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A Volatiles Analysis Case Study Evaluating the Petroleum System, Pay Zones, Seals, Chemical Compartments, and Potential Pays Zones from a Gulf of Mexico Well in the Main Pass Field Using Legacy, Oil Based Mud, and PDC Bit Cuttings, with Tie Ins to Wireline and Seismic Data

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ABSTRACT

We analyzed organic and inorganic volatiles from Cantium's Gulf of Mexico OCS-G 04903 A008 ST1 well cuttings, Main Pass 41 Field; the well was drilled with oil-based mud (OBM). This 2018 sidetrack produces from deep sand. Unpreserved wet cuttings from the top 600 ft of the sidetrack and the lower 2600 ft of the sidetrack were analyzed utilizing rock volatiles stratigraphy (RVS). Unpreserved cuttings were high graded to individual sand grains to remove residual mud. The producing interval was identified using RVS parameters including the presence of non-water-soluble aromatics, biological products like methylethylketone (oil soluble byproduct from consumption of n-butane), oil soluble sulfides, and compositional parameters like gas-oil ratio (GOR). At least 9 different parameters correctly identified the pay sand, agreeing with wireline analysis. RVS data also indicated separate chemical compartments/seals correlating to seismic, residual oil saturations, evaluated biological activity, and identified on potential for up dip/shallower pays and oil migration, reducing risk.

RVS, developed by Advanced Hydrocarbon Stratigraphy and available through Baker Hughes as Volatiles Analysis Service, analyzes entrained organic and inorganic volatile chemistries of geological materials; i.e., cuttings and/or core. RVS custom built/developed cryotrap-mass spectrometry

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systems gently extracts, identifies, and quantifies volatiles. Samples are fresh cuttings/core hermetically sealed at the well, or unsealed/legacy materials up to several decades old.

The Gulf of Mexico can be very challenging for geochemistry of cuttings. The young and cold unconsolidated sands lack sufficient diagenesis to form native fluid inclusions. Polycrystalline diamond compact (PDC) bits, OBM, and unpreserved samples further complicate matters. RVS analysis succeeds in the Gulf of Mexico as RVS analyzes fluids/gases entrained in tight pore spaces/cracks of individual sand grains, is highly sensitive, and is insensitive to OBM. Successful analysis of legacy unpreserved cuttings offers new opportunities for well postmortems, petroleum system analysis, and mature asset exploration. RVS offers new inexpensive exploration insights from legacy cuttings and cores, such as the Texas Bureau of Economic Geology maintains, from 5000+ wells in a 100 mile radius of New Orleans.

INTRODUCTION

The goals of this study were two-fold. First, to provide meaningful data on the petroleum system to Cantium on the sidetrack of the Gulf of Mexico OCS-G 04903 A008 well in the Main Pass 41 Field, Block 30 (MP30 A8 ST1). Second, to demonstrate that rock volatiles stratigraphy (RVS) could overcome the multiple challenges associated with the nature of the cuttings samples being submitted for analysis and the environment from which these cuttings were collected in the shallow Gulf of Mexico offshore environment.

RVS has previously demonstrated its ability to produce meaningful and actionable data for a variety of applications and subsurface questions ranging from post mortems, by-passed pay identification, source rock potential, thermal maturity studies, mapping oil migration conduits, and evaluating sites for carbon capture utilization and sequestration activities among others by directly measuring various volatile organic and inorganic subsurface chemistries entrained in rock samples, typically cuttings or core (C. M. Smith and Smith, 2020; M. Smith and Smith, 2020; Smith et al., 2020; C. Smith et al., 2021; M. P. Smith et al., 2021; Smith and Smith, 2021). Providing information on the petroleum system, especially on potential pay not observed in the wireline logs or in proximity to the borehole, is within the capabilities of RVS, provided viable samples are available. This made the second goal of the study supremely important, could available legacy, unsealed oil-based mud (OBM) polycrystalline diamond compact (PDC) bit cuttings be used as viable samples.

There are multiple challenges associated with the cuttings samples available; these can be broken down into four general categories: the legacy nature of the samples; the rock samples were PDC bit cuttings; OBM had been used during drilling; and finally the environment where the cuttings were from; the young, cold, and unconsolidated sediments of the Gulf of Mexico. These challenges create a situation where the easily accessible hydrocarbons (HCs) have been lost (legacy unsealed sample), the bottle being relied upon to contain residual chemistries (i.e. the rock sample) after initial losses could be generously described as problematic (combination of PDC bit cuttings and unconsolidated sediment), and there has been significant contamination of the samples by OBM.

There are a variety of techniques that can acquire organic geochemical data from rock samples such as rock evaluation pyrolysis, fluid inclusion studies, saturate-aromatic-resin-asphaltene medium pressure liquid chromatography (SARA/MPLC), and gas chromatography (GC) (in addition to its variants such as GC-mass spectrometry [GC-MS] and comprehensive two-dimensional gas chromatography [GCxGC] among others). Some of the challenges with these techniques and the type of sample available have previously been discussed as have the advantages of being able to utilize legacy cuttings samples (M. Smith and Smith, 2020). Many, if not all, of these and other common techniques suffer from at least one of the challenges listed utilizing the available cuttings samples. If core is available, some of these techniques may be

applicable even with these challenges, though the use of core, in the shallow Gulf of Mexico is more likely percussion side wall cores (SWC), which represents a higher cost, risk, and provides significantly less stratigraphic coverage than is available with cuttings.

In terms of legacy samples, certain techniques that rely on sealing cuttings at the well site in jars/cans or using a relatively recent unsealed sample will simply not be applicable, if the samples are ~2 years old at the time of analysis (Thompson, 1978). PDC bit cuttings also present significant challenges for techniques like fluid inclusion analyses that may not be impacted by the age of the sample or the mud system used given how traumatized the rock samples are by the drilling process as compared to rock bit cuttings (van de Graaff and Felder, 2014; M. Smith and Smith, 2020).

OBM is a significant challenge for several organic geochemical techniques and an issue that the RVS technology was specifically designed to address by stopping the analysis after the C10 HCs. Halting the RVS analysis at the C10 range insulates RVS from the effects of OBM. The base oil used for preparing OBM is typically diesel that predominantly consists of C11+, though some minority population of C10 HCs may be present (Hunt, 1995b; Grace, 2003; Gad, 2005; Date, 2020). Other OBM bases derived from oil also typically consist of C11+ HCs (Rossini, 1960; Hunt, 1995b; Beck et al., 1996; Anderson et al., 2003). In the case of synthetic or vegetable derived base oils, these do not analyze the same as typical liquid HCs found in the subsurface (olefins, esters, etc.) and can be identified by RVS. The ability of RVS to analyze cuttings drilled with OBM is important because OBM significantly impacts the quality of organic geochemistry data that can be obtained from cuttings (Sanei et al., 2020)

The nature of the young, cold, and unconsolidated sediments that make up the shallow Gulf of Mexico also represent significant challenges. Techniques that may be able to overcome some of the challenges discussed above, especially analyses of fluid inclusions, are challenged since the conditions for diagenesis to form native fluid inclusions are not readily present (Smith, 1990, 1992, 1993, 1995; Goldstein and Reynolds, 1994; Ward, 2017; Becker, 2018)

To demonstrate that RVS could overcome these various challenges comparisons are made between RVS data and the logs and seismic data acquired by Cantium. Positive correlations, including those that could be expected and/or explained from first principles, relating to chemical composition of oils, phase relationships, and microbial processes, provide confidence that RVS can overcome these challenges.

LOCATION AND SETTING

Cuttings samples analyzed by RVS came from the MP 30 A8ST1. The well is in the shallow/shelf (drilling floor elevation of 115 ft) Gulf of Mexico in the Main Pass 41 Field, Block 30, off the coast of Louisiana; see [Figure 1](#) for location. The well is a sidetrack that was drilled in 2018 by Cantium off the original A8 parent borehole. The MP30 A8 was drilled in 1988 to 8534 ft true vertical depth (TVD) by Texaco and recorded a maximum borehole temperature of 162°F (72°C). The sidetrack kicked off from the original borehole at 3628 ft TVD (4062 ft measured depth [MD]), deviated at an angle of 32–34°, and has a total depth (TD) of 7044 ft TVD (8090 ft MD).

The sidetrack was drilled to investigate potential sand targets apparent on seismic, including some that may be sealed by a fault the borehole crosses; see [Figure 2](#). The fault does serve as a seal and a pay zone has been identified and is now under production. Apparent residual HCs are observed at various positions in the borehole. A deeper sand target thought to be a potential pay zone was also part of the planned drilling program but could not be reached due to high pressure conditions. Subsequent drilling confirmed that this sand contained oil.

The shallow/shelf Gulf of Mexico sediments offshore Texas and Louisiana are frequently described as unconsolidated “terrigenous” sediments brought in from the various river systems that empty into the Gulf of Mexico and are primarily silicates; quartz and clay being the most abundant (Ward, 2017). Examination of the cuttings showed no apparent consolidated sediments and those sections of the wellbore with high gamma ray response appear to be “gumbo” shales.

Well Name ● OCS-G 04903 A008 ST1

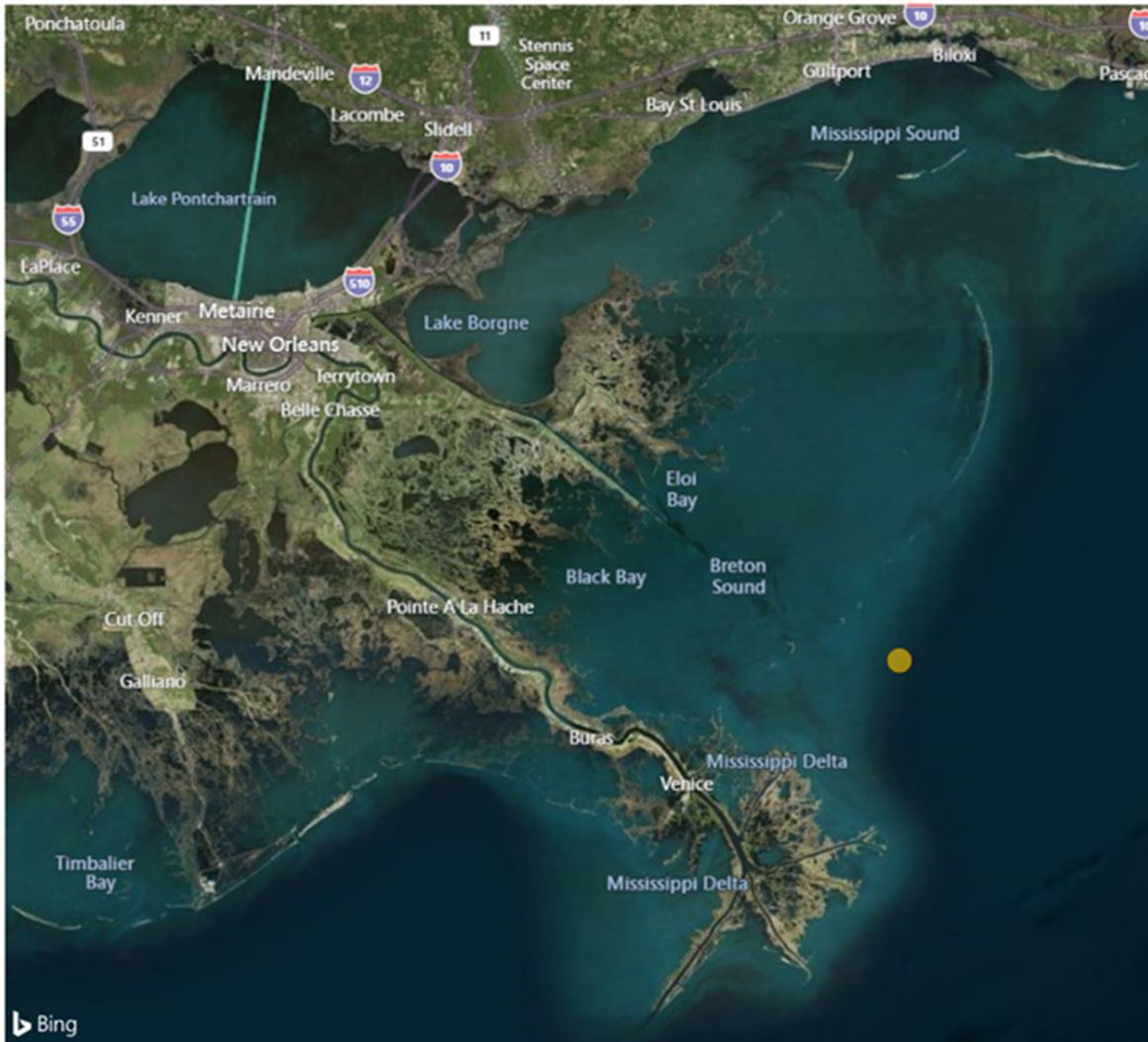


Figure 1. Aerial map of the Louisiana Gulf Coast indicating the position of MP30 OCS-G 4903 A8 ST1.

MATERIALS AND METHODS

Seismic, logs, and survey data for the sidetrack were provided by Cantium. Wireline data for the parent borehole came from the OWL database maintained by Lexco.

The technology, methodology, and workflow for RVS on legacy/unsealed samples, including PDC bit cuttings, has previously been described (M. Smith and Smith, 2020). Briefly, the RVS technology uses 0.4 cc of cuttings per sample. In the case of legacy unsealed cuttings, the sample is first crushed with 2 tons of force over 0.5 in² surface area in a brass vessel interfaces to the vacuum system and is then subjected to two vacuum extractions (at 20 mbar and then at 2 mbar). No solvents or heating are applied to the samples. The vacuum gently extracts all HCs

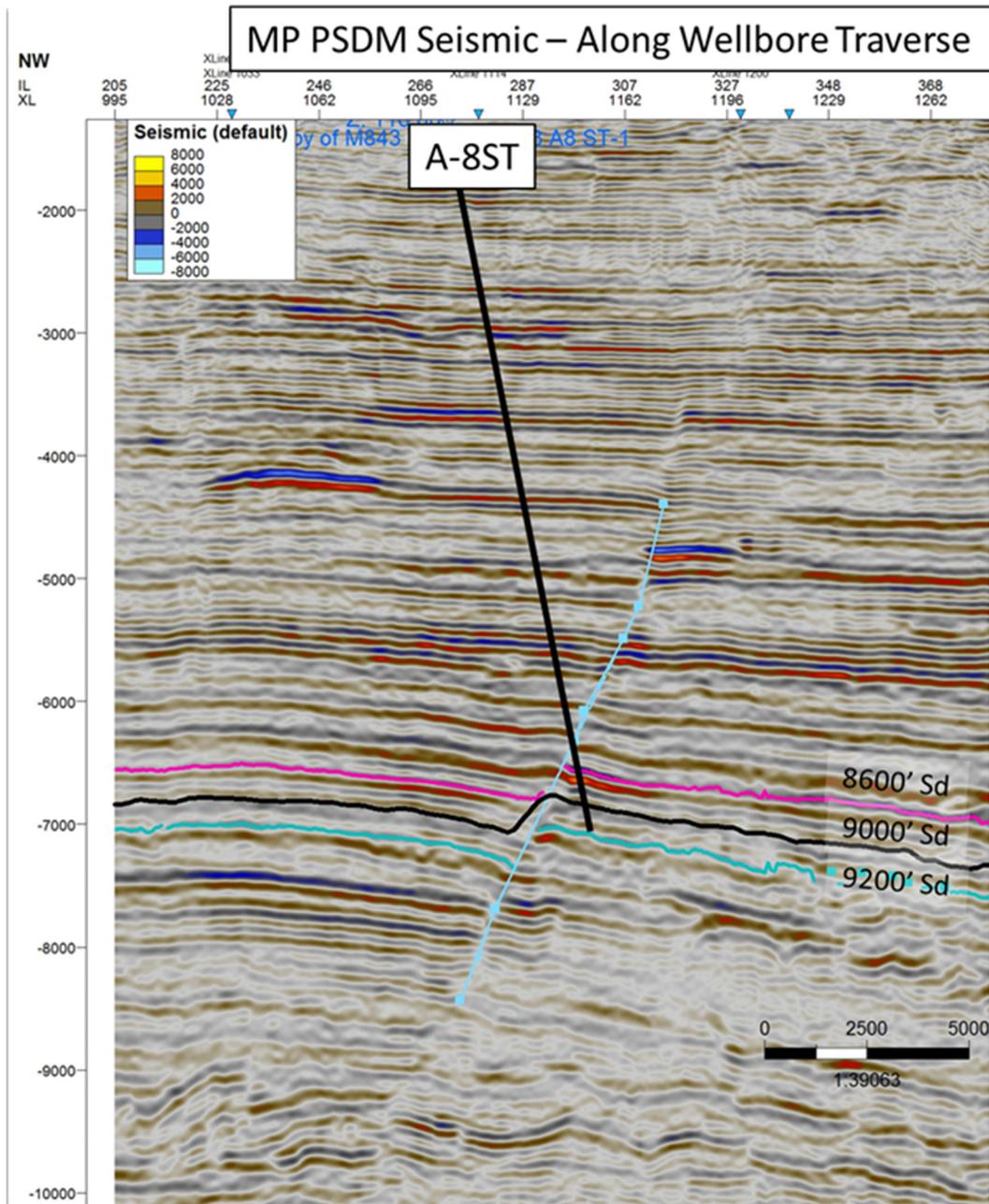


Figure 2. Seismic and well bore trajectory of the sidetrack. Fault and sands of interest are highlighted.

up to the C11 range by bringing liquid HCs to their boiling point at room temperature, as well as a significant portion of the remaining liquid HCs into the C13 range. This process also extracts several other organic and inorganic compounds including biological byproducts, various sulfur species, carbon dioxide, etc. Extracted volatiles are frozen on a liquid nitrogen cold trap. After

a given vacuum extraction is complete the non-condensable gases are submitted to a quadrupole MS for analysis before beginning to warm the cold trap. As the cold trap warms frozen volatiles, ethane and higher are released via sublimation and analyzed by the MS. The sequential release of volatiles by the cold trap allows for a separation stage similar to a gas chromatography column, but with several advantages including already operating under vacuum conditions which greatly increases sensitivity. Combined with the MS, this system of crushing, vacuum extractions, and liquid nitrogen cold trap, allows for the gentle extraction, separation, identification, and quantification of over 35 different volatile compounds. The analysis cuts off at C10, despite having access to higher order HCs.

Sample preparation of the MP30 A8ST1 OBM PDC bit legacy cuttings for analysis involved several extra steps due to the lithology of the cuttings and the condition in which they were received. The wet cuttings were sent from Core Labs' facilities in Broussard, Louisiana, directly to AHS's lab in Tulsa, Oklahoma. The wet cuttings were allowed to gently air dry for several days, with occasional stirring in a well-ventilated room; this allowed for the gently removal of the residual OBM. While this aeration may have resulted in some losses of the volatile analytes of interest, past experimentation has shown that most of the volatile analytes come from the tight pore spaces, micro cracks, and fresh surfaces that are opened and exposed immediately upon crushing. Once the cuttings were dry, they were high graded to remove the residual mud and select individual sand grains; **Figure 3** is a cuttings sample before and after high grading.

The cuttings were averaged over intervals ranging from 10 to 30 ft; a denser sampling was used in intervals of interest such as the pay zone sand intervals. Unless otherwise noted, all depths are in MD. Two intervals were submitted for RVS analysis, an upper section starting at the top of the sidetrack 4070–4700 ft MD and a lower section that went to TD, 5420–8090 ft MD.

COMPARISON OF RVS TO WIRELINE DATA

The logs indicated a sand from ~7730–7780 ft MD as a pay zone; see **Figure 4**. While this sand has a relatively high gamma ray response compared to other sands encountered, there is a clear high resistivity response present. Subsequent side wall cores confirmed the presence of oil.

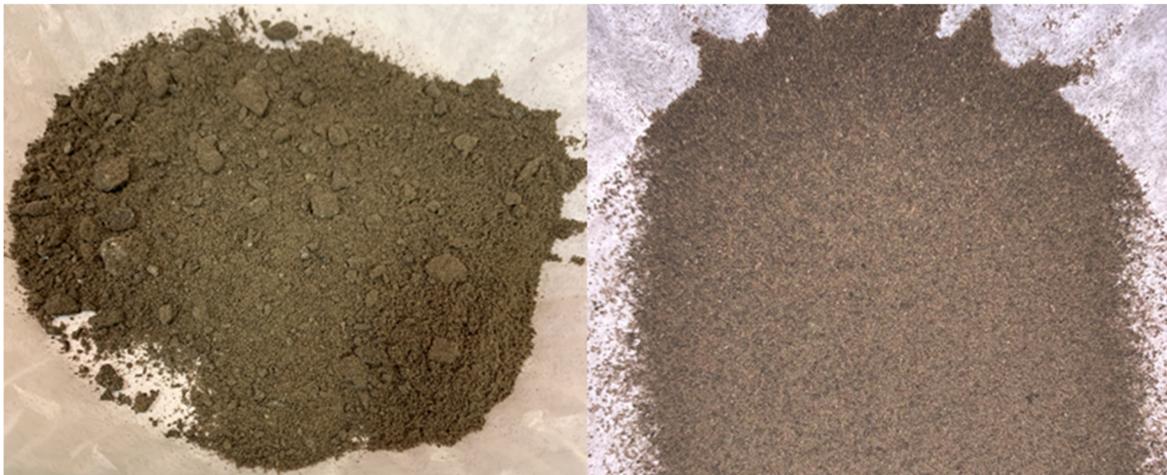


Figure 3. Example of cuttings sample (left) after drying but before high grading and (right) after high grading.

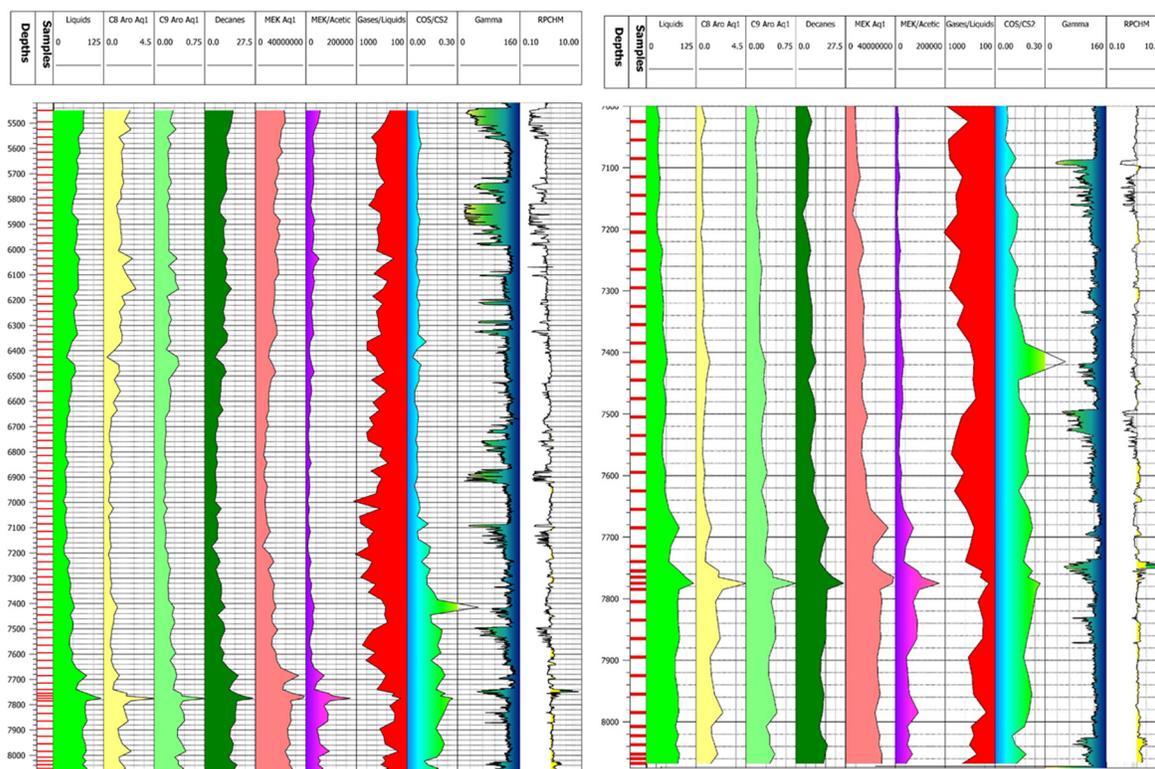


Figure 4. Comparison of selected RVS datasets and compositional parameters to log data. Left panel shows covers of complete lower section. Right panel expanded for pay zone. Aq1 refers to Aliquot 1, this is the data acquired at the 20 mbar vacuum extraction. If no aliquot is indicated the data comes from the sum of both vacuum extractions.

Several direct measurements and compositional parameters from the RVS data, shown in [Figure 4](#), indicate the pay zone. The overall liquid HC response picks out the pay zone as do most of the individual liquid HC species. Methyl ethyl ketone (MEK, also called 2-butanone) also identifies the pay zone. While the highest responses in the borehole for many of these signatures are in the pay zone, several show responses to a sandy shale at -7695 ft MD.

Compositional parameters can be applied to assist in the identification of the pay zone. Three are shown in [Figure 4](#). Perhaps the best is the ratio of MEK to acetic acid. Both are produced from biological activity but have very different phase relationships: MEK is hydrophobic/oil soluble; conversely acetic acid is hydrophilic/water soluble (Rumble, 1987; Hunt, 1995a; Røe Utvik, 1999; Skaare et al., 2007; Skaare et al., 2011). Thus, the ratio of the two can help identify phases, provided microbes are present; a high MEK/acetic acid ratio presumably indicate the presence of oil, though the highest values may be near the oil water contacts where the biological by-products would be locally produced and in the highest abundance. Evaluating the amount of detected gas versus liquid HC molecules, very similar to a gas-oil ratio (GOR), also identifies the pay zone as having the lowest ratio in the borehole, not necessarily unexpected because of the abundance of liquids, but also because HC gases are generally more soluble in water than HC liquids (Rumble, 1987).

Finally, the ratio of carbon disulfide (CS₂) to carbonyl sulfide (COS) is somewhat helpful in evaluating the pay zone. The sourcing of these sulfides in the subsurface is not well understood, though they are known to be present in the atmosphere and generated in marine environments;

their presence in the subsurface may be related to depositional environments, which have previously been observed with unconformities in cores (C. M. Smith and Smith, 2020; Lennartz et al., 2020; M. Smith and Smith, 2020). While both COS and CS₂ are hydrophobic, at standard temperature and pressure (STP) conditions the CS₂ is roughly twice as soluble in water as COS (Rumble, 1987). The ratio of COS vs. CS₂ can provide information about phase relationships; in [Figure 4](#), the second highest ratio value is observed at the base of the pay zone indicating the presence of an environment with reduced water content.

In the shallower interval of the well that was analyzed the wireline coverage was not complete, starting on the third cutting sample submitted to RVS. An interesting relationship that was observed in this section of the well were a series of four discrete relatively high HC liquids responses. These were correlated to likely residual accumulations, see [Figure 5](#).

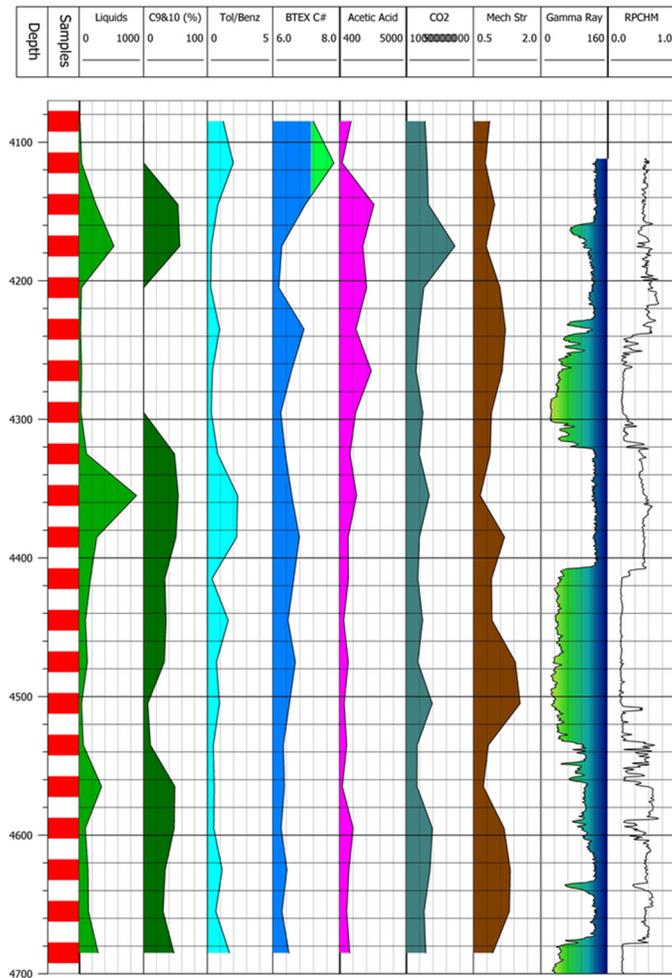


Figure 5. Selected RVS datasets and compositional parameters compared to log data. Many of the enhanced liquid responses correspond to depths where residual HCs could be interpreted in the wireline data. Interestingly, the samples with high HC liquid values have the lowest mechanical strength, suggesting that the HC Liquids may possibly be active as a lubricating agent during the crushing process. BTEX C# interpretations are not possible when the ratio of toluene to benzene is very high due to migration; this is not an issue in the analysis of this section of the borehole.

COMPARISON OF RVS TO SEISMIC DATA

Figure 6 shows a series of relationships that appear to undergo stepwise changes at various positions, perhaps the most apparent at ~6200 ft TVD. These changes strongly suggest that different chemical compartments (oxidative environments, HC compositions, and phases) are present both in relation to this feature but also at other depths. Aligning the RVS data with the seismic data, most of these stepwise changes are likely associated to the presence of the fault that the borehole crosses, (Fig. 6). The changes in the HC composition, transitioning from high benzene/low hexanes to low benzene/high hexanes, suggests moving from a water-rich environment to one less so, based on the solubility of these molecules. A similar trend is present in the ratio of COS/CS₂. Discrete stepwise changes are observed in the absolute quantities of COS, CS₂, and CO₂ at this depth. These indicate the presence of different chemical compartments; depths shallow to the fault are in a more reducing environment whereas depths deeper than the fault are in a more oxidative environment. The stepwise increase in CO₂ is also likely linked to subsurface pressure, appearing to be consistent with observations made by Cantium during drilling.

Multiple factors control the presence of CO₂ in the subsurface in terms of its sourcing and solubility; one of the key parameters controlling subsurface solubility of CO₂ is reservoir pressure (Klara, 1990; Carr et al., 2003; Sasaki et al., 2014; Zhang et al., 2015; Barclay and Mishra, 2016). These data also suggest that the fault is competent to hold back CO₂ and the interval below the fault may be usable for carbon capture storage activities. The composition of the HCs, reflected in the American Petroleum Institute (API) gravity of the gasoline range liquid HCs measured,

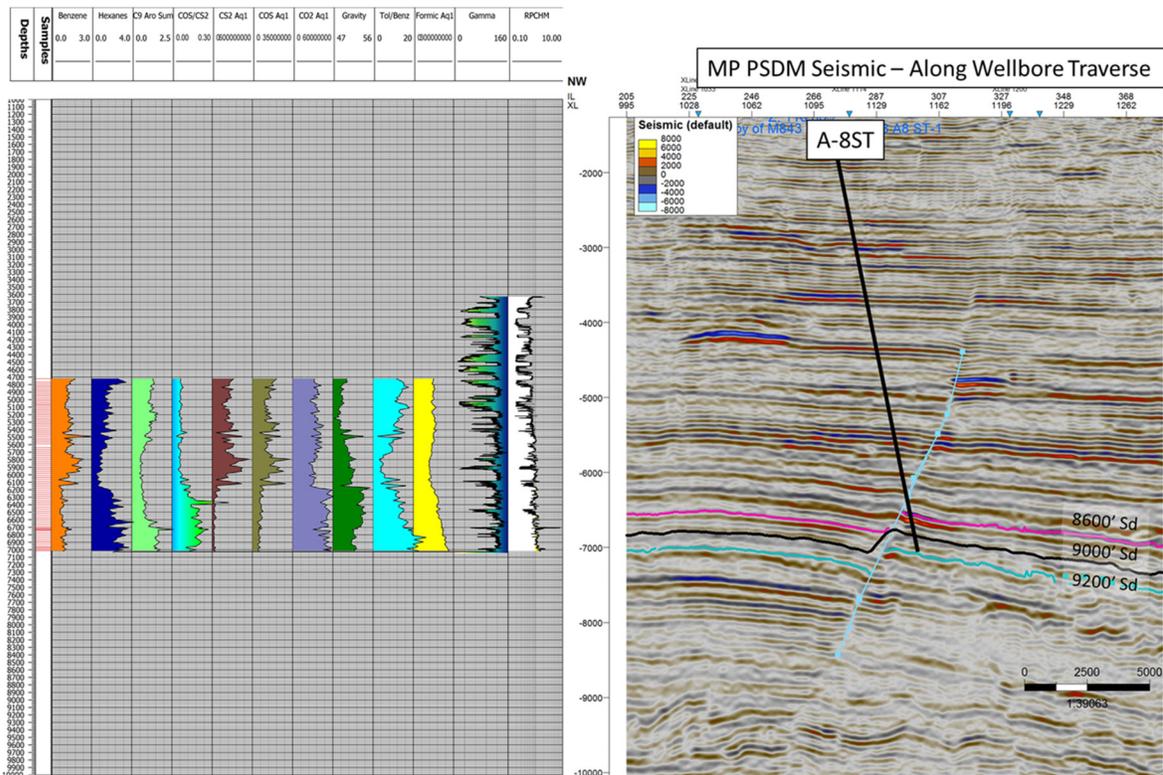


Figure 6. Selected RVS data and compositional parameters with log data presented in TVD aligned with seismic data; path of the sidetrack borehole and fault are indicated.

shows a significant transition, going from a denser composition above the fault to a lighter composition below the sealing fault, largely due to the greater abundance of aromatics in the aqueous phase above the fault. The lightest HC liquid composition is observed directly below the fault. Although this is not a pay zone, if the fault serves as a seal, it is feasible that a population of light, volatile, and mobile liquid HCs would concentrate below it. The ratio of toluene to benzene also indicates oil migration in the borehole; produced crudes tend to have molar ratios of 3 or less, but values as high as 5 occasionally observed (Rossini, 1960; Smith, 1968; Lord et al., 2018). In RVS data, values ≥ 3 are flagged as potential oil migration signatures; values in excess of 5 require significant subsurface processes to alter the composition of the liquids HCs; see M. Smith and Smith (2020) for a detailed discussion. Approximately 300 ft before the fault, the ratio is ~ 5 ; however, throughout the rest of the evaluated section, the ratio is typically ≥ 10 . These data strongly suggest that there is significant vertical migration of oil throughout the borehole, but the migration is significantly interrupted at the fault which serves as a sealing feature.

While not directly related to the seismic data, there are other transitions present in the HC data and possibly the ratio of COS to CS₂, that seem to indicate the presence of other potential “phases.” For example, while hexanes show a stepwise increase below the fault feature indicating a less water/mole oil-like phase, the C9 aromatics undergo a stepwise increase at ~ 6620 ft TVD suggesting a change in phase. This is likely indicative of the presence of residual oil vs. oil, an interpretation that may be supported by the wireline data which appears to show residual HCs in several of the low gamma ray zones below the fault.

EXPANDED RVS PETROLEUM SYSTEM ANALYSIS

In addition to the aspects of the petroleum system discussed in relation to the wireline and seismic data, there are other important aspects of the petroleum system that the RVS data reveal.

A key point of interest to Cantium is proximity to pay and by-passed pay indicators. In **Figure 6**, the formic acid increase is a fairly consistently increasing gradient from the fault to TD. Such a gradient is typically indicative of approaching a HC accumulation; the gradient continues to increase past the pay zone in the well strongly suggesting a deeper prospect (C. M. Smith and Smith, 2020). Cantium had intended to drill to test a deeper sand, but was unable to do so because of drilling concerns. Subsequent drilling confirmed the presence of a deeper oil accumulation.

There were also prospects for shallower pay towards the top of the sidetrack in the analyzed upper section of the borehole. The first two cuttings samples cover a depth range not adequately covered by the logs, see **Figure 5**. At the top of the upper section the sidetrack starts in a sand that is documented from the wireline of the original borehole. The sample at 4145 ft MD has the highest acetic acid observed in this section of the well. The sample at 4115 ft MD contains the lowest acetic acid in the section and a composition of the aromatic HCs (benzene, toluene, ethylbenzene, xylenes aka BTEX) similar to that of produced crude. The average carbon number of BTEX (BTEX C#) HCs in produced crudes is 7.48 with a lower range of 7.13 (Rossini, 1960; Smith, 1968; Lord et al., 2018). We have found that when these values are achieved or approached in RVS data it is indicative of pay zones and less water content. At the top of the section (4070–4160 ft MD), the transition from high BTEX C# values (4070–4130 ft MD) and the lowest acetic acid response in the section (4100–4130 ft MD) to BTEX C# values < 7.13 and the highest acetic acid response in the section (4130–4160 ft MD) suggests the presence of an oil-water contact between 4115 and 4145 ft MD and a shallow oil accumulation. The possibility of an accumulation at this depth may be supported by completions in nearby wells to the south that perforated a shallow sand, possibly the same being considered here (based on information retrieved from the OWL database).

The RVS data also provides detailed information about the apparent distribution of the HCs within the pay zone sand from ~ 7750 – 7780 ft MD. **Figure 7** shows the distribution of various paraffins (alkanes) and naphthenes (cycloalkanes) by carbon number in the pay zone. While the

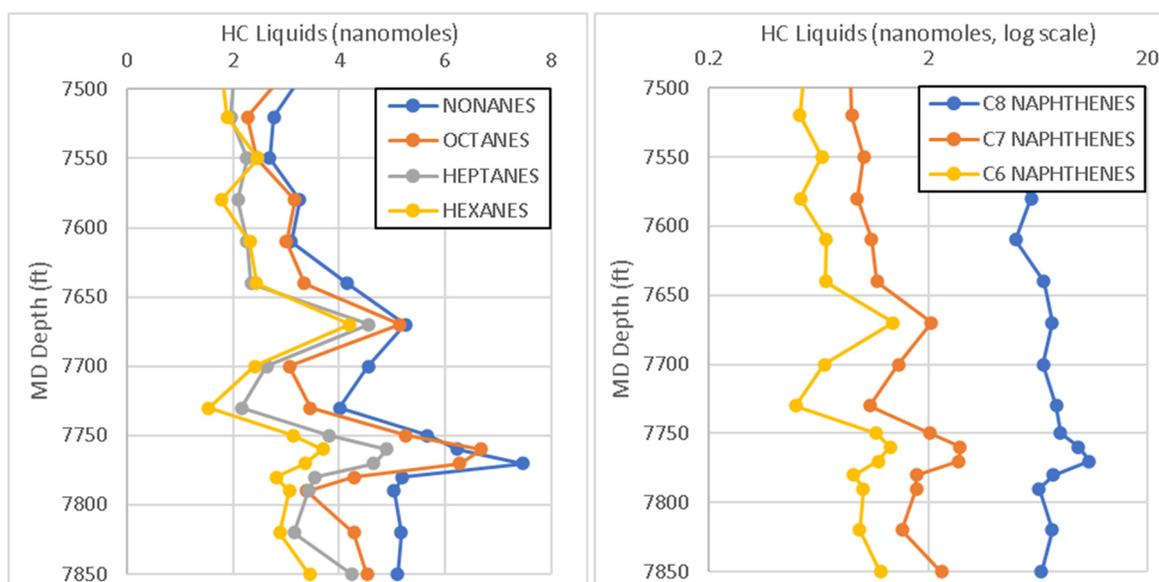


Figure 7. Paraffins (left) and naphthenes (right) distribution by depth. Note that as the carbon number increases the trend of maximum response in the pay zone appears to shift deeper.

data favor the less volatile HC liquids, the distributions suggest a density gradient within the pay zone; liquids with the lower carbon numbers (less dense) are located towards the top of the pay zone and the higher carbon number HCs (more dense) are located towards the bottom of the pay zone.

The biological activity that produces MEK, which facilitates the identification of the pay zone, has altered the HC composition of the pay zone. This alteration is observed in the relationship between butanes and MEK. N-butane is the feedstock for the production of MEK (Hunt, 1995a). The MEK response is in opposition to the moles of butanes in and about the pay zone (Fig. 8). The inverse relationship suggests the biological activity is prolific enough that feedstock molecules are depleted faster than they are replenished via diffusion or other mechanisms. There is evidence that biological activity has impacted the amount of oxygen present in the cuttings at these depths (data not shown).

CONCLUSIONS

The combination of sample parameters, PDC bit cuttings, OBM, legacy materials, and the young, cold, and unconsolidated sands from the shallow Gulf of Mexico, present significant challenges to traditional methods of collecting actionable organic geochemical data. In this study several meaningful correlations between the RVS data and other datasets such as logs and seismic were demonstrated. These correlations not only replicated information generated from these other datasets, such as pay zone identification, but provided new insights when combined with these datasets, such as evaluating the effects of the fault on the petroleum system. RVS data also provided insights into the petroleum system separate from combinations with these other datasets. The successful prediction of a deeper oil accumulation, the identification of potential bypassed pay at the top of the sidetrack, and the HC distributions and effects of biological activity in the pay zone are information that would not be obtainable with the other tools utilized on the MP30 A8ST1. The correlations not only demonstrate that RVS can generate

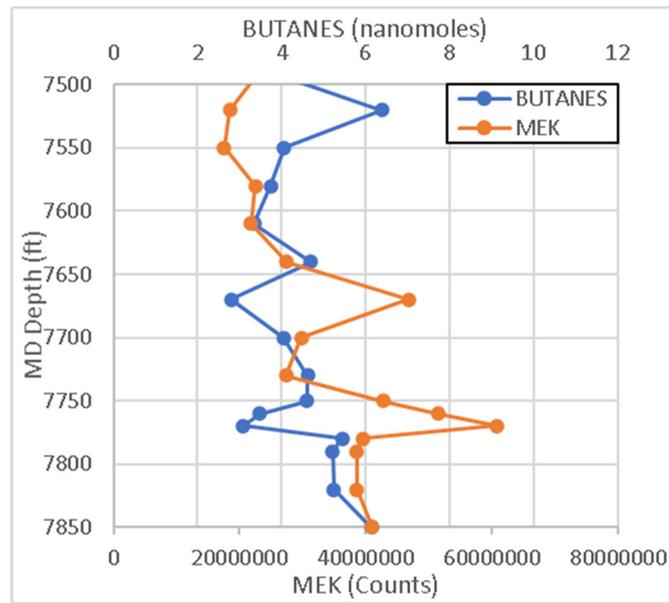


Figure 8. Butanes and MEK content measured by RVS in and proximal to the pay zone sand.

meaningful and actionable geochemical data from the analysis of the entrained volatiles, overcoming the challenges discussed with this sample type, but that it is a powerful tool that can provide new and actionable information in the shallow Gulf of Mexico setting.

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