COMPARISON OF CUTTINGS- AND CORE-BASED VERTICAL GEOCHEMICAL PROFILES & IMPLICATIONS FOR TIME-LAPSE PRODUCTION GEOCHEMISTRY IN

UNCONVENTIONAL RESERVOIRS

A Thesis

by

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Submitted to the Graduate and Professional School of Texas A&M University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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ABSTRACT

This study demonstrates a comparison of a High-Resolution Gas Chromatography (HRGC) analysis of drilling cuttings and sidewall cores from the same oil well, with the purpose of determining how well the two sample types are correlated; and to discuss their potential implications on further geochemical analyses such as Time-Lapse Geochemistry (TLG) and more specifically Production Allocation (PA). We used HRGC to determine the peak-height ratios (PHRs) shared between the two sample types. We then compared these PHRs with produced oil samples from the same well to determine if cuttings provide the same accuracy of geochemical information as core extracts. Our results show a strong correlation of peak-height ratios, both between cuttings and core samples, as well as between cuttings and produced fluid samples, in the range of primary peaks n-C15 to n-C27. Trends in peak-height ratios also mimic petrophysical logs, which suggests cuttings are also representative of geologic characteristics, such as depositional environments and specific organic matter content. The implication of this research is such that it is indeed possible that cuttings may serve as a substitute for sidewall core samples when setting up the geochemical reference profile needed for TLG and PA. Because cuttings are a byproduct of every well (compared to core which requires specific tools and operations to extract), substituting core plugs with cuttings samples when setting up vertical reference profiles would imply a substantial cost savings for Exploration & Production (E&P) companies.

DEDICATION

I hereby dedicate this thesis to the advancement of petroleum geochemistry, and the application of geological concepts to augment the crossover of research and innovation between the Geosciences and Petroleum Engineering; as is the mission of the joint-research program of the Crisman Institute for Petroleum Research, and the Berg-Hughes Center for Petroleum and Sedimentary Systems.

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To my friends and colleagues, inside and outside of the department, I thank you for making my experience at Texas A&M University both worthwhile and enjoyable. Especially through what has been one of the most challenging years in recent history, stemming from the Covid-19 pandemic, its associated effects on society, and our way of life.

Lastly, I would not be in this position to begin with if it were not for my parents, Mary & Geoff Scherer and my brother Will Scherer, who have supported my career aspirations and professional development every single day.

iv

CONTRIBUTORS AND FUNDING SOURCES

Contributors

This work was supervised by a thesis committee consisting of Professor Franco Marcantonio, Alan Yu, Mauro Becker, and Mukul Bhatia of the Department of Geology and Geophysics, and by Professor Jeffrey Spath of the Department of Petroleum Engineering at Texas A&M University.

Apache Corporation made access to the cuttings samples, prior core extract geochemical analysis, and digital logs available to our team for the purposes of this project. Dr. Daniel Xia and Dr. Changrui Gong, of Apache Corporation, have also contributed their time and knowledge as subject matter experts.

All other work conducted for the thesis was completed by the student independently.

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The contents of this work are solely the responsibilities of the authors and do not necessarily represent the official views of the Department of Geology and Geophysics, the Crisman Institute for Petroleum Research, or the Berg-Hughes Center for Petroleum and Sedimentary Systems.

ii

NOMENCLATURE

APA	Apache Corporation
C#	Hydrocarbon Compound, # indicating the number of Carbon atoms
D&C	Drilling & Completions
DRV	Drained Rock Volume
FID	Flame Ionization Detector
GC	Gas Chromatography
GC-MS	Gas Chromatography and Mass Spectroscopy
GCXGC	2-Dimensional Gas Chromatography
GR	Gamma Ray (well log)
HRGC	High-Resolution Gas Chromatography
OBM	Oil-Based Mud
PA	Production Allocation
PHR(s)	Peak-Height Ratio(s)
QC	Quality Control
QEXQ	Quantitative Light Hydrocarbon Extraction
TLG	Time-Lapse Geochemistry
VB	Visual Basic
WBM `	Water-Based Mud
XRF	X-Ray Fluorescence

TABLE OF CONTENTS

ABSTRACT	ii
DEDICATION	iii
ACKNOWLEDGEMENTS	iv
CONTRIBUTORS AND FUNDING SOURCES	v
NOMENCLATURE	viii
TABLE OF CONTENTS	ix
LIST OF FIGURES	xiii
LIST OF TABLES	xiii
1. INTRODUCTION	1
1.1 Overview of Time-Lapse Geochemistry1.2 Project History	1 4
2. METHODOLOGY	6
 2.1 Data Acquisition	6 7 9 13 15 18
 RESULTS & DISCUSSION	20 20 22 30

Page

5. CONCLUSION	35
6. RECOMMENDATIONS FOR FUTURE RESEARCH	37
7. DATA CONTINUITY	43
REFERENCES	39
APPENDIX A	40
APPENDIX B	41
APPENDIX C	

LIST OF FIGURES

Page

Figure 1	Gas Chromatogram Metrics	1
Figure 2	Reference Profile Workflow	2
Figure 3	Production Allocation Workflow	3
Figure 4	Samples as Received	7
Figure 5	Samples after Preparation	8
Figure 6	First Subset Sampling Interval	9
Figure 7	Sample HRGC Summary Sheet	13
Figure 8	Primary vs. Intermediary Peaks	14
Figure 9	Chromatograph Indexed using Malcom TM	16
Figure 10) Unindexed Chromatogram of Whole Oil	20
Figure 11	Unindexed Chromatogram of Cuttings Sample	20
Figure 12	2 Sample Index of Core Sample	21
Figure 13	3 Sample Index of Cuttings Sample	21
Figure 14	Sample Type Distribution	22
Figure 15	5 Vertical Reference Profile 1 & 2	25
Figure 16	5 Vertical Reference Profile 3 & 4	26
Figure 17	Vertical Reference Profile 5 & 6	27
Figure 18	3 Vertical Reference Profile 7 & 8	28
Figure 19	Vertical Reference Profile 9 & 10	29
Figure 20) Geological Calibration of Vertical Reference Profile	32
Figure 21	Kerogen Type and Maturity	33

LIST OF TABLES

Page

1. INTRODUCTION & PROJECT BACKGROUND

Overview of Time-Lapse Geochemistry

Time-Lapse Geochemistry (TLG) applied to unconventional reservoirs is a methodology based on laboratory analysis, which involves using high-resolution gas chromatography (HRGC) to find geochemical signatures (also known as "fingerprints"). Geochemical fingerprints are patterns in the data output of an HRGC analysis that are unique to the hydrocarbons originating from a specific source rock. While the overall composition of oils are similar in the hydrocarbon compounds they contain, one can differentiate oils by investigating the relative abundances of each of the many hydrocarbon compounds contained within an oil sample. One such method is by identifying peak-height ratios (PHRs) that are unique to an interval. Alternatively, some groups use either absolute peak-heights or peak-area ratios (see Figure 1). We elected not to use peak-area ratios (the ratio of area under a peak from its mathematical integration) because they are often too small to be useful when processed by our chosen Schlumberger MalcomTM geochemical integration software. In addition, absolute peak



Figure 1: Chromatograph depicted the three different metrics used for geochemical fingerprint: Peak-Height Ratio, Peak-Area Ratio, and Absolute Peak Heights.

heights are less stable and consistent than peak-height ratios (Jweda et al., 2021) so we did not use that method either.

By finding these identifying ratios in either cores or cuttings, a geochemist can establish a vertical geochemical profile to serve as a reference when comparing produced fluids to these fingerprints. Produced oil samples are tested with the same HRGC instrument and using a linear algebraic commingling equation, it is possible to decipher the relative contributions of oil from between 2 and 6 different formations collected at different times at the wellhead (McCaffrey and Baskin, 2016), (Liu, et al., 2017) and (Liu, et al., 2020). Prior studies show that since the number of different



Figure 2: A generalized workflow of the steps necessary to set up vertical reference profiles for Time-Lapse Production Allocation, adapted from (Jweda et al., 2021).

compounds in oil and gas is so great, even extremely similar oils are able to be differentiated from one another when using peak-height or peak-area ratios (McCaffrey and Baskin, 2016). A generalized workflow is shown in Figure 2 and Figure 3.

By monitoring the chemistry of produced fluids of a well, we can gain a greater understanding of the origins of the contributing fluids and track how the individual oil contributions of a commingled fluid change through the production lifecycle of a well. TLG analyses have provided insight into Reservoir Quality, Frac Height/Intensity, Frac Hit identification, and changes in Drained Rock Volume (DRV), (Liu, et al., 2020). By considering these various methods, one may gain additional insight into the effectiveness



Figure 3: A generalized workflow of Time-Lapse Production Allocation after a vertical reference profile is established, adapted from (Jweda et al., 2021).

of engineering challenges such as vertical and horizontal well spacing, completion designs, and parent-child interference.

The traditional method for setting up the in-situ vertical profile for reference is by taking sidewall cores during a well's drilling (see Figure 2). While sidewall coring is often an effective method for preserving the hydrocarbons contained within a rock sample, the process can be expensive, both financially and in the time it adds to drilling and completing a well. Alternatively, drill cuttings, the ground-up rock material created from the drill bit grinding the formation rock, are a byproduct of every well, and require little additional capital and labor to collect, sort, and catalog. Even when cores are used, the cost for TLG is between 1 and 2% of the cost of production logging (McCaffrey and Baskin, 2016).

While cuttings are more vulnerable to chemistry changes caused by drill bit heat, contamination from drilling fluid interactions, and volatile loss during storage, they are still in use by the industry for production geochemistry, particularly from water disposal wells (Liu, et al., 2020). While there is a recent study comparing core and cuttings for the RockEval pyrolysis analysis (Sanei, et al., 2020); there is no such study available that presents both a quantitative and qualitative comparison of the use of cuttings and core specifically from the same well for TLG. This research aims to compare cuttings and core samples from the same well, along with produced oil chemistry to evaluate the applicability of using cuttings samples when setting up vertical reference profiles for TLG.

Project History

This project originated as a research topic proposed to the members of the Crisman Institute for Petroleum Research, who voted unanimously to fund this project aimed at increasing the affordability and effectiveness of TLG for use in the Energy Industry. Crisman members supporting this project include Chevron, Halliburton, Schlumberger, Apache, BP, CNOOC, Enverus, ExxonMobil, Marathon Oil, Pioneer Natural Resources, Santos, Southwestern Energy, and University Lands.

Partnering with Apache Corporation, specifically Dr. Changrui Gong and Dr. Daniel Xia, our research group was able to come up with the idea to first see if enough hydrocarbons remained in cuttings samples to be detectable by a HRGC instrument. If so, we also wanted to determine whether the data gained from cuttings is able to be correlated with data from core extracts, and produced oil from our study well. The motivation for this work to reduce the cost associated with Time-Lapse Geochemistry analyses. While already regarded as one of the more cost-effective methods of reservoir monitoring and production allocation, the use of cuttings in place of core would reduce drilling and completions (D&C) time and expense, allow data sparse areas to be infilled using cuttings collected on prior wells, and provide an additional means of calibrating existing core samples.

For this study, both the core and cuttings come from the same well, a direct comparison that will add value to the growing body of literature on TLG. The well is located in Texas in an unconventional petroleum play. The exact location of the well is undisclosed at the request of Apache Corporation. The well finished D&C in September of 2017; and sidewall cores were taken to be analyzed with HRGC and Pyrolysis (RockEval). It is important to note that the well in our study was drilled using Water-Based Mud (WBM), so we do not expect the samples to be heavily contaminated from drilling fluids. Other studies have found that cuttings acquired with Oil-Based Mud (OBM) may be too contaminated to use in a reference profile (Jweda et al., 2021). Apache sampled, sorted, and stored the cuttings until our study began in the year 2020. Apache Corporation also periodically sampled fluids from the well and analyzed their composition using HRGC.

2. METHODOLOGY

Data Acquisition

This project involved the collection, analysis, and interpretation of both physical and digital data. The physical data came in the form of 142 bags of cuttings, each representing a range of depths between 15 and 30 feet (4.6-9.1 meters) per bag. The total depth coverage of these samples is 2709 feet (825.7 meters). Apache shipped the samples from a field office to our laboratory on the grounds of Texas A&M University in the fall of 2020. We then proceeded with our sample preparation workflow, which included transfer into new bags, weighing, labeling, checking for contamination, and then sealing to reduce further evaporation of hydrocarbons in the sample.



Figure 4: Cuttings samples as received from Apache Corporation in paper envelopes. Cuttings are sorted similar to core boxes, where the top left is stratigraphic high and the bottom right is stratigraphic low.



Figure 5: Cuttings after they were transferred into resealable sample bags to reduce further sample degradation due to evaporation. Bags are labeled to include depth interval, mass, formation tops, and flags for possible contamination.

Apache also provided a library of digital data pertinent to the well and study area included Digital Logs (.LAS format), X-Ray Fluorescence of sidewall cores, Gyrodata (Well Deviation) survey, Geologic Well Prognosis (Geoprog), Pyrolysis Source Rock Analysis (RockEval), as well as raw HRGC data of produced oils and sidewall cores. This digital information is in a centralized repository to ensure consistent access for researchers, while maintaining the confidentiality of provided data.

Cuttings Data Processing and Analysis

As previously mentioned, there were two major milestones of our project, first to determine if there were enough hydrocarbons left in the sample to create a geochemical signature

detectable by the HRGC instrument, and next to compare the geochemistry of the cuttings to that of the core and produce oil samples, which had previously been analyzed by Apache in 2018.

For our first phase of the project, we began by identifying a small subset of 12 total samples cuttings samples. Of the 12 samples, eight were unique samples; the other four were two sets of duplicate samples that we used as an internal control to ensure the instrumentation was providing consistent and repeatable results. The criteria for these samples were that they were within the approximately 1000-foot (305 meter) depth range of the core samples. In addition, we selected a higher resolution of samples within the approximately 200-foot (60 meter) depth interval of the produced oil samples depicted by Figure 6.



Figure 6: Visual depiction of the sample range for the first phase of our research. All samples are within the core extract GC results, with extra resolution within the range of produced oil GC results.

By only sampling the cuttings that were within the range of core and/or produced oil sample

depths, we would be able to conduct a preliminary assessment of both the quality and accuracy

of geochemical information received from our cuttings samples. We also used this smaller subset to ensure the project remained within our financial budget in the case that the theory was not worth continuing with further. If we determined that the information, we received from the cuttings would have the potential to be sufficient for TLG and PA analyses, we would then sample a much larger depth range of cuttings samples.

The second subset of cuttings samples would then be purely complimentary to our original dataset and fill in the depth interval gaps to ensure we were recording a continuous interval of PHRs to compare with the core and produced oil data.

Laboratory Analysis

For the laboratory analysis of our cuttings, we elected to use Stratum Reservoir in Houston, TX to perform the HRGC analysis. We specifically made this decision as they are the same laboratory that processed the original sidewall core samples on behalf of Apache in 2018, so that we could ensure scientific control with the sample preparation procedures, instrumentation, internal standards, and data reporting. In addition, we also elected to use Apache's internal oil sample to calibrate our results and to ensure the consistency of the gas chromatographs between our samples and subsets.

Upon receipt of our samples the Stratum Reservoir laboratory washed the samples using their procedure for samples collected with WBM, inspected the cuttings samples for potential contamination, picking to remove contamination, a light hydrocarbon extraction and finally a HRGC analysis of the extract samples.

Gas Chromatography (GC) is an analytical method used to separate the chemical constituents, typically of organic molecules and gases, and detect their relative abundances

within a sample. Gas chromatographs are common laboratory instruments that are widely used for organic composition determination across a wide range of industries. Specific to petroleum geochemistry, GC has a history in fingerprinting conventional oils since the late 1980s (Kaufman, 1990). Geochemists currently use GC to tackle the challenges of determining geochemical characteristics of unconventional petroleum systems (Jweda et al., 2017). Because tight-rock unconventional petroleum systems are by definition low-permeability rock properties, it can be more difficult to assign fingerprints to specific formations (which is even more challenging in stacked resource plays). The first method proposed to extract these end-member fingerprints was by way of extracting light hydrocarbons from a core sample, usually taken from the sidewall of a well, as opposed to sampling produced fluid as common on studies of conventional petroleum systems (Liu et al., 2017).

In order to define the intermediary peaks between the primary interparaffin (n-alkane) peaks, a High-Resolution Gas Chromatography (HRGC) was used instead of traditional GC instruments. A HRGC instrument consists of additional upgrades such as longer flight tubes and magnets, which significantly increases the ability to detect small contributions of hydrocarbon compounds found in very low concentrations. While HRGC continues to be one of the standard instruments for geochemical fingerprinting of unconventional petroleum systems, Two-dimensional Gas Chromatography (GCXGC) has been proposed in recent years as a new iteration that has shown the potential to resolve between 1000-3000 compounds in whole oil samples, as compared to HRGC, which detects between 100-300 compounds (Liu et al., 2020). For purposes of this study, HRGC should provide the necessary resolution for the project objectives.

Results of the HRGC analysis came as both Microsoft Excel Spreadsheets (.xlsx) and Flame Ionization Detector (FID) gas chromatographs in (.D folder format). Stratum Reservoir delivered the chromatograph information for each individual sample and the internal standard, Excel spreadsheet summaries of each individual sample one of which can be seen in Figure 7 below, an overall Excel spreadsheet summary of all the samples (including metadata, peak-area, and peak-height), and an Excel spreadsheet summary of each subset's quantitative light hydrocarbon extraction (QEXQ).

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	STDATUM			Peak Label	Compound Name	Ret. Time	Area	Height	ppm* (Area)	ppm* (Hght)	Peak Label	Compound Name	Ret. Time	Area	Height	ppm* (Area)	ppm* (Haht)
	SIRAIUM		EXTRACT GC	IC4	lso-alkane C4						IP16	Isoprenoid C16	48.444	5105	1189	18.63	9.41
	RESERVOIR			NC4	Normal Alkane C4						NC15	Normal Alkane C15	49.865	9268	2724	33.81	21.55
				IC5	lso-alkane C5						NC16	Normal Alkane C16	53.738	5988	1890	21.85	14.95
Company:	Texas A&M University	Client ID: A		NC5	Normal Alkane C5						IP18	Isoprenoid C18	55.686	3409	679	12.44	5.37
Country:	UNITED STATES	Project #: HH-107356		22DMB	2,2-Dimethylbutane						NC17	Normal Alkane C17	57.409	4527	1294	16.52	10.24
Basin:		Lab ID: 6132444263			2 3-Dimethylbutane						IP19	Isoprenoid C19 (Pristane)	57.774	3250	629	11.86	4.98
Block:		Sample Type: Cutting			2.3-Dimenyibulane						PHEN	Phenanthrene	58.836	472	116	1.72	0.92
Field:		Sampling Point:		3MP	3-Methylpentane						NC18	Normal Alkane C18	60.900	3320	1015	12.11	8.03
Well Name:	Phase 1	Collection Date:		NC6	Normal Alkane C6						IP20	Isoprenoid C20 (Phytane)	61.363	2656	482	9.69	3.81
Latitude:	0	Formation:		22DMP	2,2-Dimethylpentane						NC19	Normal Alkane C19	64.224	2970	830	10.84	6.57
Longitude.	Ŭ	Top Depth:		MCP	Methylcyclopentane						NC20	Normal Alkane C20	67.394	2856	812	10.42	6.43
GC Method:	G02G	Bottom Depth:		24DMP	2,4-Dimethylpentane						NC21	Normal Alkane C21	70.426	2093	620	7.64	4.90
Sample Pre	p: NOPR	Depth Units:		223TMB	2,2,3-Trimethylbutane						C25HBI	Highly Branch Isoprenoid C25	70.696	226	48	0.83	0.38
Extract GC	Traco		C2210040 D	BZ	Benzene	8.131	81	38	0.30	0.30	NC22	Normal Alkane C22	73.327	1894	536	6.91	4.24
LAUACO			G3210049.D	33DMP	3,3-Dimethylpentane						NC23	Normal Alkane C23	76.108	1617	453	5.90	3.59
					2-Methylbevane						NC24	Normal Alkane C24	78.779	1360	387	4.96	3.06
				23DMP	2.3-Dimethylpentane						NC25	Normal Alkane C25	81.350	1200	334	4.38	2.64
	9 6 9			11DMCP	1.1-Dimethylcyclopentane						NC26	Normal Alkane C26	83.821	1029	282	3.76	2.23
				3MH	3-Methylhexane						NC27	Normal Alkane C27	86.207	939	257	3.43	2.03
				1C3DMCP	1-cis-3-Dimethylcyclopentane						NC28	Normal Alkane C28	88.506	738	195	2.69	1.55
				1T3DMCP	1-trans-3-Dimethylcyclopentane						NC29	Normal Alkane C29	90.724	765	195	2.79	1.54
				3EP	3-Ethylpentane						NC30	Normal Alkane C30	92.879	536	140	1.96	1.11
				1T2DMCP	1-trans-2-Dimethylcyclopentane						NC31	Normal Alkane C31	94.957	452	113	1.65	0.89
				NC7	Normal Alkane C7	40,400	07000	40000	404 57	404 57	NC32	Normal Alkane C32	96.973	440	94	1.61	0.74
				ISTD MCH	Internal Standard	10.420	27839	12838	101.57	101.57	NC33	Normal Alkane C33	98.925	419	99	1.53	0.79
				113TMCP	1 1 3 -Trimethylcyclopentane						NC34	Normal Alkane C34	100.626	470	00 77	1.72	0.69
				ECP	Ethylcyclopentane						NC36	Normal Alkano C36	102.706	300	53	1.41	0.01
	ດ ທ 4			124TMCP	1,2,4-Trimethylcyclopentane						NC37	Normal Alkane C37	104.799	281	16	1.49	0.42
	и мс1 мс1		234 NC35 NC36 NC38 NC38 NC39 NC40 NC41 NC41	123TMCP	1,2,3-Trimethylcyclopentane						NC38	Normal Alkane C38	107.000	125	40 27	0.46	0.00
	NC13 NC13 NC	C17 9 9 9 9 9 9 9 9 9 15 8 3 12 8 3 2 12 8 3 12 8 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9		TOL	Toluene						NC39	Normal Akane C39	112 802	410	39	1.50	0.22
	1 T T T T T T T T T T T T T T T T T T T	1 IP1 8 1 IP1 8 1 IP2 8 1 I		NC8	Normal Alkane C8						NC40	Normal Alkane C40	116 480	482	48	1.00	0.38
ы д	North Martin Like North			IP9	Isoprenoid C9						NC41	Normal Alkane C41	120.651	289	30	1.05	0.23
				EB	Ethyl-benzene								120.001	200	00	1.00	0.20
EGC parame	eters Thompson ¹	Mango ²	Halpern ³	MXYL	<i>m</i> -xylene												
Pristane/Phytar	не 1.22 А. BZ/л С ₆	P1	Tr ₁														
Pristane/nC17	0.72 B. TOL/n C ₇	P ₂	Tr ₂	NC9	Normal Alkane C9												
nC 18/nC 19	0.60 C. (n C ₆ +n C ₇)/(CH4M CH) 1.12 I. Isoheptane Value	5N₁	Tr ₄	IP10	Isoprenoid C10												
nC17/nC29	5.92 F. n C ₇ /MCH	N ₂	Tr ₅	PB	Propyl-benzene												
nC 18/(nC 18+nC 1	9) 0.53 U. CH/MCP	6N ₁	Tr ₇	NC10	Normal Alkane C10	26.616	54	. 17	0.20	0.13							
nC17/(nC17+nC2	29) 0.9 R. n C ₇ /2MH	K1	Tr ₈	IP11	Isoprenoid C11												
CP1Marzi ⁵	1.1 H. Heptane Value	5N1/6N1	C ₂	NC11	Normal Alkane C11	31.878	146	48	0.53	0.38							
Normal Paraffin	s 27.4 MCH/n C7	P ₃ /N ₂	C ₃	NC12	Normal Alkane C12	36.806	624	207	2.28	1.64							
Isoprenoids	8.4 mpXYL/n Cs	In(24DMP/23DMP)	C ₄	IP13	Isoprenoid C14	37.554	334 650	99	1.22	0.79							
Cycloparaffins Branched (iso-)	nC6/nC7	Expulsion Temp ^e C	C ₅	NC13	Normal Alkane C13	40.321	5208	1642	2.40 19.00	12 99							
BTX aromatics	0.0			IP15	Isoprenoid C15	44.886	3313	974	12.09	7.71							
Resolved unkno	owns 64.0			NC14	Normal Alkane C14	45.771	10316	3164	37.64	25.03							
¹ Thompson, H	K.F.M., 1983.GCA:V.47, p.303. ² Mango, F.D., 1994.GCA: V.58	8, p.895. ³ Halpern,H.I.,1995,AAPG Bull.: V.79, p.801. ⁴ Hur	t, 1979 ⁵ M arzi, 1993, OrgG; 20, 1301.	Company:	Texas A&M University		Client ID:	Α									
Well Name	e: Phase 1	Proiect #:HH-	107356	Well Name:	Phase 1		Project #:	HH-10	7356								
Depth:	-	Lab ID: 613	2444263	Depth:			Lab ID:	61324	44263								
Collection D	Date:	File Name: G32	10049.D	Collection Date	9:		File Name	: G3210)049.D		* based on	initial weight of rock extracted					

Figure 7: Sample High-Resolution Gas Chromatography Summary of one of the cuttings samples used in our analysis. The left most page contains metadata and chromatograph, while the next two pages contain each of the detected compounds along with their retention time, area and height of the compound peaks.

Chromatography Data Analysis

While Stratum Reservoir did provide information on the major peaks including their retention times, areas, and heights, it is often the minor (sometimes termed "intermediary") peaks that tend to form the identifying PHRs of a hydrocarbon sample (see Figure 8).



Figure 8: Sample chromatograph showing "Primary Peaks" (typically normal alkanes and isoprenoids) as well as the "Intermediary Peaks", which often do not include named hydrocarbon compounds, but are important in the geochemical fingerprinting process.

The first step within the Schlumberger Malcom[™] software workflow is to import the FID data. For our final analysis, we imported both the cuttings FID data, the core FID data, and the produced fluid FID data, so that the software program would try to identify the best ratios that are shared across our sample library.

Upon importing data into the program, I used our reference internal standards to index each peak. Peak indexing calibrates each chromatograph to one another to account for the small variations in retention time between sample chromatographs. These small variations may occur due to a number of factors including the environmental conditions of the laboratory, how long the instrument is used, and operator errors. When corrected with the indexing procedure, the variations in retention time are negated and do not affect the final analysis.

For this indexing procedure, we used the Kovat's retention index (Kovat, 1958) to normalize the retention time of the n-alkane primary peaks to a system-independent constant, which allows for easier comparison among many samples. This indexing procedure is a standard practice in the analysis of chromatographs. The standard formula for the Kovat's index is as follows:

$$I = 100 * [n + \frac{\log t_x - \log t_n}{\log t_{n+1} - \log t_n}]$$

Where the Kovat's Index (*I*), is a function of the number of carbon atoms in the n-alkane peak (*n*), and the retention time (*t*). Thus, for n-alkane peaks we get their representative number of carbon atoms *100 (so n-C12 = 1200, n-C25 = 2500, etc.). The intermediary peaks between the n-alkanes will have an index number that related to the difference in retention time between the n-alkane above and below the intermediary peak, as well as the difference in retention time between the intermediary peak and preceding n-alkane primary peak. The workflow to establish the Kovat's Index in the Malcom[™] program is quite straightforward and involves first identifying the n-alkane primary peaks on a reference chromatograph (usually the internal standard, since it is typically high quality and included in each subset of data). Then performing a visual quality check (QC) on each of the chromatograph to ensure the program is correlating the correct peaks. If there is a mismatch, the software user may quickly correct this by manually selecting the n-alkane primary peak. While the software automates much of the mathematics of

the indexing operation, we have validated the results by using the open-source OpenChrom[™] software and performing a Kovat's index using Microsoft Excel[™].

Once the user identifies the primary peak (n-alkane) Kovat's indices, the software will automatically identify and correlate the intermediary peaks, determine peak-height, peak-area, and their corresponding ratios (see Figure 9). This data comes as a matrix in either spreadsheet or comma-separated value format for data analysis outside of the Malcom software.



Figure 9: Two chromatographs, which have been indexed to one another after the indexation process in the Schlumberger Malcom program. The n-alkane primary peaks of n-C16 and n-C17 (1600 and 1700 in Kovat's index) can be seen along with the intermediary peaks identified with their Kovat's numbers.

Determination of Identifying Ratios

Following the creation of our Kovat's indices, we are able to compare the ratios found in our

samples. The parameters used to identify PHRs in the Malcom program were a minimum ratio

value of 0.1 and a window of 20, meaning the software compared a given peak to the nearest 20

primary- and intermediary peaks when generating the ratio matrix.

The matrix was loaded as a spreadsheet into Microsoft Office where the data is then grouped according to sample type (Internal Standard, Produced Oil, Core, and Cuttings) and sorted by depth. Each column in the spreadsheet represents an individual sample, and each row represents a specific peak-height ratio as shown below in Table 1.

	G3210486.TIC	G3210456.TIC	G3210457.TIC	G3210458.TIC	G3210459.TIC
1216.9/1232.21	6.9675	5.0664	4.3543	5.0210	3.7070
1232.21/1246.38	0.5904	0.3273	0.3853	0.3061	0.3618
1246.38/1257.47	1.3275	1.2136	1.8330	1.3806	1.5878
1246.38/1259.89	1.9121	1.0764	0.7467	1.0274	1.1287
1257.47/1259.89	1.4404	0.8869	0.4074	0.7441	0.7109
1257.47/1270.24	0.3413	0.2670	0.1394	0.2198	0.1616
1257.47/1277.05	0.2243	0.2380	0.2781	0.2301	0.2348
1259.89/1270.24	0.2370	0.3011	0.3423	0.2954	0.2273
1259.89/1277.05	0.1558	0.2684	0.6826	0.3092	0.3303
1270.24/1277.05	0.6573	0.8914	1.9944	1.0466	1.4532
1270.24/1280.81	2.5543	4.0399	3.8118	3.6540	4.9304
1277.05/1280.81	3.8861	4.5322	1.9113	3.4912	3.3928

Table 1: Peak-height ratio matrix for analyzed samples. Rows represent the peak-height ratios, and each column is a separate sample.

To identify the relevant ratios, we first needed to compare the ratios found in the cuttings and core with those found in the produced oil samples. The idea is that since the oils have their origin in the formations from which the cuttings and core originate from, the range of ratio values for a specific row of produced oil samples will be the minimum and maximum values for a representative ratio found in the cutting's samples. We calculated the minimum and maximum value of oil samples for each ratio using the MIN and MAX macro functions within Excel. Core and cutting cells were then highlighted (using the conditional formatting function) if their value fell within the range of a given ratio from the produced oil samples. After the samples were highlight, we used KUTOOLS for Excel and a Visual Basic (VB) script, which allowed me to determine the number of highlighted values in a row of cuttings samples based on the fill color of that cell. The code VB Script is from extendoffice.com, shown below:

Sub DisplayFormatCount() Dim Rng As Range Dim CountRange As Range Dim ColorRange As Range Dim xBackColor As Long Dim xFontColor As Long On Error Resume Next xTitleId = "KutoolsforExcel" Set CountRange = Application.Selection Set CountRange = Application.InputBox("Count Range :", xTitleId, CountRange.Address, Type:=8) Set ColorRange = Application.InputBox("Color Range(single cell):", xTitleId, Type:=8) Set ColorRange = ColorRange.Range("A1") xReturn = 0For Each Rng In CountRange qqq = Rng.Value xxx = Rng.DisplayFormat.Interior.Color If Rng.DisplayFormat.Interior.Color = ColorRange.DisplayFormat.Interior.Color Then xBackColor = xBackColor + 1End If If Rng.DisplayFormat.Font.Color = ColorRange.DisplayFormat.Font.Color Then xFontColor = xFontColor + 1End If Next MsgBox "BackColor is " & xBackColor & Chr(10) & "FontColor is " & xFontColor

End Sub

Using this method the raw number of samples highlighted, and their percentage of the total sample set (based on the row) are calculated. This was repeated for the core samples, and then once more for both the cuttings and the core samples together. Using conditional formatting again allows us to visualize the quality of our ratios with a red-yellow-green color grading to indicate the proportion of samples that were within the "oil range" for a specific ratio. This provided both quantitative and visual information on the suitability of specific ratios to describe core and cutting samples.

A quality metric was created to assign rank values on how well the core and cuttings samples were correlated to one another based on a specific ratio. Of the 169 unique ratios generated by the Malcom software for our core, cuttings, and oil samples, the 10 highest quality ratios were selected to be depicted in this publication.

Data Visualization

After determining these 10 identifying "type-ratios", the ratios are graphically plotted in Excel to show the trend of ratio values through vertical depth. Core, cuttings, and the produced oil samples analyses were plotted to identify how well the sample types correlated to one another.

After adding organizing the data in this way, geologic context was added to our visualization through the addition of petrophysical log curves with the same depth scale as our core, cuttings, and oil samples. This last step of our methodology is paramount to this study as it reflects that the PHRs seen within our samples are geologically controlled, which we would expect.

3. RESULTS & DISCUSSION

First Subset (Proof-of-Concept)

The first lab analysis results delivered as part of this study were from the first subset of samples, where the objective was to determine whether there was a detectable signal contained within the cutting samples. While we expected some signal degradation due to evaporation and hydrocarbon fractionation during its storage, we were not initially sure of whether the intensities of the primary and intermediary peaks would be sufficient for a geochemical analysis.

By an initial visual analysis of the chromatograms generated from our first subset we do see that there is a detectable signal that appears to be mostly similar to the chromatogram from the whole oil internal standard.



Figure 10: Unindexed chromatogram of an internal whole oil standard representing the expected (highest quality) HRGC response.



Figure 11: Unindexed chromatogram of a cutting sample in our first subset

By comparing Figure 10 and Figure 11, we can see that while we are able to detect a signal in the cutting samples, the response is significantly degraded compared to our standard whole oil sample. Specifically, we notice that the hydrocarbon compounds lighter than n-alkane C12 are mostly missing or barely detectable in our cuttings samples. However, when the intermediary peaks are examined we do see that an initial comparison can be made on the visual level, shown here in Figures 12 and 13:







Figure 13: Gas chromatograph of cuttings showing paraffin (P-#) and intraparaffin (I-#) peaks.

Furthermore we have noticed that hydrocarbon compounds from n-alkane C12 to nalkane C15 have a higher quality in core extracts than in cuttings, however above n-alkane C15 this is less apparent, and there are even some compounds that appear to be better preserved in cuttings than in the core extracts, see Appendix A, B, and C. Though the absolute counts of the compounds differ by nearly an order of magnitude, because our study deals with PHRs and not absolute values, there should be enough information contained within the cuttings chromatograms to verify that we may proceed with additional analysis of the larger subset of cuttings samples.

Second Subset (Full Geochemical Profile)

The second subset consisted of an additional 28 cutting samples for a total of 38 individual depth intervals between the two subsets of data. In total our final geochemical analysis included 191 individual samples comprised of 107 sidewall core samples, 43 produced oil samples, 38 cutting samples, and 3 samples of our whole oil standard (Figure 14).



Figure 14: Relative proportions of each sample type contributing to our final geochemical analysis

Though we had a significantly larger number of core samples than cuttings samples, this is to be expected as a core sample represents a specific absolute depth, while cuttings samples represent a range of depths with intervals of 15-30 feet (4.6-9.1 meters).

When calculating the percentage of the how many samples contained a specific PHR as detailed on pages 15-18 of the Determination of Identifying Ratios subsection of the Methodology section it became apparent that, in general, the correlation of the PHRs of cuttings and core to that of the produced oil became stronger beyond n-alkane C15. Based on similar research presented at the 2021 AAPG image conference by Richard Patience, of Applied Petroleum Technology (APT), hydrocarbons lighter than n-alkane C15 are prone to evaporate from stored samples, where hydrocarbons heavier than n-alkane C15 have been shown to remain in samples at detectable quantities for up (and potentially beyond) 20 years. Thus, it is no surprise that the 10 representative PHR ratios we identified for this study are indeed heavier than the n-alkane C15. Additionally we did not account for hydrocarbons heavier than n-alkane C26 in our study since the aim of this study was to establish a baseline proof-of-concept for using cutting samples as an alternative to core. It was also observed that hydrocarbon compounds heavier than n-alkane C26 had considerably lower abundances than the hydrocarbon compounds between n-alkane C15 and n-alkane C26. While our study also included the analysis of hydrocarbon compounds between n-alkane C12 and n-alkane C15, the GC responses of these compounds were similar lower in abundance than the range of n-alkane C15 to n-alkane C26 and as such were determined not to be of significance for this study.

The plots for our 10 representative PHRs show the value of a given PHR plotted on the xaxis against vertical depth plotted on the y-axis. The exact depths of the samples are not given to ensure the confidentiality of our proprietary cutting samples. The cutting samples are symbolized as orange dots and the core samples as blue. Additionally, six of our produced oil samples from prior production allocation analyses. In general, one can observe in Figures 15a/b, 16a/b, 17a/b, 18a/b, and 19a/b that the values of these PHRs are quite similar between the core extract and cutting samples. Specifically, we see in Figure 16a, 16b, 18a, 19a, and 19b that in much of our depth interval the PHR values are nearly identical between the core and cutting samples.

Observing that PHR values in cuttings similar to those found in the core extract samples suggests that cuttings could be used interchangeably or at least complimentary to core extract samples. However, the key factor for determining whether cuttings are suitable for production allocation is how similar the PHR values found in the cutting samples to those found in the produced oils. In Figure 15a, 15b, 17a, and 18b we can clearly see that cutting samples actually provide a stronger correlation to the produced oil samples than the core extracts. In Figure 18a and 19a we see that the core samples provide a slightly stronger correlation, and alas in Figure 16a, 16b, 17b, and 19b, the difference in correlation between the core/cutting samples and the produced oil samples in negligible. One such theory of why cutting samples may provide a better correlation is that by nature of their collection during the drilling process they represent a range of depths more similar to that of a produced oil sample, whereas core extracts only represent a small portion of the overall rock and therefore may contain a higher instance of outliers. Also if the location a core sample is taken is lower in total organic carbon (TOC) the rock within a few feet above and/or below the sidewall plug, it may not be representative of the specific zone within the formation.



Figure 15a & 15b: Plot showing the vertical reference profiles (x-axis of PHR and y-axis of depth in feet) for the 1530.71/1537.24 (15a) and 1537.24/1554.32 (15b) PHRs



Figure 16a & 16b: Plot showing the vertical reference profiles (x-axis of PHR and y-axis of depth in feet) for the 2041.39/2059.78 (16a) and 2108.79/2114.52 (16b) PHRs



Figure 17a & 17b: Plot showing the vertical reference profiles (x-axis of PHR and y-axis of depth in feet) for the 2253.1/2259.68 (17a) and 2452.35/2468.83 (17b) PHRs



Figure 18a & 18b: Plot showing the vertical reference profiles (x-axis of PHR and y-axis of depth in feet) for the 2664.97/2674.6 (18a) and 2069.74/2073.23 (18b) PHRs.



Figure 19a & 19b: Plot showing the vertical reference profiles (x-axis of PHR and y-axis of depth in feet) for the 1952.81/1965.36 (19a) and 2118.95/2130 (19b) PHRs.

The final portion of our analysis was to contextualize the trends and correlations we observed in our 10 representative PHRs with geological information. Our hypothesis was that the trends observed, particularly the inflection points of a depth curves, were geologically controlled. By using well logs and formation, it was possible to construct a few figures that show these controls. Adding this contextual evidence is important as it highlights that both cutting and core samples can reflect changing geological properties in a stratigraphic section.

Geological Context

Figure 19 depicts a gamma ray (GR) well log adjusted to be the same scale are the PHR ratios of 2664.97/2674.6 and 2253.1/2259.68. A gamma ray log specifically shown to depict the differences in lithology (and consequentially depositional environment) through our well section. The lighter (white/tan) colored sections of our log tend to be either carbonate or sandier or siltier (siliciclastic) in lithology, the darker brown sections are shalier facies. Additionally, interpreted rock packages (horizons) are overlain on the well log, and are extended across the PHR plots as well. What is important to notice in Figure 20 is that groups of PHRs in both the cutting and core extracts appear to be grouped in clusters bounded either above and/or below by these horizons and of similar lithologies reflected by the gamma ray log. In addition, these horizons are often also associated with the major inflection points of changing PHR trends. This suggests that there is enough geochemical information in both cuttings and core samples to different lithotypes, especially when there are multiple facies types. While there could be some influence of biological factors in forming the differences between rock types, we find from the SRA that the

kerogen type and maturation level are clustered very closely (see Figure 21), and do not exhibit as much separation as the PHR trends through the vertical section.





Figure 21: On the left, Hydrogen Index (HI) is plotted against Oxygen Index (OI) to show Kerogen Type. On the right, HI is plotted against Tmax to represent both Kerogen Type and Maturity. Plots adapted from Weatherford Laboratories Source Rock Analysis (SRA).

However it is also important to mention that with our given equipment and resources we cannot determine the exact chemical composition of each intermediary peak (and therefore the components of PHRs). This is not the aim of our study as it is generally not necessary to know which compound every Kovat's Index number is representative of. PHRs do not need to be named and the exact representative PHR Kovat's Indices will vary in different petroleum systems and geographies. In essence, there is no single PHR or set of PHRs known that will be ubiquitous across basins, so this workflow will need to be repeated for each geography that TLG and PA will be applied to.

As previously mentioned, the cuttings for this well were collected during the drilling and completion of the well in September of 2017. The cuttings then were stored in a company warehouse in unknown conditions until we received them approximately three years after collection. The time in storage has no doubt degraded the GC response, which is apparent when compared to the whole oil internal standards such as the difference between Figure 10 and Figure 11. While it is likely we may have received better defined, or even just more results, we do find that there is more than likely enough hydrocarbons left in the samples after three years of storage to perform TLG and PA analyses with a reference profile based on these samples.

Lastly, this study represents one single well in one specific geography. The comparison of core and cuttings GC geochemistry on the same well so far is unique in the publicly available literature domain, but our study is only one data point, and though our results are certainly promising, there is still the potential for varied results when this comparison is scaled up to include multiple wells and geographies.

5. CONCLUSION

While cuttings have been used in geochemical studies in the past (including GC, HRGC, and GCXGC based studies) there has not yet been an investigation on the suitability of cuttings as an alternative sample for core extracts that has included a comparison of the two sample types from the same well. This study has filled this gap in the literature and presented a workflow, interpretation, and results that show that there is strong evidence that cuttings can either supplement or perhaps even replace core extract samples as the rock analyzed to set up the reference profiles used in TLG and PA, provided WBM (not OBM) is used to drill the well. Our findings mirror prior studies such as (Jweda et al., 2021) who found that the nC15+ range of hydrocarbon compounds could be compared between core and cuttings with a high confidence.

The workflow for using cuttings for TLG and PA is largely the same as using core plug extracts. It is expected that the HRGC response from cuttings will be diminished in strength compared to core extracts and especially produced oil, though we have found in our study that PHRs are preserved even after significant compound fractionation due to storage over the course of three years.

We have found that there is a strong correlation between cuttings and core samples in a case study of 10 representative PHRs. The small separation between PHR values and similar trends throughout the vertical section are evidence that supports this observation. In some PHRs, the cuttings actually represent a stronger correlation to produced oil samples than core extracts. Therefore, it is concluded that cuttings can indeed serve as an alternative for core extracts when

setting up the vertical profiles used as a reference to compare produced oil samples to for TLG and PA.

There is still work to be done on this topic, primarily quantifying the impact of other variables such as geographical location, the chemistry of drilling fluid used (particularly if oil-based fluids are incorporated), and the age and storage method of the cuttings. While this study primary looks at the vertical changes in hydrocarbon geochemistry, the spatial variability is another factor that could be quantified using similar workflows, but with samples taken from the horizontal portions of a well.

In summation, we have found evidence that cuttings would be appropriate to create the vertical profiles for used in TLG analyses, at least in some cases. Because similar results were found in both the cuttings and the core it is less apparent what utility of core extracts would favor the additional cost and time required to collect core samples, other than analyses involving hydrocarbons lighter than n-alkane C15. Because there is lateral heterogeneity in oil and gas composition on a basin scale, multiple vertical profiles often need to be established to ensure there is a reference close to the well location under study. To solve this, cuttings may be appropriate to use when infilling data sparse areas (McCaffrey and Baskin, 2016).

6. RECOMMENDATIONS FOR FUTURE RESEARCH

Beyond this study, there is undoubtedly more work to be done to truly understand the effectiveness of cuttings samples, as well as the type and amount of useful information that can be derived from their geochemical analysis. That being said, during the course of our research a number of questions arose, whose answers would be complimentary to our work, those include looking at multiple well locations in the same study, the influence of drilling fluid composition, determining under what time and storage conditions fractionation is most likely to occur, and horizontal changes in geochemistry.

The first idea is to look at multiple wells across one petroleum system. This analysis would allow the confirmation that our results are not an outlier. It also would have the interesting implication of showing how the selected PHRs vary spatially across a basin, especially if the wells are in different regions of the same play. Even more so this investigation could discover how kerogen type and maturity affect the PHRs if there is variability in that regard between a set of wells.

Next, since we have cuttings and core samples from a well drilled with WBM, we do not expect hydrocarbon contamination to come from the drilling fluids in our study. If instead we had a well that was drilled using Oil-Based Mud (OBM), or a combination of the two there is the potential for contamination which could skew for our results. A recent study by Sanei et al., 2020 suggests that proper washing and sample preparation can mitigate OBM contamination, as it did not appear to affect their RockEval analysis. However, it still needs to be determined how OBM may show up on HRGC, what contaminated samples may look like with HRGC, and if the level

of contamination is low enough for TLG and PA analyses. Jweda et al., 2021 has argued against this notion and found cuttings collected with OBM are too contaminated for analysis.

Because our samples underwent a period in storage which was not insignificant, it would be interesting to investigate the effect of storage on sample quality. This is especially important in the quality of cuttings as the greater surface area compared to core plugs means that evaporation and fractionation may be more probable and proceed more quickly than in core plugs. Therefore, a study that includes samples of multiple ages (i.e. fresh collected, 1 year, 3 year, 5 year, 10 year...) could lend some insight into how quickly samples are degraded and at what point if any, do they become unacceptable to use with current HRGC instrumentation. Another factor is the conditions in which the samples are stored physically. Our samples were received with each cutting sample stored in paper envelopes. A study on the type of storage container would be helpful to set up the best practices for cuttings storage moving forward, and also set another standard to determine whether samples would be suitable for a HRGC analysis.

Lastly, one interesting research direction would be to study the horizontal changes in geochemistry through PHRs. The idea would be to collect cuttings (or even core plugs) from the horizontal portion of a well to see if changes in PHRs can be observed in the second dimension along the lateral length of the well. If changes are in fact observed this could be used to verify geosteering operations and quantify how variable the overall geochemistry of a source rock/target interval is.

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APPENDIX A



CORE + CUTTINGS QUALITY OF PHRS



APPENDIX B

CUTTINGS QUALITY OF PHRs



41

APPENDIX C

CORE QUALITY OF PHRs



42

DATA CONTINUITY

The raw and processed data used for this research have been sanitized of identifying information (i.e. Well Name, Exact Depths, Location, etc.) and will be accessible for those who wish to repeat the analyses detailed in this study. Copies of this data will be managed by the author of this study whom you may reach at either <u>dscherer@tamu.edu</u> or <u>flatirongeo@gmail.com</u>. Additionally, a copy will be available at the Berg-Hughes Center for Petroleum & Sedimentary Systems which will be accessible with author approval.