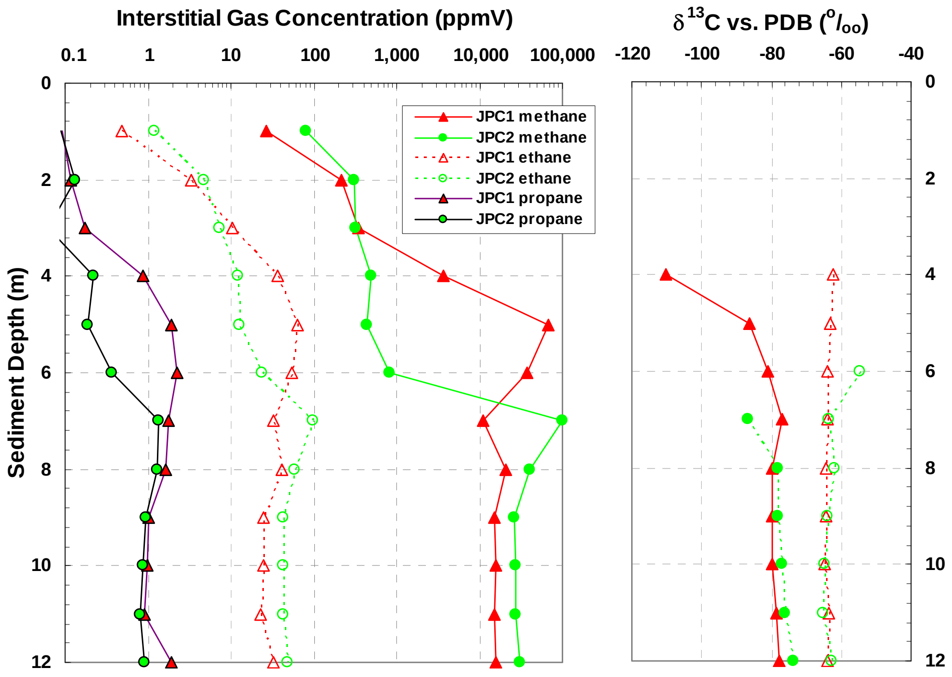

Figure 2. Depth profiles of C_1-C_3 gas concentrations and C_1-C_2 carbon isotope ratios.

Interpretation of Analytical Results

The methane depth profiles of **Figure 2** increase several orders of magnitude in the first 6 m. This is indicative of biogenic methane, which predictably increases dramatically with depth through the sulfate-reducing zone in near-surface marine sediments (Claypool and Kaplan, 1974, Martens and Berner, 1974, Bernard, 1979, Abrams, 1996a). This is because there is typically an upward flux of light hydrocarbon gas into the bottom waters, and the sediment column loses gas into the overlying water by diffusion. A concentration gradient is maintained in the top several meters of sediment as long as gas diffuses and migrates from below (Bernard, 1978, Bernard, 1979).

Whereas hydrogen sulfide was not measured in the cores of this study, the sections exhibited a strong hydrogen sulfide odor when being processed, corroborating the conclusion that the cores penetrated through the anaerobic sulfate-reducing zone, the sulfate-methane transition zone (SMTZ), below the depth of sulfate depletion, and into the zone of high-activity methanogenesis (Claypool and Kaplan, 1974, Barnes and Goldberg, 1976, Bernard, 1978, Bernard, 1979, Iversen and Jørgensen, 1985, Orcutt *et al.*, 2005). Also supporting this conclusion is the depth profile of the stable carbon isotopic ratio of methane. Methane-isotope profiles through the entire sulfate reducing zone in two Gulf of Mexico cores are very similar to profiles of **Figure 2** (Bernard, 1979). Stable carbon isotope ratios of biogenic methane are also generally accepted to be in this range (Galimov, 1968, Stahl, 1975, Schoell, 1983, Berner and Faber, 1988, Schoell, 1988, Berner and Faber, 1996, Abrams, 1996b, Prinzhofer and Pernaton, 1997, Blair, 1998, Hoefs, 2004, Milkov and Dzou, 2007).

The natural presence of 2 to 5^+ ppmV levels of C_{2+} alkane gases interstitially dissolved in the top 5 m of marine sediments has historically served as a good indicator of traces of migrating thermally-sourced gas (Bernard, 1977, Bernard, 1978, Cole *et al.*, 2001, Abrams, 2005) because ethane, propane, the butanes, and the pentanes are not locally produced and sustained at more than a few ppmV concentration levels (Claypool and Kvenvolden, 1983, Berner and Faber, 1988, Schoell, 1988). Ethane is apparently microbially produced in sediments to a small extent (Davis and Squires, 1954, Welhan *et al*., 1980; Oremland, 1981, Taylor *et al*., 2000; Hinrichs *et al*., 2006).

The olefins including ethene and propene, reported by Oremland (1981) and by Bernard (1978), are ubiquitous in the recent marine environment, and are now routinely measured in marine sediments at sub-ppmV concentrations (TDI-Brooks SGE sediment gas database), though these compounds are too labile to persist in thermogenically derived fluids (Hunt, 1979, Tissot and Welte, 1984).

Figure 3 plots the sum of the C_{2+} gases vs. the total alkane gases for sections of the two Jumbo cores, as well as over 2,000 deepwater sediment cores we have previously analyzed offshore Nigeria, Angola, and Indonesia. However, these cores were limited in length to less than 6 m, whereas the cores of the current study reached 12 m into the sediment. This log-scale plot spans several orders of magnitude. It serves to illustrate the general range of background concentrations of light hydrocarbon alkane gases in marine sediments and also illustrates several sites that contain trace to macro thermogenic gas seepage.

The distribution of plotted points illustrates that background levels of total-alkane-gases in marine sediments typically range from about 1 to 500 ppmV, whereas typical concentrations of C_{2+} hydrocarbons range from about 0.02 to 5 ppmV. The 1%, 20%, and 100% lines represent percent-by-volume boundaries. Volumes of gases are proportional to their molar quantities; therefore, these lines also represent mole fractions of 1%, 20%, and 100%. Note that a value approaching 100% means that essentially all of the gas is ethane, propane, and above, with insignificant fractions of methane. Gases of this composition are rarely encountered, and perhaps exist due to fractionation of the gas by hydrates, bacterial degradation/oxidation, or even the physicochemical fractionation effects of migration.

Mole fractions of the C_{2+} alkane gases from 1% to 20% in a reservoired gas or high-flux natural gas seep would be clearly indicative of a thermogenic "wet gas" source (Rice, 1980) but **Figure 3** demonstrates that in near-surface marine sediments the non-thermogenic background levels of ethane and propane are typically high enough with respect to the background methane to also produce these "wet gas" compositions. Such mole fractions are not extraordinary in normal near-surface marine sediments, as is illustrated by the plot. However, when the non-methane alkane fraction falls in this percentage range and the methane concentration is high compared to background in an SGE program, then the sample typically deserves further consideration as exhibiting at least a trace of thermogenic gaseous hydrocarbon component.

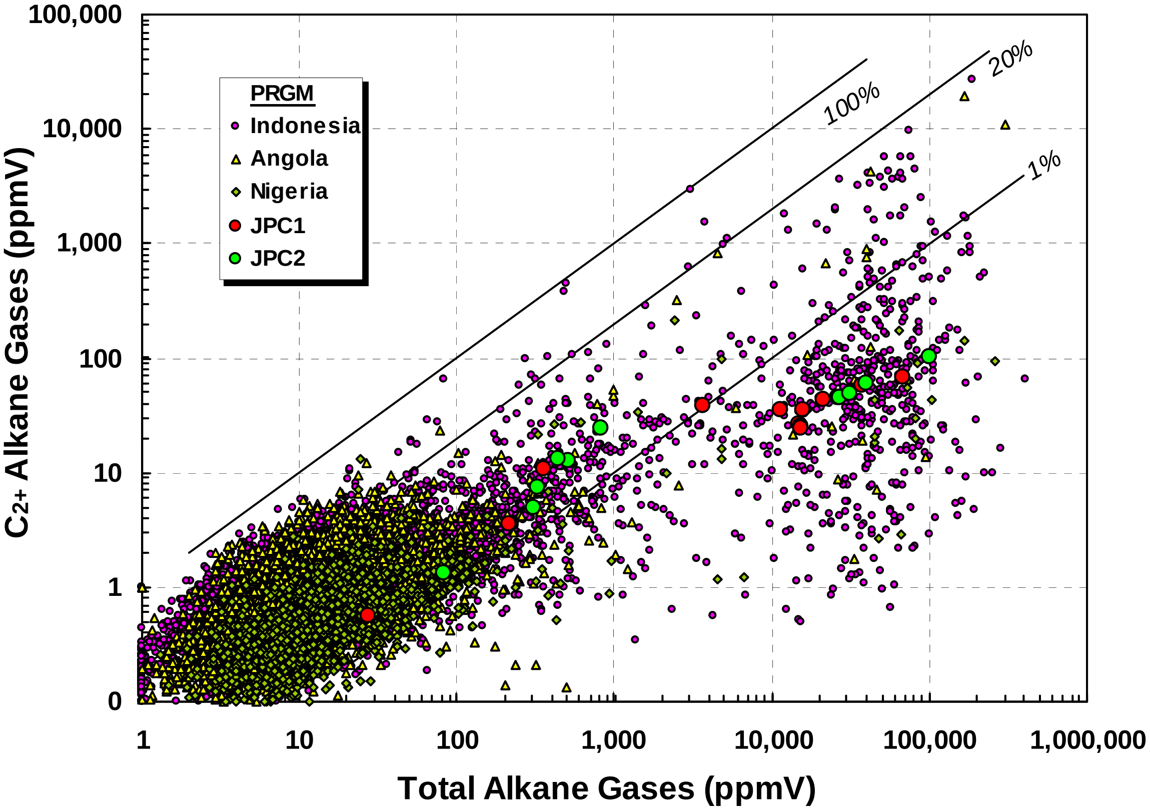

Figure 3. C_{2+} Alkane Gas vs. Total Alkane Gas values for samples of this study (blue squares) and for 2,000^{+} other near-surface sediments.

The deeper sections of the JPC samples plot above typical background, but below the 1% line, thus exhibiting low fractions of C_{2+} hydrocarbon gases. This typically reflects sediments containing higher than background levels of biogenic gas. However, the ethane in these sections is an order of magnitude higher than is typical for biogenic sediment gases, typically interpreted as containing a trace component of migrating thermogenic gas mixed with local biogenic gas. Such mixing could mask the signature of the thermogenic gas by diluting it with biogenic methane to the point that molecular and methane isotope compositions are misleading (Bernard *et al.*, 1977a). For these reasons, we also compare ethane/ethene ratio to the total alkane gas concentration in an effort to further discern the source of the gases in the cores of this study.

The background ethane and ethene concentrations are typically stable in marine shelf sediments such that the ethane/ethene concentration ratio groups around a value of about 0.5, meaning that ethene is about twice the concentration of ethane (Bernard, 1978). Each of the “first 5” light hydrocarbons, methane, ethene, ethane, propene, and propane, is present at interstitial concentrations above 0.01 ppmV in shelf, slope, and deepwater sediments due to microbial activity. Microbial activities in near-surface marine sediments decrease seaward with increasing water depth due to lower organic loading and decreasing temperature, and the interstitial levels of the light hydrocarbons decrease accordingly (Reeburgh, 1983; D’Hondt, 2002; D’Hondt *et al.*, 2004). 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 unity (Bernard, 1978).

Figure 4 plots the ethane/ethene ratio against the concentration of the total alkane gases for each Jumbo core section. We have included the data from SGE programs in Angola, Nigeria and Indonesia for comparison. Also plotted is a horizontal red line representing an ethane/ethene ratio of unity. This line meets a diagonal red line that represents the arithmetic product of the ethane/ethene ratio and the concentration of total alkane gases in ppmV. Conceptually, this diagonal line marks an arbitrary above-background SGE screening threshold for a combination of the two parameters in a single sample. Points plotted above the composite red line represent samples that exhibit anomalously high amounts of alkane gas as well as more ethane than ethene. The further to the right-and-above the line the sample plots, the more robust and definitive is the evidence for a thermogenic gas component in the sample. Points that plot near or below the unity line do not have sufficient ethane to have them classified as thermogenically-sourced to any material degree.

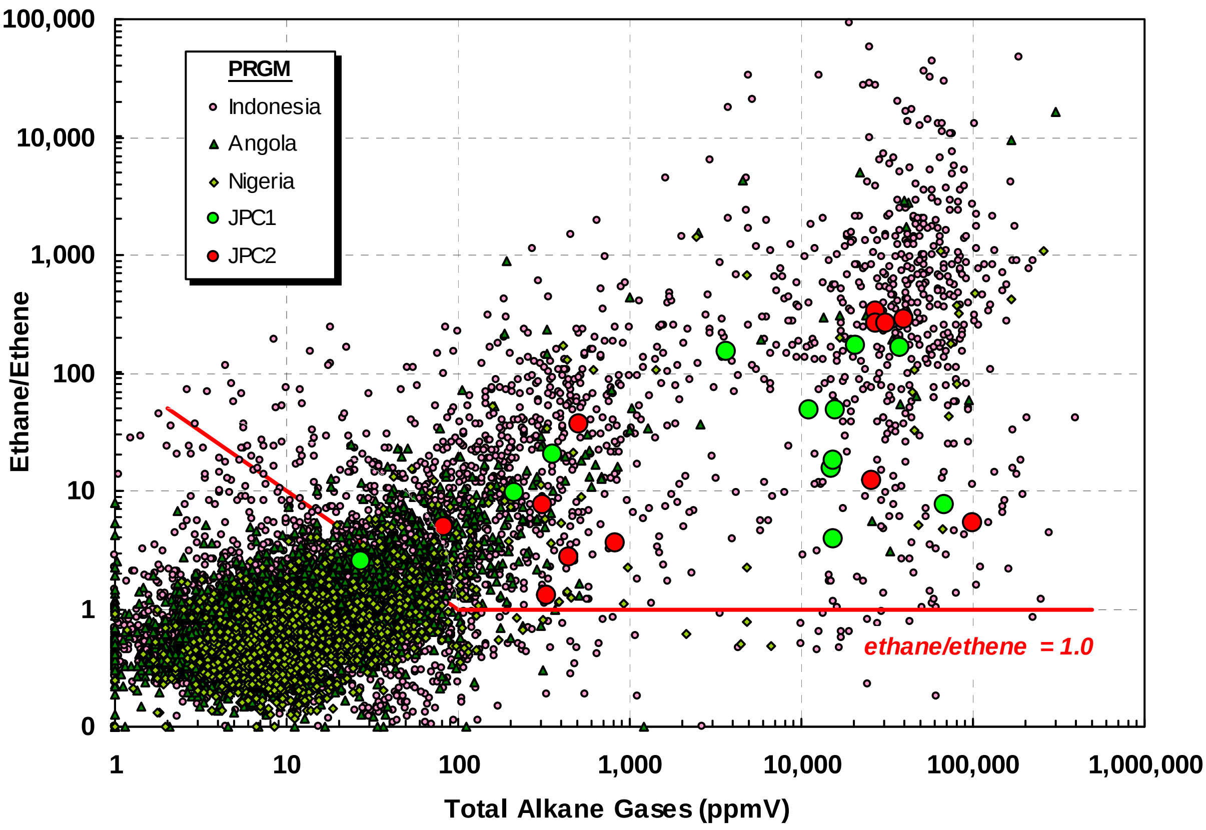

Figure 4. Ethane/ethene ratio vs. total alkane gases in sediments.

The gases in the deeper JPC sections plot clearly in the zone that would normally be interpreted as containing an unambiguous thermogenic gas component. However, propane concentrations and stable carbon isotope ratios of methane and ethane must also be considered.

Figure 5 is a plot of the JPC gases analyzed for stable carbon isotope ratios, plotting the carbon isotopic composition of methane vs. that of ethane. The **red** line indicates the empirical trend line for this gas isotope pair from a worldwide sampling of natural gases (Faber, 1987). Samples plotting close together on the line indicated a co-genetic source of thermogenic gas. The trend line also indicates more mature gases with less negative stable isotope compositions (trending upper-right). The JPC seep samples are plotted as **red triangles**. The figure legend shows several other classifications of points plotted. The black dots represent some produced gases from around the world, but excluding the Gulf of Mexico. The other symbols represent produced gases from the Gulf of Mexico region, and their labels represent the type of source rock, as determined from biological marker analysis of associated oil.

None of the core samples of this study plot near the trend line for a known thermogenic source rock. They plot in line with an extended extrapolation of the co-genetic trend line in a direction of extreme immaturity (dashed red line), though there are no known thermogenic gases in this range.

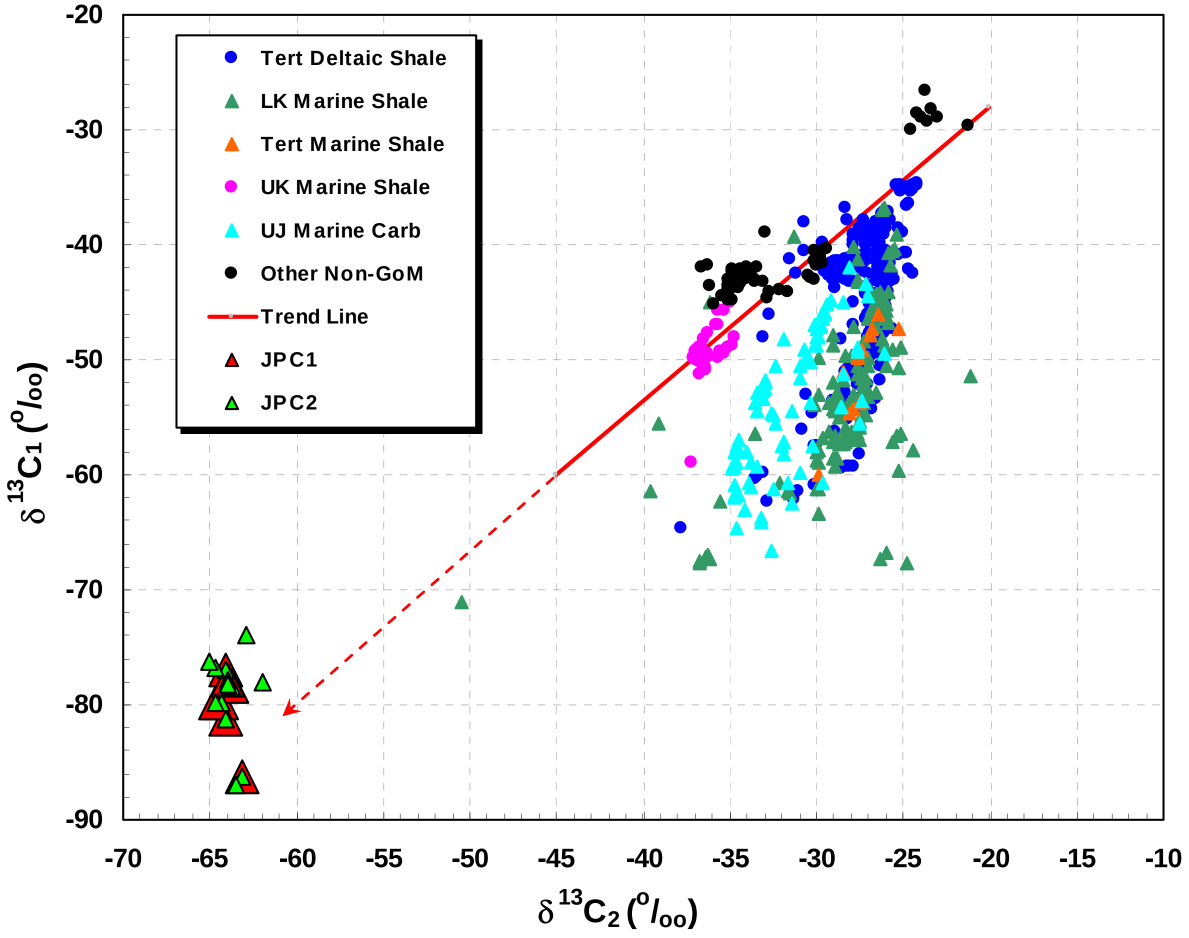

Figure 5. "Faber" Plot of methane vs. ethane isotopes in two Jumbo cores of this study and other natural gases.

Figure 6 is a so-called Natural Gas Plot of the gases analyzed for carbon isotope ratios in the current study, plotting the isotopic composition of methane, ethane, propane, n-butane, and n-pentane as a function of the reciprocal of the carbon number of each gas (Chung *et al.*, 1988; Rooney *et al.*, 1995). This plot is used to differentiate natural gases that are derived from a single source from gases that are mixtures derived from two or more sources. A linear trend supports a co-genetic origin, whereas a non-linear fit suggests that the gas accumulation is a mixture of gases, a chemically altered gas or a gas derived from a structurally heterogeneous carbon source. The empirical trend lines for each set of gases can be compared to those from a worldwide sampling.

Natural gases associated with the various oil families in produced oils of the Gulf of Mexico and an immature gas from offshore Indonesia are also represented on this figure. Plotted as dashed lines are the average isotopic compositions of each C_1 through C_4 or C_5 component from several dozen or more produced gases representing each oil family's source. The trends illustrated by these dashed lines are distinct for each oil family. The non-linearity of most of the dashed lines is indicative that many of the produced thermogenic gases in the Gulf of Mexico have a biogenic methane component (Milkov and Dzou, 2007). A line shifted downward (isotopically lighter gases) in this plot compared to the other family source lines indicates a less mature source for gases.

The data from the two JPCs plot together and indicate an extremely immature source. The trend of the gas compositions is markedly different from that of reservoired gases in our world-wide database. Milkov and Dzou (2007) extrapolate the trend line of the Natural Gas Plot to conclude that the initial methane from the onset of thermocatalytic cracking could be isotopically lighter than the accepted range for thermogenic methane, or that "secondary microbial" methane might explain methane isotopic compositions between the ranges of known thermogenic and biogenic sources. However, the extremely light isotopic compositions of the ethane samples reported in the two Jumbo cores from Indonesia cannot be explained by either of those mechanisms.

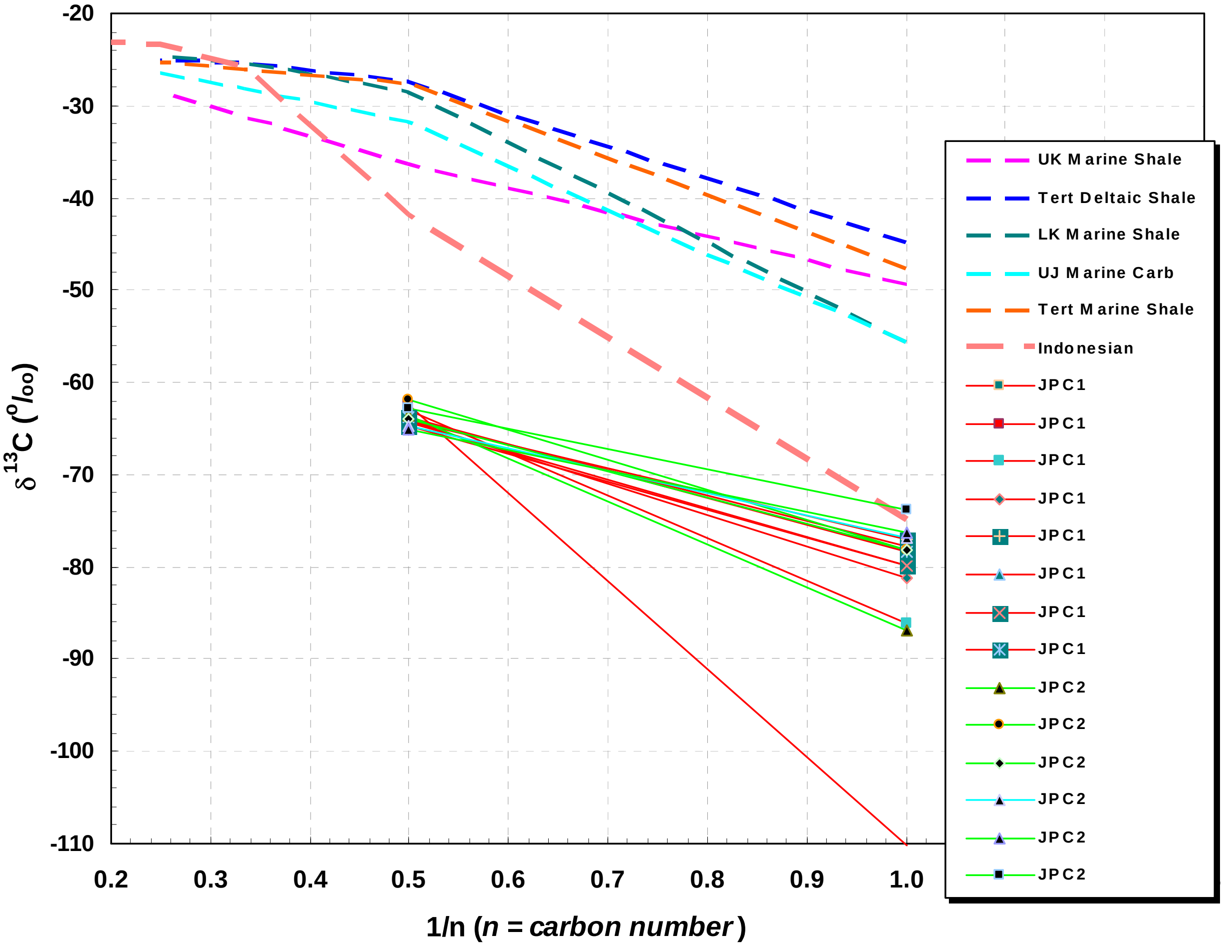

Figure 6. Natural Gas Plot of C_1 through C_3 hydrocarbon gases in selected samples.

Prinzhofer and Pernaton (1997) concluded that methane isotopic compositions can possibly be fractionated-lighter during migration, and by inference, ethane isotopic compositions could be similarly fractionated. However, any natural formation migration mechanism that preferencially retards the upward movement of one isotope of carbon in thermogenic methane so as to fractionate the initial "eluting" methane product would also act to chromatographically remove ethane from the initial eluent gas product. In other words, any natural formation forming a chromatographic filter sufficiently effective to isotopically fractionate methane (given the mere 6% difference in molecular weight of the ^{13}C and ^{12}C methane stable isotopic moities as well as their identaical tetrahedral shapes) would act to completely extract any migrating ethane from the initial eluent (given the 88% difference in the molecular weight of ethane vs. methane and their radically different molecular shapes). Thus, the mechanisms proposed by Milkov and Dzou (2007) and by Prinzhofer and Pernaton (1997) are not the most likely explanations.

Conclusions

We believe the interstitial gases of both of these Jumbo cores to be completely biogenic in origin. Evidence illustrated by **Figure 2** and **Figure 3** includes: (1) the trend of gas concentrations with depth indicates that the cores penetrated the bottom of the sulfate reducing zone; (2) the concentration of propane is an order of magnitude lower than that of ethane, and ethane is 3 orders of magnitude lower than methane. These levels and depth trends all compare well with biogenic gas profiles in the literature. Even though ethane concentrations are higher than typical biogenic gases in near-surface sediments, any trace of thermogenic gas mixed with the local biogenic methane would have also contained propane at levels approaching ethane (ref. TDI-Brooks database of thermogenic seepage); (3) the stable carbon isotope ratios of methane are fully in the biogenic range and those of ethane are in a range much lighter than is known and accepted for natural thermogenic gas.

Figure 4 is not a good interpretive tool in this case. This tool is in wide use for SGE studies, but apparently should be applied only for gases sampled above the bottom of the sulfate-reducing zone. **Figure 5** and **Figure 6** both illustrate that the JPC gases fall well outside the range of known thermogenic gas compositions, and the tools represented by both plots indicate insignificant mixing of biogenic and thermogenic gas.

It is extremely rare to be able to use the tools of **Figures 5** and **Figure 6** for biogenic gases because such gas in near-surface sediments do not typically contain sufficient ethane or propane concentrations for carbon isotope ratio measurements. The two 12 m long cores of this study have allowed us to plot isotope ratios of biogenic gases for comparison to known thermogenic gas families and other macro-seep gases acquired during deepwater SGE surveys. We believe this biogenic composition set to be indicative of the deepwater anaerobic methanogenesis zone on a world-wide basis. Indeed, similar gases in previous seep studies could be misinterpreted as having a trace thermogenic component, which would now be interpreted as fully biogenic by comparison to gases of this study.

We believe the ethane of these samples to be microbially produced or even more likely to be the diagenetic daughter product of decomposing and very labile microbially produced ethene. If a degradation product, this ethane would reflect the original isotopic composition of the bacteriogenic ethene from which it derived, as isotopic fractionation effects would be small with the substantially complete ethene degradation inferred by the measured concentrations of ethene in the cores. The ethane isotopic ratios reported here were measured at about $-64^{o}/_{oo}$ vs. PDB, which is significantly lighter than even the least mature thermogenically-derived ethane considered in the literature. Future efforts to measure the isotopic composition of sediment ethene, as well as ethene degradation experiments, will likely provide further insights.

References

Abrams, M.A. 1992. Geophysical and geochemical evidence for subsurface hydrocarbon leakage in the Bering Sea, Alaska. Marine and Petroleum Geology, V. 9, 208-221.

Abrams, M.A. 2005. Significance of hydrocarbon seepage relative to petroleum generation and entrapment. Marine and Petroleum Geology, 22, pp. 457-477.

Abrams, M.A. 1996a. Distribution of subsurface hydrocarbon seepage in near-surface marine sediments, in D. Schumacher and M. A. Abrams, eds., Hydrocarbon migration and its near-surface expression: AAPG Memoir 66, p. 1-14.

Abrams, M.A. 1996b. Interpretation of methane carbon isotopes extracted from surficial marine sediments for detection of subsurface hydrocarbons. In: Schumacher, D., Abrams, Hydrocarbon migration and its near-surface expression: AAPG Memoir 66, p. 139-166.

Abrams, M.A. 2005. Significance of hydrocarbon seepage relative to petroleum generation and entrapment. Marine and Petroleum Geology, 22, pp. 457-477.

Abrams, M.A. and Dahdah, N.F. 2011. Surface sediment hydrocarbons as indicators of subsurface hydrocarbons: Field calibration of existing and new surface geochemistry methods in the Marco Polo area, Gulf of Mexico. AAPG Bulletin, 95(11), 1907-1934.

Anderson, R.K., Scalen, R.S., Parker, P.L., and Behrens, E. W. 1983. Seep Oil and Gas in Gulf of Mexico Slope Sediment. Science, V. 222 (4624), pp. 619-621.

Barnes, R.O. and Goldberg, E.D. 1976. Methane production and consumption in anoxic marine sediments. Geology, 4, 297-300.

Bernard, B.B., Brooks, J.M. and Sackett, W.M. 1976. Natural gas seepage in the Gulf of Mexico, Earth Planet. Sci. Lett., 31, 48-54.

Bernard, B.B., Brooks, J.M. and Sackett, W.M. 1977a. A geochemical model for characterization of hydrocarbon gas sources in marine sediments, in Proceedings of the Ninth Annual Offshore Technology Conference, OTC 2934 (May 1977) Houston, pp. 435-438.

Bernard, B.B., Brooks, J.M. and Sackett, W.M. 1077b. Light hydrocarbons in recent continental shelf and slope sediments, Journal of Geophysical Research, 83, 4053-4061.

Bernard, B.B, 1978. Light hydrocarbons in marine sediments, Ph.D. dissertation, Texas A&M University, Technical Report 78-5-T, Texas A&M Press, 144p..

Bernard, B.B. 1979. Methane in marine sediments, *Deep-Sea Research, 26*, 429-443.

Bernard, B.B.1982. Geochemical Prospecting for Petroleum and Natural Gases. In: Workshop Report on Basic Research in Organic Geochemistry Applied to National Energy Needs, 1980. National Technical Information Service Report. CONF-801249, pp. B7-B33.

Berner, U. and Faber, E. 1988. Maturity related mixing model for methane, ethane and propane, based on carbon isotopes. Org. Geochem, V. 13(1-3), pp. 67-72.

Berner, U. and Faber, E. 1996. Empirical carbon isotope/maturity relationships for gases from algal kerogens and terrigenous organic matter, based on dry, open-system pyrolysis. Org. Geochem., V. 24(10/11), pp. 947-955.

Bjoroy, M. and Ferriday, I. 2002. Surface geochemistry as an exploration tool: a comparison of results using different analytical techniques. In: Near-Surface Hydrocarbon Migration: Mechanisms and Seepage Rates, American Association of Petroleum Geologist Hedberg Conference, Vancouver, BC, Canada, April 7–10, 2002.

Blair, N. 1998. The $\delta^{13}C$ of biogenic methane in marine sediments: the influence of deposition rate. Chemical Geology, 152, 139-150.

Brooks, J.M. and Carey, B.D. 1986. Offshore surface geochemical exploration: Oil and Gas Journal, v. 84, p. 66-72.

Brooks, J.M., Cox, H.B., Bryant, W.R., Kennicutt II, M.C., Mann, R.G., and McDonald, T.J. 1986. Association of gas hydrates and oil seepage in the Gulf of Mexico. Org. Geochem., V. 10, pp. 221-234.

Cameron, N.R. and White, K. 1998. Surface Geochemical Exploration continues to progress global deepwater frontiers, IBC 'Oil and Gas Developments in West Africa', London, 25-26 October.

Chung, H.M., Gormly, J.R. and Squires, R.M.,1988. Origin of gaseous hydrocarbons in subsurface environments: theoretical considerations of carbon isotope distribution. In: M. Schoell (Guest-Editor), Origins of Methane in the Earth. Chem. Geol., 71: 97-103 (special issue).

Claypool, G. and Kaplan, I.R. 1974. The origin and distribution of methane in marine sediments. In: Kaplan, I.R. (Ed.), Natural gases in marine sediments, Plenum New York, pp. 99-140.

Claypool, G.E. and Kvenvolden, K.A. 1983. Methane and other hydrocarbon gases in marine sediments. Annual Review Earth Planet Science, 11, 299-327.

Cole, G. A., Yu, A., Peel, F., Requejo, R., DeVay, J., Brooks, J., Bernard, B., Zumberge, J, and Brown, S. 2001. Constraining source and charge risk in deepwater areas, WorldOil magazine, Vol. 222:10, October.

Davis, J.B. and Squires, R.M., 1954. Detection of microbially produced gaseous hydrocarbons other than methane. Science, 119, 381-382.

Debnam, A.H. 1969. Geochemical Prospecting for Petroleum and Natural Gas in Canada. Geol. Survey of Canada. Bull. 177: 26 pp.

Devine, S.B. 1977. Soil Hydrocarbon Geochemistry, a Potential Petroleum Exploration Tool in the Cooper Basin, Australia. Journal of Geochemical Exploration, V. 8, pp. 397-414.

D'Hondt, S., Jorgensen, B.B., Miller, D.J., Batzke, A., Blake, R., Cragg, B.A., Cypionka, H., Dickens, G.R., Ferdelman, T., Hinrichs, K.-U., Holm, N.G., Mitterer, R., Spivack, A., Wang, G., Bekins, B., Engelen, B., Ford, K., Gettemy, G., Rutherford, S.D., Sass, H., Skilbeck, C.G., Aiello, I.W., Guerin, G., House, C.H., Inagaki, F., Meister, P., Naehr, T., Niitsuma, S., Parkes, R.J., Schippers, A., Smith, D.C., Teske, A., Wiegel, J., Padilla, C.N., and Acosta, J.L.S. 2004. Distributions of microbial activities in deep subseafloor sediments. Science, 306, 2216-2221.

D'Hondt, S., Rutherford, S., and Spivack, A.J. 2002. Metabolic activity of subsurface life in deepsea sediments. Science, 295, 2067-2070.

Dickens, G.R., Paull, C.K., Wallace, P., and Party, O.L.S. 1997. Direct measurement of *in situ* methane quantities in a large gas-hydrate reservoir. Nature, 385, 426-428.

Duscherer, W. 1980. Geochemical Methods of Prospecting for Hydrocarbons. Oil and Gas Journ.,V. 78, No. 48, pp. 194, 199-202, 204, 207, 208.

Emery, K.O. and Hogan, D. 1958. Gases in Marine Sediments. AAPG Bull., V. 42, pp. 2174-2188.

Faber, E. and Stahl, W. 1984. Geochemical surface exploration for hydrocarbons in the North Sea. AAPG Bulletin, 68, 363-386.

Faber E. 1987. Zur Isotopengeochemie gasförmiger Kohlenwasserstoffe: Erdöl-Erdgas-Kohle, v. 103, no. 5, p. 210–218.

Faber, E. W., J. Stahl, M. J. Whiticar, J. Lietz, and J. M. Brooks, 1990, Thermal hydrocarbons in Gulf Coast sediments, in Gulf Coast oils and gases: Proceedings of the Ninth Annual Research Conference, SEPM and Mineralogist Foundation, New Orleans, October 1, p. 297–307.

Fenn, I.J. 1940. An Hypothesis for the Origin of Certain Geochemical Anomalies Associated with Petroleum Accumulation. In: Rosaire, E.E. (Author) Symposium on Geochemical Exploration Geochemical Prospecting for Petroleum. Bull. of American Assoc. of Petroleum Geologists, Vol. 24., No. 8, pp. 1400-1433.

Fleischer, P., Orsi, T.H., Richardson, M.D., and Anderson, A.L., 2001. Distribution of free gas in marine sediments: A global overview. Geo-Marine Letters, 21, 103-122.

Frank, D.S., Sackett, W.M., Hall, R., and Fredericks, A.D. 1970. Methane, Ethane, and Propane Concentrations in the Gulf of Mexico. AAPG Bull., V. 54, pp. 1933-1938.

Galimov, E.M. 1968. Isotopic Composition of Carbon in Gases of the Crust. Internat. Geol. Rev., V. 11, No. 10, pp. 1092-1104.

Heeschen, K.U., Hohnberg, H.J., Haeckel, M., Abegg, F., Drews, M., and Bohrmann, G., 2007. *Insitu* hydrocarbon concentrations from pressurized cores in surface sediments, Northern Gulf of Mexico. Marine Chemistry, 107, 498-515.

Hinrichs, K.-U., Summons, R.E., Orphan, V., Sylva, S.P., and Hayes, J.M. 2000. Molecular and isotopic analyses of anaerobic methane-oxidizing communities in marine sediments. Organic Geochemistry, 31, 1685-1701.

Hinrichs, K.U., Hayes, J.M., Bach, W., Spivack, A.J., Hmelo, L.R., Holm, N.G., Johnson, C.G., and Sylva, S.P., 2006. Biological formation of ethane and propane in the deep marine subsurface. Proceedings of the National Academy of Sciences of the United States of America USA, 103, 14684-14689.

Hoefs, J., 2004. Stable Isotope Geochemistry, 5th. Springer Verlag, Berlin.

Horvitz, L. 1939. On Geochemical Prospecting. Geophysics, V. 4, No. 3, pp. 210-228.

Horvitz, L. 1945. Recent Developments in Geochemical Prospecting for Petroleum. Geophysics, V. 10, pp. 487-493.

Horvitz, L. 1969. Hydrocarbon Geochemical Prospecting After Thirty Years. In: W.B. Heroy (Editor), Unconventional Methods in Exploration for Petroleum and Natural Gas. Southern Methodist University Press, Dallas, pp. 205-218.

Horvitz, L. 1981. Hydrocarbon prospecting after forty years, in B. M. Gottleib, ed., Unconventional methods in exploration for petroleum and natural gas II;: Dallas, Texas, Southern Methodist University Press. p. 83-95, 1981.

Horvitz, L. 1985. Geochemical exploration for petroleum. Science, 229, 821-827.

Hunt, J.M. 1979. Petroleum Geochemistry and Geology. W.H. Freeman, San Francisco, 617 pp.

Iversen, N. and Jørgensen, B.B. 1985. Anaerobic methane oxidation rates at the sulfate-methane transition in marine sediments from Kattegat and Skagerrak (Denmark). Limnology and Oceanography, 30, 944-955.

Jones, V.T. and Drozd, R.J. 1983. Predictions of oil or gas potential by near-surface geochemistry. AAPG Bulletin, 67(6), 932-952.

Karim, M.F. 1964. Some Geochemical Methods of Prospecting and Exploration for Oil and Gas. Ph.D. Thesis, University of Southern California, 227 pp.

Kartsev AA 1959. Geochemical methods of prospecting and exploration for petroleum and natural gas. Los Angeles, University of California Press, p. 349.

Kennicutt, M.C., Brooks, J.M., and Denoux, G.J. 1988. Leakage of deep, reservoired petroleum to the near surface on the gulf of Mexico Continental slope. Marine Chemistry, 24, 39-59.

Kvenvolden, K.A. 1988. Methane hydrate-a major reservoir of carbon in the shallow geosphere. Chemical Geology, 71, 41-51.

Kvenvolden, K.A. 1993. Gas hydrates-geological perspective and global change. Reviews of Geophysics, 31, 173-187.

Laubmeyer, G. 1933. A New Geophysical Prospecting Method. Zeitschrift Fur Petroleum, V. 29, No. 18, pp. 1-4.

Logan, G.A., Abrams, M.A., Dahdah, N.F., and Grosjean, E. 2009. Laboratory methods for evaluating migrated high molecular weight hydrocarbons in marine sediments at naturally occurring oil seeps. Organic Geochemistry, 40, 365-375.

Mani, D., Patil, D.J., and Dayal, A.M. 2011. Stable carbon isotope geochemistry of adsorbed alkane gases in near-surface soils of the Saurashtra Basin, India. Chemical Geology, 280, 144-153.

Martens, C.S.and Berner, R.A. 1974. Methane production in the interstitial waters of sulfate depleted marine sediments. Science, 185, 1167-1169.

Martens, C.S. and Berner, R.A. 1977. Interstitial water chemistry of anoxic Long Island Sound sediments. 1. Dissolved gases. Limnology and Oceanography, 22, 10-25.

McConnell D., Gharib, J., Henderson, H.-W., Danque, A., Digby, A, and D. Orange, D. 2008. Seep-hunting in deepwater for frontier basin prospectivity assessment: Multibeam echosounders and seismic data detect seeps enhancing hydrocarbon exploration potential, WorldOil Magazine, Vol. 229 No. 4, April.

McDermott, E., 1940. Geochemical Exploration (Soil Analysis) With Speculation About the Genesis of Oil, Gas, and Other Mineral Accumulations. American Association of Petroleum Geologists Bulletin, V. 24, pp. 859-881.

Milkov, A.V. and Dzou, L. 2007. Geochemical evidence of secondary microbial methane from very slight biodegradation of undersaturated oils in a deep hot reservoir. Geology, V. 35(5), pp. 455-458.

Orcutt, B., Boetius, A., Elvert, M., Samarkin, V., and Joye, S.B. 2005. Molecular biogeochemistry of sulfate reduction, methanogenesis and the anaerobic oxidation of methane at Gulf of Mexico cold seeps. Geochimica et Cosmochimica Acta, 69.

Oremland, R.S. 1981. Microbial formation of ethane in anoxic estuarine sediments. Applied and Environmental Microbiology, 42, 122-129.

Pflaum, R. 1989. Gaseous hydrocarbons bound in marine sediments, Ph.D. dissertation, Texas A&M University, Technical Report 98-3-T, Texas A&M Press, 156p.

Philp, R.P. and Crisp, P.T. 1982. Surface Geochemical Prospecting Methods Used for Oil and Gas Prospecting. Journal of Geochemical Exploration, V. 17, pp. 1-34.

Price, L.C. 1986. A critical overview and proposed working model of surface geochemical exploration. In: Pflaum, R.C. (Ed.), Unconventional Methods in Exploration for Petroleum and Natural Gas, Proc. 4th South. Methodist Univ. Symp., pp. 254-304.

Prinzhofer, A., and Pernaton, É. 1997. Isotopically light methane in natural gas: bacterial imprint or diffusive fractionation? Chemical Geology, 142, 193-200.

Reeburgh, W.S. 1983. Rates of biogeochemical processes in anoxic sediments. Annual Review of Earth and Planetary Sciences, 11, 269-298.

Rice, D.D. 1980. Chemical and Isotopic Evidence of the Origins of Natural Gases in Offshore Gulf of Mexico. Transactions of the Gulf Coast Association of Geological Societies, V. 30, pp. 203-213.

Rooney, M.A., Claypool, G.E. and Chung, H.M. 1995. Modeling thermogenic gas generation using carbon isotope ratios of natural gas hydrocarbons. Chemical Geology, 125, pp. 219-232.

Rosaire, E.E. 1940. Geochemical Prospecting for Petroleum. In: Symposium on Geochemical Exploration. American Association of Petroleum Geologists Bulletin, V. 24, pp. 1400-1433.

Sackett, W.M. 1977. Use of Hydrocarbon Sniffing in Offshore Exploration. Jour. Geochem. Explor., V. 7, pp. 243-254.

Schoell, M. 1983. Genetic Characterization of Natural Gases. AAPG Bull., V. 67, No. 12, pp. 2225-2238.

Schoell, M. 1988. Multiple origins of methane in the Earth. Chemical Geology, 71, 1-10.

Sokolov, V.A. 1933. The Gas Survey as a Method of Prospecting for Oil and Gas Formations. Technika, NGRI, No. 1, February.

Stahl, W. 1975. Carbon Isotope Ratios of Natural Gases (in German). Erdol und Kohle, V. 28, pp. 188-191.

Taylor, S.W., Lollar, B.S., and Wassenaar, L.I. 2000. Bacteriogenic ethane in near-surface aquifers: implications for leaking hydrocarbon well bores. Environmental Science and Technology, 34, 4727-4732.

Tissot, B.P. and Welte, D.H., 1984. Petroleum formation and cccurence, 2nd Springer-Verlag, Berlin.

Welhan, J.K., Hunt, J. M., and Berman, J. 1980. Volatile C1-C7 organic compounds in surface sediments from Walvis Bay. Geochimica et Cosmochimica Acta, 44, 1767-1785.

Whiticar M. J., Faber E. and Schoell M. 1986. Biogenic methane formation in marine and freshwater environments: CO2 reduction vs. acetate fermentation - isotope evidence. Geochim. Cosmochim. Acta, 50, 693-709.

Whiticar, M.J. 2002. Characterization and application of sorbed gas by microdesorption CFIRMS. In: Near-Surface Hydrocarbon Migration: Mechanisms and Seepage Rates, American Association of Petroleum Geologist Hedberg Conference, Vancouver, BC, Canada, April 7–10.